

Investigation of height of electrolyte retention by glass-mat separators in gravitation field

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Abstract

One of the limitations to use glass felt separators (AGM type) in sealed rechargeable cells of high capacity and big height can be their inability to keep the uniform distribution of electrolyte by the height in the gravitation field. The influence of various factors (separator height, degree of its compression, electrolyte density) on separator ability to keep the initial uniform distribution of electrolyte has been investigated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Separator; AGM type; Lead-acid batteries; Distribution of electrolyte by the height

1. Introduction

One of the main preconditions for encapsulation of the lead-acid battery is the efficient run of the oxygen cycle encompassing such stages as evolution of oxygen on the positive electrode, transport of oxygen from the positive electrode to the negative electrode, reduction of oxygen on the negative electrode. Considering that the transfer of oxygen in gas phase is significantly quicker than its molecular diffusion in liquids, one of the ways to increase efficiency of the oxygen cycle is creation of gas channels in the inter-electrode gaps securing filtration of oxygen from the positive electrode to the three-phase interface of the negative electrode.

To achieve this end, at present a wide use is made of the electrolyte immobilization principle, when the entire electrolyte is contained in the pores of the electrode block (electrodes and separators). In this case, the structure of the separator should consist of both tiny pores filled with electrolyte and securing ionic conductivity, and large gas pores through which oxygen filtration occurs. As a separator material a wide use is made of a glass-mat separator. Such a separator is noted for good resilience securing positive contact of the separator with the electrodes, zero wetting angle, high stability in acid, high porosity (90–95%), ability to adapt to defects of the surface of the plates and high thermal stability.

The major restriction for use of the glass-mat separators in high capacity batteries noted for a significant height could be their inability to secure uniform distribution of electrolyte over the height in the gravitation field. Draining of electrolyte will result in lower capacity of the battery, non-uniform distribution of current generation processes, lower active mass utilization factor, creation of conditions for non-uniform distribution of oxygen recovery process, which in turn leads to extra heating of the top section of the battery.

The aim of this work is the determination of extent of effect of various factors (height of the separator, degree of its compression, density of electrolyte) on ability of the glass-mat separator to retain electrolyte in the gravitation field. It is evident that selection of design of the high capacity encapsulated battery depends on solution of this problem. Either it will have a traditional single-tier structure, or there would be necessary to limit its height by modification of the geometry of the electrodes, application of the multi-tier design, use of a horizontal design of the electrode block.

2. Experimental part and discussions

The mechanism of electrolyte draining in the separator should be described by the process of passage of the liquid with certain physical characteristics (viscosity, density, wetting, etc.) through the porous body under action of gravitation forces. In approximation, the porous structure of the separator could be described by the model of intersecting capillaries with average radius R , non-straightness value β .

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As average radius one should consider such radius of capillaries which secures the same volume of liquid passing through the porous system as the real separator with certain function of pore distribution by radii. The problem concerning the movement of liquid under action of differential pressure (ΔP) in a separate capillary is solved on the basis of evaluation of distribution of velocity of movement of streams over the section of the capillary which could be described by the known equation [1]

$$V = \Delta P \frac{R^2 - r^2}{4\eta} \quad (1)$$

where V is the velocity of movement of stream of liquid at a distance r from the center of the capillary with radius R , η the viscosity of liquid. Then we will derive the quantity of liquid passing through the section of the capillary $r + dr$ in unit of time

$$W = (2\pi r dr)V \quad (2)$$

Having inserted (1) into (2) and integrating by r in limits (0, R) we will get the quantity of liquid flowing through the section of the capillary with radius R in time τ

$$W = \frac{\pi \Delta P \tau R^4}{8\eta} \quad (3)$$

Thus, it follows from the derived Eq. (3) that the rate of loss of electrolyte by the separator should depend both on state of the separator material, and characteristics of the electrolyte. However, one should take into account that in the real separator the loss of liquid occurs only via the through pores. The blind-end and ring pores will continue to retain electrolyte. Besides, a certain volume of pores associated with fine pores will also retain electrolyte due to action of capillary forces (F_c), capable of compensation of gravitation forces (F_{gr}), instrumental in movement of electrolyte. It is known that capillary forces are proportional to the surface tension, cosine of the wetting angle and inversely proportional to the radius. Thus, with certain radius of the capillary (R_{lim}) there would be realized the equality $F_c = F_{gr}$, which is the precondition for retention of electrolyte in the pores with radius $R \leq R_{lim}$. It is evident that increase of extent of separator compression will not only retard the velocity of electrolyte draining in accordance with (3), but will increase the volume of pores with radius equal or less than critical.

The above statement indicates that draining of electrolyte over the height of the separator does not result in its complete dry-out. Conventionally, there are two types of pore volumes in the separator: (1) pores that persistently retain electrolyte; (2) pores through which draining (loss) of electrolyte occurs.

Since the movement of electrolyte is not the movement of the infinite column of liquid through the porous body, and there is initial limited quantity of solution and its initial level (H_0), then formally there occurs the movement of upper level of electrolyte over porous volume of the second type.

Losses of liquid associated with lowering of this level could be described by the ratio

$$dW = \pi R^2 N \beta dH \quad (4)$$

where N is the number of openings of pores in the cross-section of the separator. Integrating (4) within limits (0, W) and (H_0 , H) we will get

$$W = \pi R^2 N \beta (H_0 - H) \quad (5)$$

Having equalized (5) and (3) we will get

$$H = H_0 - \frac{\Delta P R^2 \tau}{8\eta N \beta} \quad (6)$$

Porosity of the separator (g) for the proposed model equals

$$g = \frac{V_{\text{pores}}}{V_{\Sigma}} = \frac{\pi R^2 N \beta}{Q} \quad (7)$$

where V_{pores} is the volume of pores, V_{Σ} the volume of separator, Q the area of cross-section of the separator. Having inserted R^2 from (7) to (6), we will get

$$H = H_0 - \frac{\Delta P g Q \tau}{8\pi \eta (N \beta)^2} \quad (8)$$

It follows from the Eq. (8) that the height of electrolyte retention will go up with increase in degree of compression of the separator. Increase in density of electrolyte (ρ) should also affect the height of electrolyte retention, but this dependence is not self-evident, since H simultaneously depends both on ΔP , and η . With decrease in density of electrolyte the viscosity will go down, which will result in higher velocity of electrolyte draining, but at the same time ΔP will decrease, which will assist in drop in rate of draining (8). Dependence of electrolyte draining velocity on its density is an important characteristic, since the battery cycling process is followed by change in density of the acid. Such dependence in future will be determined by empirical method.

3. Experimental part and discussions

3.1. Experimental method

As the object of investigation the use was made of the glass-mat separator SKIN –1.05. The strip of the separator measuring 900 mm × 40 mm was placed between vinyl plastic plates in gap of 2 mm. After placing the separator in the unit its both halves were uniformly compressed over the entire length by means of bolts and nuts. The structure assembled in this way was placed horizontally into the bath filled with electrolyte to impregnate the separator for 2–3 days. After impregnation the unit was mounted vertically into the beaker for collection of drained liquid and the entire structure was sealed by means of the polyethylene envelope to prevent loss of electrolyte through

evaporation. The unit was held in the vertical position for 15 days. At the end of this time the unit was disassembled in the vertical position and the separator was cut into nine parts each of which was weighed separately. After that the curve of dependence of electrolyte distribution over the height of the separator was built. The change in degree of compression of the separator was achieved by placing several layers of separator in the gap of the unit. As electrolyte the use was made of sulfuric acid with density 1.10 and 1.28 g/cm³.

3.2. Effect of degree of compression of the separator

One to four layers of the separator were placed in the gap of the unit. The degree of compression of the separator was determined by the equation

$$K = \left(1 - \frac{a}{n\delta}\right) 100\% \quad (9)$$

where a is the magnitude of the gap of the unit, n the number of layers of the separator, δ the thickness of the separator. As electrolyte the use was made of sulfuric acid with density 1.28 g/cm³. Fig. 1 shows the results of the experiment on

evaluation of the effect of degree of compression of the separator on distribution of electrolyte over its height.

It follows from data of Fig. 1 that losses of electrolyte by the separator with degree of its compression 0% (one layer), in total, amounts to 36% of its initial content. In this case there is a monotonous drop in content of the electrolyte over the height of the separator. At a height of 800–900 mm, losses of electrolyte amounted to approximately to 50%, and in the lower section, maximum 5%. The increase in the degree of compression of the separator when placing two to four layers in the gap results in significant reduction of losses of electrolyte (Fig. 1a). Similar conclusions were drawn earlier in analysis of the Eq. (3), from which it follows that losses of electrolyte drop with decrease in porosity of the separator ($g \sim R^2$), which in turn is proportional to the degree of compression of the separator.

Thus, by increasing the degree of compression by placing the respective number of layers of the separator in the inter-electrode gap (IEG) one can achieve the practically complete retention of electrolyte over the height of the separator. However, one should keep in mind that increase in the number of layers of the separator is equated to decrease in its porosity and hence reduction in absolute quantity of

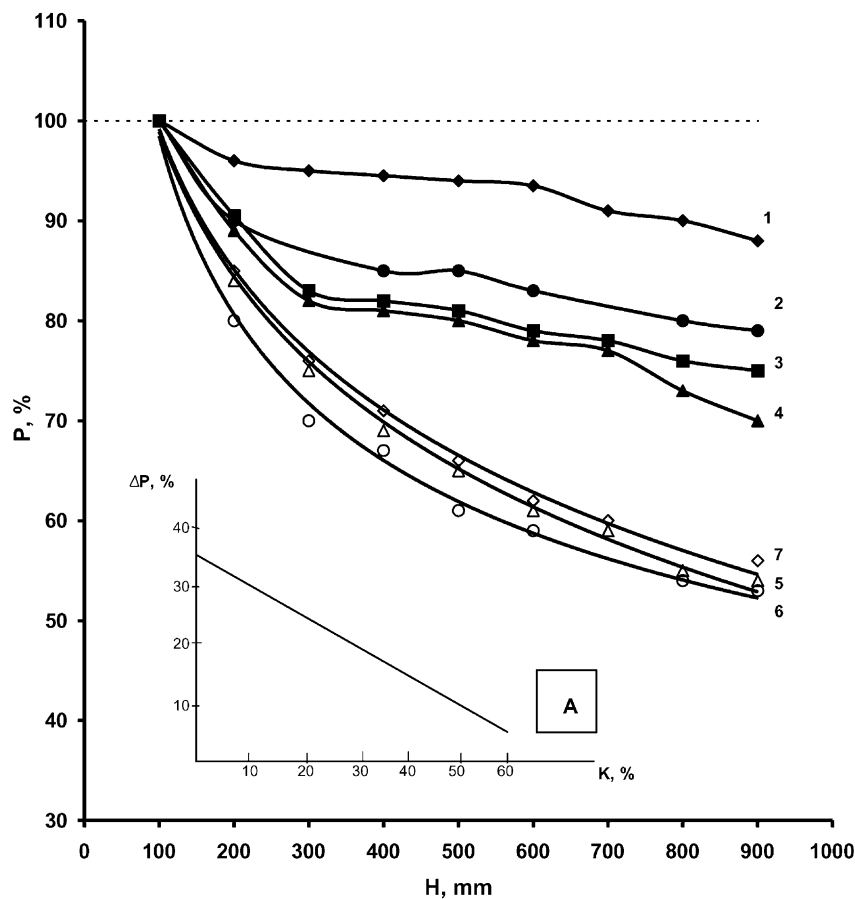


Fig. 1. Distribution of electrolyte by separator height. Number of layers in inter-electrode gap: one (5, 6, 7); two (3, 4); three (2); four (1). $P = (P_1/P_2)100\%$, where P_1, P_2 accordingly weights of 1/9 of separator band before and after testing. (a) Dependence of relative losses of electrolyte upon separator compression degree (K). P is the relative separator weight change after testing.

acid in IEG. Considering that acid in the lead-acid battery is an active participant of the current generation process (3.36 g H₂SO₄/Ah) it should be expected that reduction in stock of acid may result in loss of capacity of the battery even if its distribution over the height is ideal.

The other negative point associated with increase in the degree of compression of the separator is a possible effect of drop in porosity on efficiency of oxygen cycle in the encapsulated batteries. It was indicated earlier that implementation of the oxygen cycle is possible in presence of gas pores in the separator through which filtration of oxygen occurs from the positive to the negative electrode. One can expect that with higher compression of the separator the volume of gas (large) pores will drop, which will result in decrease in efficiency of the oxygen cycle.

3.3. Effect of density of electrolyte

In accordance with the earlier analysis the draining rate of electrolyte does not unequivocally depend on its concentration. On one hand, with decrease in density of the electrolyte (ρ), ΔP drops, which decreases the draining rate of electrolyte, since in accordance with (3) $W \sim \Delta P$. On the other hand drop in density of acid is followed by reduction in its viscosity, which improves the draining rate, since $W \sim \eta^{-1}$. Thus, establishment of the dependence $W = f(\rho)$ is best to be made by empirical method. This relationship is extremely important, since in the cycling process of the battery there takes place the change in the concentration of acid and one should be confident that drop in density of the acid upon discharge does not entail the irrevocable decrease in level of electrolyte in the separator.

For the experimental evaluation of the effect of density of the acid on the electrolyte retention, its distribution over the height was investigated with design degree of compression of 0–70% (one to four layers) with the use of acid with density of 1.10 and 1.28 g/cm³. The results are shown in Fig. 2.

It is seen from Fig. 2 that with one layer of the separator (degree of compression 0%) the density of acid does not influence the nature of distribution of the electrolyte over the height of the separator. With the use of two and three layers one can speak about weak effect of the density of acid on the nature of distribution of the electrolyte. So with two layers the total loss of electrolyte with density of 1.10 g/cm³ amounts to 76.9% and with density of 1.28 g/cm³, 79.7%. However, with use of four layers (degree of compression 62%) one can see a significant difference in the slope of curves $P = f(H)$. With the use of acid with density of 1.10 g/cm³ the said curve lies significantly lower than for the acid with density of 1.28 g/cm³. Total volume of loss of electrolyte for the first case amounts to 80% and for the second case –92%. Such a complicated nature of relationship $P = (H, \rho)$ is associated with simultaneous action of a number of factors. For explanation of observed experimental facts one could suggest the following model of the process.

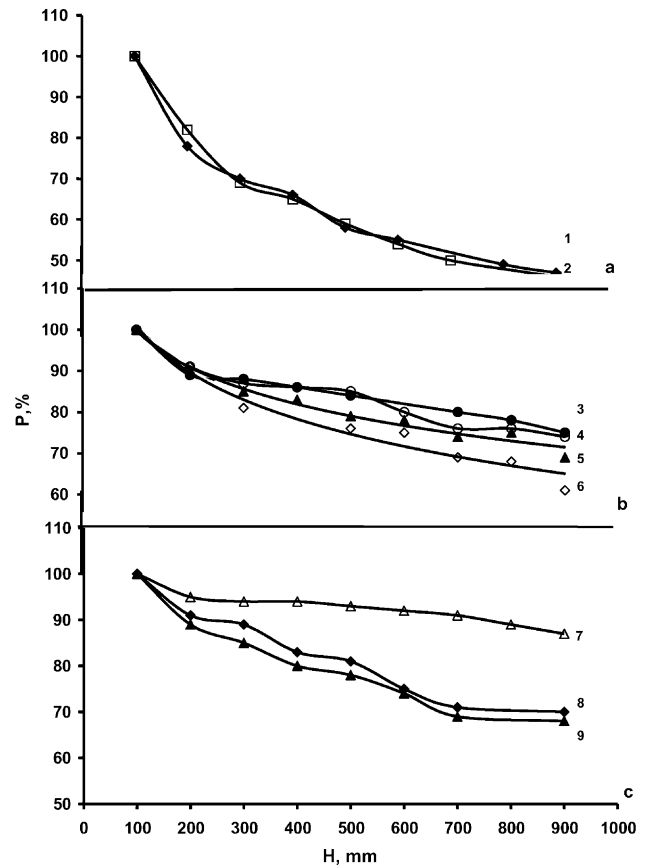


Fig. 2. Curves of electrolyte distribution by separator height at compression degree 0% (a); 28–37% (b); 62% (c) and electrolyte density 1.10 g/cm³ (2, 4, 6, 8, 9) and 1.28 g/cm³ (1, 3, 5, 7).

With lower degree of compression of the separator the latter is noted for large pore structure and electrolyte drains down the separator at a rate described by the Eq. (3) over the vertical through pores and is retained on the stable basis in blind-end and ring pores. In accordance with the Eq. (3) the electrolyte drain rate depends on its density through pressure difference ΔP and viscosity of the electrolyte η . The pressure difference is related to the acid density by means of the evident ratio $\Delta P = \rho V$, where V is the volume of the electrolyte in the separator. It is known [2] that in the range of densities 1.10–1.28 g/cm³ the viscosity will change in the linear manner with increase in density of acid, i.e. $\eta = a\rho$, where a is a proportionality factor. Having inserted ratios into (3) we will get

$$W = \frac{\pi V \tau R^4}{8a} \tag{10}$$

It follows from (12) that the drain rate does not depend on the density of the electrolyte, as it follows from Fig. 2.

However, as degree of compression of the separator increases and size of pores diminishes, the noticeable role in retention of electrolyte is played by capillary forces. The magnitude of the capillary pressure (p_c), defining the level of filling the pores, is proportional to $\cos \theta \gamma/r$, where θ is the wetting angle, γ the surface tension.

It is known [2] that the magnitude of surface tension increases with increase of density of the electrolyte, which results in growth of the capillary pressure and increase in level of filling the pores of the separator with electrolyte at expense of larger pores. Thus, with higher degrees of compression, the drop in density of the electrolyte leads to a noticeable increase in its losses by the separator.

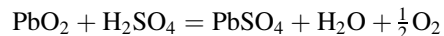
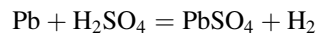
Thus, the presented data indicates that in the range of degree of compression 0–40% and density of the electrolyte 1.10–1.28 g/cm³, the acid concentration poorly affects the nature of its distribution over the height of the separator, which allows the stability of electrolyte retention in the course of charge–discharge cycles to be expected.

3.4. Effect of contact of the separator with the electrodes on distribution of electrolyte over the height of the separator

For evaluation of the effect of contact of the separator with the real electrodes on the height of the electrolyte retention, the separator was placed in the test unit between the strip cut out of the electrode. The system electrode/separator/electrode assembled in the unit was impregnated in the horizontal position for 48 h and was further held in the vertical

position for 14 days. The results of evaluation of the distribution of electrolyte over the height of the separator with degree of compression 0, 38 and 58% are shown in Fig. 3.

It is seen from the Figure that with the same number of layers of the separator the curves $P = f(H)$ for the system electrode/separator lie significantly lower than the similar curves for the system vinyl plastic/separator. Formally, there can be three reasons. Firstly, the difference in the uniformity of thickness of vinyl plastic plate and the electrode could result in different degree of compression of the separator. The thickness of vinyl plastic is sufficiently uniform over the surface, while the thickness of the real electrode is not uniform along its surface. Secondly, there is a possibility of re-distribution of electrolyte between the separator and porous electrode. And finally, self-charge of the electrode, corrosion of current collectors take place in the course of the test, which binds a certain quantity of acid to sulfate according to the reactions



Effect of the non-uniformity of degree of compression on the slope of the discussed curves is not evidently a determining

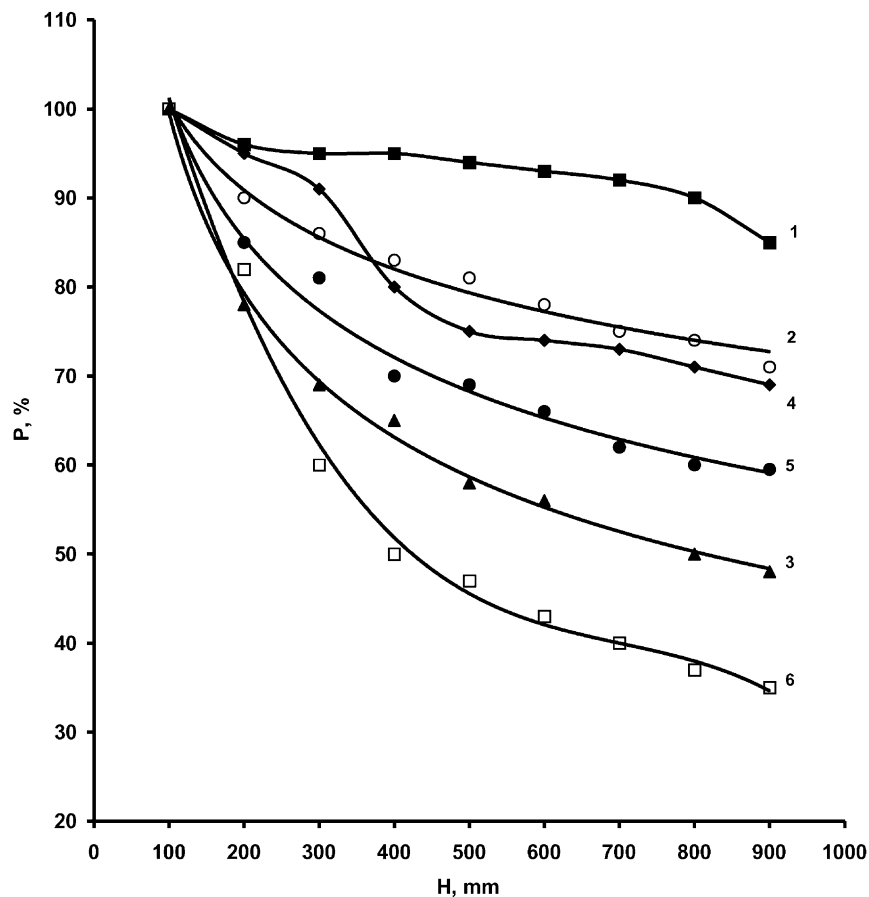


Fig. 3. Distribution of electrolyte by separator height. Number of layers: one (1, 4), two (2, 5), three (3, 6). System of electrode/separator: 4–6; system of vinyl plastic/separator: 1–3.

Table 1
Relative loss of acid by separator

Systems	Relative loss of acid (%)			
	Number of layers of separator layers			
	One	Two	Three	Four
Separator — vinyl plastic (A)	63.2	79.7	82.3	92.0
Separator — electrode (B)	54.7	70.3	71.3	78.8
A/B 100%	86.6	88.2	86.7	85.6

factor, since with the zero degree of compression (one layer of the separator) the curves $P = f(H)$ for the system electrode/separator lie noticeably lower. Re-distribution of electrolyte between the elements of the block is also unlikely, since the lengthy preliminary impregnation should secure complete filling of the pore spaces of the elements of the block in accordance with their pore structures. The third suggestion is favored by the fact that in the course of the test the mean density of the electrolyte dropped from 1.28 to 1.20 g/cm³. It is important to note that the degree of compression, while affecting the total loss of acid by the separator, does not affect the magnitude of shift of the curves with transition from the contact with vinyl plastic to the contact with porous electrode. It is seen from Table 1 that regardless of the degree of compression of the separator, drop in the content of the acid in the separator for the system electrode/separator amounts to 85.6–88.2% of the drop of acid content for the system vinyl plastic/separator.

Thus, one can suggest that the contact of the separator with the electrode results in higher loss of acid due to its binding in the electrode, which is not an irrecoverable loss of electrolyte.

4. Conclusions

Investigation of the effect of state of the separator on the degree of electrolyte retention showed that through increase in the degree of compression of the separator it is possible to secure up to 90% of retention of electrolyte in the separator

800 mm high. The maximum quantity of acid in the separator corresponds to the relative degree of compression of approximately 40–50%, while the degree of electrolyte retention amounts to 82%.

Effect of concentration of acid on the degree of electrolyte retention depends on the degree of compression of the separator. With the degree of compression 0–40%, the acid density affects but little its distribution over the height of the separator. With the degrees of compression over 50–60% drop in the acid density results in increase of its losses in the separator.

Thus, increase in the degree of compression of the separator is the major means for electrolyte retention over its height. However, this can result in reduction of volume of large gas pores and, consequently, in decrease of efficiency of the oxygen cycle. Optimization of electrolyte do takes place in the cycling process of the electrode block. In the initial moment the pre-impregnated block has practically no gas pores and upon charge oxygen has minimal resistance to its movement upwards to the sub-cover space, than to the movement through the separator filled with electrolyte. In this moment the efficiency of the oxygen cycle is extremely low and there takes place a buildup of pressure inside the battery. With decomposition of water the content of electrolyte in the block decreases till the separator pores are freed and the mechanism of filtration of oxygen through the separator to the negative electrode becomes possible. The efficiency of oxygen cycle rises, losses of oxygen drop and the optimization of quantity of acid in the block occurs. Based on this mechanism, the drop in volume of gas pores in the separator upon its compression should not noticeably affect the efficiency of the oxygen cycle.

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