

## Evaluation of hollow, glass microspheres used as an additive in positive, lead/acid battery paste

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### Abstract

New materials and electrode designs provide the possibility for dramatically improving the performance of lead/acid batteries. This paper investigates the use of lightweight, hollow, glass microspheres as a filler in the positive paste of lead/acid batteries. The paste density for this study was varied from 1.53 to 4.27 g cm<sup>-3</sup> where the low number is associated with a high loading of glass microspheres. All the plates fabricated exhibited good mechanical properties. The capacity (ampere hour) performance of the paste was evaluated with plates having similar thicknesses and porosities. The utilization of the paste, defined as the ampere hours discharged divided by the stoichiometric capacity of the paste, was plotted against the specific rate, defined as A g<sup>-1</sup> of paste. The data show that at the higher specific rates, the plates with glass microspheres performed much better than those without glass microspheres. The data also suggest that there is an optimum loading for the glass microspheres in the paste.

### Introduction

The lead/acid battery has a number of inherent characteristics that make it attractive for many applications. The battery has high volumetric energy density, high specific power and power density, high energy efficiency, and low initial cost. The many different uses found for the lead/acid battery testify to these strengths. However, the lead/acid battery exhibits low specific energy (i.e., energy per weight) which limits its usefulness in more demanding applications such as electric vehicles.

The theoretical specific energy of the lead/acid battery is 176 W h kg<sup>-1</sup>. The specific energy actually achieved depends on the discharge rate but is only about 20% of the theoretical capacity. The major reason for the lead/acid battery's inability to obtain higher specific energies is that much of the active material in both the positive and the negative electrodes is not discharged. This non-reacting active material provides structure and conductivity to the plates but does not contribute to the reaction.

The effect of different additives on the performance and life of lead/acid batteries has been reported previously [1-7]. Some of the additives

investigated include carbon black, carboxymethylcellulose (CMC), silica gel, and fibres (Dynel floc). The effects these additives have on the performance and life of the positive past are summarized by Dietz [1]. Synthetic graphite was investigated as an additive to tubular positive plates by Baker *et al.* [2]. They concluded that synthetic graphite increased porosity and reduced structural coherence. They also suggested the possibility of electro-osmotic pumping by additives with a high zeta potential. Tokmaga *et al.* [3] evaluated the effect of anisotropic graphite as an additive for the positive paste and found that active material utilization improved remarkably. This improvement in utilization was attributed to the increase in the porosity of the plates. One common effect of all these additives, however, is to decrease the density of the active mass, since the specific volumes of the additives are invariably greater than that of the active material.

The hollow, glass microspheres investigated in this paper had a true density of  $0.22 \pm 0.03 \text{ g cm}^{-3}$ . The spheres had a solid surface which prevented any liquid from penetrating to their hollow centers. The microspheres are commercially available and are employed as a filler in plastics for automotive parts and explosives. The low density additive allows the density of the active paste to be varied over a wide range. Since the glass microspheres are chemically inert in the environment and nonconductive, the effect of paste density on the specific charge performance of the paste can be studied independently of other effects.

The performance of electrodes having different amounts of glass microspheres in the paste was evaluated by discharging the electrodes at several discharge rates. The wet paste density for these plates varied from 1.53 to  $4.27 \text{ g cm}^{-3}$ . All the electrodes used the same production grids and had similar thicknesses. Plates with, and without, glass microspheres were hand pasted so that they could be compared directly. The hand-pasted plates without glass microspheres were also compared with equivalent, machine-pasted production plates. The porosity of all the plates was similar but the hand-pasted plates exhibited lower porosities than the production plates. The reason for this difference in porosity is not known, but variability in paste preparation for both the hand-pasted and machine-manufactured plates is believed to be responsible. The exact manufacturing parameters for the production plates are not known since they were taken from stock and not manufactured specifically for these experiments. All the plates were tested with an excess amount of electrolyte and negative material so that the positive electrode was the limiting electrode. The tests were performed at an ambient temperature of  $43.3 \text{ }^\circ\text{C}$  ( $110 \text{ }^\circ\text{F}$ ).

The results of the discharge tests are presented by plotting positive active material utilization as a function of the specific rate. Utilization is determined by dividing the discharged ampere hours by the stoichiometric capacity of the paste. The specific rate is the ratio of discharge current to paste weight. The plots therefore allow comparisons to be made between the different plates on a per gram basis.

## Experimental

A Barton-type lead oxide containing about 22% free lead was used to formulate the paste. The glass microspheres were mixed with the lead oxide before the water or acid was added. For every pound of lead oxide in the mix, 30 ml of  $\text{H}_2\text{SO}_4$  (density,  $1.4 \text{ g cm}^{-3}$ ) and 50 ml of  $\text{H}_2\text{O}$  were added over a 20 min period. Additional water was added to the mix until the desired paste density was obtained. For paste with glass microspheres, the desired paste density occurred when the paste density stopped increasing with the addition of water and started to decrease. Apparently, the additional water was needed to 'wet' the glass microspheres. The amount of water added to the mix was proportional to the loading of glass microspheres in the mix. A KitchenAide mixer was used to mix the paste, and its density was determined by weighing a given volume of the wet paste. The viscosity of the paste was not measured.

Different pastes were formulated for this study. A paste free from glass microspheres was made and used as a comparison for pastes containing the glass microspheres. The pastes with the glass microspheres had values of 1.1, 2.2, 4.4 and 6.6% by weight, of glass microspheres to lead oxide. The wet paste density for these mixtures ranged from 1.53 (6.6%) to  $4.27 \text{ g cm}^{-3}$  (paste without glass microspheres).

Plates were fabricated with the above described pastes by hand pasting production grids. The cast grids were 10.5 cm (4.25 in.) high, 10.8 cm (4.5 in.) wide, and 0.196 cm (0.077 in.) thick. The grids weighed 63 g and used a lead/antimony (2.75%) alloy. After pasting, the plates were wrapped in plastic and cured for a minimum of 72 h. The plastic prevents moisture loss and the curing process produces heat, but no measurements of either temperature or humidity were taken. After the plastic was removed, the plates were dried at room temperature for a minimum of one week. The goal for the curing process was to produce hand-pasted plates that performed similarly to the production plates. All the plates fabricated had approximately the same thickness (i.e., 0.085 in.) and similar porosities. The porosity was determined by weighing a cured plate both before, and after, it had been soaked in water. This method is used in Eagle-Picher's densitometer [8]. Information on the various plates tested is given in Table 1.

A minimum of two cells was fabricated for each plate type. All cells consisted of three plates separated by conventional separators. The center plate was the positive plate being tested, and the outer plates were production negative plates. The cells contained an excess amount of electrolyte. The excess electrolyte and negative material were to ensure that the positive electrode was the limiting electrode. In previous work [9], half-cell electrodes verified that the positive plates used in these experiments were limiting when discharged under similar experimental conditions.

The positive electrodes were formed *in situ* with  $1.10 \text{ g cm}^{-3}$  of  $\text{H}_2\text{SO}_4$ . The electrodes were charged at a constant current (i.e.,  $8.8 \text{ mA cm}^{-2}$ ) until 125% of the stoichiometric ampere hour capacity was reached. The stoi-

TABLE 1

Positive plate characteristics

Plate type	Paste density ( $\text{g cm}^{-3}$ )	Plate thickness ( $T_{\text{avg}}$ ) (mm)	Paste weight ( $W_{\text{avg}} \pm \Delta W$ ) <sup>d</sup> (g)	Stoichiometric capacity <sup>b</sup> ( $C_{\text{avg}}$ ) (A h)
Production plate <sup>a</sup>	4.27	2.29	84.61 $\pm$ 0.0	18.96
Hand pasted, 0% glass microspheres loading	4.19	2.12	77.69 $\pm$ 6.84	17.41
Hand pasted, 1.1% glass microspheres loading	3.34	2.05	58.15 $\pm$ 2.95	12.89
Hand pasted, 2.2% glass microspheres loading	2.53	2.21	58.55 $\pm$ 0.25	12.83
Hand pasted, 4.4% glass microspheres loading	2.09	1.96	39.33 $\pm$ 0.47	8.44
Hand pasted, 6.6% glass microspheres loading	1.75	N.A. <sup>c</sup>	43.22 $\pm$ 0.17	9.08

<sup>a</sup>Paste density for production plate supplied by the manufacturer.

<sup>b</sup>Stoichiometric capacity was estimated from the lead oxide weight in paste.

<sup>c</sup>Plate thicknesses for these plates are not available (N.A.).

<sup>d</sup>Mean average deviation for plates tested.

chiometric capacity of the electrodes was estimated from the electrode paste weight (see Table 1). All formation charges were performed at an ambient temperature of 43.3 °C (110 °F). After formation, the specific gravity of the acid in the cell was increased to 1.30  $\text{g cm}^{-3}$ .

After the acid adjustment, the cells were cycled. The cycle tests consisted of constant-current discharges where the discharge rate was adjusted so that the amperes per gram for the test electrode varied from 0.01 to 0.12. All discharges were to a cut-off voltage of 1.75 V.

After each discharge, the cell was charged at a constant current (8.8  $\text{mA cm}^{-2}$ ) until a clamping voltage of 2.45 V was reached. The cell voltage was regulated at the clamping voltage until 110% of the previously discharged ampere hours were returned. All charge and discharge tests were performed at an ambient temperature of 110 °F. The cell voltage, current, ampere hours, and temperature were recorded for each charge and discharge.

## Results and discussion

Figure 1 shows a magnified (309 $\times$ ) view of the glass microspheres. Typical diameters for the microspheres are from 20 to 50  $\mu\text{m}$ . Figure 2 shows a relatively heavy concentration of glass microspheres (4.4%) in cured paste at the same magnification. The microspheres appear to be uniformly distributed in the paste. When other pastes with different loadings of glass microspheres are viewed under the microscope, the same uniform distribution

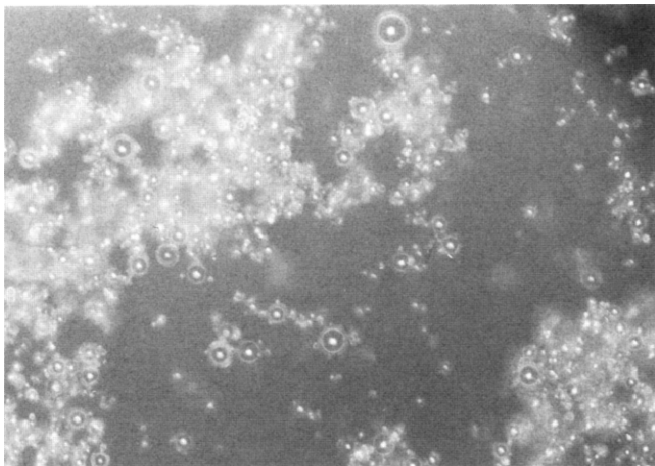


Fig. 1. Glass microspheres (309 $\times$  magnification).

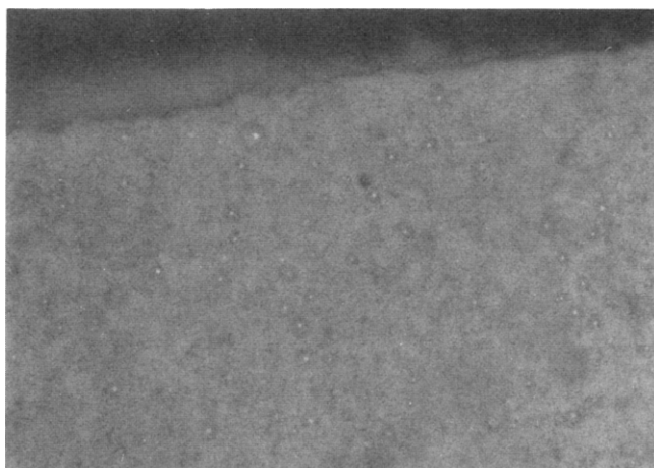


Fig. 2. Cured paste with glass microspheres (309 $\times$  magnification).

is observed. Also, no damaged microspheres were detected with the microscope. The hand-pasting operation did not appear to damage the microspheres, but it is not known whether or not commercial mixing and pasting operations would do damage. The ease with which the microspheres mixed with the lead oxide, and the uniform distribution of microspheres in the paste are important for any future industrial application.

The wet-paste density for the different hand-paste mixes is shown in Fig. 3. The paste density for the mix without glass microspheres was  $4.27 \text{ g cm}^{-3}$  ( $70 \text{ g in.}^{-3}$ ) and was the same as that used in the production plates. The Figure shows that as the weight per cent. of glass microspheres is

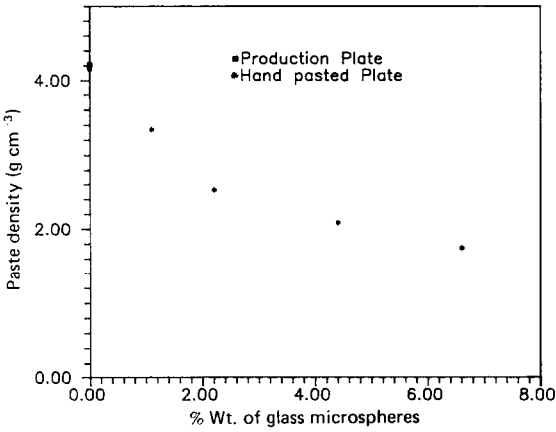


Fig. 3. Paste density vs. wt.(%) of glass microspheres.

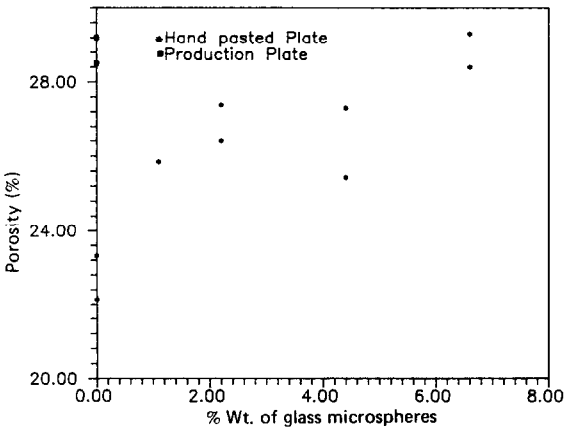


Fig. 4. Porosity vs. wt.(%) of glass microspheres.

increased, the paste density decreases, but not in a linear manner. The curve is flatter at the higher loadings of glass microspheres than at the lower loadings.

Figure 4 shows the porosities of the production plate and the different hand-pasted plates. The production plate had the highest porosity while the porosities of the hand-pasted plates were all very similar. The amount of water required to make the plate porosities similar for the different mixes was difficult to determine. The addition of the microspheres to the paste necessitated an increase in the amount of water.

The addition of the glass microspheres and the extra water produced a paste that was easy to apply to the grids. The ease with which the grids were hand pasted indicates that the microspheres might be beneficial in improving the machine pasting of positive plates. The cured plates did not crack and had a hard surface. On a volume basis, the microspheres are

actually less expensive than the lead oxide. All these considerations indicate that the addition of glass microspheres to the paste of lead/acid batteries could be commercially viable.

The test results are plotted in Figs. 5–10. Utilization of the positive active material is plotted as a function of the specific discharge rate in all the Figures. Utilization is defined as the ampere hours discharged divided by the stoichiometric capacity of the paste, and the specific rate is defined as  $A\ g^{-1}$  of paste. Since the stoichiometric capacity is proportional to the paste weight, the test results are also displayed on a per gram basis.

Figure 5 shows the data for the hand-pasted plates in the absence of glass microspheres in the mix. The solid line shown in the Figure is a linear, least-squares regression-curve-fit to the data. The coefficient of correlation, which is a measure of the accuracy of the curve fit to the data, is also provided in Fig. 5. The two dashed lines shown parallel to the solid line represent the standard error of estimate. The vertical dashed line shown in the Figure is drawn at the specific rate, which corresponds to the 1 h rate. The 1 h rate is similar for all the plates (i.e., from 0.06 to 0.07  $A\ g^{-1}$ ).

The utilization curve for the production plates is shown in Fig. 6. The curve is similar to the utilization curve for the hand-pasted plates in the absence of glass microspheres shown in Fig. 5. The two curves, along with the other experimental curves, are plotted in Fig. 11. The hand-pasted plates provide a good approximation to the production plates, even though the hand-pasting operation introduces variability into the plate fabrication process.

The utilization curves for the hand-pasted plates containing 1.1, 2.2, 4.4, and 6.6% by weight of glass microspheres to lead oxide are shown in Figs. 7 through 10, respectively. The curves show that the utilization increases when glass microspheres are added to the paste. The increase is greatest at the higher discharge rates and is negligible at the low discharge rates. At the high discharge rates the difference can be significant. The utilization for the plate with a 4.4% by weight loading of glass microspheres is four

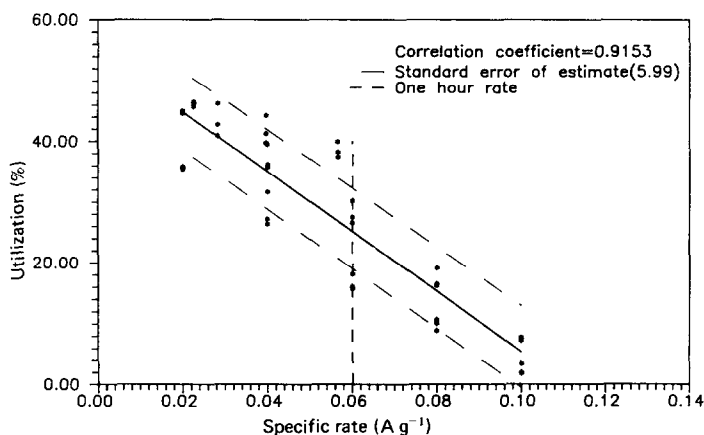


Fig. 5. Utilization for hand-pasted plates (no glass microspheres).

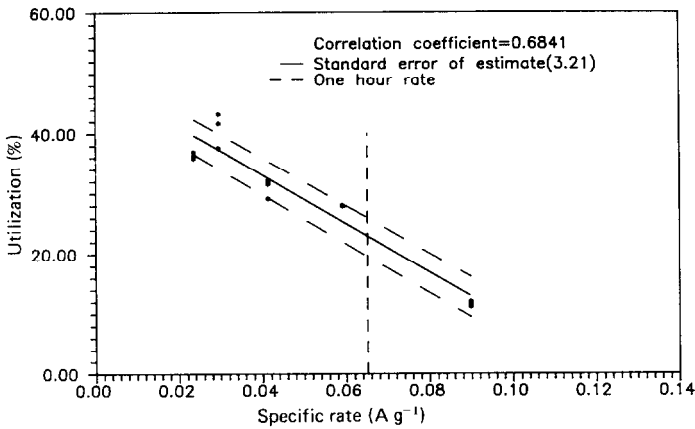


Fig. 6. Utilization for production plates (no glass microspheres).

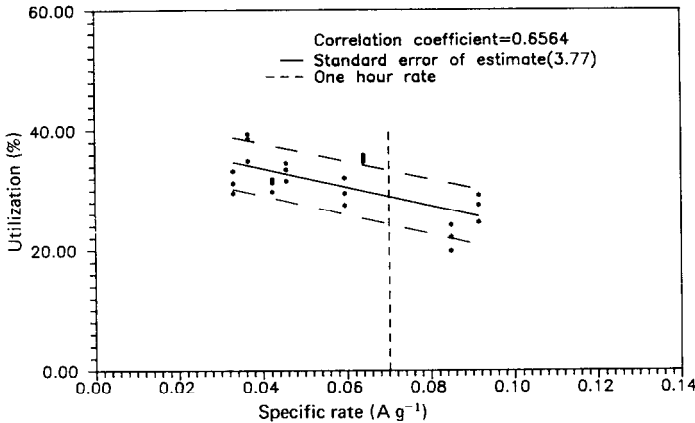


Fig. 7. Utilization vs. specific rate (1.1% by wt. of glass microspheres).

times that of the plates without microspheres at a  $0.1 \text{ A g}^{-1}$  specific rate. All the curves are shown in Fig. 11 so that they can be compared more easily. The utilization increases with the glass microsphere loading until a maximum is attained. The maximum occurs at approximately the 4.4% by weight of microspheres loading ratio.

The curves displayed in Figs. 5–11 can be more accurately modelled in three parts. At the low rates, most of the material that can react (i.e., 50–60%) does react. The amount of material that reacts is reduced at the higher rates where diffusion becomes more important. At the highest rates only the material immediately adjacent to the electrolyte has an opportunity to react. The low and high rate portion of the curves could be approximated by straight lines with a small slope. The portion of the curve where diffusion plays a major role, at the medium rates, would need to be approximated with a power curve. The straight line curve fit, shown in all the Figures,



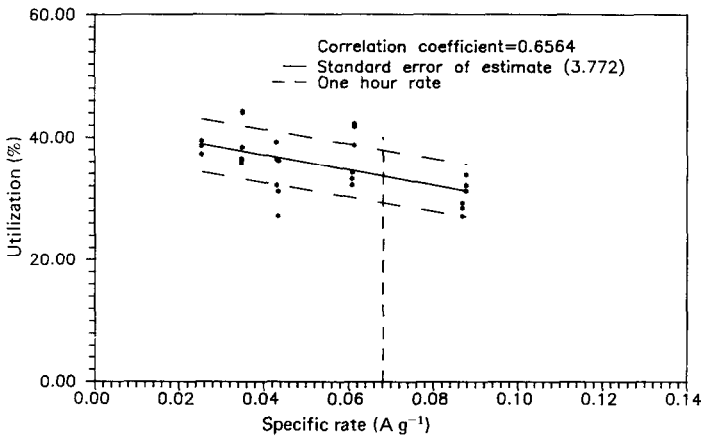


Fig. 8. Utilization vs. specific rate (2.2% by wt. of glass microspheres).

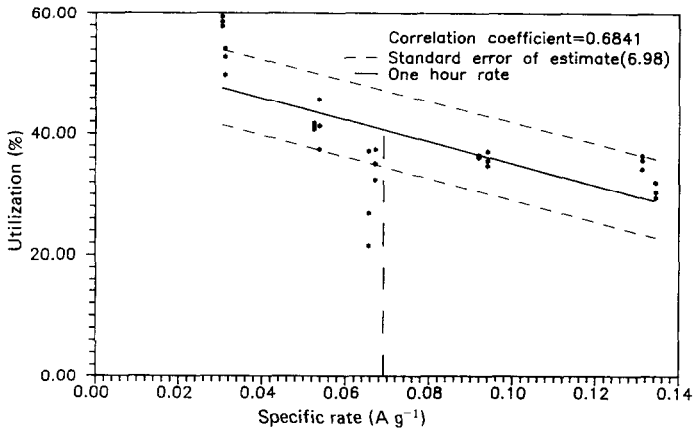


Fig. 9. Utilization vs. specific rate (4.4% by wt. of glass microspheres).

will obviously not model these regions accurately, but it is used to order and help visualize the results.

The improvement in utilization for plates with glass microspheres occurs at the medium and high rates. Ion diffusion in the positive plate is recognized as an important limiting mechanism for lead/acid batteries [10–12]. The mechanism that improves the utilization is believed to be related to diffusion. The glass microspheres reduce the positive paste density so that the amount of active material in the plate is reduced while the plate's surface area and pore volume remain essentially unchanged. Each gram of active material is therefore surrounded by a larger volume of electrolyte for reaction.

The electrolyte that discharges the positive plate can be separated into two components. One component is associated with the electrolyte in the positive plate's pores, and the other component comes from the bulk electrolyte between the plates. The pore electrolyte that reacts can be estimated from

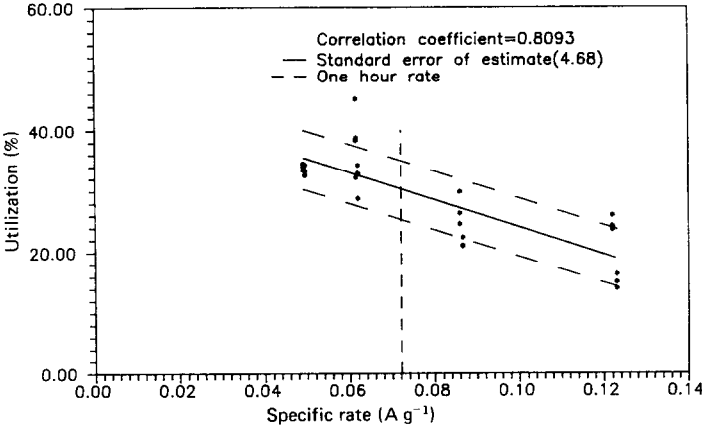


Fig. 10. Utilization vs. specific rate (6.6% by wt. of glass microspheres).

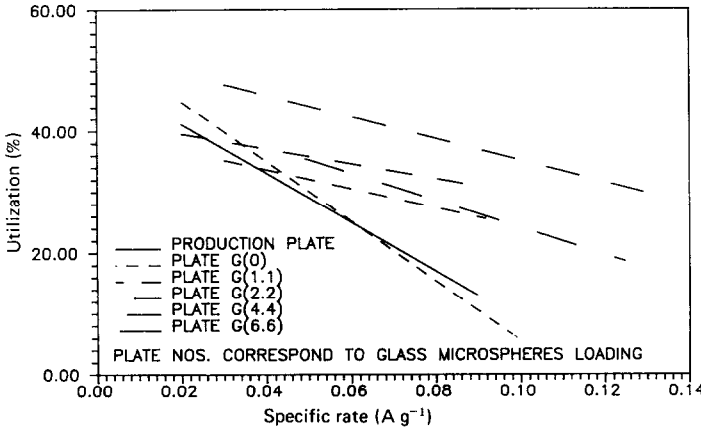


Fig. 11. Combined plot of utilization vs. specific rate.

a plate's pore volume and the change in electrolyte concentration during the discharge. The change in concentration is assumed to be the difference between the initial concentration,  $C_i$ , and the concentration associated with the end of discharge voltage, 1.75 V.

$$\Delta C = C_i - C_f$$

$$C_i = 5.04 \text{ mol l}^{-1}$$

$$C_f = 0.2784 \text{ mol l}^{-1}$$

The battery's discharge capacity associated with the pore volume is

$$C_{DP} = (nF\Delta C)V_p \tag{1}$$

where

$V_p$  is the plate's pore volume,  $n$  is the 2 electron transfer,  $F$  is 96 493 coulombs mol<sup>-1</sup>, and  $\Delta C = C_1 - C_2 = 4.762$  mol l<sup>-1</sup>.

The utilization,  $U_p$ , of active material attributable to the pore electrolyte can be calculated by dividing eqn. (1) with the stoichiometric capacity of the plate

$$U_p = C_{DP}/C_s \quad (2a)$$

where

$C_s = C_F W_p$  (Stoichiometric Capacity), and  $W_p$  = plate's paste weight;  $C_F = 806.8$  A s g<sup>-1</sup>.

When the expressions for  $C_{DP}$  and  $C_s$  are substituted into eqn. (2a) and rearranged, the expression for the pore utilization is

$$U_p = [nF\Delta C / (C_F \cdot \rho)] \rho V_p / W_p \quad (2b)$$

where

$\rho = 1.300$  g cm<sup>-3</sup> (initial electrolyte specific gravity)

Equation (2b) can be simplified to

$$U_p = C_p \gamma \quad (2c)$$

where

$\gamma = \rho V_p / W_p$

and

$C_p = nF\Delta C / C_F \cdot \rho = 0.876$

The pore utilization is therefore directly proportional to the nondimensional ratio of electrolyte weight in the plate to paste weight,  $\gamma$ . This ratio is important at the high discharge rates where only the electrolyte immediately adjacent to the active material will have an opportunity to react. In fact, the ratio can be viewed as a figure of merit for a plate's performance at high discharge rates.

Table 2 shows this figure of merit (i.e., the ratio of electrolyte weight in the plate's pores to the active material weight in the plate) for different loadings of glass microspheres. The figure of merit increases as the per cent. loading of glass microspheres to active material increases. The calculated pore utilization, based on eqn. (2), and the measured utilization at the specific rate of 0.1 A g<sup>-1</sup> for plates having different loadings of glass microspheres are also shown in Table 2.

The pore utilization approximates the measured utilization for plates having no glass microspheres (i.e., the production plate and the 0% hand-pasted plate) at this discharge rate. For these plates, most of the electrolyte consumed in the reaction comes from the plate's pores. At higher glass microsphere loadings, the percentage of the measured utilization attributable to the electrolyte in the pores is less. The bulk electrolyte therefore contributes more to the utilization of the lower-paste-density plates than to the higher ones.

The diffusion process in the lead/acid batteries is complex [10-16] and not amendable to closed form solutions. However, an estimate of the con-

TABLE 2

Figure of merit and utilization ( $0.1 \text{ A g}^{-1}$ )

Plate type	Pore volume ( $\text{cm}^3$ )	Porosity (%)	Paste weight (g)	Figure of merit (%)	Pore utiliz. (%)	Measured utiliz. <sup>a</sup> (%)
Production plate	7.325	30.52	84.61	11.25	9.86	11.64
Hand pasted, 0% glass microspheres loading	5.4127	22.72	80.2	8.72	7.65	5.02
Hand pasted, 1.1% glass microspheres loading	6.087	25.84	64.1	12.34	10.81	24.57
Hand pasted, 2.2% glass microspheres loading	6.102	26.89	58.4	13.58	11.9	30.32
Hand pasted, 4.4% glass microspheres loading	5.918	26.41	35.21	16.8	14.73	33.12
Hand pasted, 6.6% glass microspheres loading	6.5476	28.85	35.13	24.22	24.22	19.94

<sup>a</sup>The measured utilization was obtained from cycled plates, and not from the plates for which the pore volume was measured. The cycled plates were from the same batch, however, as the plates used to establish pore volume, porosity, and the figure of merit.

tribution the bulk electrolyte makes to the utilization in plates with glass microspheres can be made using the utilization curve for the hand-pasted plates with no glass microspheres, Fig. 5. The estimate is based on the assumption that at a given current density ( $\text{A cm}^{-2}$ ), the contribution of the bulk electrolyte to utilization will be the same for all the plates. This assumption is founded on the idea that at a given current density, the distance the bulk electrolyte will diffuse into a plate will be the same for all the plates.

The amount of material that reacts should be proportional to the diffusion distance, while the total amount of material in the plate will be proportional to the plate thickness. For uniform plates, utilization should therefore be proportional to the diffusion distance divided by the plate thickness. Since the glass microspheres are uniformly dispersed throughout the plate (i.e., have no preference for either the interior or surface of the plate), and the plates all have the same thickness and surface area, the bulk electrolyte utilization should be the same for all the plates operated at the same current or current density.

The bulk electrolyte utilization,  $U_B$ , for any plate can be found from the data for plates not having glass microspheres, Fig. 5, if the discharge currents for the plates are equal. The specific rate,  $S_R$ , is defined as

$$S_R = I_d / \rho_p V \quad (3)$$

where

$I_d$  = discharge current,  $\rho_p$  = paste density,  $V$  = paste volume.

Equation (3) shows that the discharge current for a specific rate is proportional to the paste density

$$I_d = \rho_p V S_R \quad (4)$$

If the discharge current,  $I_d$ , in eqn. (4) represents the current for a plate with glass microspheres at some specific rate,  $S_R$ , then an equivalent specific rate,  $S_E$ , can be defined for a plate with no glass microspheres which operates at the same current. The equivalent specific rate is

$$S_E = I_d / \rho_0 V \quad (5a)$$

where  $\rho_0$  is the paste density of the glass-microsphere-free paste.

When eqn. (4) is substituted into eqn. (5), the equivalent specific rate is equal to the specific rate multiplied by the ratio of the paste densities

$$S_E = \rho_p / \rho_0 S_R \quad (5b)$$

The utilization at the equivalent specific rate for plates without glass microspheres, defined as the equivalent utilization,  $U_E$ , will be equal to its pore utilization,  $U_{PE}$ , plus the bulk utilization

$$U_E = U_B + U_{PE} \quad (6a)$$

where

$U_{PE}$  = pore utilization for hand-pasted plates without glass microspheres  
= 7.65% (Table 2 – Pore utilization for hand-pasted (0%) plates).

The bulk utilization for all the plates discharged at a given current,  $I_d$ , is

$$U_B = U_E - U_{PE} \quad (6b)$$

The procedure for determining the bulk utilization of a plate with glass microspheres discharged at a specific rate,  $S_R$ , is to first determine the utilization for hand-pasted plates without glass microspheres, Fig. 5, at the equivalent specific rate,  $S_E$ . The bulk utilization can then be determined from eqn. (6b).

Table 3 provides a comparison between the measured and estimated utilization for plates discharged at the specific rate of  $0.1 \text{ A g}^{-1}$ . The pore utilization was calculated previously, and is shown in the Table for the reader's convenience. The effective specific rate is calculated with eqn. (5b) and is used with Fig. 5 to determine the utilization for hand-pasted plates without glass microspheres. The bulk utilization is calculated using eqn. (6b). The sum of the pore and bulk utilizations gives the total estimated utilization, and is shown alongside the measured utilization, Table 3.

The comparison between the estimated and measured utilizations is good. The estimated numbers are reasonably accurate and represent the trend of increasing utilization with an increasing ratio of glass microspheres to active material. The utilization estimate does not, however, predict the decline in utilization for the plate with the highest loading of glass microspheres.

Another mechanism is believed to be responsible for the decline in utilization at the higher loadings of glass microspheres. Their addition provides a more favorable ratio of positive active material to electrolyte in, and near, the plate, but the non-conducting spheres also act to isolate, physically and

TABLE 3

Comparison between estimated and measured utilization

Plate type	Effective specific rate	Pore utiliz.	Bulk utiliz.	Total estimated utiliz.	Measured utiliz. <sup>a</sup>
Production plate	0.1	9.86	0	9.86	11.64
Hand pasted, 0% glass microspheres loading	0.1	7.65	0	7.65	5.02
Hand pasted, 1.1% glass microspheres loading	0.08	10.81	8.35	19.16	24.57
Hand pasted, 2.2% glass microspheres loading	0.06	11.90	17.35	29.25	30.32
Hand pasted, 4.4% glass microspheres loading	0.05	14.73	22.35	37.08	33.12
Hand pasted, 6.6% glass microspheres loading	0.042	24.22	26.35	50.57	19.94

<sup>a</sup>The measured utilization was obtained from cycled plates, and not from the plates for which the pore volume was measured. The cycled plates were from the same batch, however, as the plates used to establish pore volume, porosity, and the figure of merit.

electrically, the active material. The benefits of having a more favorable balance of active material to electrolyte will, at some ratio of glass microspheres to lead oxide, be offset by a loss of contact or conductivity in the active material. The loss in conductivity can interfere with the plate formation process and can act to isolate portions of the active material during discharge. The 6.6% weight loading of glass microspheres to lead oxide has a high volume ratio of glass microspheres to positive active material (i.e., 2/3–3/4 by volume). The loss in conductivity, or some other limiting mechanism, is not surprising for this high volume ratio of glass microspheres to positive active material.

The increase in the specific volume of the paste containing glass microspheres improves utilization. This improvement results from a better balance between the positive active material and two components of the electrolyte: one associated with the pore electrolyte, and the other associated with the bulk electrolyte near the plate. The ratio of pore electrolyte weight to the positive active material weight is used as a figure of merit to characterize the pore utilization improvement. The utilization improvement associated with the bulk electrolyte is dependent on the current density. For a given specific rate, the current density of a plate with low paste density is less than a plate with high paste density. The smaller current density allows more of the bulk electrolyte to diffuse into the plate and participate in the reaction.

The specific charge performance for pastes containing different amounts of glass microspheres was investigated in this paper. The analysis and results were presented on a per gram basis of active material. The improvement in

specific performance of a plate utilizing glass microspheres, however, may result in an increase in the battery's volume. The increased volume would degrade the density performance (i.e., energy or power per volume) of the battery. In many applications, improving specific performance at the cost of reducing density performance is acceptable.

## Summary and conclusions

Utilization of the positive active material in lead/acid batteries can be increased by the addition of glass microspheres to the paste. The improvement becomes large at high specific rates (i.e., amperes per gram). The improvement is hypothesized to result from the increase in the specific volume of the paste, which provides a better balance between the positive active material and the electrolyte in, and near, the positive plate.

Although many materials used as additives will increase the specific volume of the paste, the glass microspheres are particularly attractive for this application due to their low density, cost, and ease of mixing with the lead oxide. From an experimental aspect, the glass microspheres can be used as a control to establish whether the paste utilization improvement with other additives is attributable to the increase in the specific volume or to some other mechanism.

The specific volume of the paste should be viewed as another parameter that can be adjusted to optimize the design of a battery. The addition of glass microspheres is an attractive method for altering the specific volume of the positive paste.

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