

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

Dean B. Edwards, Philip W. Appel and Brian Hammond

Department of Mechanical Engineering University of Idaho, Moscow, ID 83843 (USA)

(Received August 7, 1991; in revised form October 29, 1991)

Abstract

This paper investigates the use of lightweight, hollow, glass microspheres in the negative paste of lead/acid batteries. The paste density for this study was varied from 2.09 g/cm³ to 4.58 g/cm³ where the low number is associated with a high loading of glass microspheres. The capacity (A h) performance of the paste was evaluated with plates having similar thickness and porosities. At low rates, the capacity of the paste with glass microspheres was reduced in proportion to the amount of microspheres used in the paste. This behavior suggests that paste conductivity is the low rate limiting mechanism for negative plates. At the higher specific rates, the performance of paste with glass microspheres was similar to the paste having no glass microspheres.

Introduction

The lead/acid battery has a theoretical specific energy of 176 W h/kg. In practice, however, the lead/acid battery only achieves about 20% of this theoretical capacity because most of the active material in both electrodes does not react. This non-reacting active material provides structure and conductivity to the plates but does not contribute to the reaction. In this paper, negative plates having paste containing hollow, glass microspheres were tested. The tests determined the amount of negative paste that reacts at different discharge rates.

In previous studies performed at the University of Idaho [1], positive plates having paste containing hollow, glass microspheres were evaluated. The test results for these plates show that the addition of hollow, glass microspheres to the paste can increase the positive active material utilization at the higher discharge rates. The glass microspheres improve paste utilization by creating a better balance between the active material and the electrolyte in, and near, the positive plate. At the lower rates, however, no benefit existed for adding glass microspheres to the paste. The negative plate experiments reported in this paper duplicated the earlier positive plate experiments but, as will be shown, with very different results.

Investigators have studied a number of other additives for use in lead/acid battery paste. These additives include carbon black, carboxymethylcellulose (CMC), silica gel and fibres (Dynel floc). Dietz [2] summarized the effects these additives have on the performance and life of the positive paste. Baker *et al.* [3] added synthetic graphite to tubular positive plates. They found that the graphite increased porosity but reduced the structural coherence of the paste. They also suggested the possibility of electro-osmotic pumping with additives of high zeta potential. Tokunaga *et al.* [4] evaluated

the effect of anisotropic graphite as an additive for the positive paste and found that active material utilization improved remarkably. They attributed the improvement to the increase in the porosity of the plates.

In the negative plate experiments, the performance of negative electrodes having different amounts of glass microspheres in the paste was evaluated by discharging the electrodes at several discharge rates. The glass microspheres are hollow spheres of borosilicate glass with an outside diameter of 20–50 μm and a specific gravity of 0.12–0.22 g/cm^3 . The same production grids were used in all the electrodes. 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. All the plates were tested with an excess amount of electrolyte and positive material so that the negative electrode was the limiting electrode. A reference electrode verified that the negative was the limiting electrode in all the tests.

Experimental

The paste was formulated with Barton type lead oxide containing about 22% free lead. Expander material consisting of barium sulfate, carbon black and lignin was added to this oxide. The hollow, glass microspheres were mixed with the lead oxide before the water or acid was added. For every 454 g of lead oxide in the mix, 30 ml of H_2SO_4 (density = 1.4 g/cm^3) and 50 ml of H_2O were added over a 20 min period. Additional water was added to the mix until the desired paste density was obtained. 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.

Different pastes were formulated for this study. A paste containing no glass microspheres was made and used as a comparison for paste containing the glass microspheres. The paste with the glass microspheres had values of 2.2% and 4.4% by weight of glass microspheres to lead oxide. The wet paste densities for these mixtures ranged from 2.09 (4.4%) to 4.27 g/cm^3 (paste with no glass microspheres).

Plates were fabricated with the above described paste by hand pasting production grids. The cast grids were 10.5 cm high, 11.4 cm wide and 0.52 cm thick. The grids weighed 44 g and used a lead–antimony (2.75%) alloy. After pasting, the plates were cured. All the plates fabricated had approximately the same thickness and similar porosities. The pore sizes and distribution in the plates were not determined. Information on the various plates tested is tabulated in Table 1.

A minimum of two cells was fabricated for each plate type. All cells consisted of five plates separated by conventional separators. The center plate was the negative plate being tested and the next two outer plates were production positive plates. In order to insure that the positive plates were fully formed, two additional production negative plates were connected on the outside of the positive plates. These outside negative plates were disconnected after formation. The cells had an excess amount of electrolyte. The excess electrolyte and positive material was to insure that the negative electrode was the limiting electrode. A half-cell electrode was monitored to make certain this was the case.

The electrodes were formed *in situ* with 1.10 g/cm^3 of H_2SO_4 . The electrodes were charged at a constant current (i.e. 8.8 mA/cm^2) until 125% of the stoichiometric Ah capacity was reached. The stoichiometric capacity of the electrodes was estimated

TABLE 1
Negative plate characteristics

Plate type	Paste density (g/cm ³)	Paste weight ($W_{av} \pm \Delta W^b$) (g)	Average stoichiometric capacity ^c (A/g)
Production plate ^a	4.58	77.17 ± 0.35	17.10 ± 0.08
0.0 wt. %	4.20	75.06 ± 7.15	16.64 ± 1.59
2.2 wt. %	2.37	49.37 ± 2.53	10.72 ± 0.55
4.4 wt. %	2.09	35.11 ± 2.32	7.38 ± 0.59

^aPaste density for production plate supplied by the manufacturer.

^bMean average deviation for plates tested.

^cStoichiometric capacity was estimated from the lead oxide weight in paste.

from the electrode paste weight (see Table 1). All formation charges were performed at an ambient temperature of 110 °F. After formation, the specific gravity of the acid in the cell was increased to 1.30 g/cm³.

After the acid adjustment, the cells were cycled. The cycle tests consisted of constant current discharges where the discharge rates were adjusted so that the test electrodes varied from 0.015 to 0.10 A/g. 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 mA/cm²) until a clamping voltage of 2.45 V was reached. The cell voltage was regulated at the clamping voltage until 110% of the previous discharged capacity was returned. All charge and discharge tests were performed at an ambient temperature of 110 °F. The cell voltage, current, capacity and temperature were recorded for each charge and discharge cycle.

Results and discussion

Figures 1–4 show the experimental results of evaluating the different plates. The Figures plot the negative material utilization, expressed as a percent of the theoretical capacity, against the specific rate. Utilization is determined by dividing the discharged capacity by the stoichiometric capacity of the paste. The specific rate is the ratio of discharge current to active material weight. The plots allow comparisons to be made between the different types of plates on a per gram basis.

Figure 1 shows the test data for the production plates. The utilization is highest at the lowest discharge rates and decreases as the discharge rate is increased. The line shown in the Figure is a linear, least-squares-regression-curve-fit to the data. All the Figures have a best fit line drawn through the data with error bars representing one standard deviation. The straight line curve fit helps order the data so that the results can be more easily visualized.

Figure 2 shows the performance of hand pasted plates with no glass microspheres. The hand pasted plates perform similar to the production plates. The similarity between the curves for the production plates and the hand pasted plates with no glass microspheres verify that the hand fabrication techniques reasonably duplicate the machine techniques used to make the production plates.

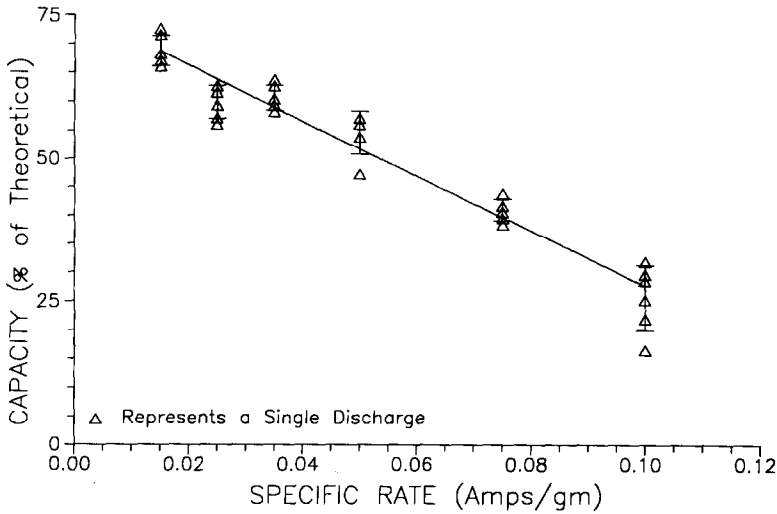


Fig. 1. Capacity vs. specific rate for production plates (no glass microspheres).

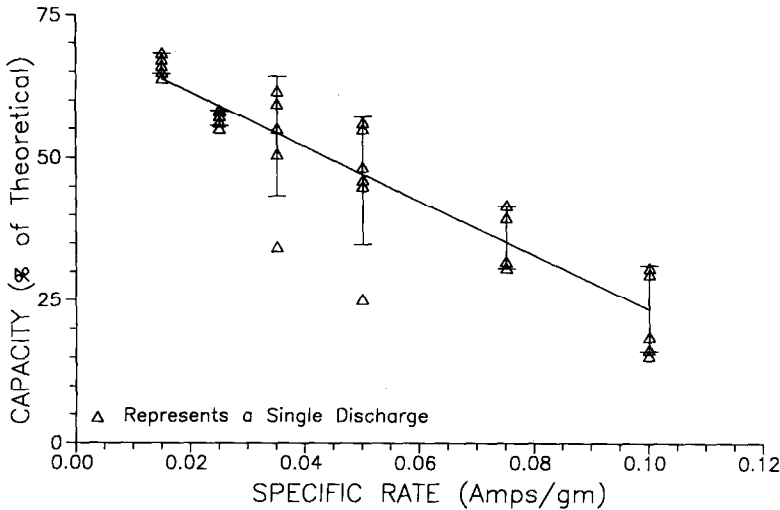


Fig. 2. Capacity vs. specific rate for hand-pasted plates (no glass microspheres).

Figures 3 and 4 show how adding glass microspheres to the paste affects paste performance. Figure 3 gives the test results for negative plates having paste containing 2.2% by weight of glass microspheres to lead oxide. Figure 5 shows all the curves for the different plate types together so that they can be more easily compared. The low rate performance for these plates is less than both the production plates and hand pasted plates having no glass microspheres (see Fig. 5). These plates, however, perform about the same at the high rates as the plates having no glass microspheres. The curve for the negative plates with the 2.2% glass microsphere paste is therefore flatter than the curves for plates having no glass microspheres. When the ratio of glass microspheres to lead oxide is increased to 4.4%, the low rate performance is further

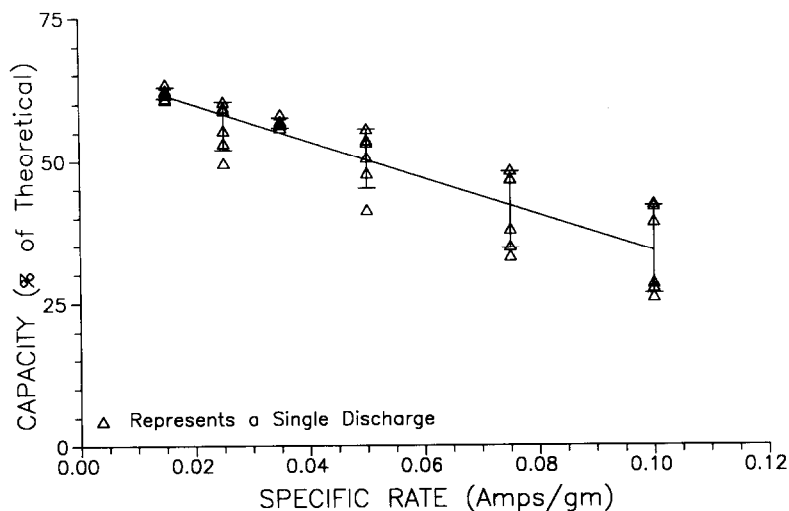


Fig. 3. Capacity vs. specific rate (2.2% by wt. of glass microspheres).

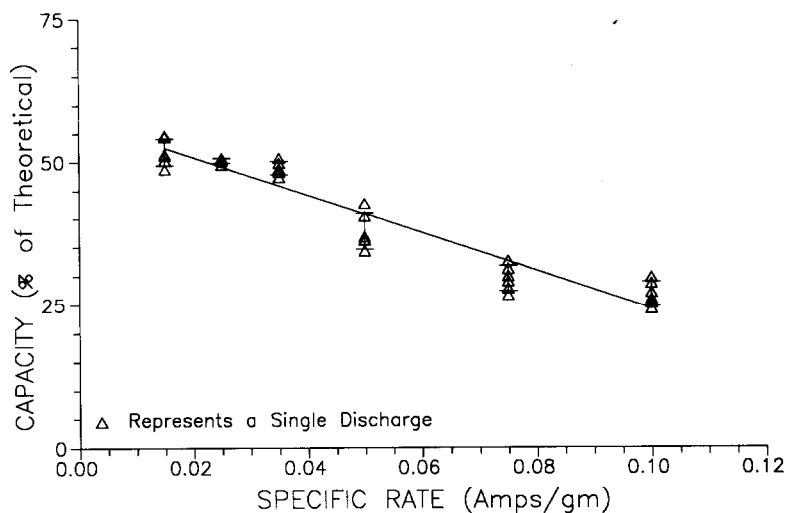


Fig. 4. Capacity vs. specific rate (4.4% by wt. of glass microspheres).

reduced, while the high rate performance is again similar to the other plates (see Figs. 4 and 5). Adding glass microspheres to the negative paste, therefore, reduces the low rate performance and has no measurable effect at the high rates.

We believe that the utilization of negative paste containing glass microspheres is reduced at low discharge rates because the glass microspheres reduce paste conductivity. Previous work [5, 6] investigated the role electronic conductivity plays in limiting the capacity of lead/acid electrodes. As a battery discharges, lead dioxide in the positive and lead in the negative is converted to lead sulfate. The lead sulfate is a very good insulator so that, during a low rate discharge, the electrode can become non-conductive and stop the reaction before all the active material is converted. The percolation

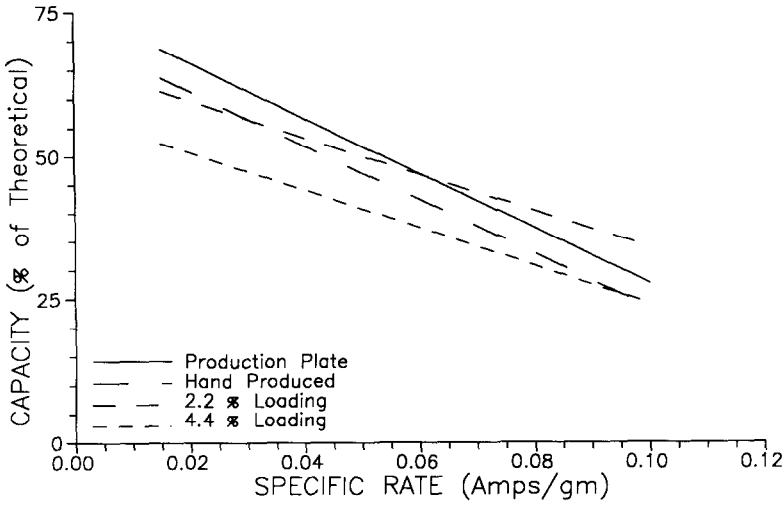


Fig. 5. Combined plot of capacity vs. specific rate.

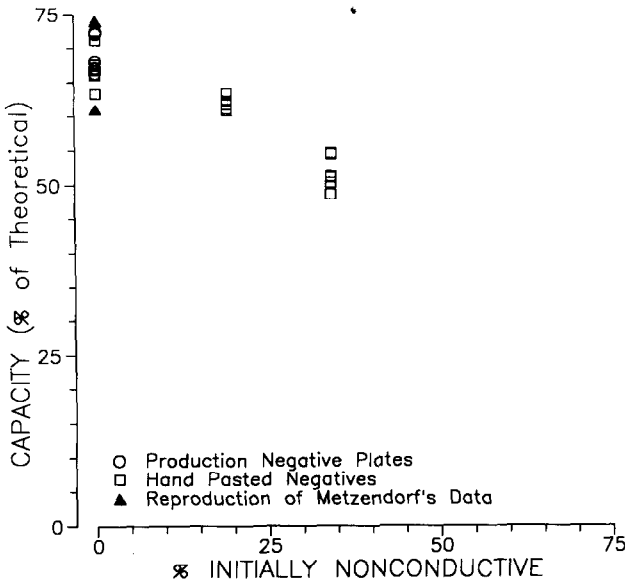


Fig. 6. Low rate (0.015 A/g) capacity vs. volume percentage of glass microspheres.

theory and the effective medium theory have been used previously to predict the conductivity of a mixture of two materials, one conductive and one non-conductive. Metzendorf [6] applied these two theories to estimate the capacity of lead/acid battery electrodes at low discharge rates.

Figure 6 shows the low discharge rate utilization for the different plate types as a function of the volume percentage of glass microspheres. The plates having no glass microspheres, both production and hand pasted, exhibit the highest utilization. Met-

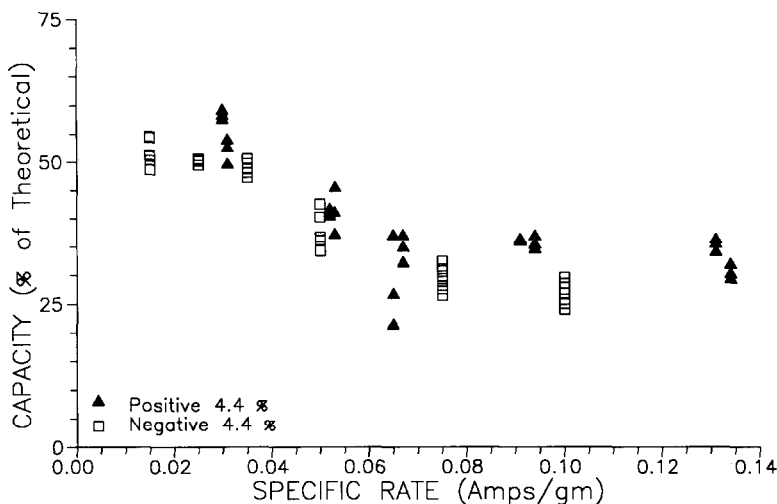


Fig. 7. Positive and negative plate comparison (4.4% by wt. of glass microspheres).

Metzendorf predicted the utilization for a negative plate to be between 61% and 74%. The lower number assumes a spherical particle shape for the negative active mass while the higher number is associated with an oblong particle shape. The utilization data for paste containing no glass microspheres fall between these two limits (see Fig. 6).

When glass microspheres are added to the paste, the paste conductivity will decrease since the glass microspheres are non-conductive. This decrease in paste conductivity will result in a lower paste utilization at low discharge rates. Figure 6 shows that as the volume percentage of glass microspheres is increased, utilization is decreased. At the lowest discharge rate (i.e. 0.015 A/g) the deviation of the data is small, as indicated by the error bars, so that the reduction in utilization with increasing volume percentage of glass microspheres definitely exists.

Qualitatively, the low rate discharge data are consistent with Metzendorf's hypothesis. A quantitative comparison is not easily performed since the glass microspheres are much larger than the particles used to model the active mass. If the glass microspheres were the same size as the active mass particles, they could simply be treated as discharged particles. In a companion paper [7], a computer program is presented that, at low discharge rates, can quantitatively model electrodes having these glass microspheres.

Work previously performed on positive plates [1] showed that the addition of glass microspheres to lead oxide improved medium and high discharge rate performance until an optimal value was achieved. This optimal value occurred around the 4.4% by weight ratio of glass microspheres to lead oxide. The optimal loading of glass microspheres in the positive plate may be interpreted as the loading where the incremental addition of glass microspheres improves electrolyte diffusion by the same amount as the paste's electrical conductivity is reduced. The acid diffusion process, usually considered to be the limiting mechanism for the positive plate in lead/acid batteries, can thus be improved until another limiting mechanism, electrical conductivity, is encountered.

If this reasoning is correct, then positive plates at the optimal and higher loading of hollow, glass microspheres, and negative plates with the same loading of microspheres,

should have similar performance. Figure 7 shows the data and best fit curves for both positive and negative plates having a 4.4% by weight of glass microspheres. The two curves are very similar and, more important, the data points at the low discharge rates for these plates are approximately the same.

Summary and conclusions

Negative pastes containing different amounts of glass microspheres were tested. The test results show that the glass microspheres reduced the negative paste capacity at low discharge rates. The loss in capacity increased with increasing amounts of glass microspheres. At the high discharge rates, the performance of all the pastes was similar. The glass microspheres had little if any effect on paste performance at the high discharge rates.

Metzendorf [6] hypothesized that the capacity of both the positive and negative electrodes was limited at low discharge rates by the electronic conductivity of the electrode. The test results for the negative electrodes having no glass microspheres was consistent with his predictions. The addition of glass microspheres to the negative paste reduces its conductivity. This decrease in conductivity is believed to be responsible for the loss in capacity experienced by the electrodes having glass microspheres.

A comparison between the negative and positive plates having 4.4% by weight of glass microspheres to lead oxide was made. The two curves and the low rate data points for the plates were very similar. The comparison shows that the optimal loading of glass microspheres in the positive plate, which is approximately at the 4.4% loading, occurs where the incremental addition of glass microspheres improves electrolyte diffusion by the same amount as the paste's electrical conductivity is reduced.

Acknowledgements

The research described in this paper was supported by the University of Idaho Seed Grant Program and the Idaho Research Foundation which filed for a patent on this work. Concorde Battery Co. was very helpful in supplying the needed materials for conducting these tests. The cycling equipment used was donated by the Electric Power Research Institute.

References

- 1 D. B. Edwards and V. S. Srikanth, *J. Power Sources*, 34 (1991) 217.
- 2 H. Dietz, *J. Power Sources*, 4 (1985) 305.
- 3 S. V. Baker, P. T. Moseley and A. D. Turner, *J. Power Sources*, 27 (1989) 127.
- 4 A. Tokunaga, M. Tsubota, K. Yonezu and K. Ando, *J. Electrochem. Soc.*, 134 (1987) 525.
- 5 J. P. Pohl and W. Schendler, *J. Power Sources*, 6 (1981) 245.
- 6 H. Metzendorf, *J. Power Sources*, 7 (1981/82) 281.
- 7 D. B. Edwards and P. W. Appel, *J. Power Sources*, 38 (1992) 281-286.