

New additives to active masses of sealed lead storage battery

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Abstract

Effect of high-collated carbon clusters (HCC; soots containing fullerenes and nanopipes) on electrode pastes structure have been studied and their positive effect on characteristics of the obtained active masses has been shown. Effect of partial hydrophobization of negative active mass (NAM) on efficiency of the closed oxygen cycle has been studied. Positive effect of fluoroplastic addition to the NAM on the oxygen reduction rate across the negative electrode has been shown.

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1. Introduction

Additives of various kinds are introduced to the active mass formula with the aim to improve electric characteristics of lead storage batteries and to prolong their life. Additives, strengthening the positive active masses (PAM), expanders of the negative active masses (NAM), inhibitors of self-charge are well known. But working conditions of an sealed lead storage battery (VRLA) impose additional requirements on additives and frequently such requirements limit their application or make it necessary to use additives of new types, which are not used in ordinary filled batteries. For example, usage of strengthening polymer organic fibers in the PAM of an sealed lead battery is not desirable due to their oxidation in the positive electrode working conditions, irreversible oxygen absorption, reduced depolarization of the negative electrode and increased rate of hydrogen evolution, which finally results in the reduced service life of a battery.

Another method of obtaining strong active masses using pastes containing tetrabasic lead sulphate (4BS) is known. Coarse crystals of PbO_2 obtained as a result of metasomatic oxidation of 4BS form a space frame, which ensures increased strength of active masses and prolonged service life of batteries [1–3]. In our papers [4,5], we have shown that the service life of the active masses obtained from the pastes containing $4\text{PbO}\cdot\text{PbSO}_4$ has been 1.6–1.8 time longer

than the service life of the active masses obtained from the ordinary pastes (PbO , $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$, $\text{PbO}\cdot\text{PbSO}_4$, PbSO_4) with some decrease in specific power characteristics. Possibility of obtaining coarse-crystalline prismatic structure of pastes by using high-collated carbon clusters (HCC) in the technological process of their preparation (fullerenes, nanopipes) is studied in this paper.

The high-collated carbon clusters (HCC) are graphite surfaces, laid of regular hexagons with carbon atoms located at the apexes. In the case of the fullerenes, such surface has a closed spherical shape [5–7], and in the case of the nanopipes, it has a shape of a hollow cylinder [8]. Such structures can be obtained at graphite atomization in an electric arc with graphite electrodes in helium shield. In this case, the soot, deposited on the walls of a gas-discharge chamber, contains up to 20% of fullerenes, the main components of which are C_{60} and C_{70} , and the soot, deposited on the cathode surface directed to the inter-electrode gap, contains extended structures, which represent graphite layers rolled in one-layer or multi-layer pipes. The HCC are distinguished by their high specific surface, chemical stability, adsorption ability and significant electric conductivity. It is felt that being absorbed on the surface of growing crystals of the sulphates, the HCC can produce great effect on overtension of separate faces crystallization depending on their adsorption ability and, finally, it can produce some effect on a shape of the growing clystalls. Effect on paste structure and characteristics of obtained active masses, soots, containing fullerenes and nanopipes, has been studied to check this assumption.

Additives, which influence on the efficiency of the oxygen cycle, are known. Thus, paper [9] shows that Sn, Se and Co

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added to the electrolyte increase conductivity of sulphate films in relation to the molecular oxygen and, hence, increase efficiency of the oxygen cycle. It is universally accepted, that oxygen electrochemical reduction (OEcR) rate is limited by its diffusion in the electrolyte. Therefore, on the one hand, the OEcR rate will be maximum at places, where separator gas channels cross the negative electrode surface, since on this boundary the thickness of the diffusion layer is minimal ($\sim 0.1 \mu\text{m}$), and, on the other hand, this surface will increase with oxygen pressure growth in the separator pores, since in this case quantity of separator pores, from which electrolyte can be displaced, increases. Spreading of the OEcR process to the depth of the negative electrode is hindered due to increased diffusion layer and a low ratio of oxygen transfer in the electrolyte. An OEcR rate can be increased by increasing the reaction surface, on which the OEcR process can be realized, for example, by increasing a quantity of gas pores in the separator. But, in this case, its resistance will increase and electrolyte reserve in the electrode block will be reduced. Possibility of expanding the reaction surface of the OEcR process at the expense of its spreading to the depth of the negative electrode by partial hydrophobization of the NAM has been investigated in this paper. The NAM surface hydrophobization will ensure some displacement of the electrolyte from surface pores of the negative electrode due to increased oxygen pressure in the separator pores at the end of the charge and will increase three-phase reaction boundary, on which the OEcR process takes place. Increase in OEcR efficiency will make it possible to intensify the charging process and to reduce its duration. Effect of the NAM hydrophobization by adding fluoroplastic suspension on the OEcR process efficiency has been studied in this paper.

2. Experimental and discussion

2.1. Additives strengthening PAM

Effect of the HCC on the structure of electrode pastes and characteristics of obtained PAM has been studied in this paper. With this purpose lead powders have been treated, using a special technology, either with a solution of fullerene-containing soot (FCS), or with a suspended of soot, containing nanopipes (NCS). The FCS was a soot, taken from the walls of the gas-discharge chamber. The concentration of the used FCS was 0.1% by weight. The NCS was a soot, taken from the cathode, containing the nanopipes with various ratios of diameter to length. The concentration of the used NCS was 0.01, 0.1 and 0.5% by weight. Lead powders, after treatment using HCC, were mixed with acid and water following the usual technology of electrode paste preparation without additional warming, then they were spread on current taps $82 \text{ mm} \times 47 \text{ mm} \times 4.2 \text{ mm}$ in size and dried. Structures of pastes, obtained from the treated and untreated HCC of lead powder, are shown in Figs. 1 and 2. It is seen,

that the pastes obtained from the treated HCC of lead powder had more coarse crystalline prismatic structure. Thus, if an average crystal size of the paste, obtained from untreated lead powder, made $1.2\text{--}1.7 \mu\text{m}$, the pastes, obtained from powders treated with NCS suspended of 0.01, 0.1 and 0.5% by weight, had crystals of average size of $2.1\text{--}2.5$, $2.3\text{--}2.7$ and $1.6\text{--}1.9 \mu\text{m}$, respectively. The average size of paste crystals obtained using the FCS solution of 0.1% by weight was $5.2\text{--}6.7 \mu\text{m}$. The X-ray diffraction analysis of such pastes showed that they consist mainly of $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ and PbO (Fig. 3). No content of $4\text{PbO}\cdot\text{PbSO}_4$ was observed in them at all. Besides, it is known [10,11] that 4BS forms in the course of preparation of pastes at temperatures of $80\text{--}90^\circ\text{C}$, and size of 4BS crystals amounts in average to $20\text{--}25 \mu\text{m}$, which noticeably surpass the sizes of the crystals formed as a result of treatment of lead powders of high-molecular carbon clusters. Thus, effect of the HCC on formation of electrode paste structure was confirmed.

After plate formation, batteries were assembled with an assembly count of $2(+)/3(-)$ and a rated capacity of 12 Ah (C_{20}) and tested by the continuous cycling method. The batteries were filled with acid with a density of 1.28 g/cm^3 . A cycle consisted of charge with a current of $0.075C_{20}$ for 3 h (the first stage) and a current of $0.0083C_{20}$ up to 120% of overcharge (the second stage) and discharge with a current of $0.125C_{20}$ to 20% degree of discharging. A control discharge with a current of C_{20} to a final voltage of 1.75 V was done for each battery every 20 cycles. Such cycling mode (not deep discharge and significant overcharge), when the electrode block was not compressed, may be considered as rapid test, since great destructive effect of oxygen bubbles on the PAM took place.

Test results of test batteries, fabricated of powders, treated with suspended of 0.01 (batteries No. 1), 0.1 (batteries No. 2) and 0.5 (batteries No. 3) NCS and 0.1% FCS (batteries No. 4), as well as of batteries, fabricated without special treatment of lead powder (batteries No. 0) are shown in Fig. 4. It is seen that the batteries with test active masses (Nos. 1–4) had higher capacity characteristics at cycling and increased life. The following patterns may be noted for batteries Nos. 0–3. Battery characteristics increased, when powders treated with the NCS with concentrations within a range of 0.0–0.1% were used. But, batteries No. 3 showed decrease in their characteristics, which points to availability of maximum permissible concentration of the NCS. It shall be noted, that pastes obtained from powders treated with 0.5% suspended of the NCS had smaller average size of crystals, than the pastes prepared using 0.01 and 0.1% suspended of the NCS. Batteries No. 4 showed excess of the capacity and life characteristics over the level of the similar characteristics of batteries No. 0 and approximately corresponded to batteries Nos. 1 and 2. Fig. 5 shows the structure of the active masses obtained from the pastes, containing 0 and 0.1% of the NCS, after life tests. It is seen, that the test PAM preserves the coarse crystalline structure till the end of the service life.

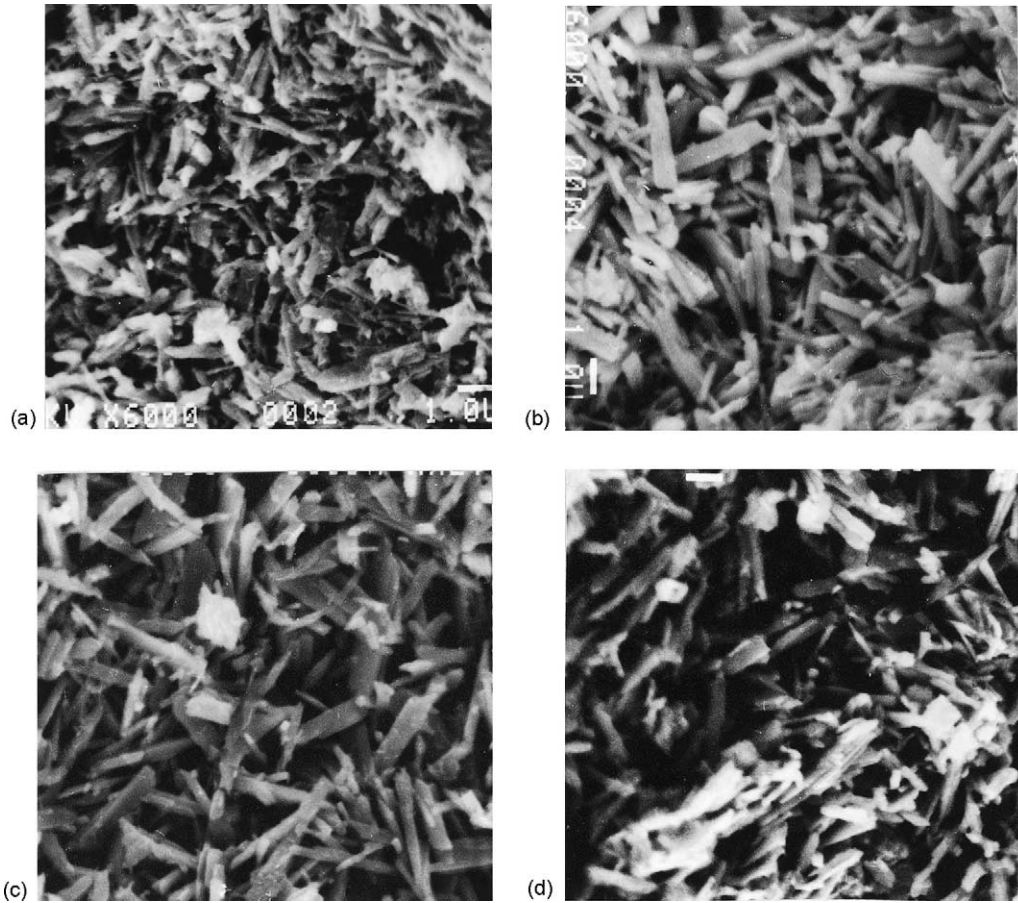


Fig. 1. Structure of pastes prepared of lead powder treated with NCS solution with 0.01% (b); 0.1% (c); and 0.5% (d) concentration; serial paste (a); magnification: 6000×.

Thus, the noted effect of the lead powder after treatment using HCC on the electrode paste structure facilitates improvement of characteristics of batteries, fabricated with their use.

Use of the HCC in the formula of the positive electrode and their effect on a value of the oxygen overcharge across

porous PbO_2 electrode shall be checked in order to evaluate their possible effect on the efficiency of charge current use. For this purpose $8\text{ mm} \times 5\text{ mm} \times 3\text{ mm}$ electrodes were fabricated from the same pastes, which were used for fabrication of plates for test batteries Nos. 0–4. After formation of such plates, anode polarization curves were plotted for them within a potential range of 1.65–2.10 V (values of electrode potentials are given in relation to the

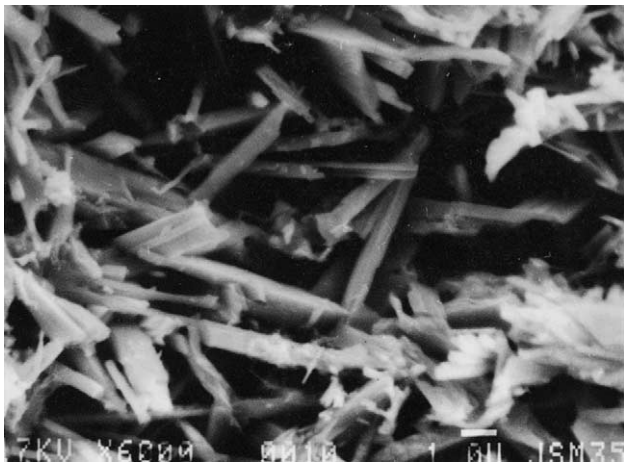


Fig. 2. Structure of pastes prepared of lead powder treated with FCS solution with 0.1% concentration of FCS; magnification: 6000×.

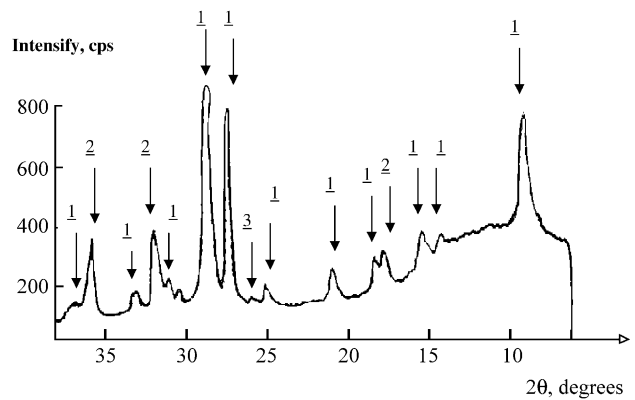


Fig. 3. The X-ray diffraction analysis of the paste. (1) $3PbO \cdot PbSO_4 \cdot H_2O$; (2) PbO ; (3) $2PbCO_3 \cdot Pb(OH)_2$.

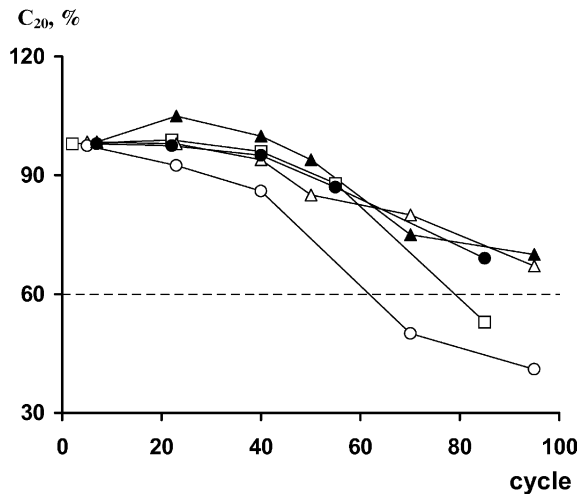


Fig. 4. Capacity of batteries with PAM obtained from pastes containing 0 (○); 0.01 (△); 0.1 (▲); 0.5% of NCS (□); and 0.1% of FCS (●) vs. number of performed cycles.

comparative chlorine-silver electrode) in acid solution with a density of 1.28 g/cm^3 . Each test were conducted at least five times. Fig. 6 shows anode polarization curves, obtained for active masses, prepared from the pastes containing 0, 0.01, 0.1, 0.5% of the NCS and 0.1% of the FCS. Fig. 6a shows, that availability of the NCS in the active mass formula has a relatively weak effect on a value of the oxygen overcharge. It may be noted, that at NCS concentrations of 0.01 and 0.1% the oxygen overcharge is somewhat higher in relation to the similar parameter obtained for the active masses, which do not contain the NCS, and for the active masses, containing 0.5% of the NCS the oxygen overcharge is lower. Thus, concerning capacity characteristics and a value of oxygen overcharge, there is a limitation of the NCS concentration, which is within 0.1–0.5%. Fig. 6b shows, that addition of the FCS to the active mass (0.1%) practically has no effect on the oxygen overcharge.

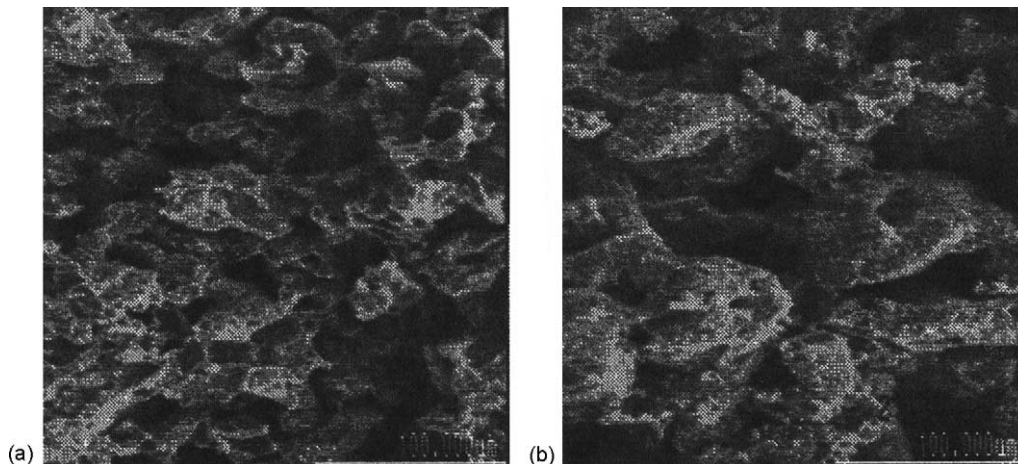


Fig. 5. Structure of positive active masses obtained from pastes containing 0% (a) and 0.1% (b) of NCS, after cycling; magnification: $500\times$.

Thus, the obtained results show that there is no negative effect of the NCS (0.01–0.1%) and the FCS (0.1%) on the efficiency of charge current use, and this, along with their positive effect on capacity and life characteristics of batteries, makes their use feasible. It is known, that prices for fullerenes and nanopipes are rather high. But this paper shows the possibility of using soots, containing these materials, with sufficiently low concentration of solutions (0.1%), which does not make battery price too high.

2.2. Partial hydrophobization of NAM

With the aim of the NAM hydrophobization in the process of electrode paste preparation, a calculated amount of fluoroplastic water suspension with 1.5–2.2 μm particles were charged into a mixer. The fluoroplastic suspension was charged on the basis of obtaining pastes with a fluoroplastic concentration of 0, 1.5, 4.5 and 7.5% by weight. The paste prepared by this way was spread on current taps $90 \text{ mm} \times 45 \text{ mm} \times 3.5 \text{ mm}$ in size, it was formed and blocks with an assembly count of 3(+)/2(–) were assembled of the obtained electrodes. The electrode blocks were placed into cells of acrylic plastic, which make it possible to take measurements of both voltage and internal pressure during the cycling process. The cells were filled with 1.28 g/cm^3 acid and were cycled till stabilization of electrode blocks electrolyte-filling (25–30 cycles). After that, the following cycle was conducted:

1. charge with 0.45 A current with 20% overcharge (the first stage);
2. discharge with 1.5 A current to a depth of 50% (the second stage);
3. charge with 0.45 A current with 50% overcharge (the third stage);
4. hold after charge without current for 17 h (the fourth stage).

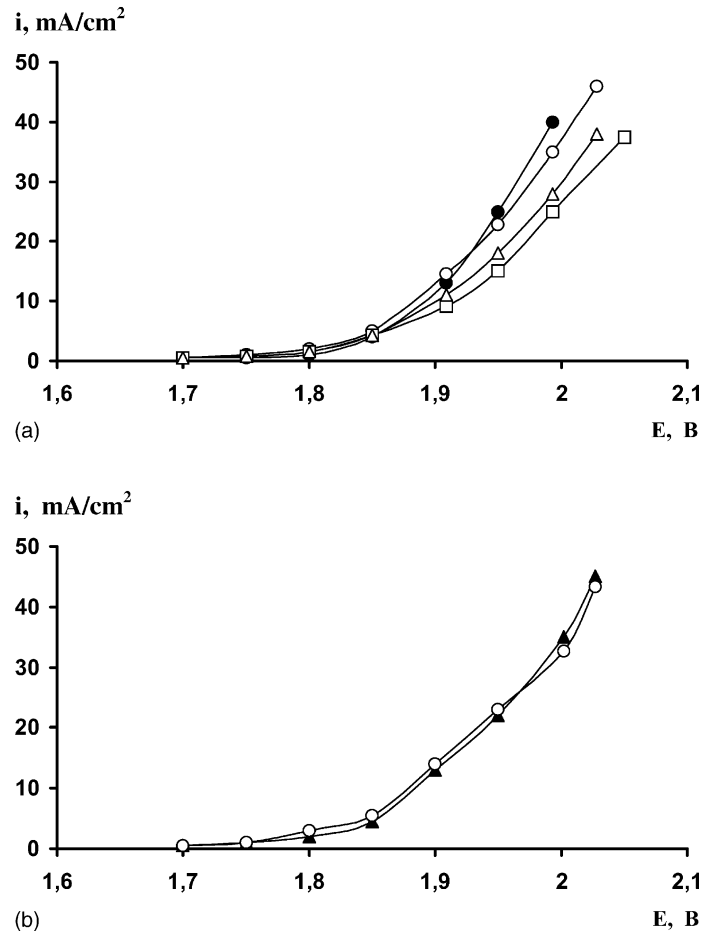


Fig. 6. Anode polarization curves for PAM obtained from pastes containing 0 (○); 0.01 (△); 0.1 (□); 0.5% (●) of NCS (a) and 0 (○); 0.1% (▲) of FCS (b).

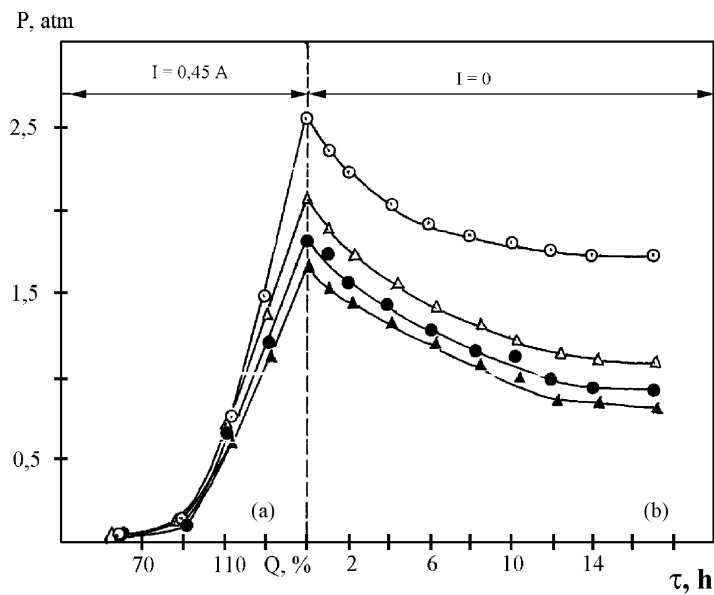


Fig. 7. (a) Internal pressure of battery models vs. degree of their charge in process of charging with 0.45 A current. (b) Dependence of internal pressure of battery models in process of their holding without current after charge. PAM contains: 0 (○); 1.5 (△); 4.5 (●); and 7.5% (▲) of fluoroplastic.

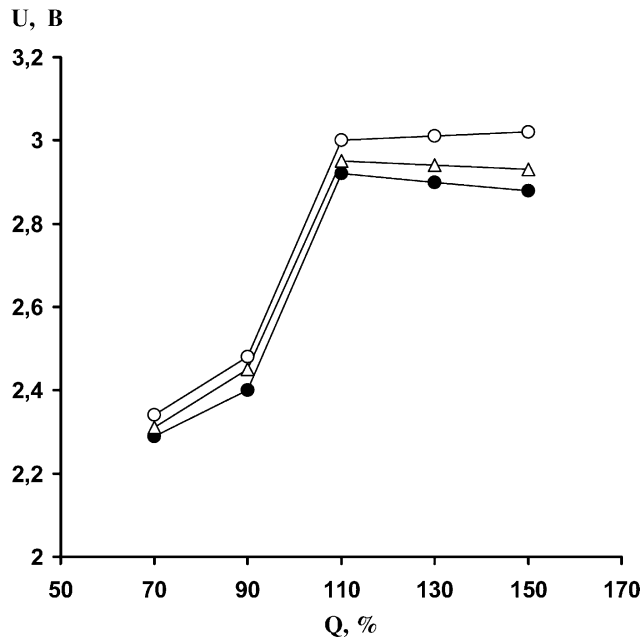


Fig. 8. Battery model voltage vs. degree of their charge in the process of charging with 0.45 A current. PAM contains: 0 (○); 1.5 (△); 4.5 (●) of fluoroplastic.

Voltage and internal pressure were periodically measured at the third stage, and only internal pressure was measured in the fourth stage. After performing the earlier mentioned cycle, it was repeated with charge current of the third stage increased up to 0.90 and 1.2 A.

Fig. 7 shows plots of the internal pressure in the cells for the third and fourth stages with a charge current at the third stage of 0.45 A versus charge duration and fluoroplastic content in the PAM. The figure shows, that addition of the fluoroplastic within the entire range under study reduces the pressure value at the end of the charge and the higher the degree of such reduction the higher fluoroplastic content and the higher degree of the overcharge. The same figure shows, that, after charge, pressure drop in the cells in the process of long holding without current, connected with OEcR across the NAM, is also considerably more intensive with increase of the fluoroplastic concentration in the active mass. All this points to the increased rate of the OEcR, connected with addition of the fluoroplastic hydrophobization additive to the NAM formula. As it was mentioned earlier, the fluoroplastic facilitates the growth of the reaction surface, on which the OEcR process is realized.

The earlier mentioned is confirmed also by the results of battery voltage measurement during the charge process (the third stage), represented in Fig. 8. The figure shows, that as the fluoroplastic content in the NAM increases, the voltage during the charge decreases. This can be connected with the fact, that the growth of the OEcR rate causes higher

depolarization of the negative electrode and, hence, decreases the voltage across the batteries.

Similar results were obtained for charge currents of the third stage equal to 0.9 and 1.2 A. The obtained patterns were well reproduced at the repeated cycling.

Thus, addition of the fluoroplastic rather effectively increases the OEcR rate at the end of the charge. But, it shall be taken into consideration, that the fluoroplast must decrease the battery capacity due to reduced NAM content in it. It was shown, that with fluoroplast content at an amount of 0, 1.5, 4.5 and 7.5%, the rated capacity C_{20} of the used models made 7.2 Ah (100%), 7.1 Ah (98.6%), 7.0 Ah (97.2%) and 6.7 Ah (93.0%), respectively. But the data given previous show, that small additions of the fluoroplastic contribute major share into the OEcR growth, and this makes it possible to recommend its concentration in the NAM at a level of 1.0–1.5%.

3. Conclusions

The paper shows the efficiency of using high-collated carbon clusters (fulleren-containing soots and soots, containing nanpipes) as additives to electrode pastes. Use of such additives in the process of paste preparation makes it possible to obtain coarse-crystalline prismatic lead sulphates, which forms active masses of increased strength at their formation. Tests of batteries with such active masses have shown their improved capacity and life characteristics. It is shown, that the content of earlier mentioned carbon materials added to the PAM has no negative effect on the value of active mass oxygen overcharge and, hence, on the efficiency of the charge current use.

The paper shows that partial hydrophobization of the NAM by introducing fluoroplastic in it results in the increased rate of oxygen electric reduction. This is caused by the growth of the reaction surface, on which the OEcR process is possible.

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