

Short communication

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

Dean B. Edwards*, Song Zhang

Department of Mechanical Engineering, University of Idaho, Moscow, ID 83844-0902, USA

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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

* Corresponding author. Tel.: +1 208 885 7229; fax: +1 208 885 9031.
E-mail address: dedwards@uidaho.edu (D.B. Edwards).

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.

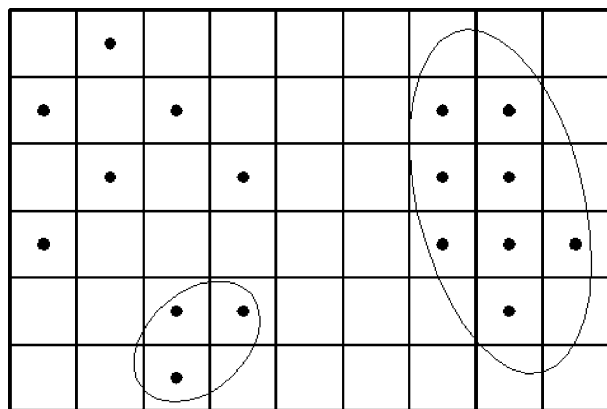


Fig. 1. Definition of nearest neighbor cluster in Percolation Theory.

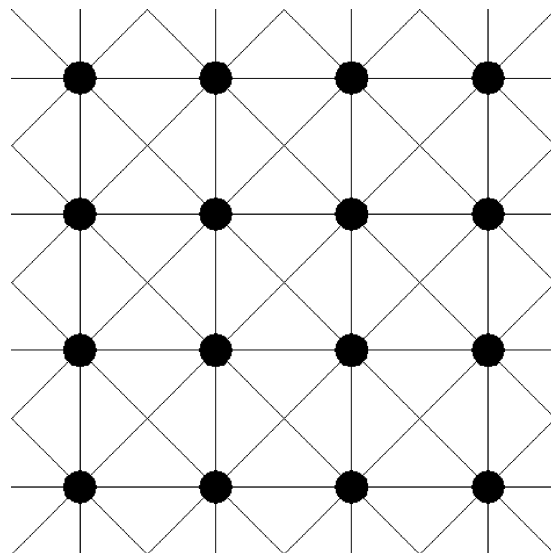


Fig. 2. Grid structure for two-dimensional computer model.

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

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