

Porosity measurements of electrodes used in lead-acid batteries

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Received 3 March 2004; received in revised form 30 August 2004; accepted 27 September 2004

Abstract

A method is presented that determines the porosity of a complete electrode plate used in lead-acid batteries. It requires only elementary equipment and is simple to operate, so that laboratory workers can use it as a routine method during manufacturing to determine the complete electrode's average porosity over a range of electrode sizes and types of both flat plate and tubular configuration. The method makes use of Archimedes' principle and uses glycerol as displacement medium. This allows for the porosity determination of both cured and formed positive and negative electrodes, without the detrimental effect of lead oxidation, which is common when using water as a displacement medium. The study showed that the method of using glycerol as a displacement medium gave on average, good repeatable results for both cured and formed positive and negative electrode plates used in the manufacture of automotive lead-acid batteries. The porosity results of the method were compared to the results obtained using Hg porosimetry, where a statistical paired *t*-test showed the two techniques to produce comparable results for all types of plates analyzed. The porosity of various plates was compared to the surface area of the respective active material of both positive and negative electrodes. These results showed unusual trends in that, depending on the manufacturing conditions, the surface area of formed positive electrodes could vary significantly from sample to sample of different batches without little change in its respective porosity. The surface area of different formed negative electrodes, however, would only vary slightly with significant changes in their corresponding porosity. The glycerol displacement method was also shown to be suitable to determine the effective porosity of cured and formed positive tubular electrodes.

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Keywords: Lead-acid battery; Electrodes; Porosity; Porosimetry; Surface area

1. Introduction

Battery technologists continue to research ways to obtain the maximum amount of capacity for each gram of material used as cathode and anode in a battery. This is especially true for lead-acid batteries, where lead is one of the heaviest elements used in commercially available battery systems and this limits the comparative capacity per mass ratio when compared to other battery systems. Manufacturers have aimed at utilizing the maximum geometric availability of active material. This is achieved by using thinner current collectors (grids) and optimizing the available surface area of the active material. In high current applications such as the starting of

a car where high current loading over short periods of time is required, the geometric available surface of the electrodes becomes important and is diffusion limited by the amount of acid that can freely flow into the porous material to react with the inner active sites [1]. Hence, the high rate of discharge is limited by the penetration depth of the acid. In turn, slow discharges are more resistant-controlled, allowing the acid time to diffuse into the interior material. Depending on the application of the battery (high or low rate discharge), the active surface area of the electrode material that is suitably exposed to the surrounding electrolyte used in lead-acid batteries is directly proportional to the amount of capacity that can be achieved during the discharge. However, the porosity of the active material influences the discharge rate by limiting the diffusion rate of the electrolyte that can penetrate the inner porous active material within an electrode. The typical

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porosity of cured and formed active material used in lead-acid batteries can range between 40 and 60%, depending on its manufacturing procedure and application [1–3].

An electrode with a high porosity and a large pore volume distribution might give good results during high power discharge applications, but if the porosity is too high, a reduction in the life cycle ability of the electrode would occur because of a decrease in the rigidity of the active material structure that would result from poor adhesion between the particles, resulting in shedding. So a trade-off between using electrodes with a lower porosity is used in order to maintain the life-cycle capability of the active material.

A distinction is made between various sizes and types of pores found in materials. The main types of pores pertaining to the lead-acid battery are the macropores and mesopores [1,4]. Macropores allow for the mass transport to occur throughout the pore system and have an average diameter between 0.05 and 5.0 μm . These make up the largest portion of voids in the active material of electrodes. Mesopores are usually a smaller fraction of the total porosity and comprise of cracks and fissures in the active material structure. These are usually between 2 and 50 nm. These capillaries, cracks, channels and crevices form the void volume of the active material framework, which is built from an initial mixture of loose lead oxide dust and an aqueous mixture of sulphuric acid [5]. Micropores are usually classified as pores with a diameter less than 2 nm and make up a very small percentage in lead-acid battery active materials.

The importance of the porosity of the active material in lead-acid battery electrodes has been widely debated and various authors have discussed the optimal porosity and its role in the battery electrochemistry during charge and discharge [1,6–8]. The importance of porosity as a function of the activity of the electrodes relates to the availability of active material sites for reactions to take place and the ease at which the electrolyte can access the active sites. The porosity of a material is related to its density about which a number of important terms should be clearly defined.

1.1. Absolute density

Other terms that are used in the industry are true, matrix, real, apparent and skeletal density. This density is obtained when the volume that is measured excludes the pores within the sample material. The absolute density is determined from the absolute volume of the material [9].

1.2. Bulk density

This is also referred to as the envelope density and is determined for porous materials where the pore spaces within the material are included in the volume measurement. For fine powders, the term “tap” density would be the same as bulk density [9].

There are a number of analytical techniques available that determine the porosity of porous material. These techniques

require expensive equipment and are usually limited to the sample size, which its sample chamber can accommodate. The most common technique used in a wide field of applications is mercury porosimetry where Hg is forced under pressure to fill the pore volume of a porous object. The rate at which the volume of Hg changes with pressure can then give an indication of the object’s porosity. Other techniques such as He pycnometry and dry-powder envelope density have been developed to determine densities of materials and are used successfully in many material based industries [9].

Some lead-acid battery manufacturers have developed their own technique using a water displacement method to determine the porosity of cured positive and negative electrodes. However, the method of using water as the displacement medium cannot be used to evaluate the porosity of the negative formed electrodes, which consist of sponge lead. The wetting of the negative formed electrode by water would accelerate the oxidation of the lead, thereby decreasing the effective pore size, and would not give a true reflection of the porosity of the active material. Instead, a method that uses glycerol as the displacement medium is proposed in order to determine the porosity of formed negative electrodes.

There seems to be a need for a quick, easy-to-use analytical method for determining the porosity characteristics of a battery electrode. The following method was developed in order to allow the technical laboratory in a lead-acid factory to evaluate, on a routine basis, both the formed and cured positive and negative electrodes and draw conclusions from the results with regards to the effective porosity of the manufactured material. The electrodes could be evaluated as a complete plate, giving an average porosity distribution across the whole electrode and not just certain sections thereof.

2. Experimental

Various samples of cured and formed active material of both the negative and positive flat plate electrodes commonly used in the manufacture of automotive batteries were analyzed for porosity using the glycerol displacement method and compared with the mercury porosimetry method. In addition, these samples were also analyzed for their BET surface area (nitrogen adsorption). Due to the limited sample chamber size, the BET surface area and Hg porosimetry analyses were performed on active material that was carefully removed from the center of the respective electrode grid. Care was taken not to crush the samples or distort the shape of the samples. This was particularly important for the analysis of the formed negative active material, where the sponge lead can very easily be distorted when handled. The glycerol displacement method, instead, was carried out on the entire plate.

The laboratory set-up and experimental details for measuring the absolute density and porosity of electrode active material by means of glycerol displacement are described below.

An electronic balance is placed on a sturdy frame structure above a suitable container that contains the glycerol and electrode to be analyzed. One end of a copper wire, bent into a hook, is allowed to extend from the bottom of the scale through a hole in the center of the frame support. The other end of the copper wire has a common crocodile clip where the plates for analysis are supported. The container used must be big enough to allow a complete battery plate to be immersed in glycerol. The container should however not be oversized, which would then require an excess amount of glycerol. The container is supported on a laboratory jack that can be easily moved up or down underneath the balance frame structure.

The plates for analysis must be sufficiently dried prior to determining their mass. The positive formed plates are dried in an oven at 110 °C for about 1 h. The negative formed plates are dried in an inert atmosphere such as nitrogen or argon. Care needs to be taken that all the sulphuric acid is washed from the plates before drying. Cured positive and negative plates are placed in an oven at 110 °C for a short period of time to ensure complete dryness before their plate mass determination. The respective mass of the dry plate is recorded before continuing with the procedure. The accurate mass of the respective grid is determined by carefully removing the active material of a cured electrode obtained from the same batch.

The dried plate to be tested is placed in a glycerol-filled container. The filled container is then placed in a desiccator, which is evacuated by a vacuum pump (about 380 mmHg) for about 0.5 h or until no more air bubbles are observed coming out of the glycerol-covered plate. The vacuum on the desiccator should be released slowly and the plate is then removed from the glycerol. The plate is allowed to stand freely in an upright position for about 0.5 h, ensuring that no contact is made with the sides of the plate. After the standing time, excess drops of glycerol hanging from the bottom of the plate should be carefully removed. The plate is re-weighed and its mass recorded. The wet plate is then suspended from the wire and crocodile clip and carefully immersed into the container filled with glycerol. The sample should not touch the sides of the container and hang freely, completely immersed in the glycerol. The supporting crocodile clip should not be immersed in the glycerol, as this will influence the results. The apparent mass of the sample suspended in the glycerol is then recorded. The analysis is carried out in duplicate on plates of the same manufacturing batch.

The following sets of experiments were performed in order to validate the method developed and determine its limits and accuracy:

1. Cured and formed positive and negative automotive flat plates were received on a monthly routine basis from a local lead-acid battery manufacturing facility. Their porosity was evaluated using the glycerol displacement method using the complete electrode. In order to verify the repeatability of the technique on various types of cured

and formed electrodes, the analysis was done in duplicate, where the average and the standard deviation were recorded. To ensure reproducibility, the electrodes were taken from the same manufactured batch. Selected electrodes from the same batch that had undergone similar electrochemical processes were further analyzed by BET surface area and Hg porosimetry. The samples for the two techniques were selected from active material taken from the middle section of duplicate electrodes.

2. A 12 V 50 Ah automotive battery was formed, where each cell of the battery was filled with a different SG sulphuric acid. It is known that the concentration of the formation acid influences the surface area and porosity of the final active material [5]. After formation, the battery was cut open, and the formed positive and negative electrodes carefully removed. The formed electrodes (+ve and -ve) were washed, appropriately dried and analyzed for their porosity by the glycerol displacement method and Hg porosimetry. The BET surface area was analyzed on duplicate plates from the same cell and the active material taken from the middle of the plates. The six cells were filled with 1.10, 1.13, 1.16, 1.20, 1.24 and 1.28 SG acid, respectively, and formed in a water bath for 62 h until 5 × C₂₀ rated capacity was achieved.
3. The repeatability and versatility of analyzing other types of electrodes were investigated by evaluating a cured and formed positive tubular electrode. A 10 rectangular spine electrode (14 cm × 1 cm per spine) was used in the study where the curing and formation conditions for each of the individual spines would be identical to that of the complete electrode. The electrode was divided by carefully cutting along the spine separator into 10 identical individual spines. The porosity of the cured active material in each spine was analyzed by the glycerol displacement method and compared for their repeatability and accuracy. The mass of the single spine, the plastic stopper and gauntlet was also taken into consideration when doing the calculations. The curing and formation conditions of the electrodes are described in a previous study [10].

3. Results and discussion

3.1. Repeatability of the glycerol displacement method to determine porosity

As was pointed out earlier, a method based on Archimedes' principle where water is the displacement medium has been used in the battery industry. However this method cannot be applied to negative formed electrodes, due to the interaction of water with the lead. For this reason, water was replaced by glycerol in the current analytical method.

Table 1 summarizes the data and the relevant important parameters when determining the porosity of the active material (AM) of a battery plate using the glycerol displacement method.

Table 1
Calculations for determining the porosity of plates by means of the glycerol displacement method

Parameter	Description or equation
A	Dry plate mass (g)
B	Glycerol soaked plate mass (g)
C	Mass of plate in glycerol (g)
D	Grid mass (g)
E	Grid density (g cm^{-3})
F	Active material mass (g) = $A - D$
G	Active material absolute density (g cm^{-3}) = $F / ((A - C / 1.264) - (D/E))$
H	Bulk density (g cm^{-3}) = $1 / (1/G + I)$
I	Specific pore volume ($\text{cm}^3 \text{g}^{-1}$) = $((B - A) / 1.264F)$
J	% Porosity = $HI \times 100$

Essentially the battery plate is dried and weighed (A). The dry plate is then immersed in glycerol and a vacuum is applied above the glycerol, so that the glycerol can penetrate the pores of the material. It is then removed from the glycerol and allowed to drip-dry so that excess glycerol is removed. Once no more surface liquid is visible, the wetted plate is weighed again (B). Now it is weighed again whilst completely immersed in glycerol (C). The grid mass of the plate (D) is based on the average mass per batch of plates, and the grid density (E) is determined using conventional methods and depends on the type of lead alloy used. Analysis of at least two plates from a batch is done simultaneously, and the average result is then reported.

The derivation of the formulae given in Table 1 will now be covered:

With reference to F in the table, the active material mass is simply the difference between the dry mass of the plate (A) and the grid mass (D).

According to Archimedes' principle, the apparent loss in mass of an immersed body is equal to the mass of liquid displaced, from which the volume of the immersed body can be determined. However the apparent loss in mass of the plate will be the sum of the apparent loss in mass of the paste on the plate and that of the grid of the plate.

The absolute density (G) of the paste is given by Eq. (1):

$$\begin{aligned}
 G &= \frac{\text{mass of dry AM}}{\text{volume of dry AM}} \\
 &= \frac{A - D}{\text{volume of plate} - \text{volume of grid}} \\
 &= \frac{A - D}{\text{volume of plate} - (D/E)} \quad (1)
 \end{aligned}$$

However the volume of the plate is equal to the volume of glycerol displaced, which equals the apparent loss in mass ($A - C$) divided by the density of glycerol at 25°C , which is 1.264 g cm^{-3} . The absolute density (G) of the paste of the plate is therefore given by Eq. (2):

$$G = \frac{F}{[A - C/1.264] - (D/E)} \quad (2)$$

The pore volume = volume of all open pores = the volume of glycerol that was soaked up by the dry plate = mass of glycerol soaked up divided by the density of glycerol. Hence the pore volume is given by Eq. (3):

$$\begin{aligned}
 \text{Pore volume} &= \frac{B - A}{1.264} \quad \text{and} \\
 \text{specific pore volume in } \text{cm}^3 \text{ g}^{-1} &= I = \frac{B - A}{1.264F} \quad (3)
 \end{aligned}$$

Now, since the total volume of the AM is the geometric volume of the AM + the pore volume, it follows that:

$$\text{Total volume of AM} = \left[\frac{A - C}{1.264} - \frac{D}{E} \right] + \left[\frac{B - A}{1.264} \right] \quad (4)$$

and the bulk density of the active material, (H), is simply the mass of active ingredient, (F), divided by the total volume of the AM:

$$\begin{aligned}
 \text{Bulk density} &= H \\
 &= \frac{F}{[(A - C/1.264) - (D/E)] + [B - A/1.264]} \quad (5)
 \end{aligned}$$

Eq. (5) can be simplified, since the geometric volume of the paste can be expressed as (F/G) and the pore volume itself is equal to (I × F). Hence:

$$\begin{aligned}
 \text{Bulk density} &= H \\
 &= \frac{F}{[(A - C/1.264) - (D/E)] + [B - A/1.264]} \\
 &= \frac{F}{[F/G] + IF} = \frac{1}{[1/G] + I} \quad (6)
 \end{aligned}$$

Finally the % porosity is given by Eq. (7):

$$\begin{aligned}
 \% \text{ Porosity} &= \frac{\text{volume of pores} \times 100}{\text{total volume of the paste}} \\
 &= \frac{IF \times 100}{F/H} = HI \times 100 \quad (7)
 \end{aligned}$$

In order to test the glycerol method for determining porosities on battery plates, duplicate plates from the same batch of battery plates were tested and some of the results are shown in Table 2. These tests were carried out on four different battery plate types: formed negative, formed positive, cured negative and cured positive.

The tabulated results show that the glycerol method gives consistent readings for the % porosity of the different plates. Both the negative and positive formed plates give, however, a slightly better average standard deviation than the cured plates. Taking into account the small standard deviations obtained, it becomes apparent that this is a workable method to determine, in situ, the porosity of battery plates.

This method will now be compared with mercury porosimetry.

Table 2
Porosity of duplicate plates using the glycerol displacement method

Type of plate	Sample 1 porosity (%)	Sample 2 porosity (%)	Average porosity (%)	S.D. (%)
Formed negative	73.07	73.48	73.28	0.29
	68.16	68.91	68.54	0.53
	67.89	67.46	67.68	0.30
Formed positive	51.45	51.86	51.66	0.29
	51.54	52.05	51.80	0.36
	49.71	50.21	49.96	0.35
Cured negative	40.62	39.49	40.06	0.80
	39.51	40.51	40.01	0.71
	36.13	35.25	35.69	0.62
Cured positive	40.70	39.68	40.19	0.72
	45.13	44.23	44.68	0.64
	41.34	42.05	41.70	0.50

3.2. Comparing the glycerol method with Hg porosimetry

Four different types of plates are being compared, namely the negative and positive formed plates, and the negative and positive cured plates. The results reported for the glycerol method represents each time the average analysis carried out on duplicate plates of the same batch, whilst the corresponding Hg porosimetry result represents only one analysis carried out on sample taken from the center of a plate from the same batch. The results are spread over a number of batches of plates obtained from the industry over a time period of 1 year. The forming and curing conditions were different depending on the type of plate and its particular manufacturing process. More studies were carried out on the formed positive plates, since this was the main area of the investigation.

Table 4

Comparison between the % porosity determined from Hg porosimetry and the glycerol displacement method for various cured and formed electrode material selected from positive or negative electrodes

Negative formed		Positive formed		Positive cured		Negative cured	
Hg por. (%)	Glycerol disp. (%)	Hg por. (%)	Glycerol disp. (%)	Hg por. (%)	Glycerol disp. (%)	Hg por. (%)	Glycerol disp. (%)
51.41	60.46	59.24	55.66	40.45	43.53	41.20	42.94
54.87	59.92	52.36	46.99	35.10	40.99	35.69	36.61
54.34	59.81	50.36	50.44	45.41	45.03	41.89	40.01
57.07	60.53	51.00	48.27	42.92	44.37	38.42	40.06
51.82	59.35	35.10	41.00	45.10	42.61	39.92	37.85
55.46	57.00	52.36	49.02	47.64	46.03	39.47	37.97
65.95	63.63	45.97	44.34	44.37	42.92	42.16	40.86
59.34	54.80	47.62	47.82	42.61	45.10		
55.21	51.17	50.44	50.36	44.34	45.97		
		47.82	47.62				
		50.32	49.11				
		46.21	47.32				
		44.86	47.41				
		51.24	48.94				
		52.51	49.39				
		53.59	50.59				
$t = 1.49, N = 9$		$t = 1.52, N = 16$		$t = 1.07, N = 9$		$t = 1.06, N = 7$	

Statistical verification was done at the 95% confidence level.

Table 3
Calculation for paired *t*-test for the negative formed plates

Hg porosimetry porosity (%)	Glycerol displacement porosity (%)	<i>d</i>	$\bar{d} - d$	$(\bar{d} - d)^2$
51.41	60.46	+9.05	-6.70	44.89
54.87	59.92	+5.05	-2.70	7.29
54.34	59.81	+5.47	-3.12	9.73
57.07	60.53	+3.46	-1.11	1.23
51.82	59.35	+7.53	-5.18	26.8
55.46	56.96	+1.50	+0.85	0.72
65.95	63.63	-2.32	+0.03	0.0009
59.34	54.80	-4.54	-6.89	47.47
55.21	51.17	-4.04	-6.39	40.8

$$\bar{d} = +2.35, \sum(\bar{d} - d)^2 = 178.9.$$

Using statistical testing, one can analyze the data obtained for both methods and decide whether there is a significant difference between the results of the two methods [11]. One starts with the null hypothesis, assuming that the two methods give the same result, and the *t*-test is carried out, which yields a *t*-value. If this *t*-value exceeds a certain critical value at a particular confidence level, then the null hypothesis must be rejected and the two methods then give significantly different results.

For samples, which are not identical but are compared by two similar techniques, the paired *t*-test is used [11]. This method is applied to the data shown in Table 3, which is for the formed negative plates only. The results shown in Table 4 are for all the plate types analyzed, and the *t*-test method was done on each group of plates separately.

Since the samples are not identical, it is meaningless to calculate the mean and standard deviation of each series, since any differences between the two methods will be swamped by differences in the samples. For each series of results, the differences (*d*) between each pair of results are calculated,

and the mean deviation (\bar{d}), is obtained. The square of the deviations from the mean deviation is calculated, and the standard deviation (s_d), of the differences is calculated using Eq. (8), where N is the number of different pairs of results.

$$s_d = \sqrt{\frac{\sum (\bar{d} - d)^2}{N - 1}} \quad (8)$$

For the results in Table 3 the data calculations for the negative formed plates is shown in the adjacent columns.

The value s_d given by Eq. (8): $s_d = \sqrt{178.9/8} = 4.73$.

Finally the t -value is determined using Eq. (9):

$$t = \frac{\bar{d}\sqrt{N}}{s_d} = \frac{2.35\sqrt{9}}{4.73} = 1.49 \quad (9)$$

For a two-tailed test, with eight degrees of freedom, the accepted critical statistical value for t at 95% confidence level ($P=0.05$) is 2.31 [11]. This shows therefore that the null hypothesis is valid and there is no significant difference between the glycerol displacement method and the Hg porosimetry method for the negative formed plates analyzed.

The data for the other plates was similarly calculated and the t -values are displayed in the Table 4. For each of these, the null hypothesis was valid, and therefore there is no significant difference between the two porosity methods.

The results in Table 4 are shown graphically in Fig. 1. The comparative results between the two techniques are indicated for each type of electrode analyzed. The linear equation shown is fitted using all the results.

Even though the statistical verification at the 95% confidence level showed that the two techniques are comparable and that the null hypothesis is valid, slight deviations from the simple linear relationship between the two techniques for all samples analyzed were observed. The graph (Fig. 1) shows the slight deviations from linearity, in particular the results of the formed negative electrodes. The porosity results obtained for these negative electrodes using the glycerol displacement method were, on average, slightly higher than the correspond-

ing values obtained using the Hg porosimetry method. This can be partially attributed to the sample preparation for the two techniques and the method of analysis. The whole negative formed electrode, after drying in an inert atmosphere, was analyzed within a few hours using the glycerol displacement method. Due to the limited size of the sample chamber used for the Hg porosimeter, the samples had to be taken from dried plates by pushing the “sponge” lead from the middle of the grid support. This could have influenced the porosity of the active material, where the soft “sponge” lead can easily distort, thereby closing the respective pores. Pavlov et al. [7] reported that Pb can also form an amalgam with Hg during the analysis procedure, thereby influencing the results of the measured porosity. He also reported that discrepancies in the porosity results can also arise from the fragmentation of the sample during preparation.

It must be remembered that the two techniques differ in their analytical methodology in that the Hg porosimetry analysis uses only a small section of the active material that was removed from the grid support. The material in the above study was always taken from the middle of the plate and was about 3 g in mass. The Hg is pressurized into the pores of the sample thereby filling most available space. Under these high pressures, certain pores in the active material can also collapse. On the other hand, the glycerol displacement method uses an entire electrode for analysis without the active material being removed from the grid support. The glycerol is only slightly forced into the pores by vacuum and relies on the volume displacement of the glycerol. The samples that have predominantly larger pores could give slightly lower results when using the glycerol displacement method as compared to Hg porosimetry, since some of the glycerol that had filled the larger pores could start to leak out due to gravity during the set rest period during analysis. All these factors can therefore contribute to the differences observed between the porosity results obtained from the two methods under investigation.

3.3. Comparison between porosity and surface area

The porosity of a material would be indirectly related to the surface area of the solid material matrix. Samples of electrodes manufactured by the local battery company were obtained on a monthly basis for more than a year and analyzed for their porosity using the glycerol displacement method and the results were compared to the BET surface area of the same material.

Fig. 2 shows the porosity plotted against the BET surface area for the same samples obtained from a number of cured and formed active material from positive and negative electrodes used in the manufacture of automotive lead-acid batteries.

The graph shows that there are clear groupings of the resulting values between the various types of active material analyzed. In theory, there should be a relationship between the surface area of a material and its porosity. The pore sizes in a lead-acid battery’s active material are usually in

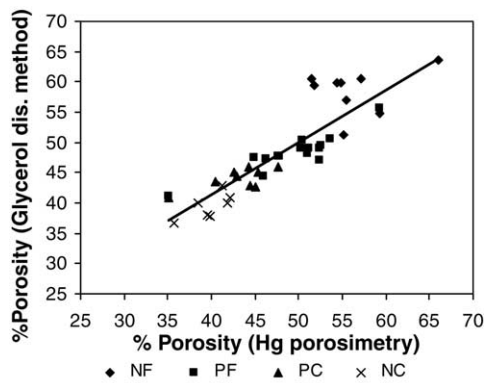


Fig. 1. Comparison between the % porosity obtained from the glycerol displacement method to that obtained from Hg porosimetry. NF = negative formed plates; PF = positive formed plates; PC = positive cured plates; NC = negative cured plates.

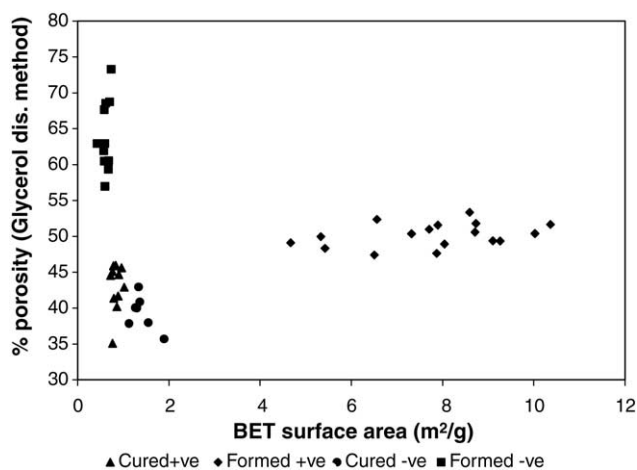


Fig. 2. Comparison of the % porosity using the glycerol displacement method vs. the BET surface area of various cured and formed active material.

the meso- and macro-range [1,7,8]. The more mesopores (smaller) a material has the smaller is the overall porosity, the greater is the surface area according to the BET nitrogen gas theory. If the material has predominantly macropores, the corresponding surface area should be relatively smaller. This can be seen from the results obtained for the formed negative active material, where the results (Fig. 2) show that it is possible to obtain a material that has a relatively large porosity with a relatively small surface area. The results also showed that different samples of the active sponge lead found on negative electrodes could have significantly different porosities but relatively similar surface area values. The porosity of the formed negative active material showed a considerable variation from 57 to 74% without any significant change in their respective surface area. This shows that the internal material's structure can change considerably during the formation time of the negative plate and can then result in an increase of the respective porosity, without significantly changing the available surface area. The increase in porosity would imply an increase in the macropores, but not necessary to the extent that it significantly changes the surface area of the available active material. The increase in macropores can also be accompanied by an increase in mesopores (cracks and crevices) within the larger pore, thereby maintaining a relatively constant available surface area.

The porosity and surface area of the cured positive and negative active material were very similar in that they reported a lower porosity and a lower respective surface area, with the negative cured material having a slightly higher average surface area. The porosity of the cured samples is between 35 and 45% and their surface area between 0.5 and 2.1 m² g⁻¹. There is not a great difference in the manufacturing process between the two cured electrodes, except that the negative cured material contains an expander consisting of very fine carbon powder, barium sulphate and lignin as an additive. These might contribute to the slightly higher surface area of the cured negative material.

The results for the positive formed active material show that the surface area of a sample could change significantly without varying the available porosity, which is the opposite to that observed for the negative formed electrode results. The surface area of the formed active material varied between 4 and 11 m² g⁻¹ with only a slight variation in the respective porosity between 45 and 50%. The active material could predominantly contain mesopores that contribute to a lower overall porosity and a much higher surface area. The larger variation in surface area from sample to sample could be due to the change in mesopores with little or no change in its respective macroporous character.

The results show that the formation conditions of the battery used during manufacturing influences the porosity and surface area of the final active material for both the negative and positive electrode.

The following investigation considered varying only one parameter, namely the concentration of the acid used during the formation, and its influence on the porosity and surface area of the final formed positive and negative active material was studied.

3.4. Porosity of electrodes as a function of formation-acid concentration

It is well known that the acid concentration used during formation influences not only the active material composition but also the porosity and surface area [5]. Furthermore, it was important to verify the unusual trend observed previously of surface area and porosity for various formed active materials (Fig. 2).

3.4.1. Positive electrode

Fig. 3 shows the porosity and surface area results for active material taken from the formed positive electrode as a function of the formation acid concentration. Two plates from the same cell were analyzed for their porosity using the glycerol

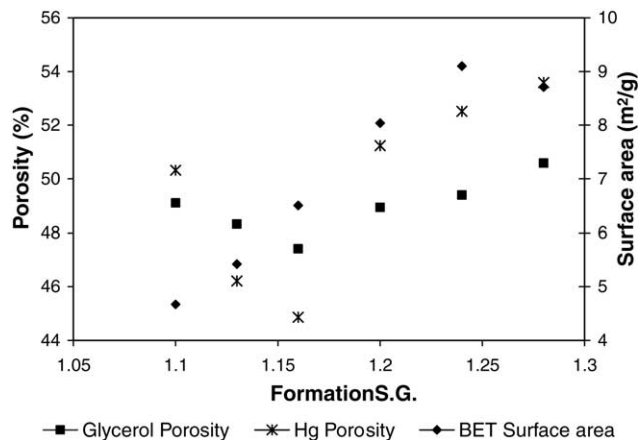


Fig. 3. Comparisons of the porosity and BET surface area of the active material from a positive electrode formed with different acid concentrations.

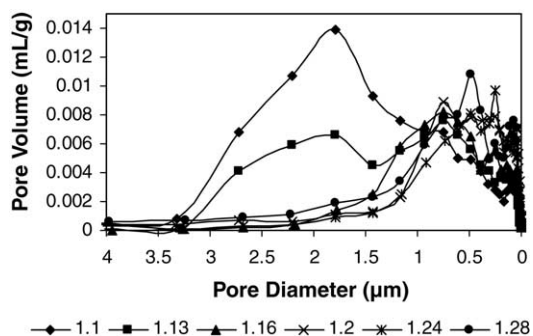


Fig. 4. Relationship between the incremental pore volume distribution and the pore diameter for the formed positive active material formed with different acid SG concentrations as determined by Hg porosimetry.

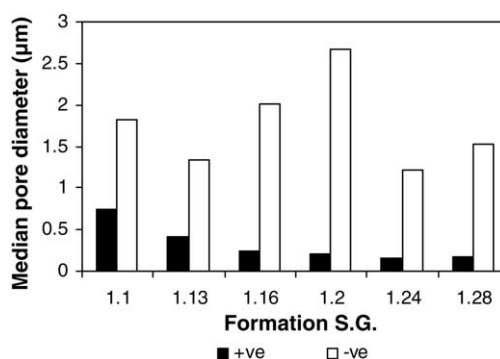


Fig. 5. Median pore diameter distribution for the formed positive and negative active material formed with different acid SG concentrations.

displacement method and active material taken from the center of another plate were analyzed by Hg porosimetry and BET surface area, respectively.

The variation of the porosity, using Hg porosimetry and glycerol displacement methods, for the positive active material shows similar trends in that the porosity of the active material at first decreases slightly as the SG of the formation acid increases, followed by an increase at SG values of 1.2 and higher. The variation in porosity with the SG of acid used for formation ranged only from 45 (1.16 SG) to 54% (1.28 SG).

The variation in the surface area for the active material with SG of the acid is significantly larger. There is an almost linear increase in surface area from 4.5 (1.1 SG) to 9 m² g⁻¹ (1.24 and 1.28 SG). This confirms the results observed in Fig. 2, where a larger variation in the surface area of the positive formed active material was observed than its corresponding porosity.

An advantage of using Hg porosimetry is that the pore volume and their size distribution of the active material can be determined at the same time. The distribution of the pore volume of the formed active material versus the pore diameter is shown in Fig. 4. The results show that the increase in surface area of the samples analyzed would have a corresponding decrease in their relative pore diameter. The corresponding median pore diameter distribution for the formed positive is shown in Fig. 5, where the median pore diameter of the active material formed with 1.24 SG acid is 0.15 μm and that of the 1.1 SG formed active material is 0.75 μm. For comparison purposes, the median pore diameter distribution for the negative electrodes is also shown, and will be discussed later.

The increase in the surface area of the active material formed with higher SG acid (Fig. 3) can be explained in terms of the material having predominantly smaller pores. The smaller pores do, however, not decrease the overall porosity of the material significantly, since there could simply be more of them at the smaller diameter. This would result in only a small increase in porosity but a significant increase in the surface area of the active material.

3.4.2. Negative electrode

The comparative porosity of the formed negative active material using the two techniques for porosity is shown in Fig. 6, together with the BET surface area determinations.

The results show that no significant change in the porosity of the negative active material occurs with a change in the formation SG acid. The porosity values obtained from the glycerol displacement method are generally higher than those obtained from the Hg porosimetry analysis. Reasons for the difference discussed previously include sample preparation techniques and the amalgam formation of lead and mercury.

Similar to the results observed in Fig. 2, the surface area of the negative formed active material that was formed over the SG range of 1.10–1.28 were very similar and within experimental error. This implies that very little influence on the active material’s surface area and porosity can be achieved by changing the formation acid concentration. There are, however, probably other factors that could influence the porosity of the negative formed active material such as the use of different expanders or formation currents, rates and temperature.

The median pore diameter for the Hg pore volume intrusion for the different formed negative active material with various formation SG acid is shown in Fig. 5. The results show that the negative formed material had a significantly larger median pore diameter than the corresponding positive

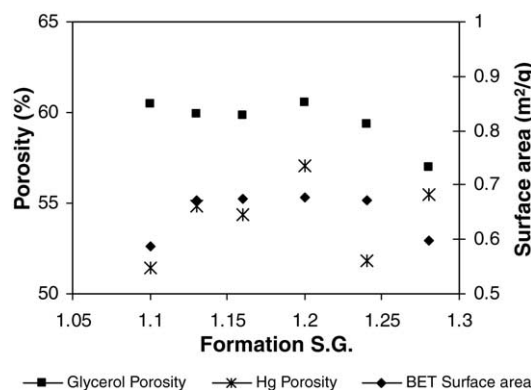


Fig. 6. Comparison of the porosity and BET surface area of the active material from a negative electrode formed with different acid concentrations.

Table 5
Summary of the density and porosity of single spines analyzed from a tubular positive cured plate, using the glycerol displacement method

Sample ID	Dry mass (g)	Glyc. wet mass (g)	In glycerol mass (g)	Mat. mass (g)	Abs. density (g cm^{-3})	Sp. pore volume ($\text{cm}^3 \text{g}^{-1}$)	Bulk density (g cm^{-3})	Porosity (%)
Cured tubular spines								
1	44.93	50.32	37.56	27.5	6.57	0.155	3.254	50.46
2	45.46	50.86	37.56	28.03	6.09	0.152	3.157	48.12
3	45.20	50.67	37.16	27.77	5.89	0.156	3.071	47.85
4	45.42	50.93	37.36	27.99	5.92	0.156	3.079	47.95
5	45.88	51.20	38.10	28.45	6.31	0.148	3.263	48.27
6	46.11	51.43	38.28	28.68	6.30	0.147	3.274	48.05
7	45.13	50.67	37.49	27.70	6.30	0.158	3.154	49.90
8	47.19	52.31	38.57	29.76	5.75	0.136	3.226	43.90
9	45.47	50.83	37.64	28.04	6.16	0.151	3.190	48.24
10	46.35	51.50	38.04	28.92	5.87	0.141	3.212	45.25
Average					6.11	0.150	3.188	47.80
S.D.					0.25	0.007	0.069	1.84

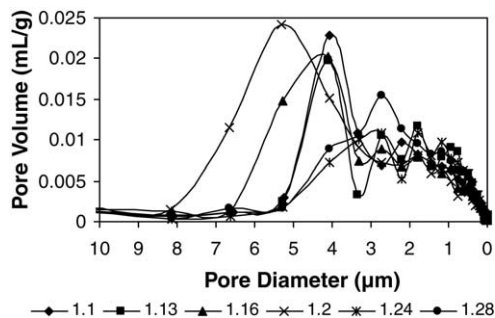


Fig. 7. Relationship between the incremental pore volume distribution and the pore diameter for the formed negative active material formed with different acid SG concentrations.

formed material. The slight variations in the median pore sizes between the samples analyzed are probably due to experimental error discussed previously. The pore volume distributions for the samples analyzed are shown in Fig. 7 and indicate that the majority of the pores are in the macroporous range.

Table 6
Summary of the density and porosity of single spines analyzed from a tubular positive formed plate, using the glycerol displacement method

Sample ID	Dry mass (g)	Glyc. wet mass (g)	In glycerol mass (g)	Mat. mass (g)	Abs. density (g cm^{-3})	Sp. pore volume ($\text{cm}^3 \text{g}^{-1}$)	Bulk density (g cm^{-3})	Porosity (%)
Formed tubular spines								
1	49.15	55.42	41.18	32.77	6.88	0.151	3.371	51.03
2	49.59	55.93	41.17	33.21	6.49	0.151	3.278	49.51
3	50.64	57.27	42.29	34.26	6.77	0.153	3.324	50.90
4	50.25	56.82	42.00	33.87	6.80	0.153	3.327	51.06
5	50.10	56.96	41.10	33.72	6.05	0.161	3.065	49.33
6	50.02	56.59	41.96	33.64	6.96	0.155	3.354	51.83
7	49.53	56.06	40.94	33.15	6.31	0.156	3.182	49.59
8	49.93	56.47	41.31	33.55	6.36	0.154	3.211	49.52
9	50.56	57.04	42.23	34.18	6.78	0.150	3.360	50.40
10	50.74	57.13	42.44	34.36	6.84	0.147	3.410	50.17
Average					6.63	0.153	3.288	50.33
S.D.					0.29	0.004	0.101	0.81

Total spine mass = lead spine + plastic + gauntlet = 17.4 g, spine density = 10.6 g cm^{-3} , glycerol density = 1.264 g cm^{-3} .

3.5. Glycerol displacement method used for positive tubular electrodes

The summary of a study that used the glycerol displacement method in the analysis of tubular cured and formed electrodes is shown in Tables 5 and 6. This study shows the viability and precision of using the glycerol displacement method for the analysis of tubular positive electrodes. The study involved the measurement of a single cured and formed 10-spine tubular electrode that was carefully separated into its individual spines. This ensured that no variation in curing or formation of the active material could have influenced the results since each spine would have been exposed to the same experimental conditions.

The results of the individual spines of a 10-spine electrode showed that the glycerol displacement technique can be used to determine the porosity of tubular electrodes with a relatively low standard deviation and span of results. The standard deviation for the porosity of the cured electrode spines was 1.84% and for the formed electrode, 0.81%.

4. Conclusion

The technique of using Archimedes' principle to determine the porosity of cured and formed plates used in the manufacture of flat plates as well as positive tubular electrodes was shown to be successful. The use of glycerol, instead of water, for determining the porosity was shown to be feasible for not only the cured plates, but also for formed negative plates, where the sponge lead is sensitive to oxidation. The method is comparable to Hg porosimetry, a well-known technique and differences between some of the results can be explained in terms of sample preparation and the formation of Pb–Hg amalgam. The technique is relatively quick and inexpensive, and can be easily implemented as a routine procedure in a manufacturing environment.

The variation of electrode porosity and surface area seems to be more evident for some plate types than others. The cured automotive electrodes (positive and negative) did not show large variations in their porosity and surface area over the range of samples analyzed.

Significant variations in the porosity of negative formed electrodes were obtained with very little change in their corresponding surface area, which can be explained in terms of its predominantly macroporous structure. This implies that during manufacturing, the active material is more prone to changes in its porosity than its surface area, and it is therefore more important to monitor porosity as a function of manufacturing conditions. The variation of the surface area of the positive formed electrodes was greater for different samples, with very little variation in their corresponding porosity, which relates to the predominantly mesoporous structure of the material. Hence, here it is then more important to monitor the surface area of such samples, which seem to be more susceptible to changes with varying conditions of manufacturing.

Many parameters influence the formation process of a lead-acid battery and the final properties of the active material. These include the formation rate, temperature, acid concentration and current strengths. Varying the acid con-

centration between 1.10 and 1.28 SG, and keeping all other parameters constant, the study showed that significant differences in the surface area of the formed positive active material can be achieved. There were only slight changes in the respective porosity. There was no significant variation in the resulting porosity and surface area of the formed negative electrodes.

The study also showed that with a certain degree of accuracy, the glycerol displacement method can be used to determine the porosity of complete cured or formed tubular positive electrodes.

Acknowledgments

The authors thank Willard Batteries for their financial contribution and for supplying battery samples used in this study. The authors also thank the South African NRF (Thrip) for their financial contribution.

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