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Short communication

A three-dimensional conductivity model for electrodes in lead-acid batteries

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Abstract

In this paper, we develop a three-dimensional conductivity model for the active material in the electrodes of a lead-acid battery. We use the model to investigate the influence that this conductivity has on battery capacity. Previous computer models used for this purpose were two-dimensional. Our three-dimensional model allows electrons to move out of a two-dimensional layer to another layer in order to find conductive pathways to an edge thereby allowing the reaction to occur. By using a number of two-dimensional layers, the actual changes in conductivity taking place in the plates can be more accurately modeled. Because of the many layers of our three-dimensional model, the total number of conductive paths is much greater than the previous two-dimensional models. We extend the two-dimensional models to three-dimensions, and compare the model capacity results with those predicted by the Percolation Theory and Effective Medium Theory. We find that the results of the three-dimensional model closely match the predictions of these theories.
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1. Introduction

The utilization of active materials in lead-acid batteries has always been lower than the theoretical stoichiometric capacity. The maximum utilization of the positive active material (PbO_2) of present day lead-acid batteries is typically less than 55% of the theoretical value [1], even at low current densities. For the negative active material (Pb), the maximum utilization is slightly higher with values of about 60% [1]. Metzendorf [2] hypothesized that the mechanism limiting the positive and negative electrodes of the lead-acid battery at low discharge rates is electrical conductivity of active materials during discharge. He showed that the electrical conductivity of powder mixtures may be described by the theories of statistically distributed networks. He also showed a good correlation between experimental data and two theories, the Percolation Theory (PT) and the Effective Medium Theory (EMT) for binary mixtures. He estimated the maximum real utilization to be 55% for the lead dioxide electrodes, and 69% for the lead electrodes.

In these theories, the structure of the active materials in the porous electrodes may be regarded as a network that contains statistically distributed resistance elements. Within this network, PbO_2 and Pb provide good electrical conductivity, while $PbSO_4$ provides poor electrical conductivity. The changing electrical conductivity of this binary mixture system can then be modeled as a phase transition problem with the Percolation Theory or the Effective Medium Theory. The difference between PT and EMT is that PT is based on a site percolation mechanism, which fits spherical structures better, while the EMT is based on a bond percolation mechanism and is a better fit for the description of spongy structures such as lead electrodes.

These theories show that at a particular ratio of conductive to nonconductive material, the conductivity of the whole system changes dramatically from one phase to another. This ratio is called the percolation threshold or critical volume fraction. With the production of $PbSO_4$ during the discharge process, one may expect that the good electrical conductivity of the reacting Pb or PbO_2 electrode will change to that of poorly conducting $PbSO_4$. This process occurs because a large portion of those conductive pathways for electron transport are blocked so that further discharge becomes impossible although not all PbO_2 and Pb have been converted to $PbSO_4$.

We have previously investigated the use of hollow glass microspheres as nonconductive additives in the paste of both the negative and positive electrodes of the lead-acid battery [3,4]. In the previous research, a two-dimensional computer

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model was developed to help predict the influence of these additives on the conductivity and the capacity of the electrodes. The influence of both spherical additives and additives having different aspect ratios can be simulated by the two-dimensional model [4,5]. However, the battery is actually a three-dimensional structure where conductive pathways can be formed out of the two-dimensional plane that is presently used to model the process. In this paper, we develop a three-dimensional model by using two-dimensional planes and allowing electron transport between planes. We compare our simulation results with the Percolation and the Effective Medium Theories.

2. Model description

Percolation Theory was introduced to mathematically model disordered systems. Examples could be a solute diffusing through a solvent, molecules penetrating a porous solid or disease infecting a community. According to the Percolation Theory [6], a conductive cluster (or conductive pathway) can be defined as a group of neighbor nodes occupied by conductive particles. Particles are called "nearest neighbors" if they are next to each other and in the same horizontal or vertical line, whereas particles touching diagonally are called "next nearest neighbors". All particles within one cluster are thus connected to each other by one unbroken chain of nearest neighbor and next nearest neighbor links, as shown in Fig. 1, where particles belonging to the same cluster are circled.

The main concept of Percolation Theory is the percolation threshold. For the lattice shown in Fig. 1, we can use p to express the probability that each site is randomly occupied, and $1-p$ is the probability that the site is empty. The percolation threshold p_c, is the smallest concentration p of sites at which an infinite cluster of sites (i.e., an unbounded cluster) emerges when sites are occupied with that concentration. For all $p > p_c$, a cluster exists extending from one side of the system to the other side.

Fig. 2 shows the nodal structure used in a two-dimensional computer model that was previously developed [5] to represent the active material in an electrode. Each solid dot is an active material node that is conductive until the node is discharged and becomes nonconductive. The node therefore acts as a switch that is closed until it is discharged at which time it becomes open.

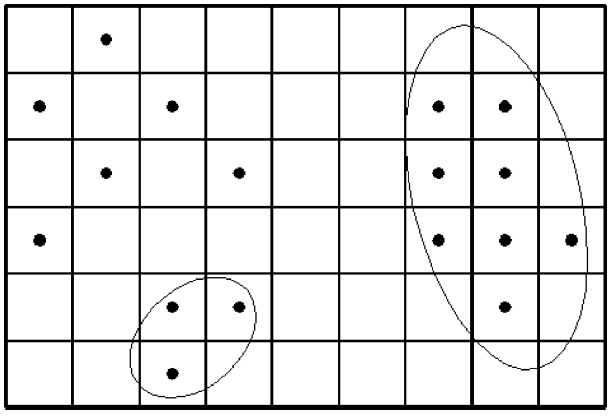

Fig. 1. Definition of nearest neighbor cluster in Percolation Theory.

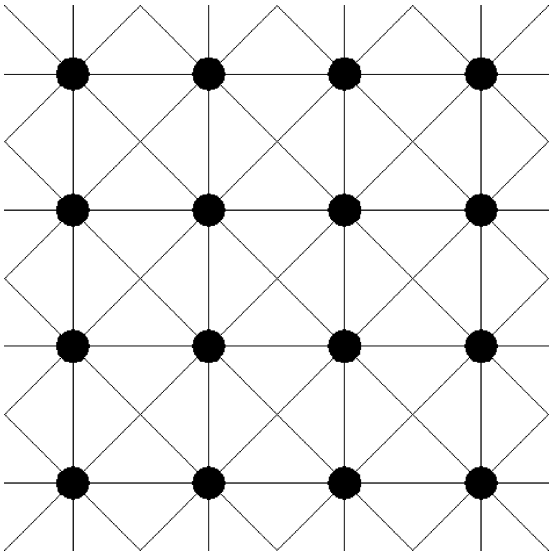

Fig. 2. Grid structure for two-dimensional computer model.

Each node is connected to the surrounding eight nodes on the same plane by eight pathways, as shown by the straight lines between the nodes. The nodes connected to each other along the horizontal and vertical pathways are "nearest neighbors" while the nodes connected through the diagonal pathways are the "next nearest neighbors" as previously described. The coordination number z is the number of contacts or pathways that one particle or node has with its neighbors so the two-dimensional model has a structure where $z = 8$.

The active material of a lead-acid battery can also be considered as a disordered binary mixture, where PbO_2 and Pb represent the good electrical conductivity phase, and $PbSO_4$ represents the poor conductivity phase. A plate can then be regarded as a square lattice which is randomly filled with conductive and nonconductive particles at those intersections. At the beginning, we assume that all the nodes have been fully charged, the concentration of PbO_2 and Pb is therefore $p = 1$. During the discharge process, p is decreasing, and each node on the grid can be randomly changed from a conductive PbO_2 or Pb node to a nonconductive $PbSO_4$ during the reaction. With the production of $PbSO_4$, there must be a threshold value p_c, at which the unbroken conductive pathway from one side of the plate to the other no longer exists; further discharge is not possible although not all PbO_2 and Pb have been converted to $PbSO_4$. The percolation threshold p_c therefore indicates the percentage of PbO_2 or Pb nodes that cannot be discharged so that the utilization can be expressed as $u = 1 - p_c$.

The computer model is based on the Monte Carlo method which generates random numbers. The model randomly chooses a node within the plate and checks the eight surrounding nodes to determine if the conductive pathway can be found to the edge of the grid. If a pathway is found, the starting node is considered discharged and marked as nonconductive. If a pathway is not found, the starting node is marked as an isolated node. In other words, if a conductive cluster can be found from a randomly chosen node to the edge, then this randomly chosen node can be discharged. If the cluster cannot be found, then the original node

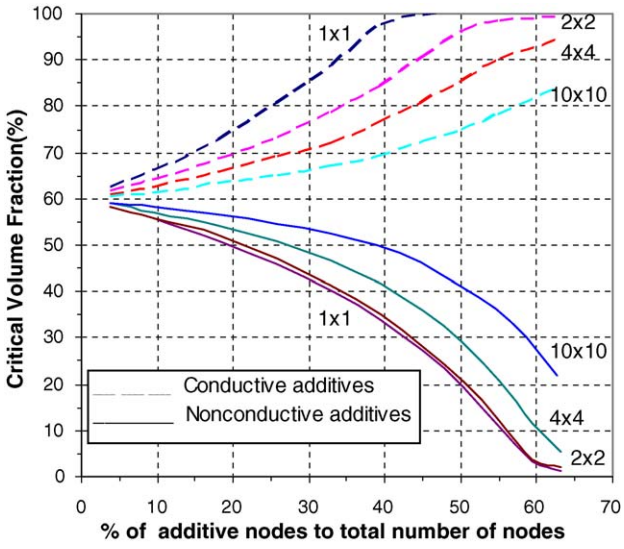

Fig. 3. Critical volume fraction of spherical additives.

is labeled isolated. After all nodes have been selected and conductive pathways have been tried, the model records the number of nodes that are either discharged or isolated. The critical volume fraction is then calculated as the ratio of discharged nodes to the initial total number of nodes available for discharge.

In Fig. 3, computer simulation results for electrodes having both conductive and nonconductive additives are shown. Here, the critical volume fractions of electrodes predicted by a two-dimensional model where each node has connections to eight other nodes (i.e. $z = 8$) are plotted versus different additive volume percentages. The different curves in Fig. 3 represent different size additives. Although all these additives have the same aspect ratio (length to width ratio), their sizes are different. For example, 1×1 means that both the conductive and the nonconductive additives are one node wide and one node long (i.e. one node), whereas 10×10 means that both additives are 10 nodes wide and 10 nodes long, etc.

This figure shows that larger-size conductive particles are not as effective as the smaller particles for improving utilization. For example, with the same 30% volume of conductive particles, the smallest 1×1 conductive particles achieve about 85% utilization which is higher than those achieved with the larger 2×2, 4×4, and 10×10 particles. Fig. 3 also demonstrates that the larger-sized nonconductive particles are less harmful to utilization than the smaller nonconductive particles. When 20% of the total volume is nonconductive particles, the plate filled with the smallest 1×1 particles has the lowest utilization, whereas the plate filled with the largest 10×10 particles has the highest utilization. The explanations for the change in capacity due to both conductive and nonconductive additives are similar. For the same volume percentage of conductive additives, the smaller particles are more widely distributed in the plates than the larger particles and therefore provide more conductive pathways. On the other hand, large nonconductive particles are more concentrated than an equivalent volume amount of smaller particles and do not block as many conductive pathways.

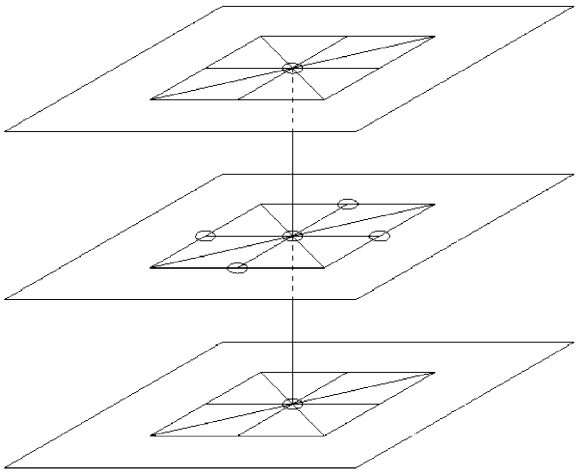

Fig. 4. Three-dimensional model structure having six nodes (four nodes in the same layer plus one node up and one node down).

Euler et al. [6] suggested that for the Pb and PbO_2 electrodes, the coordination number z is approximately eight (i.e. $z \approx 8$). Our two-dimensional model illustrated in Fig. 2 uses this structure ($z = 8$), which is equivalent to the nearest and the next to the nearest neighbor structure discussed in Section 1. However, for this paper we will investigate the three-dimensional structures shown in Figs. 4 and 5 that have coordination numbers z equal to 6 and 10, respectively. The three-dimensional structure where $z = 6$, shown in Fig. 4, has each node connected to its four nearest neighbors in the same layer and two nodes in the immediate adjacent layers. The 10-node construction is illustrated in Fig. 5. Here, besides the four nearest neighbor nodes, the four next to the nearest neighbor nodes in the same layer are also included. When the two nodes in the two immediate adjacent layers, one above and one below the current layer, are counted, the coordination number becomes 10.

In our three-dimensional models, we represent the boundary between the electrode and the electrolyte as a discharged layer. This discharged layer prevents electrons from flowing into the electrolyte from the electrodes and is a simplification that allows

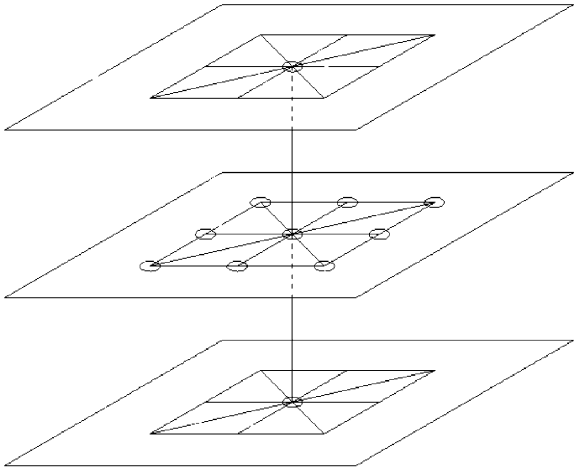

Fig. 5. Three-dimensional model structure having 10 nodes (eight nodes are in the same layer plus one node up and one node down).

us to extend our algorithm. The edges of the different layers are where the current collector of the grid is located, which was also the case for the two-dimensional model. When the program checks a random node on one of the outside discharged layers, the program knows that no conductive pathway exists and will proceed to randomly pick another node.

3. Results and discussion

To verify the accuracy of our conductivity model, simulation results were compared with the values predicted by the Percolation Theory and Effective Medium Theory. First, the two-dimensional model was tested where only the four nearest surrounding nodes, $z=4$, were considered. The average utilization of 10 program runs using a grid size of 1024×1024 is 41%. Since $p_c = 1-u$, we can predict the percolation threshold $p_c = 1-0.41 = 0.59$. This value matches with the percolation threshold of the $z=4$ square lattice given by Stauffer and Aharony [7], which equals 0.592746, it also matches the value that was given by Scher and Zallen [8], which equals 0.59 ± 0.02.

When, the four next nearest nodes were added as neighbors so that eight nodes surrounding a particular node was checked, the average utilization of 10 program runs using a grid size of 1024×1024 was 60%. Unfortunately, we could not find the theoretical value for a two-dimensional lattice where $z=8$ for comparison, but the model results approximately matches those experimental values by Bode [1] of 55% for the positive electrode and 60% for the negative electrode.

For the three-dimensional case the thickness of the electrode is important. The distances between the wires for a typical grid are approximately 6.4 mm while the electrode thickness is approximately 1.8 mm. The selection of the number of layers in our model is a trade off of accuracy versus computer requirements and running time. For example, if we use 1024×1024 nodes to model the electrode material in one grid square, then we would need approximately 288 layers to model the electrode thickness to the same accuracy. Obviously, the number of nodes would be very large (i.e. 288 million). Although computer requirements could be too high to make this approach practical, the utilizations of the same plate modeled by different number of layers converges to a certain value as the number of layers increases. The number of layers at which this occurs is small enough to make the method practical.

Fig. 6 shows the results of the computer simulations for the 6-node and 10-node structure and the corresponding running time of a Pentium III 866 MHz CPU, 256 M RAM computer working on Windows 2000 professional edition operating system. We also tried to run our model on a dual Pentium IV 1.8 GHz XEON CPU; 2 G RAM Dell Blackstone workstation. Surprisingly, this workstation with Windows XP professional edition operating system was not significantly faster than the PC aforementioned. For example, we found that the difference between the two computers was only about 5 min for the 15 layer case.

The results of the three-dimensional model were compared with values predicted by the Percolation Theory. To verify the accuracy of our 6-node model (i.e. $z=6$), we compared our results with theoretical results [6–8]. From Table 1, we see that for the 6-node structure, the utilization was 65.3% after 17 layers were used. The rate at which the utilization changed was slow as more layers were added so that we decided to stop after 17 layers. The percolation threshold, for this case is therefore $p_c = 1-0.653 = 0.347$. For this cubic lattice structure, Stauffer and Aharony [7] gave the theoretical percolation threshold as $p_c = 0.3116$, whereas Scher and Zallen [8] gave a value of $p_c = 0.31 \pm 0.02$. The model gives a reasonable estimate to these theoretical values as shown in Table 1.

For the $z=10$ structure, according to Table 1, after the number of layers has been increased to 14, the utilization converged to about 75.9%, so that the percolation threshold $p_c = 1-0.759 = 0.241$. This number is very close to the $p_c = 0.24 \pm 0.02$ theoretical percolation threshold Scher and Zallen [8] gave for three-dimensional lattices having a coordination number of eight. Our percolation threshold estimate is also only 0.005 lower than the value that Stauffer and Aharony [7] suggested for Body Center Cubic (BCC) lattices where $z=8$ (i.e. $p_c = 0.246$). We were not able to reference a value for a three-dimensional structure where $z=10$. From Fig. 6, we see that for both three-dimensional structures analyzed (i.e. $z=6$ and 8) that

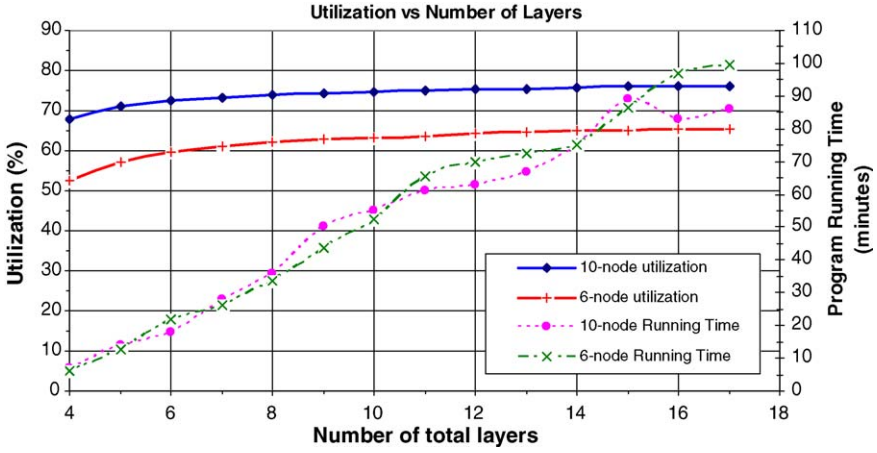

Fig. 6. Utilization and program running time vs. number of layer in model.

Table 1
Utilization and program running time for different number of layers (6-node and 10-node model)

Number of layers	Utilization of 6-node model (%)	6-Node model running time (min)	Utilization of 10-node model (%)	10-Node model running time (min)
4	52.5	6.1	67.9	7
5	57.0	12.7	70.9	14
6	59.5	21.8	72.4	18
7	60.9	26.1	73.3	28
8	62.1	33.5	73.9	36
9	62.7	43.5	74.4	50
10	63.1	52.3	74.6	55
11	63.7	65.3	74.9	61
12	64.2	69.7	75.3	63
13	64.7	72.3	75.5	67
14	65.0	75.2	75.7	75
15	65.1	86.3	75.9	89
16	65.2	96.8	75.9	98
17	65.3	99.4	75.9	86

after about 10 layers, the change in utilization is relatively small and probably does not warrant using the additional layers.

4. Summary and conclusions

In this paper, we compared the capacity predicted by both two- and three-dimensional computer models with theoretical values given by the Percolation Theory. For the two-dimensional $z=4$ structure, the simulation results of $p_c=0.59$ matched perfectly with those theoretical percolation thresholds given by Stauffer and Aharony [7] and Scher and Zallen [8]. For the two-dimensional $z=8$ structure, the theoretical percolation thresholds could not be found for comparison but the simulation results approximately matched the experimental results as reported by Bode [1].

The simulation results of the three-dimensional models compare favorably with those theoretical values predicted by the Percolation Theory. For the $z=6$ structure, the utilization of the three-dimensional simulation using 17 layers was 65.3%. This value is slightly lower than that predicted from the theoretical three-dimensional Percolation Theory, 68.8%. For the $z=10$ structure, although we could not find the theoretical value, the result given by our model using 17 layers was 75.9% and matched the theoretical percolation threshold (i.e. $76\pm0.02\%$) for the Body Center Cubic (BCC) lattices where $z=8$ [6].

Acknowledgements

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References

[1] H. Bode, Lead-acid Batteries, Wiley, New York, 1977.
[2] H. Metzendorf, The capacity limiting role of the electronic conductivity of the active material in lead-acid batteries during discharge, J. Power Sources 7 (1982) 281–291.
[3] D.B. Edwards, P.W. Appel, Conductivity model for lead-acid battery electrodes discharged at low rates, J. Power Sources 38 (1992) 281–286.
[4] D.B. Edwards, P.W. Appel, T. Stalick, Modeling the effects of electrolyte diffusion and paste conductivity on lead-acid battery performance, J. Power Sources 46 (1993) 49–60.
[5] D.B. Edwards, S. Zhang, Influence of different aspect ratio additives on the performance of lead-acid batteries, J. Power Sources 135 (2004) 297–303.
[6] K.J. Euler, R. Kirchhof, H. Metzendorf, Electronic conductivity of battery active masses—a limiting factor, J. Power Sources 5 (1979) 255–262.
[7] D. Stauffer, A. Aharony, Introduction to Percolation Theory, revised 2nd ed., Taylor & Francis, 1994.
[8] H. Scher, R. Zallen, Critical density in percolation processes, J. Chem. Phys. 52 (1970) 3759–3761.