Glasnik hemičara i tehnologa Bosne i Hercegovine

Bulletin of the Chemists and Technologists of Bosnia and Herzegovina

2012

39

Print ISSN: 0367-4444

UDC: ________________________

Online ISSN: 2232-7266

Original Scientific Article

29-33

The Impact of the Content of Lead Oxide on the Porosity and Volume of the Pores, Paste and Active Mass of the Positive Electrodes-Pasted Flat Plates of Lead-Acid Batteries

Avdić N.[a]

[a]*University of Sarajevo, Faculty of Science, Department of Chemistry, Zmaja od Bosne 33-35, 71000 Sarajevo, Bosnia and Herzegovina*

Article info
Received: 30/11/2012
Accepted: 14/12/2012

Keywords:
lead-acid batteries,
porosity,
paste and active mass

***Corresponding author:**
E-mail: technoprocur@yahoo.com
Phone: 00-387-33-279862
Fax: 00-387-33-649-359

Abstract: Porosity and the volume of the pores of active mass of lead-acid layout battery are one of the key factors that determine the capacity and their lifetime. Increase of pore diameter enables flow of sufficient quantitiy of electrolyte into the bulk active mass and, as a consequence, enables its maximum conversion. Smaller diameter of the pores in the same volume of active mass provides a larger surface area which has again a consenquence of higher capacity for the ephemeral dischargings, but also faster filling in of the pores with the compenents of electrochemical reaction, which in turn reduces their lifespan. The aim of this work was to consider the impact of different content of the lead oxide in lead powder as the main component in the production of these batteries regardings this phenomenon.

INTRODUCTION

Basic characteristics due to which lead baterry surpasses other chemical sources of electricity are high energy performances and relatively simple and developed technology of production. These high energy characteristics are influenced by the adequate structure and composition of the active mass that provides water supply and shunt of the electricity on each point of platinum. The last processes take place in two stages.Charge transport in solid porous phase is achieved by electron movement; in the pores at the plate surface, charge transport is maintained by ions of the electrolyte. Good organization of these processes requires the necessary presence of an optimal relationship between the solid phase and its pores. During filling in and emptying, the solid porous mass is changing due to its composition and weight, and the pores are doing the same due to its volume and diameter.

In order to have a long battery life time, the structure of active mass has been improved, which ensured strength and electrical conductivity of the porous mass, availability of ions of the solution in each point of platinum and reversibility of the process of charge-discharge (Pavlov 2011). There is a series of operations through which the production of positive electrodes of the lead battery goes, starting from the choice of its granulation and its phase composition, preparation of the paste with a certain phase composition and density, ripening of the paste and finally building the structure of the active mass and organization of the components duting the formation.

During the production of electrodes there are certain tolerances defined by technology in terms of quality of powdera, pastes, ripening and formation of the active mass. All this can significantly affect the quality of the battery and especially if is in use one or the other limit of tolerance in regarding parameters.

Active mass represents very porous electrode which is formed by precisely defined conditions from the various phases of the initial paste. Having in mind that different components composing the initial paste which are characterized by different physical attributes (shape, diameter of the particles, stoichiometric composition, electrical conductivity, oxidation rate), it is normal to expect different physicochemical attributes of the active mass.

On the basis of electronic-microscopic observations of the active mass (Pavlov, Bashtavelova, 1984) the structure of the active mass is determined. The smallest element are separated PbO2 crystals and they are grouped into porous agglomerates consisting of a sequences of single crystals. Through grouping of crystals the pores are formed and the combination of crystals and micropores in one agglomerate builds microstructure of positive active mass, which represents the first structural level. Agglomerates of different shapes of diameter and microstructures are associating with each other in a spatial skeleton. It contains macropores that form channels which interupt whole cross section of the platinum. The combination of skeleton of the macropores formes microstructure of positive active mass, which forms a second structural level. The idea is that macropores found in skeleton level structure serve as a major transportation system for the movement of ions between the electrolyte volume and agglomerate inside of the platinum. Micropores constitute the main part of the area on which cirulates the electrochemical reactions, and the macrostructure serves as one mechanical skeleton that conduct electricity and form ionic transport system. (Pavlov, 1984; Pavlov, St. Ilija, Papazov, Bashtavelova, 1984)

The structure of the active mass made with lead powder changes during exploitation and, after more than 25% of its life span, the content of large pores is increased. Acording to some authors, this increase is consequence of oxygen evolution at the PbO_2 surface due to the overfilling. Platinums made of synthetic 4PbOPbSO4 when passes 25% of the life span does not contain such deep pores and are quite compact and on its surface the swelling is observed.

The structure of the positive active mass (Pavlov, Papazov, 1986) after the formation is similar to the structure of the initial paste.

Many authors have studied the processes that occur during the preparation of pastes, method of mixing of lead dust, acid and water, the duration of the mixing process, the temperature at which this process takes place, and drying processes and the formation of platinum, with a range of presented facts about ways of running of chemical reactions (chemistry) during these processes and factors that influence the formation of the structure of active mass. As during the tests examined in this work, all the active mass have been simultaneously treated and were subjected to the same parameters during the preparation of differences midst discrepancies of mentioned influenced are eliminated and omitted.

EXPERIMENTAL

The amount of 2 kg of the paste was prepared in the laboratory mixer (Scheme 1). In the mixer the leaded dust is first added (Table 1) and then a solutions of sulfuric acid and water, alternately in equal installments. The recipe for paste with its characteristics was given in Table 2. Lattice lubricated with paste (5.5% Sb, As 0.14%) lead alloy capacity of 36Ah were subjected to standard regime of ripening, drying and aftewards, the forming. Determination of total volumes of the pores and their distribution is made on the mercury pores meter Autopores 9200. Probations of active mass were observed by scanning electron microscope Joel T200.

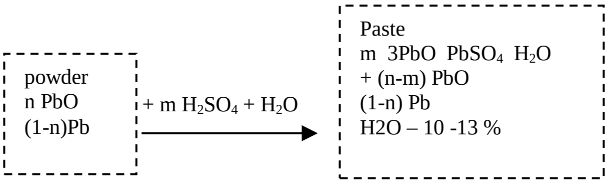
Table 1: Gradings analysis of lead powder.

	63%PbO			67%PbO			72%PbO			75%PbO			79%PbO		
	Tg	(%)	∑%	Tg	(%)	∑%	Tg	%	∑%	Tg	(%)	∑%	Tg	(%)	∑%
+125	0.12	2.4	2.40	0.10	2.0	2.0	0.20	4.0	4.0	0.26	5.20	5.20	2.60	2.60	2.60
-125 +90	0.08	1.6	4.00	0.10	2.0	4.0	0.14	2.8	6.8	0.09	1.80	7.00	1.80	1.80	4.40
-90 +63	0.25	5.0	9.00	0.16	3.20	7.2	0.26	5.2	12.0	0.12	2.40	9.40	3.40	3.40	7.80
-63 +40	0.98	19.6	28.6	0.67	13.4	20.6	0.61	12.2	22.2	1.55	31.1	40.4	24.2	24.20	32.0
-40 +32	0.19	3.8	32.4	0.06	1.20	21.8	0.24	4.80	27.0	0.10	2.00	42.4	0.60	0.60	32.6
-32 +0	3.38	67.6	100	3.91	78.2	100	3.55	73.0	100	2.12	57.6	100	67.4	67.4	100

The conditions of making of the paste are such, that all the sulfuric acid reacts with PbO and as the result 3PbOPbSO4H2O is formed during which process the part of non-reacted PbO and metallic lead remain in the paste which does not participate in the reaction. Phase composition of the paste - Scheme 1 (Ratio 3PbOPbSO4H2O, PbO, Pb) depends on the content of PbO in powder and quantities of used acid. (Pavlov, 1988).

Table 2: The recipe for positive paste with density and consistency.

% PbO	addid to 1 kg powder H_2SO_4 (g)	H_2O (ml.)	Paste densyti g/cm^3	Consist-ency circles
63	45.37	100	3.85	20
	60.49	88	3.63	20
67	45.37	83	3.95	20
	60.49	68	3.80	20
72	45.37	75	4.00	20
	60.49	55	3.81	20
75	45.37	80	3.98	20
	60.49	60	3.90	20
79	45.37	72	4.00	20
	60.49	58	4.03	20



Scheme 1: Phase composition of the paste.

The amount of water added to create a paste was within the limits of 10-13%. It determines density and consistency of paste. Paste consistency was maintained by constant (20 laps) changings of the amount of added water. In this way pastes with different density were obtained.

Table 3: Chemical analysis of paste and active mass.

	Paste (%)				Active mass (%)			
PbO	Pb	PbO	$PbSO_4$	Pb	PbO	$PbSO_4$	PbO_2	Pb^{2+4+}
63	10.64	73.76	15.24	0.95	19.22	11.36	68.98	88.02
67	7.44	77.50	14.52	0.40	13.47	11.62	74.55	88.02
72	1.73	82.84	14.52	0.15	12.51	12.20	75.10	87.61
75	1.48	83.11	14.52	0.15	13.58	10.90	74.42	88.00
79	3.47	81.24	15.24	075	15.18	9.59	74.42	84.01

RESULTS AND DISCUSSION

As the paste was made with constant consistency, with the parameter that defines the relationships between the particles under dynamic conditions, the presented pastes have different densities. Density dependence of paste from the content of PbO in powder at constant consistency is given in Table 2. The table shows that when making pasta with a variety of PbO in order to maintain the consistency of paste constant with increasing % PbO in powder, the density of the paste has been increased. Also, from the same table is visible that in order to maintain the consistency of paste with an increase of content of acid, density of paste decreases. The results in the agreement with literary data listed in (Illiev, Pavlov 1974.)

Determination of total volume of pores volume and their distribution per diameter in the positive active mass was made on the mercury pores meter AUTOP 9200, Micrometritics.

The selected probe was placed in a small container, under vacuum filled with mercury and the pressure was gradually increase. During given amount of pressure certain quantity of mercury fills the pores of a given radius, the relationship between pressure (p) and radius (r) is given by the following equation:

$$r = \frac{2 \cdot \sigma - \cos\varphi}{p}$$

Where is: σ - surface tension of mercury, a cos φ its wetting angle. Volume of the pores of a given radius is determined by the amount of mercury that fills the pores. These measurements make it possible to measure the total porosity of the sample expressed in (cm3 / g) materials, the total surface of the pores (cm2 / g) and distribution of the pores per radius. In the calculations applies cylindrical model of the pore. The accuracy of the method is 5-8%.

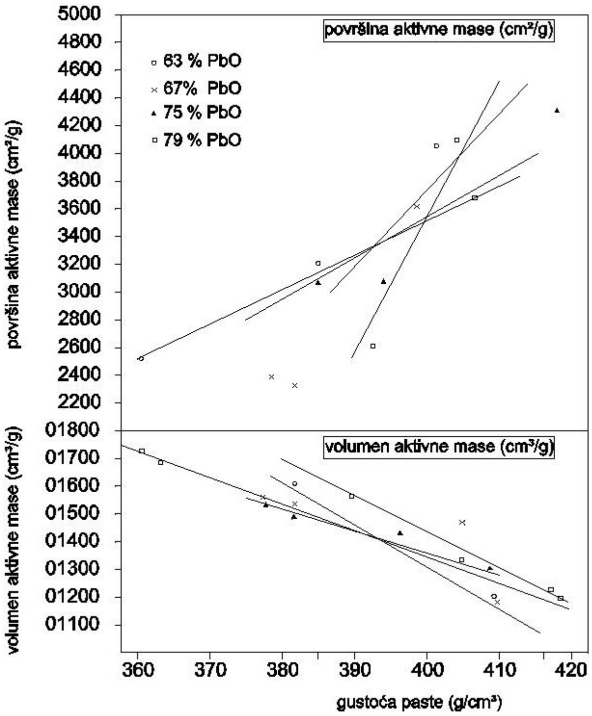


Figure 1: Surface area and volume of the paste, depending on the density of pastes.

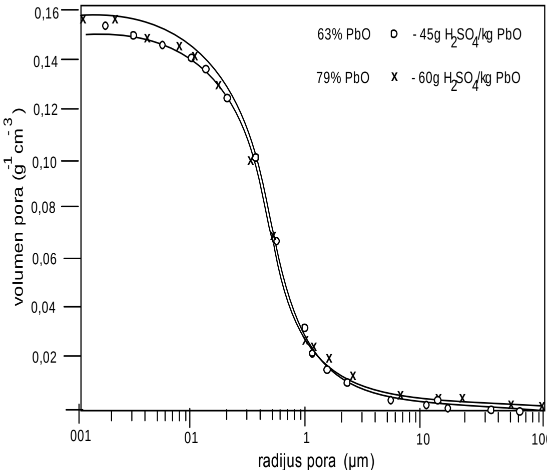


Figure 2. The distribution of pore per radius of the pastes of 63% and 79% PbO in powder with 45 and 60g H_2SO_4/kgPbO.

This independence can be explained through this - the diameter of PbSO4 crystals $3PbO \cdot PbSO_4 \cdot H_2O$ is almost the same as the PbO particle, so increasing the content of three-basic sulfate at the expense of decreasing of the content of PbO does not affect the volume and surface of the pores. These parameters are determined mainly with density of the paste. In Picture 1 the dependence of the surface and volume of the pores volume from density of the obtained pastes given in Table 3 is given

From the Figure 1 it is visible that with increasing the density of paste, there is a general tendency of decrease of the volume of pores and increase of the total surface of pores of the paste. This can be explained by the fact that with increasing the density of the paste relative amount of small pores increases and the surface is defined precisely by the quantity of small pores. In the field of density technology, the volume of pores is within the limits from 0.12 to 0.13 g/cm3.

In Figure 2 the distribution of the volume of pores per radius, for pastes prepared with 63 and 79% PbO in powder with 45 and 60g H2SO4/kg PbO is given. It can be seen that for the pastes made from various oxides there is no difference in the distribution of the pores per radius and total volume of pores of the paste. The curve shows that the quantity of pores is very small with a radius larger than 10μm and basic pores have a radius in the range 0.1 - 2μm. Inflexed point of curve of the distribution gives the middle radius of the pores that are located, in the tested paste, in the range from 0.4 to 0.5 um.

Poregrammes of other tested pastes are not different from poregrammes presented in figure 2.

All pastes in the tested range of composition, reagarding lead oxide powder and sulfuric acid, crystallise as $3PbO \cdot PbSO_4 \cdot H_2O$, but do not have a clearly defined crystalline form (iow. create crystals without forms). These small crystals are visible in Figure 3. Lengths are 2.3 width are about 2 -0.5 μm and are grouped into the crystalline agglomerates. Among crystals of the paste pores are created with average diameter of 0.5 μm which correspondes to data obtained by analysis through pore-meters, Figure 2.

Agglomerates among themselves create large pores, as shown in Picture 4. Their length is about 10μm, and their volume is about 0.005 cm3 / g (Figure 3). So, the total porosity is determined by small pores, which volume is of over 80%, and not the big ones, which means that they are within much smaller quantity.

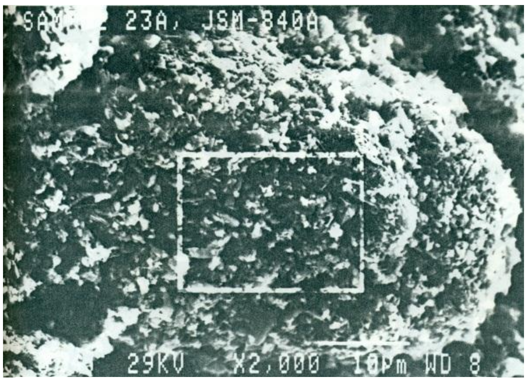


Figure 3: Structure paste made from 63% PbO in powder and 45 g H_2SO_4/kg PbO.

Tests have shown that changes in the content of PbO in powder makes no major changes in the characteristics of the paste, and paste made in such wide range interval of under the rust treatment and leaded dust, can be used in the technology manufacture of batteries.

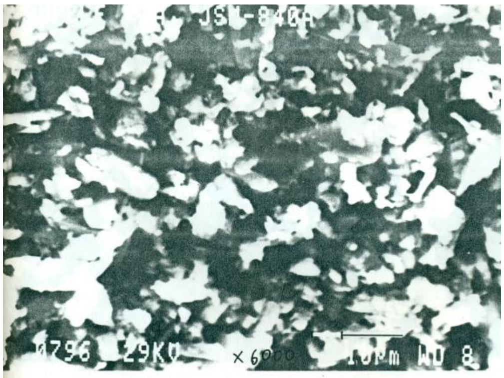


Figure 4: Structure paste made from 79% PbO in powder and 60g H_2SO_4/kg PbO.

Poregrammes of established active mass are given in Figure 5. Poregrammes are given only for two active mass, as all the others are very similar. These poregrammes talks about a small reduction in overall volume of the pores. The increase of the middle radius of the pores from 0.4 -0.5 μm of the paste and on 0.8 - 0.9 μm for the active mass was also observed.

Figure 6 shows the dependence of the volume of the pores and the pore surface of the active mass in regards the density of the paste.

There is no visible certain dependence of the pore surface of the active mass in regards to the density of pastes, and there is a tendency of reduction of the pores volume of the active mass with increase of density of the paste. The results of measurements of the volume and the surface area of pores of all pastes says that there is no specific dependence of these parameters on the content of PbO in powder and the amount of sulfuric acid used for making paste.

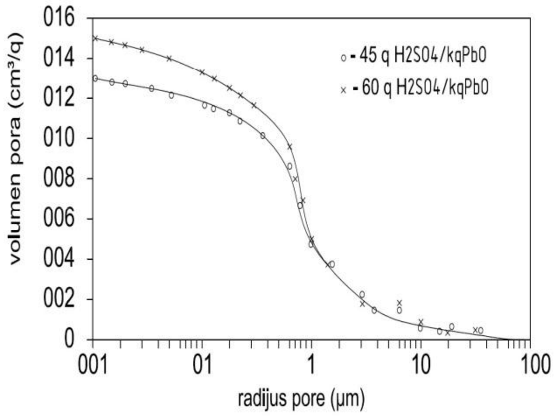


Figure 5: The distribution of pore per radius of the active mass made of 63% and 79% PbO in powder with 45 and 60g H_2SO_4/kgPbO.

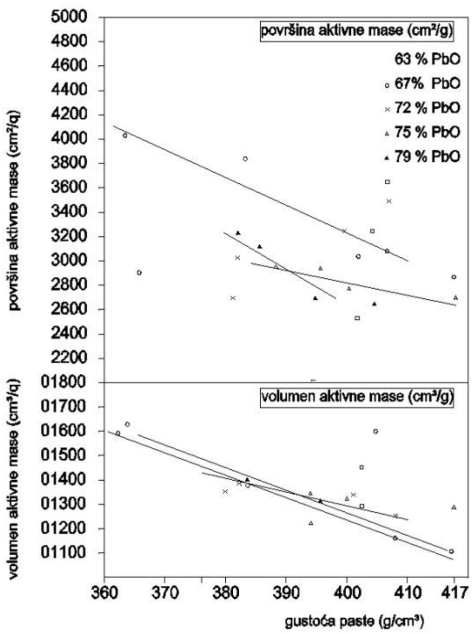


Figure 6: Surface area and volume of the active mass, depending on the density of pastes.

That independence can be explained by the fact, as proved by the results of other researchers, that thediamatres of the particles of PbO and $3PbO \cdot PbSO_4 \cdot H_2O$ are approximately the same and changing relations between the two phases of the paste does not affect the change of porosity.

CONCLUSIONS

These results suggest that changes in the content of PbO within leaded powder during the testing interval (63% - 79%) does not affect the structure and porosity of the paste, regardless the change of the phase composition of the paste. Structure and porosity of the paste compounds by shape and diameter are approximately equal and thus changes of the relationship of these two phases, which means changes in the phase composition of the paste, shows no effect on the structure and porosity of various paste.

The structure and porosity of the active mass does not change with the changing content of PbO in powder. As shown by other studies the structure of the active mass determines mainly the structure of the starting paste.

REFERENCES

Avdić N.,(2006) An Influence of the Lead oxide structure changing to the Energy and exploitation characteristich of a LeadBattery, *6-th Scientific/Research Symposium with International Participation, „Metallic and Nonmetallic Inorganic Materials"*Zenica.

Iliev V., Pavlov D.(1979) *Bulgarian Academi of Sciencis*, Sofija.

Pavlov D., (2011) Lead-Acid Batteries: Science and Technology. *Elsevier*, Amsterdam

Pavlov D., (1984) Powes Sources for Electric Vehicles. *Elsevier*, Amsterdam

Pavlov D., Iliev V., Papazov G., Bashtavelova E., (1974) *J electrochem*. **8**.

Summary/Sažetak

Porozitet i volumen pora aktivne mase olovnih namaznih akumulatora jedan su od ključnih faktora koji određuju kapacitet i njihov životni vijek. Povećanjem dijametra pora ostvaruje se mogućnost pristupa dovoljne količine elektrolita u unutrašnjost aktivne mase a time i njeno maksimalno iskorištenje. Manji dijametar pora za isti volumen aktivne mase obezbjeđuje veću površinu što je posledica opet veći kapacitet za kratkotrajna pražnjenja, ali i brže popunjavanje pora komponentama elektrokemijske reakcije, što opet smanjuje njihov životni vijek. Razmotrimo utjecaj različitog sadržaja olovnog oksida u olovnom prahu kao osnovne komponente u proizvodnji ovih baterija na navedene pojave.