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A universal way for gas–liquid flow control in the design of hermetical lead-acid batteries☆

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ABSTRACT

The paper demonstrates the capabilities of our technique of implementation of the oxygen and hydrogen cycles in hermetically sealed lead-acid batteries with forced gas feed to the pores of the working electrodes. It is based on optimization of the porous structures of the separation materials and gas-absorbing electrodes, reducing free gaps in the interelectrode gap down to the large pores of the working electrodes. Such a structure of the interelectrode gap matrix provides a fine-jet gas flow (the filtration transfer mechanism is realized); the excessive pressure in the interelectrode gap (in the separator pores) exceeds the capillary pressure on the electrode pores, as a result, the gas displaces the electrolyte from some pores of the electrode and these pores get partially filled with the gas. The fine-jet gas flow is characteristic of fine-porous separators tightly fitting to the electrode surface.

The authors offer methods to increase the rate of gas absorption on the working (lead and lead-dioxide) electrodes based on compulsory gas feed into the electrode pores, which are practically cost-free but allow designing of completely hermetical batteries. It is especially important now in the development of hermetical lead-acid batteries which should replace valve-regulated ones.

1. Introduction

The possibility of creating hermetical batteries of new generation, which would not be inferior to the open systems in their capacity characteristics and lifetime, is based on the implementation of gas cycles (release and absorption of gas in the battery) with the use of working electrodes functioning as the gas-diffusion electrodes in fuel elements.

The directed selection of separation materials to provide the creation of common interelectrode space, which enables the gas-diffusion flow to be effectively managed, is a basic task in improving valve-regulated lead-acid batteries and designing hermetically sealed ones. Here we demonstrate the capabilities of our technique at realization of the oxygen and hydrogen cycles in hermetically sealed lead-acid batteries with forced gas feed to the pores of the working electrodes.

Let us consider in brief some macrokinetic regularities of the gas–liquid flow management at charging of hermetical batteries. How gas passes through separation materials is analyzed in Ref. [2]. Three types of the ratio between the structures of the interelectrode gap and electrode with various mechanisms of gas feed and absorption have been resolved and conditionally called the coarse-jet, fine-jet, and combined flows. Fig. 1 schematically shows the gas flow mechanisms within the interelectrode gap in the battery at charging.

At coarse-jet flow (Fig. 1 (I, I′)), the gas on passing the separator has the pressure P_0 but its excessive pressure ΔP ($P_0 = P_{atm} + \Delta P$) is lower than $4\sigma/D_2$ ($\Delta P \ll 4\sigma/D_2$ ($D_1 \gg D_2$)), which prevents the gas from getting into the electrode pores, and its absorption takes place on the frontal surface of the electrode only (σ being the surface tension). Coarse-jet flow is typical of coarse-pore rigid woven separators poorly adjacent to the electrode, with a noticeable separator–electrode gap.

At fine-jet flow (Fig. 1 (II, II′)), the gas has its excessive pressure $\Delta P \geq 4\sigma/D_2$ ($D_2 \gg D_1$), and gas ionization occurs in the electrode pores. Such a type of flow is characteristic of very fine-porous, soft separators with no regular structure, which are tightly adjacent to the electrode surface.

Combined flow (Fig. 1 (III, III′)) is characterized by gas absorption starting with course-jet flow, which then turns into fine-jet one because the pressure in the gas phase continues rising and reaches a value sufficient for the gas to enter the electrode pores. The gas is absorbed both on the frontal electrode surface and in the largest pores.

Fig. 2 presents the calculated values of the transitional characteristics of gas pressure in the interelectrode gap of hermetical batteries (a) and gas ionization currents (b) for several flow modes

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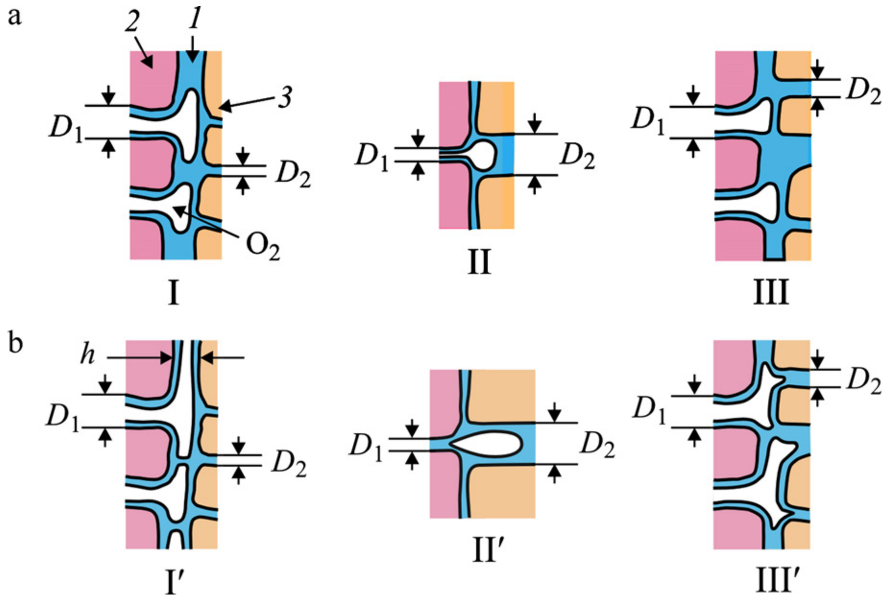

Fig. 1. Gas flow mechanisms in the interelectrode gas of the battery at charging: I, I′ – coarse-jet flow ($\Delta P \ll 4\sigma/D_2$; $D_1 \gg D_2$); II, II′ – fine-jet flow ($\Delta P \geq 4\sigma/D_2$; $D_2 \gg D_1$); III, III′ – combined flow. I, II, III are for the beginning of gas absorption; I′, II′, III′ are for the instance of stationary state establishment. D_1 – the diameter of the largest separator pores; D_2 – the diameter of the largest electrode pores. 1 – electrolyte solution; 2 – separation; 3 – pores of the electrode.

in a layered porous medium: the coarse-jet mode, fine-jet mode, and combined mode of gas flow.

Fig. 3 shows ranges of pore sizes of the separation matrix and electrode filled with gas (dashed): 1 – size distribution of pores for the electrode; 2 – that for the separation matrix.

We have shown experimentally [1] that the fine-jet and combined flows in the interelectrode gap of the battery, finally, provide high rates of gas ionization at charging. However, the fine-jet flow is preferable not only due to its provision of higher reliability of the system but also due to a lower gas filling degree of the interelectrode gap, which influences the Ohmic voltage loss at charging.

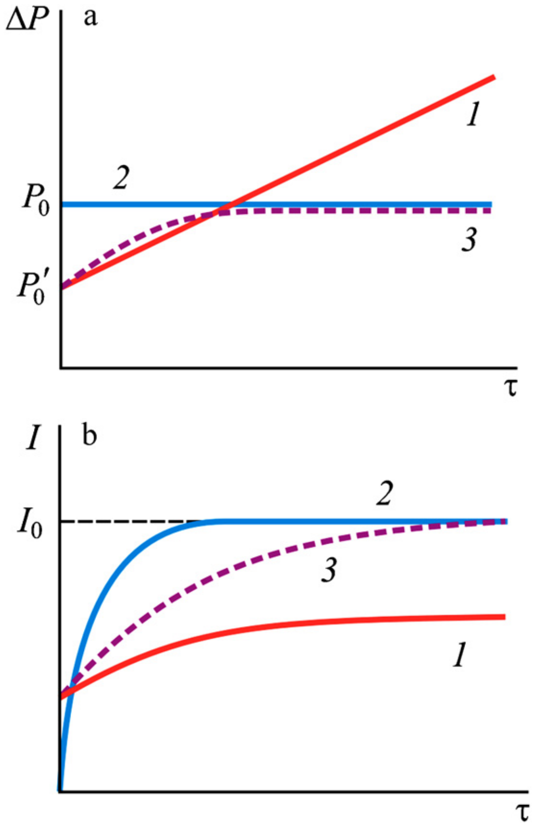

Fig. 2. Calculated values of the transitional characteristics of gas pressure in the interelectrode gap of hermetical batteries (a) and gas ionization currents (b) for several flow modes in a layered porous medium: 1 – the coarse-jet mode ($\Delta P \ll 4\sigma/D_2$; $D_1 \gg D_2$); 2 – the fine-jet mode ($\Delta P \geq 4\sigma/D_2$; $D_2 \gg D_1$); 3 – the combined mode of gas flow. ΔP is the excessive pressure in the gas phase; P_0 – the gas pressure in the electrolyte, *I* – the gas absorption current.

2. Experimental

Our working electrochemical cell was designed as a mock-up of the hermetical self-dosing lead-acid battery – a three-electrode tight-assembly block with one gas-generating electrode (at the center) and two gas-absorbing ones (by sides) with a layer of separation material between (Fig. 4). Besides, two symmetrically arranged high-capacity lead-dioxide and lead electrodes were used as auxiliary ones to avoid extra gas release. The electrode block assembled in the said sequence was placed between two Vinyplastic^{TM} plates with permanent pressing. Battery sulfuric acid (an aqueous H_2SO_4 solution, $d = 1.28\,g\,cm^{-3} + Na_2SO_4$ added to $d = 1.30\,g\,cm^{-3}$) served as the electrolyte.

The rate of electrochemical oxygen reduction was measured potentiostatically by current changes of cathode polarization of the charged lead electrode when gaseous oxygen entered to the separator–electrode system. The rate of hydrogen oxidation on the lead-dioxide electrode was measured similarly, save switching of the positive and negative electrodes in the scheme.

Formed plates of the lead (the thickness 1.00 mm) and lead-dioxide (the thickness 1.16 mm) electrode of the 12 SAM-28P aircraft lead-acid batteries (Electroistochnok Corp.) were used as working gas-generating and gas-absorbing electrodes. Working 3 cm × 4 cm electrodes were cut from these plates.

Samples of glass absorptive matrices of several types and acid-resistant asbestos paper (which forms an almost ideal porous

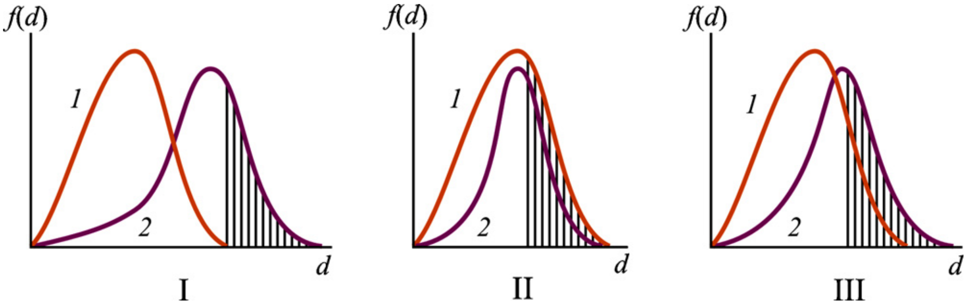

Fig. 3. Range of pore sizes of the separation matrix and electrode filled with gas (dashed): 1 – size distribution of pores for the electrode; 2 – that for the separation matrix. I – the coarse-jet mode ($\Delta P \ll 4\sigma/D_2$; $D_1 \gg D_2$); II – the fine-jet mode ($\Delta P \geq 4\sigma/D_2$; $D_2 \gg D_1$); III – the combined mode of gas flow.

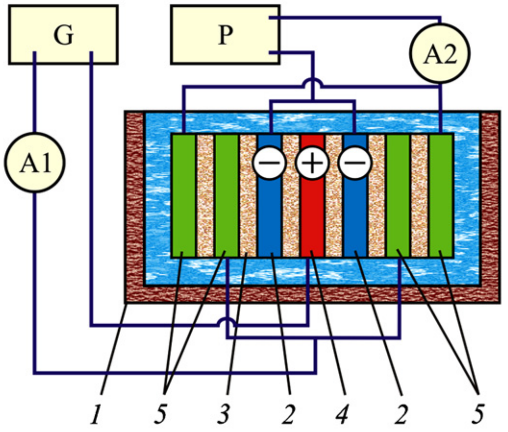

Fig. 4. A scheme of the cell for exploring the oxygen reduction reaction on the lead electrode: *G* is a galvanostat, *P* – a potentiostat, *A*1 and *A*2 are ampermeters, 1 – a cell, 2 – porous lead electrodes for oxygen absorption, 3 – a separator, 4 – a lead-dioxide oxygen-generating electrode, 5 – auxiliary electrodes.

structure of the interelectrode gap) were applied as separators. The programs of the examined porous matrices measured by means of contact reference porometry [3] are presented in Fig. 5.

As is seen from Fig. 5, the separator samples taken are highly porous systems, their total porosity being 90–95%.

The formed electrodes are less porous systems with the porosity not exceeding 40–50% (Fig. 5). The size of the large pores in the lead-acid battery electrodes is in accord with the porous structure of the separation materials tested, which should provide effective gas absorption on the working electrodes at charging.

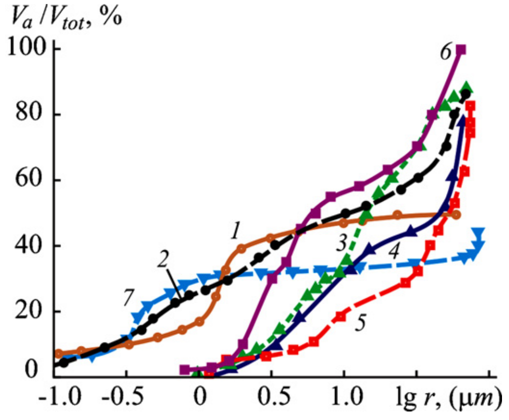

Fig. 5. Radius distributions of the pore volume of the lead electrodes and several porous matrices: 1 – the lead electrode; 2 – "blue" asbestos; 3 – porovinyl; 4 – PPF-70; 5 – glass fiber; 6 – the Keratech group AGM; 7 – the lead dioxide electrode.

3. Studying oxygen absorption on the lead electrode under forced gas feed

Fig. 6 depicts the dependences of the efficiency of oxygen ionization (*Ia*/*Ig*) on the lead electrodes in battery mock-ups with the separators made of the glass absorptive matrices ("Keratech group", the thickness 0.58 mm), glass fiber and asbestos matrices on the oxygen release rate (*Ig*) on the lead-dioxide electrode.

As is seen from Fig. 6, the oxygen ionization efficiency (the absorption/release current ratio) in the conditions simulating battery high-current recharging can achieve 60 and 80–100% for the glass absorptive and asbestos matrices, respectively.

The higher efficiency of oxygen absorption in our hermetical mock-ups with the asbestos separator is due to the ideal coincidence of its porous structure with that of the electrodes and tighter adjoining to the working electrodes' surface.

Figs. 7 and 8 show the gas filling degree of the negative lead electrode in several models of hermetical lead batteries: 1 – asbestos fiber, 1′ – the same with gas feed from both sides, 2 – glass fiber, 3 – PPF-70 (Petrianov's perchlorovinyl filters).

The amount of gases in the negative electrode was estimated from the current drop curve for oxygen reduction on the lead electrode after turning polarization off (Fig. 9).

As follows from Fig. 7, high rates of oxygen reduction are achieved at low gas filling degrees, not higher than 5–15% of the pore volume.

The linear dependence of current on the gas pore surface of the lead electrode (Fig. 10) points to the predominant contribution of these pores to the total current. The gas pore surface of the negative electrode was calculated by the gas filling degree of the electrode and the radius distribution of pore volumes (Fig. 5). The intensity of

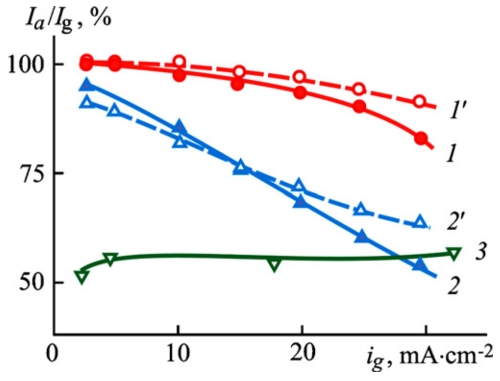

Fig. 6. Influence of the way of gas feed to the lead electrode on the relative rates of its ionization in several models of hermetical lead batteries: 1, 1′ – asbestos; 2, 2′ – glass fiber; 3 – the Keratech group AGM 1, 2, 3 – one-side feed; 1′, 2′ – two-side feed.

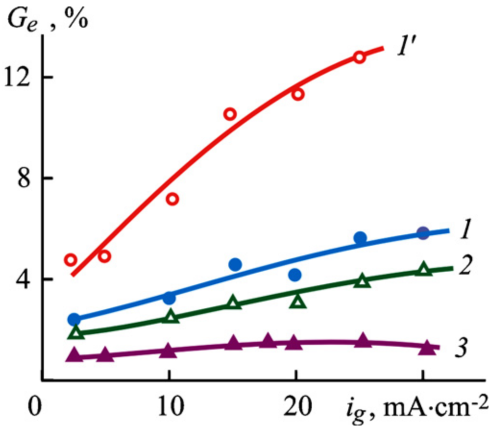

Fig. 7. Gas filling degree of the negative lead electrode in several models of hermetical lead batteries: 1 – asbestos fiber, 1′ – the same with gas feed from both sides, 2 – glass fiber, 3 – PPF-70.

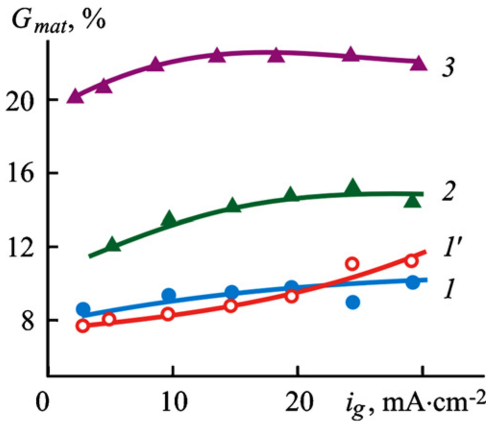

Fig. 8. Gas filling degree of the separation matrices in several models of hermetical lead batteries: 1 – asbestos fiber, 1′ – the same with gas feed from both sides, 2 – glass fiber, 3 – PPF-70.

the process under the electrolyte film on the pore walls calculated from the $I - S_{\text{газ}}$ slope is 4–6 mA cm^{-2}.

By the way, the intensities of the processes under films on the gas-filled cadmium and lead electrodes are close to each other [1].

Thus, a universal way of managing the gas–liquid flow at charging batteries has been developed. It is based on optimization of the porous structures of the separation materials and gas-absorbing electrodes, reducing the separator–electrode gap down to the diameter of the largest pores of the working electrodes. Such a structure of the interelectrode gap matrix provides a fine-jet gas flow (the filtration transfer mechanism is realized); the excessive pressure in the interelectrode gap (in the separator pores) exceeds the capillary pressure on the electrode pores, as a result, the gas displaces the electrolyte from some pores of the electrode and these pores get partially filled with the gas. Even a 5–10% gas filling degree of the working electrodes leads to an increase in the oxygen ionization rate by two orders of magnitude and equals it with the gas release currents at charging by hour modes. The fine-jet gas flow is characteristic of fine-porous separators tightly fitting to the electrode surface (to make the separator–electrode gap hermetical).

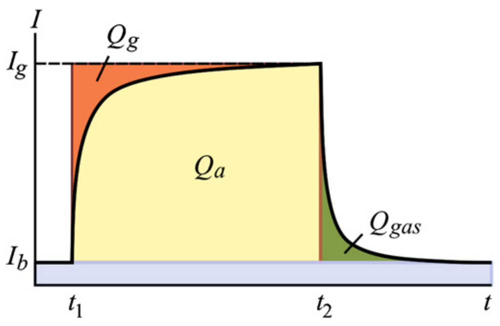

Fig. 9. Variations of the cathode current on the porous lead electrode at oxygen feed into the separator–electrode system t_1 is the onset of oxygen release; t_2 the instant of switching off the galvanostatic circuit of oxygen release; Q_g and Q_a are the quantities of electricity spent for release and absorption of oxygen; Q_{gas} the quantity of electricity spent for ionization of the oxygen in the pores of the electrode.

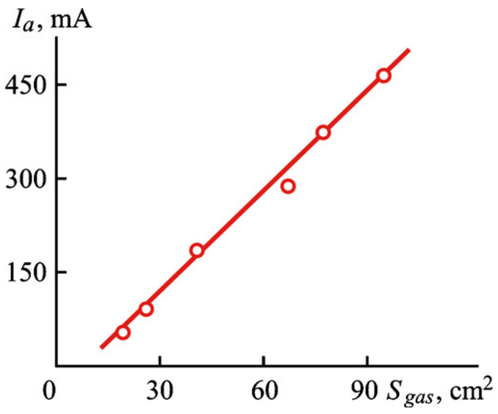

Fig. 10. Oxygen reduction current as a function of the area of gas sites in the pores of the lead electrode (two-side gas feed). The working area of the electrode is 5.25 cm^2 × 2.

4. Studying hydrogen ionization on the lead-dioxide electrode under forced gas feed

Let us proceed to the hydrogen cycle macrokinetics in lead-acid batteries.

Fig. 11 shows the curve of potentiostatic turning on of the porous lead-dioxide electrode on hydrogen feed to it. t_1 is the hydrogen release onset.

Fig. 12 depicts the influence of the hydrogen release rate on the ionization rate on the porous lead-dioxide hydrogen-filled electrode (an asbestos matrix).

In order to make sure that the experimentally measured currents in the potentiostatic circuit are hydrogen oxidation currents rather than anode hydrogen-stimulated oxygen release currents, we have compared our coulombimetric and volumetric data obtained in the same experiments. It has been found that the

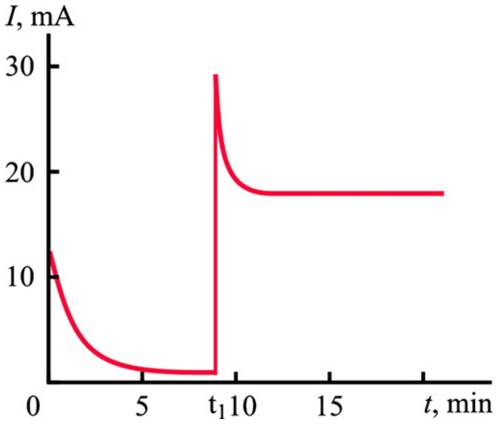

Fig. 11. Curve of potentiostatic turning on of the porous lead-dioxide electrode on hydrogen feed to it. t_1 is the hydrogen release onset E = 1.25 V (MSE).

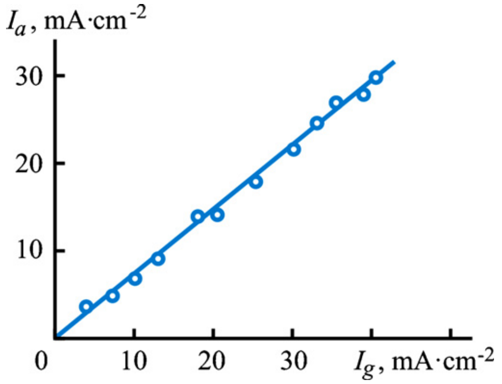

Fig. 12. Influence of the hydrogen release rate on the ionization rate on the porous lead-dioxide hydrogen-filled electrode (an asbestos matrix) $E = 1.25$ V (MSE).

amount of gas collected volumetrically matches that calculated from coulombimetric data with a 10% accuracy. The latter was calculated as the difference between the integrals of the hydrogen release current in the gas-generation circuit and the current of its assumed oxidation on the electrode under study in the potentiostatic circuit (Fig. 13).

Fig. 14 presents the dependence of the hydrogen ionization efficiency at several release rates in lead-acid mock-ups with tight assemble of the electrodes with the separators studied (the Keratech group matrix and the asbestos one).

In the whole, it should be noted that the hydrogen cycle efficiency in our mock-ups is somewhat lower than that of the oxygen cycle. It does not exceed 50% for the glass absorption matrix separator. When the separator is made of the asbestos matrix, the hydrogen absorption efficiency is higher and can reach 72%.

The obtained values of the hydrogen absorption degree are also caused by partial filling of the pores of the lead-dioxide electrode with hydrogen and show the principal possibility of hydrogen cycle implementation in hermetical lead-acid batteries.

The state of the surface of the lead-dioxide electrode determined by its polarization is another factor influencing the hydrogen ionization rate. The results obtained in our work show that the increase of the potential of the lead-dioxide electrode from 1.25 to 1.40 V (MSE) results in an increase of the hydrogen absorption efficiency (Fig. 15).

Therefore, the usage of the principle of forced hydrogen feed to the lead-dioxide electrode pores also enables raising the hydrogen ionization rate up to currents close to the hydrogen ionization currents on the negative electrodes at charging. The degree of hydrogen ionization enhancement still depends of the gas filling degree of the electrode, determined by the structure of the interelectrode gap. Just as in the case of oxygen ionization, the process of hydrogen ionization is mainly located under electrolyte films in the pores of the electrode, where its intensity is few mA cm^{-2}. Our studies and results obtained point to the principal possibility of using the lead-dioxide electrode for hydrogen cycle implementation in lead-acid batteries.

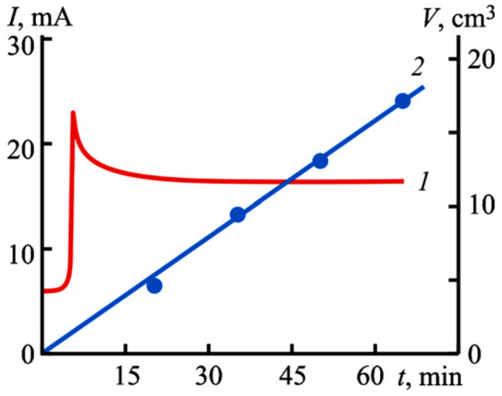

Fig. 13. Comparison of coulombometric (1) and volumetric (2) experiments at hydrogen ionization on a porous electrodes made of lead dioxide (an asbestos matrix). The hydrogen release current is 48 mA, the electrode dimensions are 3.0 cm × 2.7 cm.

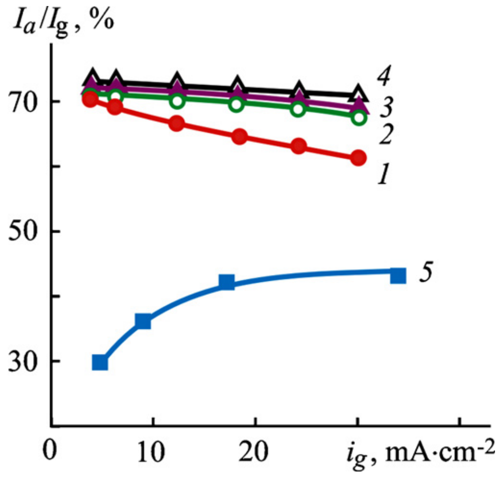

Fig. 14. Influence of the density of asbestos separation matrices on the hydrogen ionization rate on porous lead-dioxide electrodes: 1 – 0.25; 2 – 0.28; 3 – 0.32; 4 – 0.35 g cm^{-3} (for comparison: 5 – the Keratech group AGM).

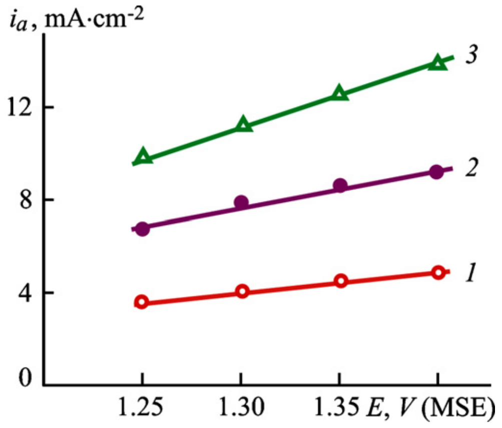

Fig. 15. Influence of the lead-dioxide electrode polarization on the hydrogen ionization rate at several hydrogen feed rates (asbestos). Hydrogen release currents are (mA cm^{-2}): 1 – 5; 2 – 10; 3 – 15.

5. Conclusions

- The principle of forced gas feed to the electrode pores was used by us to implement the oxygen and hydrogen cycles in hermetical lead-acid batteries.
- However, the macrokinetic regularities of gas ionization on the working electrodes have much in common with those observed in hermetical NiCd and NiMH batteries [1]:
  - The gas ionization rate can really be increased by two orders of magnitude by means of forced gas feed to the electrode pores.
  - The intensity of gas reduction rises with the gas filling degree of the working electrodes.
  - The character of changes of the reduction current and that of the pressure value in the interelectrode gap in time points to the quick establishment of the stationary state of the system.

- When the pore structures of the separator and electrode are related optimally, a united gas–liquid network in the interelectrode gap is formed to provide the filtration mechanism of gas transfer to the surface of the electrode.
- Provided that the gas filling degree is optimal, gas ionization mainly proceeds on the surface of the pores of the working electrodes under electrolyte films of a micronic thickness with an intensity of few mA cm^{-2} independently of the electrode material nature.

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