

## STRUCTURAL CHANGES IN THE ACTIVE MASS OF THE NEGATIVE ELECTRODE OF THE LEAD/ACID BATTERY DURING CHARGING

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(Received January 8, 1990)

### Summary

An investigation is made of changes in the structure of the active mass of the negative electrodes of lead/acid batteries during charging. It is shown that, in the initial period of charge, reduction of lead sulphate proceeds mainly in the contact region of lead, lead sulphate and electrolyte. A method based on impedance measurements is suggested for determining the porosity of the active mass. By comparison of results from impedance and standard porosimetry methods, it is found that a considerable part of the negative electrode does not participate in the electrochemical process.

### Résumé

Le changement de la structure de la masse active de l'électrode négative de l'accumulateur de plomb est étudié. Il est démontré que la période initiale du processus de charge se déroule en premier lieu au contact des trois phases: plomb, sulphate de plomb et l'électrolyte. Une méthode permettant d'obtenir la porosité de la masse active à partir des mesures d'impédance est proposée. La combinaison des méthodes d'impédance et de porosymétrie a permis de démontrer qu'une partie considérable de la mass active de l'électrode négative de l'accumulateur de plomb ne participe pas au processus électrochimique.

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### Introduction

Pasted plates in lead/acid batteries are typical porous electrochemical systems and their behaviour is mainly determined by the parameters of the

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porous structure of the active mass, *i.e.*, surface area and the character of the porosity. The dependence of the available capacity on the structural parameters of the active mass has been clearly shown [1] for the negative electrode. In particular, a linear relationship has been established between the capacity and the square of the surface area.

Various characteristics of the negative electrode (*e.g.*, capacity and charge acceptance) are determined by features of the active-mass structure, especially by the contribution of lead and lead sulphate crystals in the electrode surface area. For example, it has been found [2] that the charging current of the lead electrode is influenced appreciably by the size of the lead sulphate crystals, *i.e.*, by the value of their surface area. At the same time, it must be emphasized that measurements of electrode surface-area usually relate to the *total* area, and that the latter is determined by both lead sulphate and lead.

The objectives of the work reported here are to investigate changes in the porous structure of the negative active mass during charging and to isolate the respective contributions of lead and lead sulphate to the total surface area. An attempt has also been made to evaluate the fraction of the porous material taking part in the electrochemical reaction.

## Experimental

Studies were conducted on pasted lead electrodes of dimensions:  $20 \times 10 \times 2$  mm. The active mass was prepared from lead dust (68% oxidized) containing 0.4 wt.%  $\text{BaSO}_4$ , 0.2 wt.% soot and 0.9 wt.% expander based on a synthetic tanning agent. After a 24-h period of curing, the electrodes were formed in a 1.08 sp. gr. sulphuric acid and then subjected to a conditioning charge in a working solution (1.28 sp. gr. sulphuric acid) in which all measurements were performed. Before undertaking impedance and structural investigations of the active mass, the electrodes were cycled (for four  $C/5$  discharge cycles) and then discharged at the  $C/20$  rate in order to obtain a uniform distribution of lead sulphate in the bulk of the active mass. The electrode potential was measured against a  $\text{Hg}/\text{Hg}_2\text{SO}_4$  reference electrode in the same working solution.

Special electrodes were constructed for conducting impedance measurements of the active mass; details of the design have been reported previously [3]. The active mass composition and electrode treatment for impedance measurements were the same as those described above. Measurements of impedance components were performed with an X-2071 automated impedance instrument. All investigations were made at 25 °C.

Before examination of structural features, the electrodes were washed repeatedly in acetone and then dried in vacuum at ambient temperature. The distribution of pore radius was determined by a porosimetry method [4] that avoided the problem of lead amalgamation normally encountered with the more common mercury-based technique.

The specific surface area of the active mass, and its changes during charging, were determined by the BET method using a Micrometrics Flowsorb II2300 unit. The specific area so determined is expressed generally in  $\text{m}^2$  per g of active mass. The weight of the electrode changes, however, during the transformation of lead into lead sulphate, and *vice versa*. This causes difficulties in the comparison of data corresponding to different states-of-charge of the active mass. Therefore, all the data were recalculated per g of lead in the fully charged lead electrode.

## Results and discussion

The value of the specific surface area determined by the BET method includes the surface of both the lead and the lead sulphate crystals in the active mass. In order to understand the mechanism of processes occurring in the active mass, however, it is interesting to determine the individual contributions of lead and lead sulphate crystals to the electrode surface area. The direct experimental determination of these two components of the total surface area appears impossible, but a simple model approach enables them to be evaluated rather easily.

Generally, the surface area of the active mass can be described by the expression:

$$S_{\text{TOT}} = (1 - x)S_{\text{Pb}} + xS_{\text{PbSO}_4} - S_{\text{Pb} \cap \text{PbSO}_4} \quad (1)$$

where:  $S_{\text{TOT}}$  is the total surface area obtained by the BET method;  $S_{\text{Pb}}$  is the specific surface area of the lead crystals;  $S_{\text{PbSO}_4}$  is the specific surface area of the lead sulphate crystals;  $S_{\text{Pb} \cap \text{PbSO}_4}$  is the surface area of contacts between the lead and the lead sulphate crystals;  $x$  is the degree of discharge.

The  $S_{\text{PbSO}_4}$  value can be obtained experimentally. The active mass is treated in a mixture of nitric acid and hydrogen peroxide in order to remove completely the lead. The lead sulphate remaining is washed in acetone and dried, and then the  $S_{\text{PbSO}_4}$  is determined by the BET method.

For  $S_{\text{Pb}}$  calculations, a simple model describing the lead crystal structure is used. It is based on two simplifications: a spherical shape is assumed for the lead crystals and their quantity is assumed to remain constant during discharge of the active mass. According to this model, the surface area of lead crystals can be calculated from:

$$S_{\text{Pb}} = S_{\text{Pb}}^0(1 - x)^{-1/3} \quad (2)$$

where:  $S_{\text{Pb}}^0$  is the specific surface area of the fully charged active mass (determined by the BET method).

From relationships (1) and (2), the surface of contacts between lead and lead sulphate crystals can be obtained readily, *i.e.*,

$$S_{\text{Pb} \cap \text{PbSO}_4} = -S_{\text{TOT}} + xS_{\text{PbSO}_4} + S_{\text{Pb}}^0(1 - x)^{2/3} \quad (3)$$

The total surface area of the active mass as a function of its state-of-charge is presented in Fig. 1. It can be seen that the area increases at the beginning of the charging process and then remains virtually constant up to the end of charging. The initial increase in  $S_{TOT}$  is obviously due not only to the growth of lead crystals but also to an 'opening' of lead and lead sulphate crystals as a result of a decrease in the contact between them. The latter can explain the unreasonable, at first sight, increase in the surface area of the lead sulphate (Fig. 1) while its quantity in the active mass falls. The decrease in the surface of contact between lead and lead sulphate crystals at the start of charging (Fig. 2) indicates that the lead sulphate reduction in this case takes place mainly at the sites of three-phase (lead, lead sulphate, electrolyte) contacts. This can explain the high value of the initial charging current that is usually observed during potentiostatic reduction of the active mass.

The specific pore volumes of the fully charged and fully discharged active mass as a function of the logarithm of the pore radius are presented in Fig. 3. The curves clearly illustrate an increase in the electrode porosity during charging. From these data, the specific surface area of the active mass can be calculated using the well-known equation connecting the pore volume,  $V$ , and its surface area,  $S$ :

$$S = 2 \int_0^V r^{-1} dV \quad (4)$$

The specific surface area of the electrode increases almost two-fold during charging (Fig. 4). Comparison of data presented in Figs. 1 and 4 demonstrates that there is a good agreement between the values of specific surface area determined by standard porosimetry and BET methods.

During charging of a discharged active mass, the reduction of lead sulphate to metallic lead results in changes in both the solid and liquid

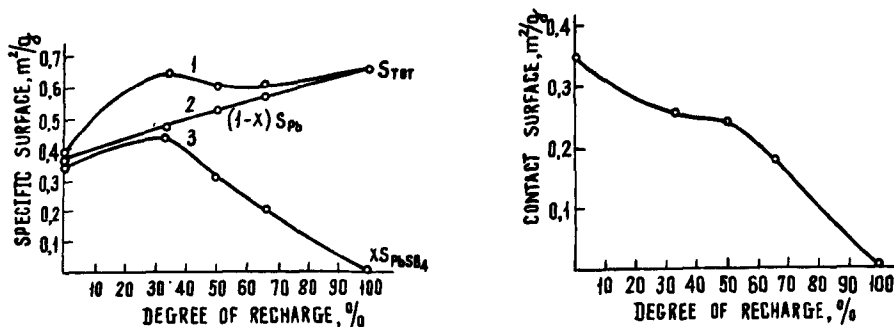


Fig. 1. Specific surface area as a function of degree of charge: (1) total surface area; (2) surface area of lead crystals; (3) surface area of lead sulphate crystals.

Fig. 2. Surface of contact between lead and lead sulphate crystals as a function of degree of charge.

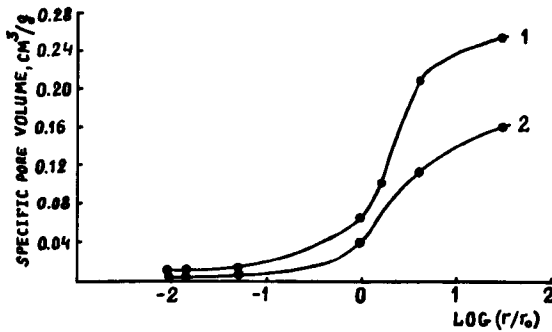


Fig. 3. Specific pore volume of active mass as a function of logarithm of pore radius,  $r_0$  is equal to  $1 \mu\text{m}$ : (1) fully charged electrode; (2) fully discharged electrode.

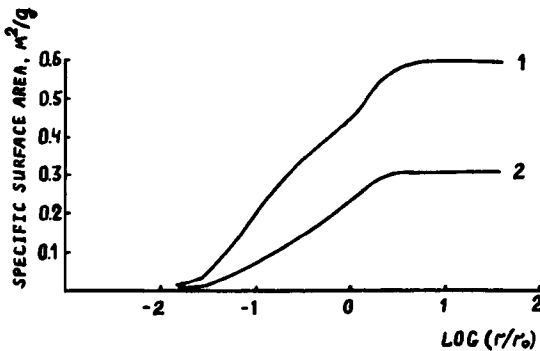


Fig. 4. Specific surface area of active mass as a function of logarithm of pore radius: (1) fully charged electrode; (2) fully discharged electrode.

phases and hence in the porosity of the active mass. Variations in the porous structure of the electrode during its operation can be detected by the impedance method.

It follows from the impedance plots given in Fig. 5, which are close to semicircles, that the surface impedance can be represented by a parallel connection of double-layer capacity,  $C_d$ , and the electrochemical resistance,  $R_F$  [5]. In this case, the impedance of the porous electrode,  $Z_e$ , in the low-frequency region (where the depth of penetration of the alternative current is many times in excess of the pore length) is given by [6]:

$$\text{Re}(Z_e) = \frac{l}{3nk\pi r^2} + \frac{1}{C_d R_F} \frac{\text{Im}(Z_e)}{w} \quad (5)$$

where:  $l$  and  $r$  are the length and the radius of pores, respectively;  $k$  is the electrolyte conductivity,  $n$  is the amount of pores.

Substitution of the pore volume,  $V_p = n\pi r^2 l$ , into eqn. (5) gives:

$$\text{Re}(Z_e) = \frac{l^2}{3kV_p} + \frac{1}{C_d R_F} \frac{\text{Im}(Z_e)}{w} \quad (6)$$

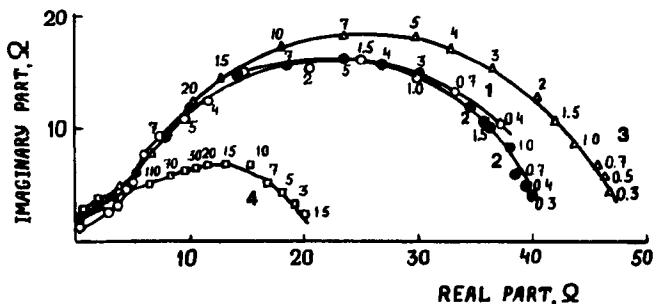


Fig. 5. Impedance diagram for active mass at different states-of-charge: (1) fully charged; (2) recharged to 66%; (3) recharged to 33%; (4) fully discharged. Numbers on curves represent frequencies in Hz.

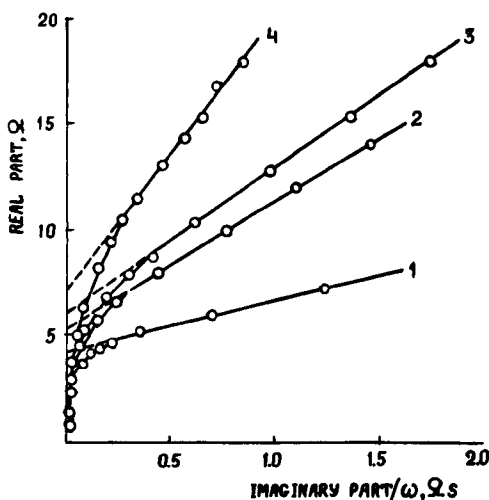


Fig. 6. A plot of real impedance component against imaginary component divided by angular frequency. Plots for electrode conditions given in Fig. 5.

The experimental data (Fig. 6) confirm the validity of eqn. (6) for analysis of the impedance of the active mass for different states-of-charge of the negative electrode of the lead/acid battery. The value of  $R_0 = l^2/3kV_p$  for different states-of-charge can be obtained by extrapolation of the linear sections of the curves in Fig. 6. These  $R_0$  values themselves do not allow the separate determination of pore length, and therefore volume  $V_p$ , but analysis of  $R_0$  as a function of state-of-charge overcomes this problem.

The dependence of the pore volume,  $V_p$ , on the quantity of electricity,  $q$ , required for reduction of the active mass is given by:

$$V_p = V_p^0 + \frac{\Delta V}{2F} q \quad (7)$$

where:  $V_p^0$  is the pore volume in the discharged electrode;  $\Delta V$  is the molar-volume change during the transformation of lead sulphate to lead in the active mass. Substitution of eqn. (7) in the expression for  $R_0$  allows  $V_p^0$  and  $l$  to be obtained directly from the impedance data, *i.e.*,

$$\frac{1}{R_0} = \frac{3kV_p^0}{l^2} + \frac{3k\Delta V}{2Fl^2} q \quad (8)$$

The value of  $l$  was determined from the slope of the plot given in Fig. 7. From the same data, the pore volume and hence the porosity of active mass (since the geometry of the electrode is known) can also be obtained. The porosity of the active mass as a function of its state-of-charge is shown in Fig. 8. The observed increase in the active-mass porosity during charging is well known [7]. The main feature of the information given in Fig. 8 is that it is determined directly during charging of the electrode. These results illustrate the scope of the impedance method to describe the behaviour of the active mass during electrode operation.

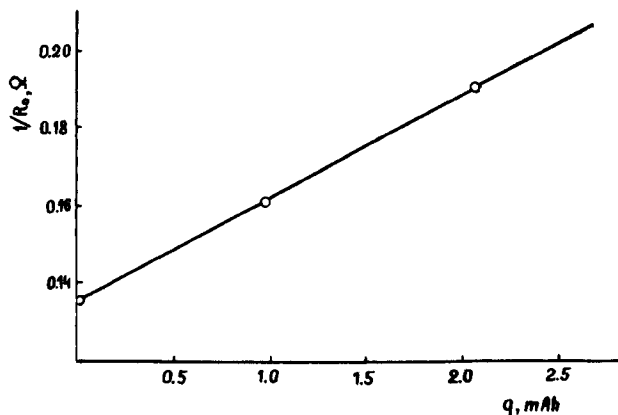


Fig. 7. Reciprocal of limiting value of real impedance component as a function of quantity of electricity passed.

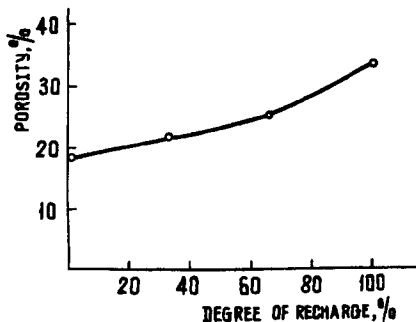


Fig. 8. Porosity of active mass as a function of degree of recharge.

The porosity values obtained by the impedance method are approximately half those determined by the standard porosimetry method. The porosity of fully charged and fully discharged electrodes obtained by the latter method is 82% and 45%, respectively. It must also be emphasized that the impedance method measures only that part of the pore volume that is reached by the alternative current. Those parts of the active mass where the alternative current is for some reason impeded (e.g., by plugging either by gas bubbles or lead sulphate crystals) do not take part in the measurements. Therefore, the impedance method must report lower values of the porosity than other (non-electric) methods. Furthermore, the results indicate that a substantial part of the active mass of the negative electrode of the lead/acid battery does not participate in the electrochemical process. This, in term, explains the much lower values of the specific surface area of the active mass obtained by the impedance method (by comparison of the differential double-layer capacity of smooth-lead and pasted-lead electrodes [3]) with respect to the values determined by the BET and porosimetry methods. The porosity obtained by the impedance method reflects those changes in the electrode structure that are interesting from the point of view of its electrochemical properties. A comparison of the results of investigations of the active-mass structure performed by the impedance method and by an independent one (e.g., standard porosimetry) provides additional information on the electrode properties.

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