Short communication

Three-dimensional conductivity model for porous electrodes in lead acid batteries

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Abstract

In this paper, the critical volume fraction (CVF) of electrodes having porosity is predicted with the help of a three-dimensional (3D) conductivity model. The model consists of a 3D lattice of nodes; which in this paper, are assumed to be identical spheres, which are in electrical contact with their neighbors. The porosity that exists between these spheres is referred to as "micro-porosity" while the porosity that occurs from having missing spheres is referred to as "macro-porosity". The critical volume fraction is the maximum utilization of an electrode's active material and occurs when the electrode's conductivity changes from being conductive to nonconductive. Previous 3D conductivity models used to determine the CVF did not account for porosity. The porosity is modeled from porosity size distribution previously determined experimentally by other researchers.

The sphere size of the model is estimated from these porosity distributions and by assuming a simple cubic (SC) lattice structure as the sphere arrangement. Because the porosity between the spheres (i.e. "micro-porosity") for such an arrangement is 48%, the sphere size can be estimated from the pore size where this value of electrode porosity occurs. Porosity smaller than this sphere size is assumed to be smaller than a single sphere, and to be counted as part of the 48% porosity that exists between the spheres. Porosity above the single sphere size is modeled with nonconductive additives having the same pore size as the porosity being modeled. This approach is therefore used to determine both the sphere size in the model as well as the influence of porosity on the critical volume fraction. The model provides reasonable estimates of the critical volume fraction of positive electrodes having porosity and agrees with experimental data.

1. Introduction

The actual utilization of the active material in a lead acid battery is always lower than the stoichiometric capacity, based on the complete reaction of the chemicals available. According to Bode [1], the highest experimental utilization of the active material in the positive plate of a lead acid battery, lead dioxide (PbO_2), is about 55% even at very low discharge rates. Bode [1] gives a slightly higher value of 60% for the utilization of the active material in the negative plate (Pb).

Metzendorf and co-workers [2,3] attributed this phenomenon of incomplete reaction of active materials in the lead acid batteries to the active material conductivity change that occurs during the discharge process. At the beginning of discharge, active materials in both electrodes, that is, lead dioxide (PbO_2) in the positive plate and lead (Pb) in the negative plate, are electrically conductive. During discharge, the active materials of both electrodes are changed to lead sulfate ($PbSO_4$), which is a good insulator. The conductivity of the whole system changes dramatically from being conductive to nonconductive when a sufficient amount of active material is converted to lead sulfate. The lead sulfate electrically isolates some of the active material and prevents it from being discharged. Metzendorf showed that the powder mixture of the active material (PbO_2 and Pb) and discharge product ($PbSO_4$) could be modeled theoretically as statistically distributed networks, and this binary mixture system could be studied with the percolation theory (PT) [4] or effective medium theory (EMT) [5].

A two-dimensional (2D) conductivity model [6] was developed to predict the highest utilization of lead acid batteries discharged at low rates. In this 2D model, only one layer of nodes was used for the electrode's conductivity structure. The effect of

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Nomenclature

r	radius of each sphere (m)
R_{sc}	pore radius in SC lattice corresponding to 48% of electrode porosity (m)
V_c	volume of a cell (m^3)
V_n	volume of a sphere (m^3)
z	coordination number, or number of contacts or pathways

different size and aspect ratio of conductive and/or nonconductive additives were analyzed [6]. The two-dimensional model was later extended to a three-dimensional model [7,8] to better simulate the thickness effect in an electrode. In both models, the nodes represented the active material both before and after the discharge reaction. The nodes were assumed to be conductive, with zero resistance, before the reaction and nonconductive, with infinite resistance, after the reactions. If a conductive pathway could be found from a particular node to the edge of a plate, then the node was classified as a dischargeable node. If the conductive pathway could not be found, then the node was classified as an isolated node and could not be discharged. At the end of the simulated discharge, for both the 2D and 3D models, all nodes would either be classified as discharged or isolated.

The coordination number z is defined as the number of contacts or pathways that one node has with its neighbors. For the 2D model [6], the conductive pathways were horizontal, vertical, and diagonal so that the configuration had a coordination number $z = 8$. Early research [3] suggested that for the Pb and PbO$_2$ electrodes, the coordination number z is approximately eight (i.e. $z \approx 8$). For the simple cubic (SC) 3D model [7,8], z has a value of six. Although these models simulated the electronic behavior of the electrodes, they did not attempt to account for porosity.

The problem of including porosity in the model can be illustrated by assuming that an electrode has 50% porosity. Does this mean that 50% of the nodes are missing? If the porosity is accommodated in this manner, then the electrode utilization would be very low and not consistent with experimental data. If the nodes are modeled as spheres with a characteristic dimension, r, then porosity can exist between the spheres, see Fig. 1. We call the porosity that exists between the spheres "micro-porosity". Any additional porosity must be achieved by eliminating spheres and disrupting the structure. We refer to the porosity which results from the elimination of spheres in the structure as "macro-porosity".

Other investigators have defined micro- and macro-porosity differently. Ferg et al. [9,10] defined that micro-pores as pores with a diameter less than 2 nm, and macro-pores as pores having an average diameter between 0.05 and 5.0 μm. Pavlov [11] suggested that the diameter of micro-pores is less than 0.1 μm and the diameter of macro-pores is greater than 10 μm. In this paper, micro-pores are considered as the pores that exist in between the spheres and this porosity will have no influence on the conductivity of the overall reactant/product system because they do not
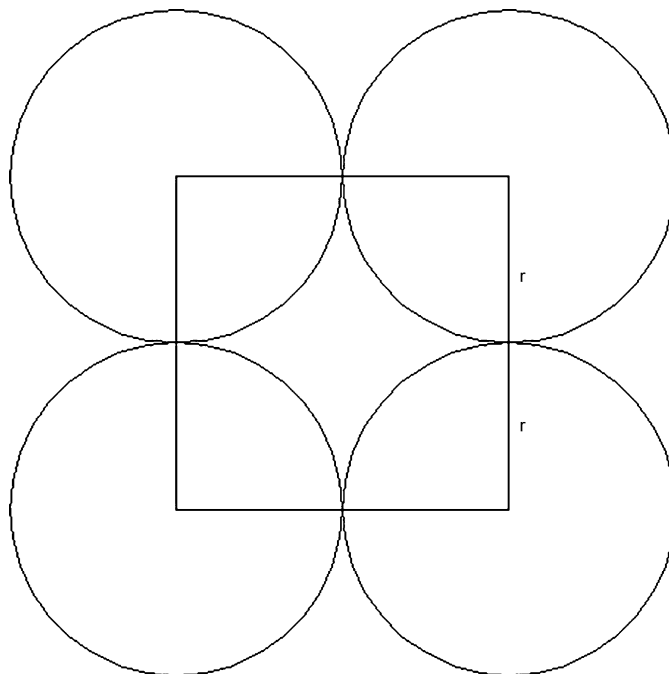

Fig. 1. Spheres in a simple cubic structure.

modify the lattice structure. On the other hand, macro-pores are those pores larger than one sphere and their distribution will cause missing spheres and will reduce the discharge capacity of the battery.

Accounting for porosity with the 2D model is particularly troublesome. In the 2D model, the critical volume fraction (CVF) for $z = 8$ is about 60% [6]. The 2D micro-porosity is defined as the difference in area between a circle and a square whose side is the same length as the diameter of the circle. This 2D micro-porosity is 23%. Because the porosity of an electrode is around 50%, an additional 27% of macro-porosity, which is defined as the porosity that occurs from having missing circles for the 2D case, is required. If this additional porosity is included in the 2D analysis, the critical volume fraction (CVF) would not be 60% but approximately 33%. This is, of course, much lower than the observed values of 55–60%. A three-dimensional model must therefore be used to accurately account for porosity.

In the 3D structure, shown in Fig. 2, the electrode was modeled with a number of layers. Previous work [7] showed that the utilization of active material having no additives or porosity converged to the approximate theoretical value when 15 or more layers were used to simulate the discharge reaction. The simulation results in both models showed good correlation to those theoretical numbers predicted by the percolation theory. For example, for the coordination number $z = 6$ and 10 structures, the 3D model predicted utilization of 65.3% and 75.9%, which compared favorably with the theoretical numbers of 68.8% and $76 \pm 0.02\%$, respectively [7].

The model used in this paper assumes that all the spheres are the same size. A scanning electron microscope (SEM) picture of a positive electrode, Fig. 3, shows that the size of the particles vary as does the size of the pores in the positive active material. Our model is not based on the reality of the complex geometry of
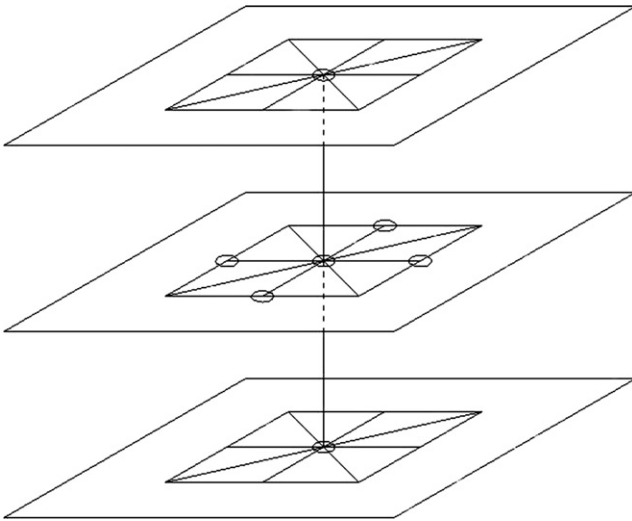
Fig. 2. Three-dimensional model structure for $z = 6$ (four nodes in the same layer and two nodes in different layers).
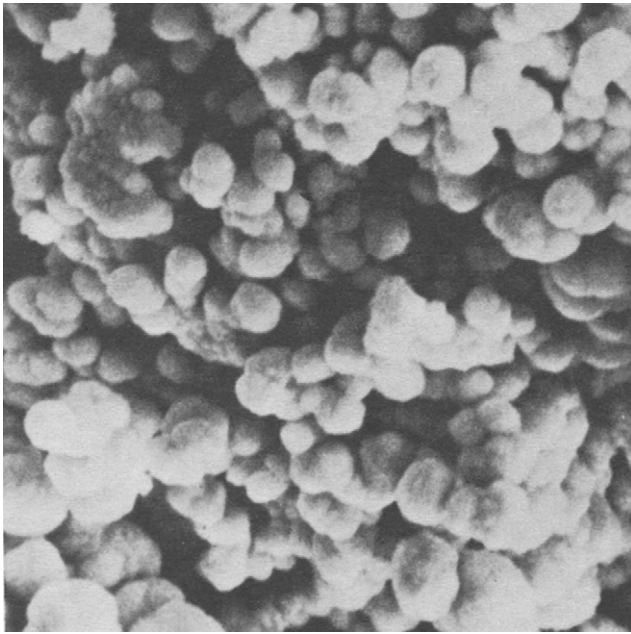

Fig. 3. Surface of a positive plate fully formed and charged, β-PbO$_2$. Magnification 1:4600 [1].

the solid and liquid phases in an electrode. However, the abstraction that this structure can be modeled with a three-dimensional structure having a single sphere size provides physical insight into both the nature and types of porosity found in electrodes. This model also provides some quantitative results that can be compared with experiments. This paper is therefore another step in developing better conductivity models for porous electrodes where porosity is also considered in the analysis.

2. Model description

In the three-dimensional conductivity models previously discussed [7], two different kinds of node structures having coordination numbers of $z = 6$ and 10 were presented. In this paper
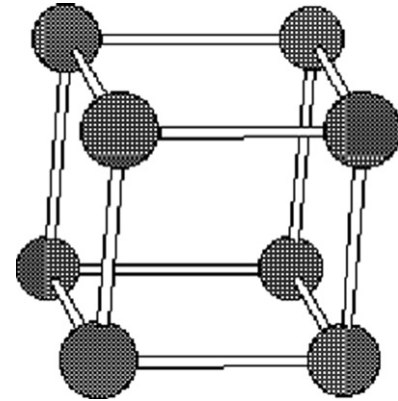

Fig. 4. Simple cubic (SC) crystal lattice structure.

we will only analyze the simple cubic lattice structure, $z = 6$. The six-node structure is shown in Fig. 2 where each node in the $z = 6$ structure is connected to its four nearest neighbors in the same layer and to two nodes in the immediate adjacent layers. This arrangement results in the simple cubic (SC) crystal lattice structure shown in Fig. 4. The micro-porosity for the simple cubic crystal lattice structure $z = 6$, can be calculated by referring Fig. 1. The radius of each sphere is given as r so that the volume of a cell V_c is equal to $8r^3$. The total volume of nodes in the cell V_n is $(4/3)\pi r^3$. The packing factor of a simple cubic lattice is

$$\frac{V_n}{V_c} = \frac{(4/3)\pi r^3}{8r^3} = \frac{\pi}{6} = 52\% \tag{1}$$

The vacant volume percentage or micro-porosity is therefore 48%.

In previous models, the porosity of active materials in the electrodes of a lead acid battery was not included. Porosity is the ratio of void space to the bulk volume of active material in an electrode. A porous body of an electrode consists of a solid framework that is transected by a system of three-dimensional, interconnected capillaries or intermediate pores that are usually uniformly distributed throughout the interior of the electrode. The capillaries or pores that form the void volumes within the electrode are described by their average pore radius R. The method of measuring the porosity of an electrode, such as the BET method [1], the use of glycerol [9], and the influence of paste composition and curing processes on the porosity have been reported by different researchers.

For the simple cubic (SC) lattice structure, we can determine the sphere size from the pore radius where the porosity of the electrode is equal to the porosity that occurs between the nodes, which would be 48% for the SC structure. In this paper, micro-pores are considered as the volume between the spheres and will have no influence on the conductivity of the overall reactant/product system because they do not modify the lattice structure. All the macro-pores that have a diameter one node or larger are modeled as nonconductive additives in this new model, because the void volume is not conductive and reduces the conductivity of the system. The pore size distribution for different grid alloy and charge methods has been reported by other
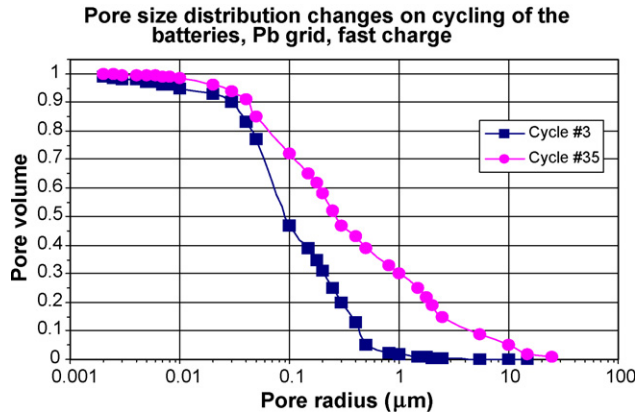
Fig. 5. Changes in cumulative pore size distribution on cycling of the batteries with Pb grid, fast charge. [11].

researchers [10,11]. Results for two different types of plates are summarized in Figs. 5 and 6 [11].

These figures show that on cycling, the pore volume of the positive active material (PAM) increases for all batteries. This means that the pore volume of the active material is increasing and becomes more open and accessible for the electrolyte. Fig. 5 [11] shows that for a battery using a lead grid and a fast charge (0.7 h discharge rate), about 90% of the total pore volume is less than 0.5 μm in the 3rd cycle, while in the 35th cycle, 90% of the total pore volume is less than 5 μm. Fig. 6 [11] shows that after 72 cycles, for a battery with a PbCaSn grid and a slow charge (15 h discharge rate), 40% of the total pore volume consist of pores having a diameter equal to or greater than 1 μm.

The pore radius, R_{sc}, is defined as the value where 48% of the porosity has pore radii smaller than this value in a simple cubic (SC) lattice. We therefore associate the micro-porosity for the SC structure with this pore radius. The sphere radius for the SC model can be estimated from the pore radius R_{sc}. Assuming that the pore volume is a sphere and equating this volume to the micro-porosity gives

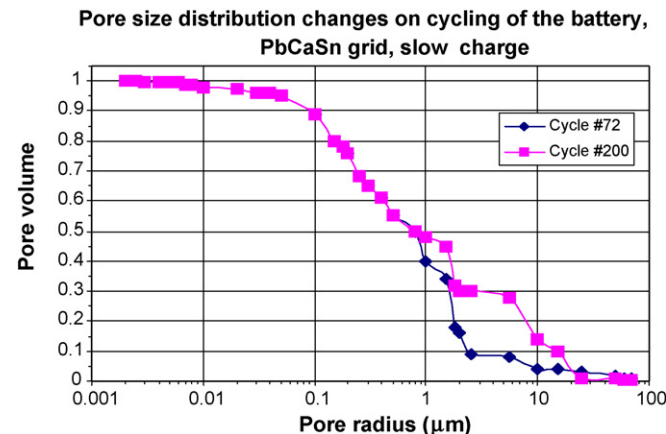$$\frac{4\pi R_{sc}^3}{3} = 0.48(2r)^3 \tag{2}$$

Fig. 6. Changes in cumulative pore size distribution on cycling of the batteries with PbCaSn grid, slow charge. [11].

So the sphere radius is

$$r = \frac{R_{sc}}{0.97} \approx R_{sc} \tag{3}$$

The relationship shows that the micro-porosity radius R_{sc} and the sphere radius r are almost identical for electrodes where the sphere size is assumed to have only one value in a simple cubic lattice structure. If we assume the porosity of the electrode is 50%, then we know that 48% of the porosity is between the nodes (see Fig. 1) and Eq. (1), while only 2% of the porosity contribute to the macro-porosity. Using Fig. 6 for the PbCaSn grid and slow charge at the 72nd cycle, we see that the pore radius R_{sc}, where 48% of the electrode porosity is attained (i.e. 96% of he total pore volume) is approximately 10 μm. From Fig. 6, we see that the remaining 2% porosity volume (i.e. 50–48%) is attributed to macro-porosity.

3. Simulation results

In this section, the macro-porosity volume is modeled with nonconductive additives, and different pore sizes are represented by different nonconductive additive sizes. The overall porosity of the electrode, which ranges from 45 to 65% [10], is determined mainly by the different paste composition, curing and formation procedures. For the cured and formed positive plate, which is considered in this paper, we assumed that the porosity of the plate before discharge is 50%. From the calculation in Section 2, the micro-porosity in the SC arrangement is 48%.

From Fig. 6, the pore volume distribution of a PbCaSn grid slow charged battery shows that the node or sphere radius size is around 10 μm. The diameter of a 2×2 node is around 20 μm, and the diameter of 4×4 and 8×8 nodes are 40 and 80 μm, respectively. From Fig. 6, the volume percentage of nonconductive additives with the pore size 1×1, 2×2, and 4×4 can be modeled with 1%, 1%, and 0%, respectively. The estimated single node size and the porosity associated with the macro-pores are summarized in Table 1.

The simulation of the 3D model of an electrode, which contains 1 vol.% of 1×1 pores, 1 vol.% of 2×2 pores, and 0 vol.% of 4×4 pores was run with 15 layers. For comparison, the previous model using 15 layers, which did not include the porosity of the electrode, gave the critical volume fraction of the SC lattice as 65.1%. This compares favorably with the theoretical value of 65% [7]. The model that includes the porosity of the electrode gave 59.2% as the critical volume fraction. The simulation results are shown in Table 2.

Table 1
Node size distribution for 3D conductivity model

	Approximate real node size from the pore size distribution	
	SC size (μm)	Percentage (macro-pores/paste volume)
1×1	10	1
2×2	20	1
4×4	40	0

Table 2
Critical volume fraction of SC lattice structure with and without electrode porosity

Porosity of electrode	Critical volume fraction of different node structure (%)
Not included	65.1
Included	59.2

4. Conclusions

In this paper, the sphere size of the conductivity model is estimated from the electrode porosity distributions where a simple cubic (SC) lattice structure was assumed. Porosity smaller than this sphere size (i.e. estimated to be 1–10 μm) is assumed to be smaller than a single node, and to be counted as part of the 48% porosity that exists between the nodes that is part of the micro-porosity. Porosity above the single node size, the macro-porosity, is modeled with nonconductive additives having the same pore size as the porosity being modeled. We showed that under these assumptions, the micro-porosity for such an arrangement is 48%, and that the sphere radius is the same as the porosity radius associated with the micro-porosity. This approach is therefore used to determine both the sphere size in the model as well as the influence of porosity on the critical volume fraction.

The model provides reasonable estimates of the critical volume fraction of positive electrodes having porosity and agrees with experimental data. From the simulation results of the 3D conductivity model that includes electrode porosity, we see that the model results, 59.2%, are close to the experimental results previously reported [1,8]. Also, from the porosity distribution of an electrode having a PbCaSn grid, we determine that the average node size of the active material in the electrode after 72 cycles was about 10 μm for the simple cubic lattice structure.

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