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Conductivity model for lead/acid battery electrodes discharged at low rates

Dean B. Edwards and Philip W. Appel
University of Idaho, Moscow, ID 83843 (USA)

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Abstract

A computer program was developed to model the conductivity of lead/acid battery electrodes during low rate discharges. The program is used to estimate the capacity of electrodes when they are limited by conductivity. Computer generated data shows good agreement with experimental capacity data obtained from testing both positive and negative electrodes at low discharge rates. These electrodes had different amounts of a non-conductive filler, glass microspheres, added to the paste. The observed correlation between the model and the experimental data supports the theory that conductivity of the active material in the electrodes is the low rate, capacity-limiting mechanism for lead/acid batteries.

Introduction

Previous work [1, 2] investigated hollow, glass microspheres used as a filler in lead/acid battery paste. The experimental results from capacity tests performed on these electrodes was consistent, at least qualitatively, with the theory that electronic conductivity of the active material limited the low rate capacity of lead/acid battery electrodes. In order to quantitatively compare the experimental results with this theory, a computer model was developed that accounted for having hollow, glass microspheres in the active material of the electrodes. This paper discusses the derivation of the model and compares the active material utilization predicted by the model to the experimental test results.

Metzendorf [3] hypothesized that the mechanism limiting the positive and negative electrodes of the lead/acid battery at low discharge rates is electrical conductivity. He showed a good correlation between two theories, the percolation theory and the effective medium theory for binary mixtures, and experimental data. These theories indicate that both the positive and negative active masses will stop being conductive at a particular ratio of conductive to non-conductive particles. Unfortunately, these theories cannot be directly applied to the case where hollow, glass microspheres are present in an electrode. The glass microspheres represent non-conductive particles that are substantially larger in area (i.e. 100 times in our model) than the particles used to model the active mass and cannot be simply treated as discharged particles.

A computer program was written to model the electronic conductivity of paste containing hollow, glass microspheres and its effect on electrode performance. The model replaces the active material in an electrode with a grid pattern of nodes which act as switches. After a node reacts during an electrode discharge, the switch is opened so that electrons can no longer use that node to find a path to the edge of the grid.

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An open node is assumed to have no conductivity while a non-reacted or closed node is assumed to have negligible resistance. As the battery discharges and the number of reacted nodes increase, the probability that a conductive path exists from a node that has not reacted to the boundary of the lead grid will decrease. If no conductive path exists, then the node will remain unreacted.

A detailed discussion of the derivation of the model and its verification for the case where no microspheres are present is discussed in the following sections of this paper.

Model development

Figure 1 shows the node structure used in the computer model to represent the active material. Each circle in the Figure is a node that acts as a switch making the node conductive or non-conductive. These nodes represent the active mass of the battery. Each node is connected to the surrounding nodes by eight pathways, as shown by the straight lines between the nodes.

The model simulates either the negative or positive active mass behavior by randomly 'choosing' a node and locating a conductive path to the edge of the grid. If a pathway is found, then the program changes the node to non-conductive and its pathways are removed from future use. If a pathway is not found, then the program leaves the node conductive.

The program can model different percentages of non-conductive blocks, of a variable size, that are randomly placed throughout the grid. The hollow glass microspheres have an actual diameter of 20 to 50 μm, and the distance between the plates' lead wires is 5 mm in the narrowest direction. This means that 100 spheres of 50 μm diameter each can fit across the 5 mm distance of the plates' lead wires.

An initial requirement that ten nodes represent each side of the non-conductive microsphere was established so that the active mass surrounding the microsphere would appear to be continuous. With this non-conductive particle size, 1000 nodes are needed per side (i.e. 100 spheres × 10 nodes). Computation time for this model, however, can be reduced if the grid size chosen is a power of two. A grid with 1024 nodes per side would satisfy the power of two requirement and would have over a thousand nodes per side.

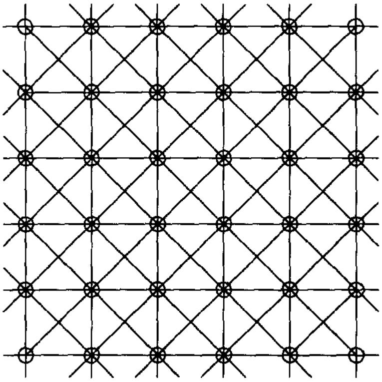

Fig. 1. Grid structure for computer model.

Figure 2 shows the case where no non-conductive blocks are present. The difference in accuracy between a grid having 1024 nodes per side and one having 512 nodes per side is very little. However, as the number of nodes per side are reduced, the percentage of nodes that react are increased. The higher reacted percentages associated with the smaller node numbers can be attributed to an edge effect, where a larger percentage of nodes is on the edge, and therefore do not need a pathway to react.

The program would check 50 random nodes simultaneously for conductive paths to the edge, before their connections were changed. As the number of nodes reacting simultaneously was increased from 1 to 10, and then to 50, no difference was seen in the results of the 512×512 matrix. Reacting 50 nodes simultaneously was shown to have little effect other than shortening the computation time.

Figure 3 shows a graph of the output from a series of 48 program runs using a grid size of 1024×1024. The graph shows that approximately 60% of the nodes found conductive pathways when there were no non-conductive blocks (i.e. glass microspheres) added to the grid. This compares favorably with what the effective medium theory (EMT) model developed by Metzendorf [3] for a spherical particle predicts (i.e. 61% of the active material reacted). Our model, however, predicts a much lower number of reacted nodes than what Metzendorf's EMT model predicts with an elongated particle shape (i.e. 74% of the active material reacted nodes). For the positive electrodes, Metzendorf found that the percolation theory (PT) gave more accurate results than the EMT. The PT predicted a 68% utilization value for positive plates. The model derived in this paper provides a reasonable estimate for the number of nodes that react in both the negative and positive plates when no glass microspheres are present.

As the non-conducting particles are added, the percent of the nodes that react decreases. A fifth order polynomial curve was used to fit the simulated computer data. This curve represents the maximum amount of material that can react based upon the conductivity model developed in this paper.

The model has a number of major limitations. It is two dimensional in nature and assumes that the conductive paths between nodes have zero resistance. In addition, the pores in a plate that have the same approximate dimensions as the glass microspheres or are larger are not included in the model. The two dimensional model will always underestimate the number of nodes that will react because the electrons are limited to move in one plane. A three dimensional model would allow an electron to move

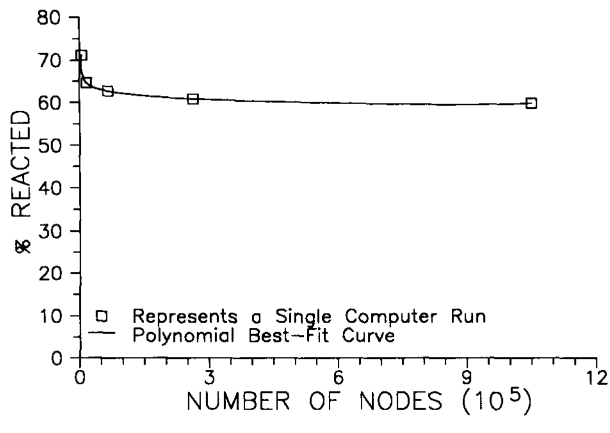

Fig. 2. Percent of reacted nodes vs. the total number of nodes.

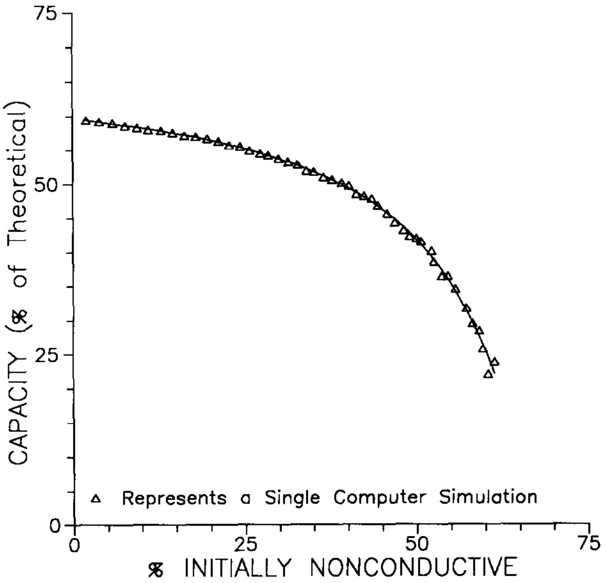

Fig. 3. Percent of reacted nodes vs. percent of non-conductive nodes.

out of its plane to find other pathways to the edge of the grid and would therefore predict a higher number of reacted nodes. If the conductive paths are given some resistance, however, the number of nodes reacting will be reduced. The two dimensional model already underestimates the number of reacted nodes so adding resistance to the conductive paths would not be desirable. A three dimensional model which includes large scale porosity and where the conductive paths have resistance would correct the major limitations of the present model.

Scher and Zallen [4] investigated a number of different two and three dimensional lattices. They found that the two dimensional lattices had higher critical percolation densities than the three dimensional lattices. Higher critical percolation densities, for our application, would correspond to a lower percentage of reacted nodes. For the two dimensional lattices they studied, the percentage of non-conductive nodes was $56 \pm 2\%$. This compares favorably with our model which predicts 60% reacted nodes.

Comparison with experimental data

In this section, results from previous tests [1, 2] on both positive and negative plates discharged at low rates will be compared with the computer model results. Table 1 provides information on plates having glass microspheres that were previously tested. In addition to these plates, production and hand pasted negative plates having no glass microspheres were also discharged at low rates and their capacity recorded [1, 2].

From Table 1, the volume percentage of hollow, glass microspheres to paste can be calculated and is shown in the last column. These calculations use a true density of 0.2 g/cm^3 for the hollow, glass microspheres as reported by the manufacturer. The

TABLE 1

Volume percentage of hollow glass microspheres to paste

Microspheres (wt.%)	Total paste weight (g)	Paste density (g/cm^3)	Weight of microspheres (g)	Microspheres (vol.%)
Negative plates				
2.2	601	2.37	9.6	19.0
4.4	605	2.09	20.0	34.5
Positive plates				
4.4	601	2.09	20.0	34.8

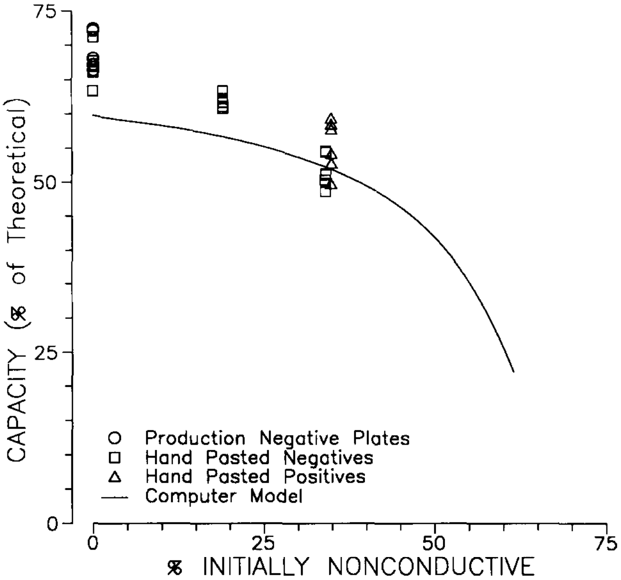

Fig. 4. Comparison between computer model and low rate discharge experimental data [1, 2].

volume percentage for both the positive and negative plates having a 4.4% ratio of glass microspheres to lead oxide are almost identical.

The negative plates were discharged at the low rate of 0.015 A/g. The discharge rate for the positive plates was 0.025 A/g. As discussed in ref. 2, this positive plate type (i.e. 4.4% ratio) had a high enough loading of glass microspheres that its performance was starting to be limited by the electronic conductivity of its active material. The only other positive plate type that had a higher ratio of glass microspheres to lead oxide (i.e. 6.6% ratio) was not tested at a low enough discharge rate to be included. Its lowest discharge rate was 0.05 A/g. The positive plate tests [1] were not originally designed to investigate the low rate performance of positive plates.

In Figure 4, the curve generated from the computer model is compared with the experimental data. The curve, which was previously shown in Fig. 3, provides a reasonable estimate to the data points and accurately represents the decrease in capacity with increasing amounts of hollow, glass microspheres in the paste. The computer model will generally underestimate the capacity because it is only two dimensional.

Although some deviations exist between the model and the experimental data, the simple model is surprisingly accurate. The model is two dimensional and does not account for changes in structure and species conductivity during discharge, but its results are still very close to the behavior of the actual battery. The model's prediction matched both Metzendorf's [3] spherical model and actual experimental data and could therefore be used by others to predict the effect that various additives might have upon battery systems. The most important result, however, is that the model and experimental data provide a convincing argument that electronic conductivity limits the lead/acid battery performance at low discharge rates.

Summary and conclusions

A computer program was developed to model the conductivity of both positive and negative electrodes at low discharge rates. The program was written so that it could model electrodes having different amounts of hollow, glass microspheres and predict the low rate capacity of these electrodes. Data generated from the computer show good agreement with the experimental capacity for both negative and positive electrodes. This good agreement provides a convincing argument that electronic conductivity limits lead/acid battery performance at low discharge rates.

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