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THE CAPACITY LIMITING ROLE OF THE ELECTRONIC CONDUCTIVITY OF THE ACTIVE MATERIAL IN LEAD-ACID BATTERIES DURING DISCHARGE*, **

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Summary

The utilisation of the active material in lead–acid batteries is known to be no more than about 60% of the theoretical value, even at low current densities. It can be shown that the maximum output is limited by a sharp decrease in the effective electronic conductivity of the active materials. Structural effects are responsible for the electrical insulation of unconverted parts of the active material of the electrodes. A mathematical model for the behaviour of the effective electronic conductivity during discharge has been developed and compared with experimental values.

1. Introduction

The phenomenon of the incomplete ampere hour yield of the active material of lead–acid batteries is well known, and over a long period many attempts have been made to explain it. Many experiments have been conducted and models developed to obtain new insight into this problem. Investigations have been carried out on the transport processes in the electrolyte in dependence on the state of discharge, as well as on the conditions during formation of lead sulfate. These resulted in two main reasons for incomplete capacity utilisation:
— the pore openings are blocked with lead sulfate [1];
— the hindrance to diffusion, caused by the non-infinite radius of the pores, leads to an impoverishment of the electrolyte in the pores [2].
Both these reasons result in the ionic conductivity in the electrodes breaking down.

**Dedicated to Prof. Dr. Ing. Karl-Joachim Euler, Kassel, on the occasion of his 60th birthday, on May 24th 1982.

Until now consideration has not been given to the possibility of changes in electronic conductivity of the active material during discharge, which may have an effect on the utilisation of the electrodes.

Generally, one assumes that the ohmic voltage drop over the active material of lead–acid batteries remains unchanged and negligibly small. This assumption may be correct in the case of discharges at high current densities, which give capacities of less than 10% of the theoretical values. However, first investigations, on which we reported previously [3], showed that discharges at medium current densities, which allowed 30 - 40% utilisation of the theoretical capacities, already showed a distinct increase in the resistance of the active material of both electrodes. Finally, in the case of very low current densities, the utilisation will be no more than about 60% of the theoretical values. Even if there is a forced flow of electrolyte through the electrodes during discharge at high current densities, the capacity will not be more than about 60%.

In view of these facts, the reasons given above do not seem adequate to explain fully the incomplete ampere hour yield. This led us to the conclusion that there must be some other factor, such as the electronic conductivity of the active material, which may play a role in limiting the utilisation.

In the following we report on investigations [5] that we have carried out to determine whether the electronic conductivity has an influence on the limitation of capacity.

2. Mathematical model

The electrical conductivity of powder mixtures may be described by theories of statistically distributed networks. In particular, the Percolation Theory (PT) [6] and the Effective Medium Theory (EMT) [7] may be used for binary mixtures with a strong difference in the conductivity of the two components [8].

The main point of both theories is the fact that at a particular composition — the percolation threshold — the conductivity of the whole system changes very quickly from the value of one component to the value of the other (see Fig. 1).

Because the structure of the active material in the porous electrodes may be regarded as somewhat similar to compressed powder mixtures, the above-mentioned theories may be used to determine the electronic conductivity of the active material [9]. This is possible if one considers the electrodes as a network of statistically distributed resistance elements. In this case the electrodes consist of a phase of good electronic conductivity (Pb or PbO_2) and a phase of poor electronic conductivity ($PbSO_4$ and H_2SO_4). Because of the production of poorly conducting lead sulfate during discharge, it may be expected that, at a critical volume fraction of lead sulfate, the electronic conductivity of the whole system changes to that of
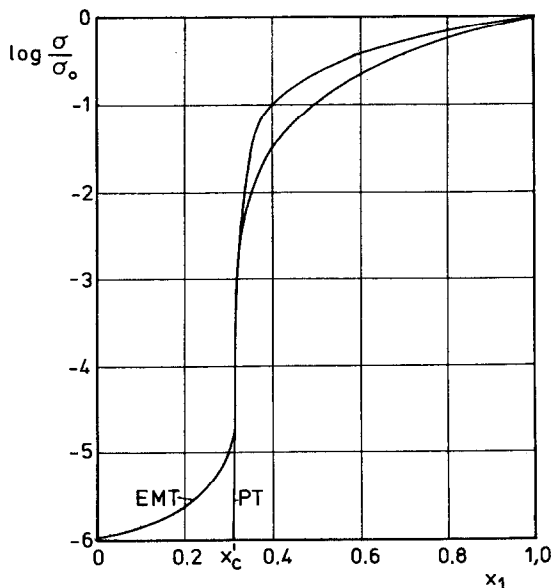
Fig. 1. Relative conductivity of a binary mixture, calculated from the Effective Medium Theory and from the Percolation Theory. The relation of conductivity ($\sigma/\sigma_0 = 10^{-6}$) and the coordination number ($k = 6$) were chosen randomly.

the poorly conducting $PbSO_4$. From this it follows that the transport of electrons is strongly obstructed, and, hence, further discharge is no longer possible, although the total conversion of Pb or PbO_2 to $PbSO_4$ has not taken place.

In the following a mathematical model is developed on the basis of the above-mentioned theories. With this model it should be possible to calculate the behaviour of the electronic conductivity of the active material during discharge, in dependence on the change in the volume fraction of Pb or PbO_2 and $PbSO_4$.

As one requirement we assume that the value of the specific electronic conductivity for each of the components remains approximately constant. This means that no change in the physical material constants is described, but only the measurable macroscopic relation between voltage and current related to a volume element of the electrode. Therefore, the specific electronic conductivity of the active material has to be understood as a mean or effective value.

In the case of the Percolation Theory we are restricted to a system in which one phase has no conductivity. Lead sulfate can be regarded as a good approximation to this. The specific conductivity, $\bar{\sigma}$, of the system is then defined as [10]:

$$\bar{\sigma} = (x_1 - x_c)^b \tag{1}$$

where $\bar{\sigma}$ is the specific conductivity of the active material, x_1 the volume fraction of the good conducting phase, x_c the critical volume fraction (percolation theory), and b is a numeric exponent [1, 7].

The critical volume fraction, x_c, depends on the coordination number k, which describes the arrangement of the resistance elements in a spatial lattice. The resistance elements may be regarded as the particles of which the active material consists. Because of the approximation for the conductivity of the non-conducting phase eqn. (1) is valid only for $x_1 > x_c$ (Fig. 1.).

In the case of the Effective Medium Theory $\bar{\sigma}$ is defined as [11]:

$$\bar{\sigma} = \frac{1}{k-2}(Q + Q^2 + 2(k-2)\sigma_1\sigma_2) \tag{2}$$

$$Q = \left(\frac{k}{2}x_1 - 1\right)\sigma_1 + \left(\frac{k}{2}x_2 - 1\right)\sigma_2$$

where x_2 is the volume fraction of the non-conducting phase and k is the coordination number. $\bar{\sigma}$ represents the effective specific conductivity of the good conducting phase (Pb or PbO) and σ_2 of the non-conducting phase, both in the before discharge porosity condition.

As mentioned above, knowledge of the coordination number is necessary for a description of the porous electrode as a spatial lattice. As long as we assume spherical particles of a single uniform size, it is very easy to determine k by simple measurement of the filling rate, f, and relating it to the corresponding spherical packing and its coordination number. However, in real electrodes the particle size is distributed over a more or less wide range. Another problem arises from the different densities of lead (11.3 g/cm^3), lead dioxide (9.6 g/cm^3), and lead sulfate (6.3 g/cm^3). This results in a change in the total solid volume during discharge, which corresponds to a change in the coordination number, and, hence, of the critical concentration, x_c. Therefore, we have to introduce another constant, the critical density, d_c. This is defined as the product of the filling rate and the percolation threshold:

$$d_c = fx_c. \tag{3}$$

d_c remains constant for coordination numbers from 4 to 12. So, if we regard the whole structure as a superposition of different local lattices [12], we are able to determine the percolation threshold as a function of the changing filling rate.

If one compares the basic relations of the PT (eqn. (1)) and of the EMT (eqn. (2)) for $x_1 > x_c$, it can be shown that the EMT also contains a term for the percolation threshold x_c, which equals $2/k$ [8]. So, by using eqn. (3), it follows that:

$$x_c = \frac{d_c}{f} = \frac{2}{k}. \tag{4}$$

To obtain a real equation for the PT a proportionality factor is introduced into eqn. (1) and we get:

$$\bar{\sigma} = \sigma_1 \left(1 - \frac{d_c}{f_1}\right)^{-b} \left(x_1 - \frac{d_c}{f}\right)^{b} \tag{5}$$

σ_1 represents the effective specific conductivity of the pure phase of Pb or PbO_2 ($x_1 = 1$), at a known filling rate f_1 (preferably f_1 should be the filling rate before discharge).

To determine the effective specific conductivity of the active material, in dependence on the state of discharge, the relation between the change of the volume fractions and the utilisation rate, r, must be considered. The utilisation rate is related to the theoretical capacity, i.e., in the case of complete conversion of the active material, r equals 1.

The change of the volume fractions means that there is a change in the relation for the pore volume of the electrode, V_e, to remain constant during discharge. Because of the lower density of lead sulfate this results in a growth of solid volume by diminishing the pore volume. Hence, for solid volumes V_1 (good conducting phase) and V_2 (poor conducting phase) it follows, having regard to the different molar volumes M_1 and M_2, that:

$$V_1 = V_{10}(1 - r) \tag{6}$$

$$V_2 = V_{10}rM_2/M_1 \tag{7}$$

where V_{10} is the solid volume of the active material before discharge.

The volume fractions are then defined as:

$$x_1 = \frac{V_1}{V_1 + V_2} = \frac{1 - r}{1 + Cr} \tag{8}$$

$$x_2 = \frac{V_2}{V_1 + V_2} = \frac{\dfrac{M_2}{M_1} r}{1 + Cr} \tag{9}$$

$$C = \frac{M_2 - M_1}{M_1}.$$

The filling rate is defined as:

$$f = \frac{V_1 + V_2}{V_e} = f_0(1 + Cr) \tag{10}$$

where f_0 is the filling rate before discharge.

By taking eqns. (8) and (10) we obtain from eqn. (5):

$$\bar{\sigma} = \sigma_1 \left(1 - \frac{d_c}{f_1}\right)^{-b} \cdot \left[\frac{1 - r - \dfrac{d_c}{f_0}}{1 + Cr}\right]^{b}. \tag{11}$$

For the EMT it follows from eqns. (2), (8), (9) and (10) that:

$$\bar{\sigma} = \frac{1}{\frac{2f_0}{d_c}(1 + Cr) - 2}\left[Q + \sqrt{Q^2 + 4\left(\frac{f_0}{d_c}(1 + Cr) - 1\right)\sigma_1\sigma_2}\right] \qquad (12)$$

$$Q = \left[\frac{f_0}{d_c}(1 - r) - 1\right]\sigma_1 + \left[\frac{M_2}{M_1}r\frac{f_0}{d_c} - 1\right]\sigma_2.$$

To calculate the effective specific conductivity of the active material we must determine the parameters for eqns. (11) and (12) (see Table 1).

TABLE 1

Parameters for the calculation of the effective electronic conductivity of the active material

	PbO_2	Pb	$PbSO_4$	Remarks
f_0	0.48	0.40		
b	1.70	1.70		[10]
d_c	0.154	0.1		PbO_2 [12]
σ_1 (S/cm)	1.35×10^2	5.3×10^3		PbO_2 [13]
σ_2 (S/cm)			1×10^{-8}	powder compressed at
M_1 (cm^3/Mol)	25.15	18.25		100 MPa
M_2 (cm^3/Mol)			48.2	

For the positive electrode a value for σ_1 is given in ref. 13. The corresponding value for the negative electrode was determined by our own measurements. The value σ_2, for lead sulfate, can be taken as a good approximation to that of lead sulfate powder compressed at 100 MPa.

The critical density is given as $d_c = 0.154$ [12]. This is valid for all spherical packings, as long as the particles are spherical. For the lead dioxide electrodes this requirement is quite well fulfilled. However, the particles of the lead electrode have a more elongated structure [5]. In this case the percolation probability changes. This can be shown in a simple example (Fig. 2) for a two-dimensional square lattice. For spherical elements every crosspoint may or may not be occupied. In the case of particles with a length to width relation of ($l/w = 2$), it follows that if one crosspoint is occupied
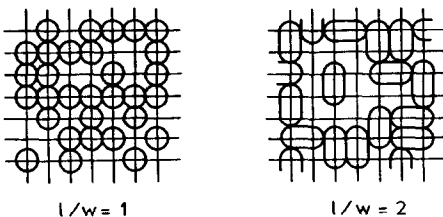

$l/w = 1$ $l/w = 2$

Fig. 2. Examples of different particle structures in a simple square lattice.

there is a probability of 1 that the neighbouring crosspoint will be occupied as well. From this Figure we learn also that the number of possible contacts changes from 4 to 6. Hence, the number of contacts is no longer equal to the coordination number of the basic lattice. In eqn. (4) we have then to set k equal to the contact number, which may be determined for three-dimensional lattices in an analogous manner to the example above.

However, the relation of length to diameter (l/d) for the particles of the lead electrode cannot be determined easily, but to a rough first approximation l/d may be set as 2. For a simple cubic lattice ($f = 0.524$) the contact number k will be 10. From eqn. (4) the critical density is then approximately 0.1.

3. Experimental

The measurements were made with 6 cells of a commercially available traction battery having a nominal capacity of 60 A h at the 20-hour rate. Each cell consisted of three positive and four negative grid-plate electrodes. The theoretical capacity of the three positive plates together was 144 A h, and for the negative plates together, 176 A h.

After an initial charge the cells were discharged for different times, the last one until complete collapse of the cell voltage. To obtain maximum output and to avoid concentration gradients in the electrodes, a low current density of 0.88 mA/cm^2, related to the geometrical surface of the positive electrodes, was applied. All sets of plates were discharged in an excess of electrolyte, to make sure that the discharge was not limited by shortage of acid. The density of the electrolyte was 1.28 g/cm^3 at 20 °C. The containers with the cells were held in a waterbath at 27 ± 0.5 °C.

When each cell completed the designated discharge it was taken off the experimental arrangement and washed under running water. The positive plates were then dried in normal atmosphere at 105 °C and the negative plates under vacuum at 60 °C. The utilisation rate and the electronic conductivity of the active material was then determined. The utilisation rate was determined by a wet-chemical determination of the amount of lead sulfate contained in the electrodes.

Conductivity measurements were made with small, square-stone like specimens of known size. They were separated from the electrodes, so that they did not contain any grid parts. The measurement was carried out by a four-probe method. To avoid errors from electrolytic current flow, an alternating current of 113 Hz was applied. Figure 3 shows a schematic outline of the arrangement.

Because the discharge varies over the plate, specimens were taken from different locations on the electrodes. The voltage drop was measured at several points on each specimen. The results were obtained by calculating the mean value of all measurements for each cell and type of electrode.
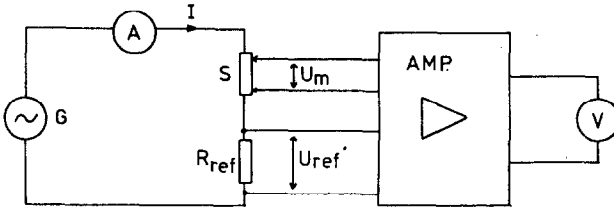
Fig. 3. Schematic outline of the arrangement for the conductivity measurement. G, generator; I, current through the specimen; S, specimen; R_{ref}, reference resistance; U_m, voltage drop over the specimen; U_{ref}, reference voltage; AMP, lock-in-amplifier.

4. Results and discussion

Figures 4 and 5 show the calculated values (straight lines) and the experimental values (single points). The theoretical lines show a sharp decrease in the effective electronic conductivity at a utilisation rate that lies distinctly below 100% for both electrodes. The conductivity drops by some orders of magnitude.
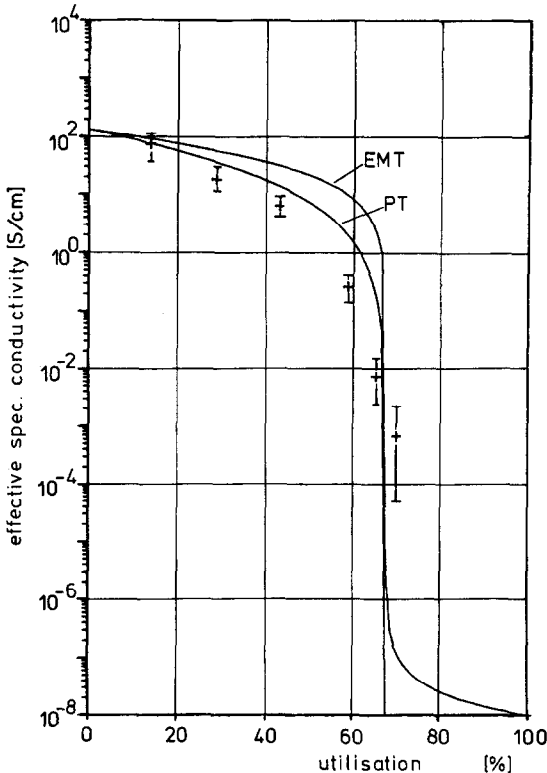

Fig. 4. Dependence of the effective electronic conductivity of the active material of a positive electrode on the utilisation rate.

A comparison of the calculated and measured values for the positive electrode shows a satisfactory coincidence (Fig. 4). The theoretical percolation threshold lies within the tolerance of the measured values. The vertical, marked tolerance lines show the variation of the measured values from which the mean values were calculated. Coincidence with the PT is better than with the EMT. This is because the EMT is based on a bond percolation mechanism, while the PT is based on a site percolation mechanism which fits spherical structures better. This results in the difference, especially in the region of the critical concentration [10]. The difference, still existing between experiment and the PT, may be related to the fact that the lead sulfate crystals are much bigger than the lead dioxide crystals. This causes a local concentration of poorly conducting material, which means a deviation from statistical distribution.

Because the examined cells have more negative than positive plates, a maximum utilisation could not be reached for the lead electrodes. Therefore, a single negative plate was discharged between two positives until voltage breakdown. The utilisation rate at this point was about 74% for the negative electrode (see Fig. 5). Here we have a better coincidence with
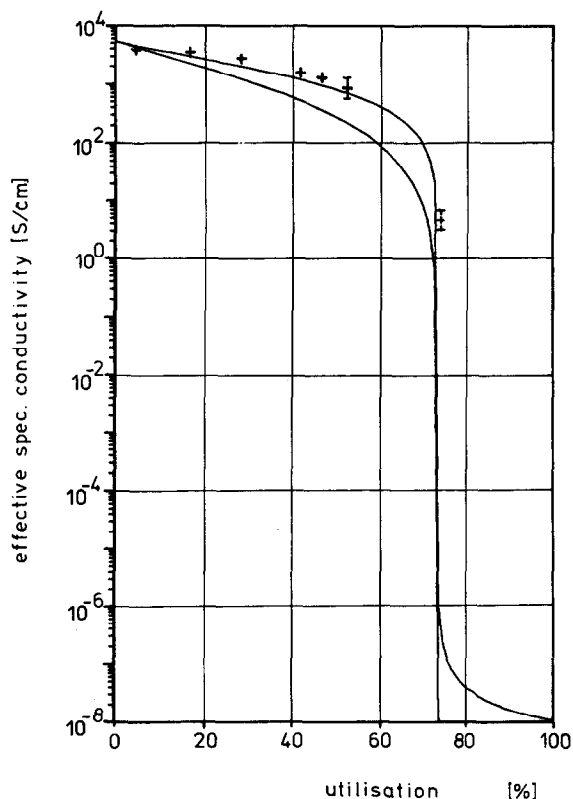

Fig. 5. Dependence of the effective electronic conductivity of the active material of a negative electrode on the utilisation rate.

the EMT because a bond percolation mechanism is a better fit for the description of spongy structures such as the lead electrodes. The congruence of experimental and theoretical values for the percolation threshold should not be overrated because of the rough estimation which was made for the critical density. But it clearly shows the tendency: the percolation threshold is pushed to better utilisation rates because of the elongated structure of the particles in the negative electrodes.

In Figs. 4 and 5 it can be seen that the utilisation rate at the beginning is greater than zero. This is due to the fact that there is always a small amount of lead sulfate in the fully charged plates.

If we relate the results of our investigation to the mechanism in the electrodes, it can be stated that a non-conductive network is produced during discharge, which insulates the unconverted parts of the active material. Hence, they can contribute neither to the conduction of current nor to the electrochemical reaction itself.

For the cells under investigation, the positive plates limited the discharge. The maximum output from the positive electrodes is 68% and from the negative electrodes, 74%. But, if we take into consideration the amount of lead sulfate present before discharge, the maximum real utilisation rate is 55% for the lead dioxide electrodes, and 69% for the lead electrodes. This is in good agreement with earlier observations [4].

5. Conclusion

The usual opinion, that the resistance of the solid matrix of the active material in lead–acid batteries remains constant and negligibly low during discharge, can no longer be held without reservation. In the case of low current densities the maximum output is limited by the breakdown of the electronic conductivity in the electrodes. From eqn. (11) it can be seen that the moment of breakdown is dependent on two factors, the critical density, and the filling rate before discharge.

The dependence on the critical density can be shown for the negative electrodes. In the case of spherical particles the calculated utilisation rate would be about 61%. However, the spongy structure makes a 74% discharge possible. This can be related to the greater number of contacts with the elongated particles. So, if it were possible to produce a similar structure in the positive electrodes, a greater utilisation rate should be possible, especially at low current densities.

If the filling rate in the plates is increased, the critical region will be reached as follows from eqn. (11), hence, the utilisation rate would be better. However, this means a decrease in porosity, which results in a greater diffusion resistance. This is not wanted at high current densities. From this we obtain a rule for optimizing the electrodes. For short discharges at high current densities, a high porosity is needed to ensure a fast diffusion of ions.

For long discharges at lower current densities, the porosity should be decreased to maintain a conducting network for as long as possible.

Acknowledgements

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