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Optimization of ratio of active masses in VRLA battery

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Abstract

The gravimetric and barodynamic methods were used to investigate the effect of ratio of active masses on efficiency of internal oxygen cycle.
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1. Introduction

A ratio of active masses (RAMs) is an important characteristic of VRLA battery, which to a great degree determines its serviceability. But presently, the problem of the RAM optimization is not solved unambiguously. For batteries working in a mode of continuous charging it is recommended to use excess of negative active mass (NAM) so that to eliminate hydrogen evolution and to compensate for its self-discharge [1]. And, on the contrary, for cycled batteries, it is recommended to use excess of positive active mass (PAM). This is due to the fact that otherwise intensive evolution of oxygen at the end of the charge and its regeneration across the negative electrode will continuously facilitate insufficient charge of the NAM and will shorten the battery service life [2]. The effect of the RAM on the efficiency of the internal oxygen cycle (IOC), including processes of oxygen evolution across the positive electrode, its transfer to the negative one and subsequent regeneration across the negative electrode, is studied in this report.

With this object in view some gravimetric and barodynamic tests of VRLA batteries have been conducted.

2. Experiment method

VRLA batteries with a rated capacity of $C_{20} = 13$ Ah with a RAM (m_{PAM}/m_{NAM}) of 0.83, 0.87, 0.91, 0.95, 1.00, 1.05, 1.10, 1.18. have been fabricated for the gravimetric tests. H_2SO_4 with a density of 1.28 g/cm^3 was used as electrolyte.

The batteries have been cycled in the following mode: discharge with current $0.23C_{20}$ for 2 h; 2-stage charge with current $0.115C_{20}$ for 2.5 h and with current $0.015–0.020C_{20}$ for 17 h. At the first stage, the batteries received 65% of the capacity removed beforehand; transient voltage was 2.35–2.40 V; overcharge was 20%. After each charge the batteries were weighed to a nearest ±0.01 g to determine water losses. Control discharge with current $0.05C_{20}$ was carried out every 20 cycles to a final voltage of 1.75 V.

Special cells, which allow to carry out electric tests of battery models with simultaneous measurements of their internal pressure, were designed and fabricated for conducting barodynamic tests. The cells were filled with 1.28 g/cm^3 acid. The cells were cycled in the following mode: discharge with current $0.2C_{20}$ for 1.5 h with subsequent charge with current $0.06C_{20}$ to 15% overcharge. The pressure in the cell was recorded at the end of the charge. After the charge the cells were held without current for 17 h, during which pressure measurements were taken. The models with a RAM of 0.83, 0.95, 1.00, 1.05 and 1.18 were tested.

3. Experiment results and discussion

Fig. 1 shows the dependence of battery summary weight losses for a period from 20 to 80 cycles on the RAM, taken within a range of 0.83–1.18. Within 1–20 cycles battery weight losses were not considered at evaluation of the summary losses, since in this period the IOC stabilization process took place due to loss of excess electrolyte in the battery separators. The figure shows that within a range of $0.95 \leq \text{RAM} \leq 1.05$ weight losses are maximum and practically they do not depend on the RAM. At $\text{RAM} \leq 0.95$ weight losses of the batteries come down and at $\text{RAM} = 0.83$

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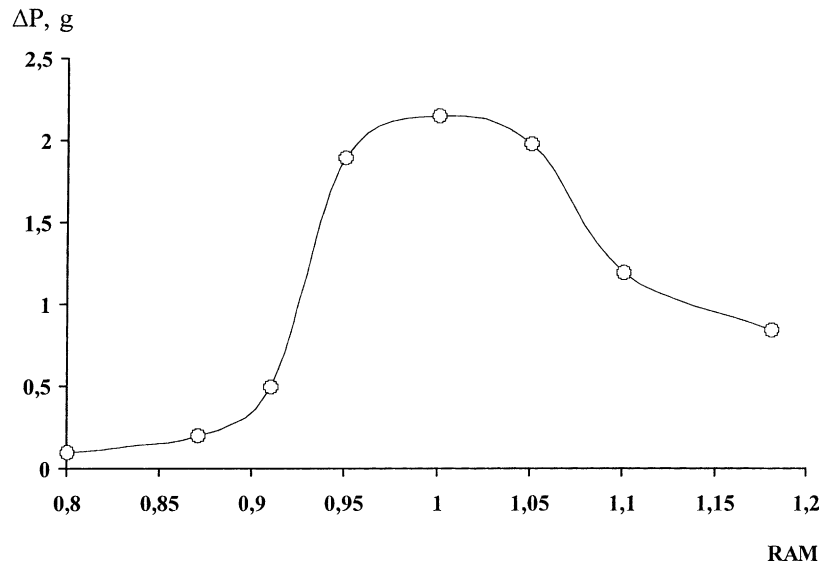*E-mail address:* lushina@mail.wplus.net (Yu. Kamenev).

ΔP, g

Fig. 1. Dependence of summery of weight losses of batteries for a period from 20 to 80 cycles on the RAM.

they make about 8% of the weight losses at RAM = 1. With RAM ≥ 1.05, the weight losses also come down, but to an essentially lesser degree, and with RAM = 1.18, they make about 40% of the weight losses with RAM = 1.

(a) Batteries with RAM < 1

The reduced weight losses mentioned above for batteries at cycling with excessive NAM can be explained on the basis of the following model of the process. It is known that the sulphate film, developed on the lead under discharging, is a barrier for oxygen diffusion to the lead active surface [3] and, hence, its development must retard the recombination process. On the other hand, at charge of positive electrodes the oxygen evolution takes place earlier than the active masses are completely formed [4] and can reach the surface of the negative plates. But till the surface of the latter, which contacts with the separator gas channel mouths, becomes completely recovered to the lead, the process of the recombination will be retarded due to low rate of the oxygen

diffusion through the negative electrode pores, filled with the electrolyte, to the lead surface able to react. It is evident, that as a content of the NAM in the battery increases, the degree of its oxidation at equal discharge modes will decrease and, hence, the efficiency of the oxygen recombination process will increase in the process of the next charge. The said may be confirmed by the evaluation of weight losses at batteries charge after their discharge to various depths. The results of this experiment are given in Fig. 2. The figure shows that the higher depth of discharge (DOD), i.e. the higher the degree of the NAM oxidation, the greater electrolyte losses at their subsequent charge for all RAM < 1 under study.

Fig. 3 shows the dependence of battery weight loss change of batteries with different RAM within one cycle on a number of cycles performed. It is seen that with increase of a number of cycles the battery weight losses depend to a lesser degree on the RAM. Here, approximation of the weight losses occurs at expense of increased efficiency of the IOC of the batteries with lower NAM content.
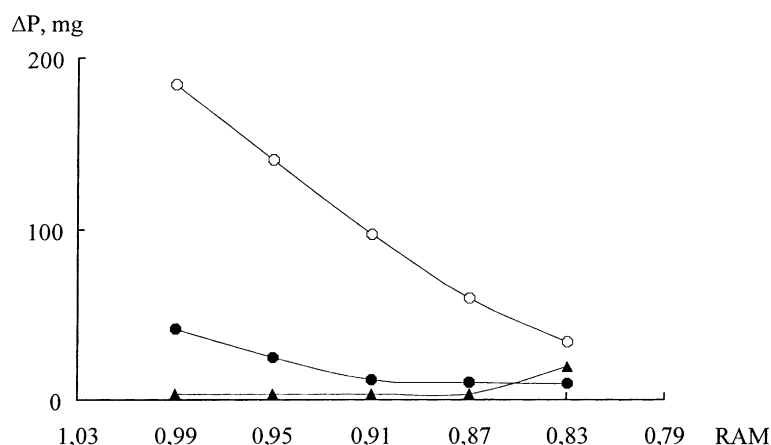
ΔP, mg

Fig. 2. Dependence of loss of weight of batteries on RAM and DOD. DOD (%): 55.4 (○), 46.1 (●) and 26.5 (▲).
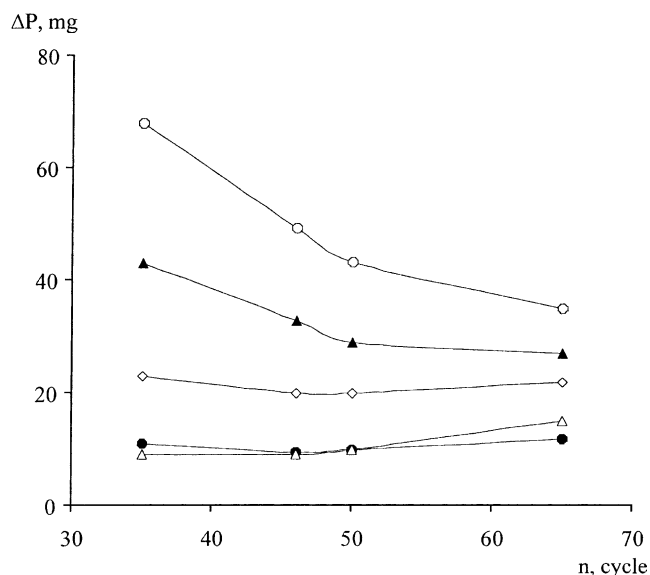
Fig. 3. Dependence of loss of weight of batteries per cycle on RAM and number of cycles performed. RAM: 1.0 (○), 0.95 (▲), 0.91 (◇), 0.87 (●) and 0.83 (△).

Table 1
Dependence of degree of saturation of the separator on RAM after 70 cycles

RAM	1	0.95	0.91	0.87	0.83
L (%)	80.0	82.5	86.2	89.5	93.0

related to increase of a number of gas channels in the separator and due to this to enlargement of the reaction surface at which oxygen recombination will take place. Thus, increased degree of negative electrode surface oxidization for batteries with low excess of the NAM can be compensated by enlargement of surface of its contact with gas channels and this finally results in increased efficiency of the oxygen cycle. But oxygen recombination rate increases in the result of considerable drop of degree of saturation of the separator and this, in its turn, must cause a deterioration of battery capacity characteristics at expense of their internal resistance. Thus, for example, a difference between the capacity of batteries with the RAM equal to 0.95 and 1.0 in 21, 41 and 71 cycles, cycled simultaneously, made 1, −1.5 and −4.5%, respectively.

A certain increase in losses of a battery with RAM = 0.83 after 70 cycles can be noted from Fig. 3. Such effect can be attributed to the fact, that a high efficiency of the IOC, typical for such batteries, and cycling conditions during this experiment, can facilitate development of the self-discharge of the NAM, which is equivalent to the reduced RAM.

Fig. 7 shows typical curves of change in pressure in the course of charge and holding without current of batteries with ratios of active masses of 0.95 and 0.83. It is seen from the Fig. 7 that sharp increase in pressure related to the oxygen evolution process corresponds to a degree of charging of about 90%. According to the data of [4] oxygen evolution across the positive electrode reaches its maximum at a degree of charging of an VRLA battery of 94%. The charge being finished, a drop of pressure takes place characterizing the efficiency of the oxygen recombination process. It is clear that with a large content of the NAM (RAM = 0.83) the efficiency of the oxygen reduction process is significantly higher than for the models with low excess of the NAM (RAM = 0.95). Fig. 4 shows the dependence of pressure increase in batteries with RAM = 0.95 and

Assuming that the electrolyte losses are caused mainly by the separator with larger pore radii than by the electrodes, one can calculate the degree of saturation of the separator (L) for batteries with various RAM by the equation:

$$L = \frac{V_{el}}{V_{sep}} = \frac{k n_{sep} \gamma_{sep} V_{sep} - \Delta P / d_{H_2SO_4}}{n_{sep} V_{sep} k}$$
$$= \gamma_{sep} - \frac{\Delta P}{n_{sep} V_{sep} k d_{H_2SO_4}} \qquad (1)$$

where V_{el} and V_{sep} are the volumes of electrolyte and separator, respectively, $d_{H_2SO_4}$ the density of electrolyte, γ_{sep} the porosity of separator, k the degree of separator compression, and n_{sep} is the number of separators in batteries.

The results of the calculations made by Eq. (1) are given in Table 1.

The table shows that degree of saturation of the separator greatly depends on the RAM. Basing on this, one can assume that increase in oxygen recombination efficiency for batteries with low excess of the NAM at prolonged cycling can be
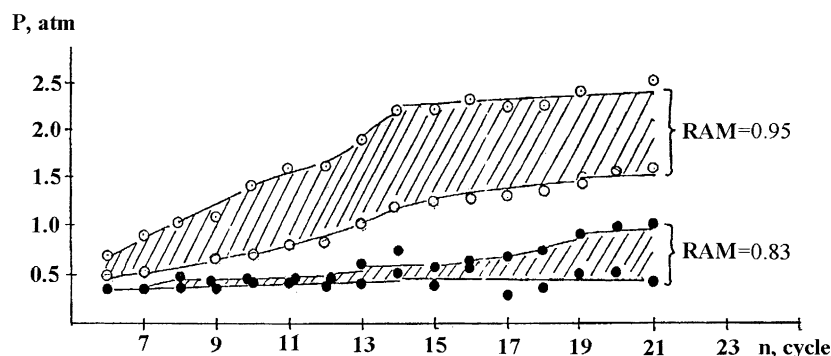

Fig. 4. Change in pressure inside battery with RAM: 0.83 (●) and 0.95 (○) on number of cycles performed.

Table 2
Pressure in cells after 17 h of holding without current

Cycle no.	Degree of discharge before charge (%)	Pressure (kPa)	
		RAM = 0.95	RAM = 0.83
40	26.0	0.04	0.03
43	15.6	0.03	0.02
44	100	0.055	0.040

RAM = 0.83 during one cycle on a number of performed cycles. The results obtained confirm the data of gravimetric studies (Fig. 3) and show that with cycling the efficiency of the IOC for batteries with low content of the NAM increases and come near to the similar values for batteries with high content of the NAM.

Paper [5] shows that residual pressure in a battery after disconnection of current and prolonged holding characterizes hydrogen pressure. Values of residual pressure in batteries with different content of the RAM after 17 h of holding without current are given in Table 2.

The table shows that hydrogen pressure in batteries with RAM = 0.83 was lower, which can be explained by more efficient IOC in them and hence by a higher depolarizing effect of oxygen on the negative electrode. In addition, it shall be noted that hydrogen pressure increases with the increase of the battery discharge depth, which is also in a good agreement with the model of the process described above.

(b) Batteries with RAM > 1

Fig. 5 shows change in battery weight losses per cycle depending on a number of cycles performed and the RAM. The losses per cycle were calculated as a mean value of 10 cycles performed in succession. It is seen from the figure that at the initial cycles with the RAM increase there is considerably reduced weight loss per cycle. But as a number of performed cycles increases the average losses to depend on the RAM a lesser degree. Here, approximation occurs at

expense of decrease in the weight for the batteries with lower RAM.

As it was noted above, the battery weight losses increase with increase of the PAM within RAM = 0.83–1.00. It was shown, that it is connected with increase in degree of the NAM oxidation at the moment when oxygen starts to evolve across the positive electrode. But with increase in the PAM content within a range of RAM = 1.05–1.18, decrease of battery weight losses was noted at charge and this points to a qualitative change of the mechanism of the RAM effect on the efficiency of the IOC.

It is evident that when excess of the PAM is significant and the previous charge is not deep, a degree of its oxidation by the moment, when the charge begins, will be high. In this case, the oxygen evolution process shall take place simultaneously. Its reduction across the negative electrode will be retarded due to availability of sulphate film on its surface. Under such conditions, oxygen evolution can result in its accumulation in separator pores and growth of oxygen partial pressure therein. This, in its turn, will increase a number of gas channels in the separator due to electrolyte displacement from the largest pores of the negative electrode and will extend the oxygen reducing reaction to the zones with the least NAM oxidation. Thus, increase of the oxygen pressure and the reaction surface must cause increased rate of oxygen reduction, increased depolarization of the negative electrode, reduced oxygen evolution and, finally, in reduced losses of the battery weight.

Fig. 6 shows dependence of the average residual pressure in the battery after charge and after 17 h without current (hydrogen pressure) on the RAM value. It is seen from the figure, that during 20–50 cycles the average growth of the residual pressure per cycle becomes considerably slower as the RAM increases (PAM content increases), and this points to the reduced rate of hydrogen evolution across the negative electrode at the expense of increase in oxygen reduction rate. In this case, it is important to note that pressure increment at
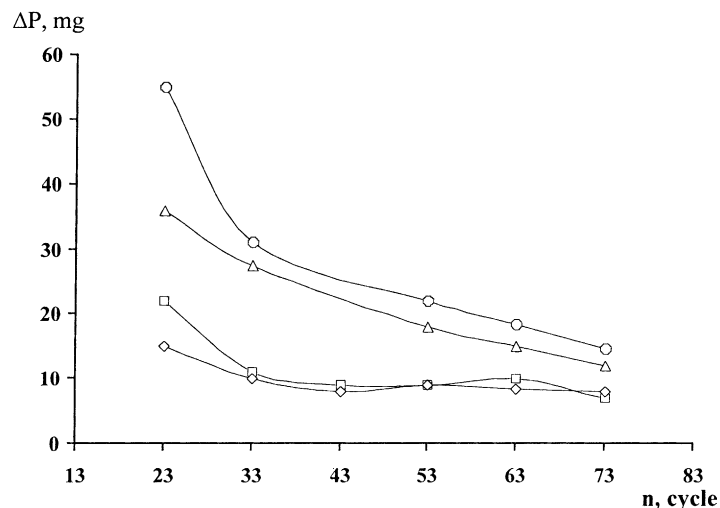

Fig. 5. Dependence of loss of weight of batteries per cycle on RAM and number of cycles performed (RAM: 1.0 (○, △) and 1.18 (◇, □).
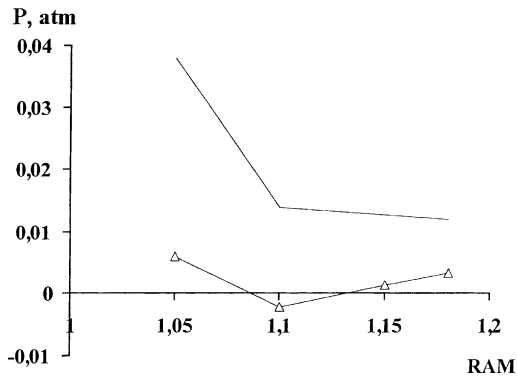
P, atm

Fig. 6. Dependence of the average residual pressure in the batteries after charge and 17 h without current on the RAM during 22–55 (—) and 77–102 (△) cycles performed.

P, atm

Fig. 7. Change in pressure inside battery with RAM: 0.83 (▲), 0.95 (○), 1.05 (●) and 1.18 (△) in the course of charge and retention without current.

the end of charging batteries with RAM = 1.18 (0.34 atm per cycle at an average) was higher than that for batteries with RAM = 1.10 (0.25 atm per cycle at an average). It is evident that this is connected with a high partial pressure of oxygen in batteries with considerable excess of the PAM at the expense of higher degree of its oxidation by the moment of charge starting. But a high efficiency of the IOC and low rate of hydrogen evolution for such batteries, finally, ensure lower weight losses at cycling.

It was noted, that with increase of a number of cycles weight losses of batteries with RAM = 1.05 become less and come to values which are comparable with weight losses of batteries with RAM = 1.10–1.18. Thus, within 77–105 cycles an average increment of pressure per the cycle "charge—17 h without current" is equal to 0.006, −0.006 and 0.004 atm, respectively for batteries with RAM = 1.05, 1.10 and 1.18. As for the case with RAM = 0.83–1.00, it can be assumed that increased water losses in the process of cycling in batteries with RAM = 1.05 cause a growth of gas channels in the separator, increase in reaction surface on which oxygen reduction takes place and increase in efficiency of the oxygen cycle and this, in its turn, suppresses the oxygen evolution process at the expense of depolarization of the negative electrode. But this must simultaneously result in separator draining, its increased resistance and reduced capacity of batteries with RAM = 1.05. The said above is confirmed by the results of the performed control discharges of batteries with the RAM equal to 1.05, 1.10 and 1.18 in the process of their cycling. Thus capacity of batteries with a RAM of 1.05, 1.10 and 1.18 by the 80th cycle was equal to 87, 96 and 98% of C_{nom}.

And, finally, Fig. 7 shows results of pressure change in batteries with RAM = 1.05 and RAM = 1.18 during the charging process and subsequent holding for 17 h after charging current disconnection. It is seen from the figure that pressure drop after disconnection of the charging current is more steep for the battery with RAM 1.18, which fact evidences a higher efficiency of the IOC and lower residual pressure after 17 h indicating that a rate of hydrogen evolution is lower than that of battery with RAM = 1.05.
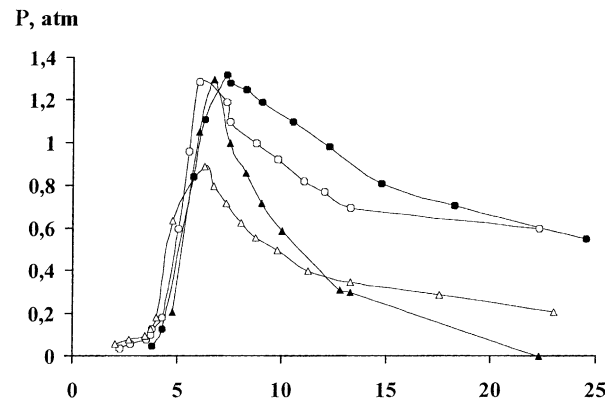
Comparing curve $P = f(\tau)$ for models with RAM = 1.18 and RAM = 0.87, one can see that in the first case the residual pressure is markedly higher than in the second case. Thus, for batteries with RAM 1.18 it is about 0.2 atm, and for batteries with RAM = 0.87 it is 0 atm. It this case, actual weight losses in batteries with higher RAM value are significantly higher. Thus, for RAM = 1.18, they are 0.01 g per cycle on the average, and for RAM = 0.83, they are 0.002 g per cycle. This confirms again, that the proposed process model, which connects weight losses of batteries with reduced rate of hydrogen evolution, is reasonable.

4. Conclusions

Effect of ratio of active masses (m_{PAM}/m_{NAM}) within a range of 0.83–1.18 on the mechanism of gas processes in VRLA battery has been studied. Gravimetric and barodynamic methods have been used for studies.

It has been shown that dependence of water losses on the RAM is of extremal character. In the field of RAM = 0.95–1.05, weight losses change faintly, and this makes it possible to consider them as independent within the given range on a RAM value. With RAM > 1.05 and RAM < 0.95 weight losses are considerably lower. In the second case, such drop is more significant.

So, use of RAM = 0.85–0.87 may be recommended for batteries, which work in the mode of continuous charge and require excess of the NAM for self-charge compensation, and this ensures minimum losses of water.

RAM = 1.10–1.18 may be recommended for batteries, which work in the mode of continuous cycling and require excess of the PAM.

References

[1] J. Manders, N. Bui, D. Lambert, Power Sources 73 (1998) 152–161.
[2] D. Berndt, Maintenance-Free Batteries: A Handbook of Battery, 1998.
[3] I. Aguf, Sbornik rabot po istochn, Toka, N14, 1991, pp. 31–36.
[4] J. Mrha, J. Jndre, M. Musilova, Power Sources 32 (1990) 303–312.
[5] H. Dietz, M. Radwan, H. Doring, Power Sources 42 (1993) 89–101.