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Influence of different aspect ratio additives on the performance of lead–acid batteries

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Abstract

In this paper, we examine the influence of different aspect ratio paste additives on the performance of lead–acid batteries. Previous computer models have been developed to investigate the influence that spherical conductive and non-conductive paste additives have on battery performance. However, many additives used in both the positive and negative plates have aspect ratios that are not spherical. We extend models previously developed for spherical additives to handle additives having different aspect ratios and find that conductive additives with high aspect ratios can improve paste utilization above that of an equal volume of spherical additives. These results suggest that very high aspect ratio conductive additives would be advantageous in improving conductivity in both the negative and positive paste.
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Keywords: Lead–acid; Battery; Capacity; Additives; Aspect ratio

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1. Introduction

The utilization of the positive active material in lead–acid batteries is typically about 50–55% of the theoretical value, even at low current densities. For the negative active material, the maximum utilization is slightly higher with values of 60–65%. If the amount of lead sulfate present before discharge and the molar volume change associated with the production of $PbSO_4$ is taken into consideration, the maximum real utilization rate is 55% for the lead dioxide electrodes, and 69% for the lead electrodes [1].

Metzendorf [2] hypothesized that electrical conductivity was the mechanism that limits both the positive and negative active materials at low discharge rates. He showed that the electrical conductivity of powder mixtures might be described by theories of statistically distributed networks. In particular, the percolation theory (PT) [3] and the effective medium theory (EMT) [4] may be used for binary mixtures with a strong difference in the conductivity of the two components. 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. The main point of both theories is that at a particular composition (the percolation threshold) the conductivity of the whole system changes very quickly from the value of one component to the value of the other.

In lead–acid batteries, electrodes can be considered as a network of statistically distributed resistance elements, that is, a phase of good electric conductivity materials (Pb or PbO_2) and a phase of poor electric conductivity materials ($PbSO_4$). These theories indicate that both the positive and negative active masses will stop being conductive at a particular ratio of conductive mass (PbO_2 in the positive active mass and Pb in the negative active mass) to non-conductive mass ($PbSO_4$ in both active masses). According to Metzendorf's findings, no more than 68% of the positive plate, and no more than 74% of the negative plate can consist of $PbSO_4$ [2].

Typically, plates have utilizations even lower than Metzendorf's predictions. The reason for this low utilization is that the batteries are typically discharged at currents where diffusion of electrolyte ions limits the reaction. This phenomenon means that most of the active material is not used during the discharge reaction. Even though these active materials are not discharged, they still serve two functions: provide structure and conductivity. As the active materials (i.e., Pb and PbO_2), are heavy and weak and not very good structural materials, the use of light, strong materials to replace the material not reacting would seem prudent.

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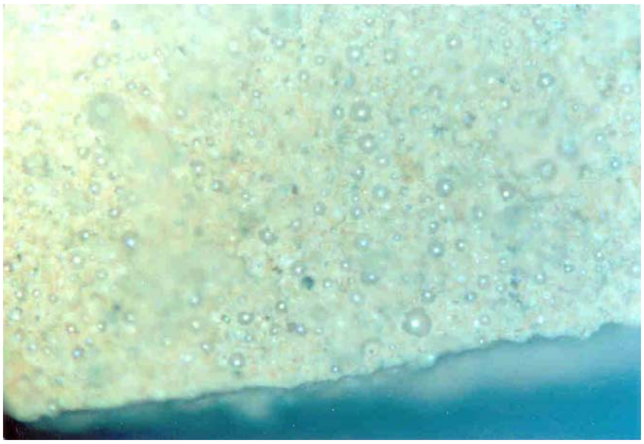

Fig. 1. Glass microspheres in the positive active material of a lead–acid battery.

We investigated the use of hollow glass microspheres as non-conductive additives in previous research [5–11]. These additives caused the specific energy (i.e., energy/weight) of the batteries to increase because of the reduction in the weight of the battery. Fig. 1 shows the glass microspheres in the positive active material of a lead–acid battery. However, as more glass microspheres are added, the conductivity of the active material eventually begins to limit capacity and not the diffusion of ions in the electrolyte.

Conductive additives could be added to both plates to increase the conductivity of the active material and improve utilization. Theoretically, with the use of spherical conductive additives, high utilizations (above 80%, for example) could be achieved. However, many additives are not spherical, and the question remains whether utilizations could be improved with different aspect ratio (length to width ratio) additives. In this paper, we investigate the use of additives with different aspect ratios, both conductive and nonconductive, and their influence on battery capacity.

In addition, the charge characteristics for both the positive and negative plates could possibly be enhanced by adding conductive additives. When a sealed lead–acid battery is operated in a partial state of discharge, it becomes increasingly difficult to charge and recover the capacity of the negative plate as the battery ages. The use of conductive additives could provide a conductive path through the discharge portion of the plate making charging easier. The benefit of this approach to recovering discharged $PbSO_4$ needs to be further investigated and verified. However, expander materials used in the negative plate [12,13] also give the additional benefit of improving the conductivity of the active material.

In this paper, we examine the influence of different aspect ratio paste additives on the performance of lead–acid batteries. Since many additives used in both the positive and negative plates are not spherical, we extend previous models developed for spherical additives so that additives having different aspect ratios can also be simulated.

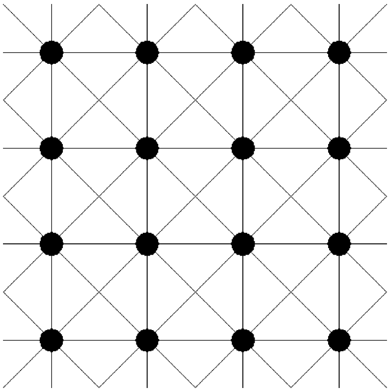

Fig. 2. Grid structure for computer model.

2. Model description

Fig. 2 shows the nodal structure used in the computer model to represent the active material. 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 closed switch until it is discharged and becomes open. Each node is connected to the surrounding eight nodes by eight pathways, as shown by the straight lines between the nodes.

The conductivity model is based on the Monte Carlo method, which solves a problem by generating suitable random numbers and observing that fraction of the numbers obeying some property or properties. The model randomly chooses a node and attempts to find a conductive pathway to the edge of the grid. If a pathway can be found, the starting node is considered discharged and marked as nonconductive. If a pathway cannot be found, the starting node is then marked as isolated. After all nodes have been selected and pathways have been tried, the model reports the number of nodes that were either discharged or isolated. The critical volume fraction is calculated as the ratio of discharged nodes to the initial total number of available nodes. The critical volume fraction is the highest utilization that can be achieved when the reaction is not limited by diffusion. In the remainder of this paper and the ensuing discussions, we will use utilization and critical volume fraction interchangeably.

The program can model different percentages of conductive or non-conductive blocks having different sizes. From previous work [5], we believe the size of a single node is about 3–5 μm, which correlates with the initial size of the lead oxide particle. However, we have not been able to conclusively verify this result experimentally. The nonconductive, hollow glass microspheres used in previous research [7–11] have a range of diameters from 20–50 μm and are relatively large compared to the hypothesized node size. Obviously, the node size is required if the results of the computer simulations are to be applied to actual battery designs.

We model the active material between the wires of a cast or expanded grid. The distance between the plate's grid wires is 5 mm in the narrowest direction. Assuming each node is about 5 μm, one thousand nodes are needed per side. This calculation means that 100 spheres of 50 μm diameters each can fit across the 5 mm span of the plate's grid wires. Computation time for this model, however, can be reduced if the grid size chosen is a power of 2. A grid with 1024 nodes per side would satisfy the power of 2 requirement and would have over 1000 nodes per side. The grid node structure, therefore, contains more than 1,000,000 nodes.

To check for mathematical stability of a 1024 × 1024 grid, smaller grid sizes were also evaluated and their results compared [9]. As the numbers of nodes per side are reduced, the percentages of nodes that react are increased. The higher reacted percentages associated with the smaller node numbers can be attributed to the edge effect, where a larger percentage of nodes are on the edge and, therefore, do not need a pathway to react.

Fig. 3 shows the computer display of a plate that is nearly discharged that has both conductive and non-conductive square additives. These squares represent additives with an aspect ratio of one including spherical additives. The green areas represent the conductive and the yellow areas the non-conductive additives. The black areas represent the charged active material while the red areas represent the discharged material. The isolated material that cannot be discharged because it is surrounded by discharged material and therefore has lost an electrical connection to the edge is represented by the blue areas.

Once the volume percentage of conductive and/or non-conductive additive particles is determined, different aspect ratios can be modeled by specifying aspect ratio input for the computer program. These additive particles can be dispersed randomly within the plate, but unlike the spherical particles, they will have an orientation that will also need to be random. In order to simplify the program, the orientations of these particles were restricted to be randomly located either in the horizontal or vertical directions within the plate, see Fig. 4.

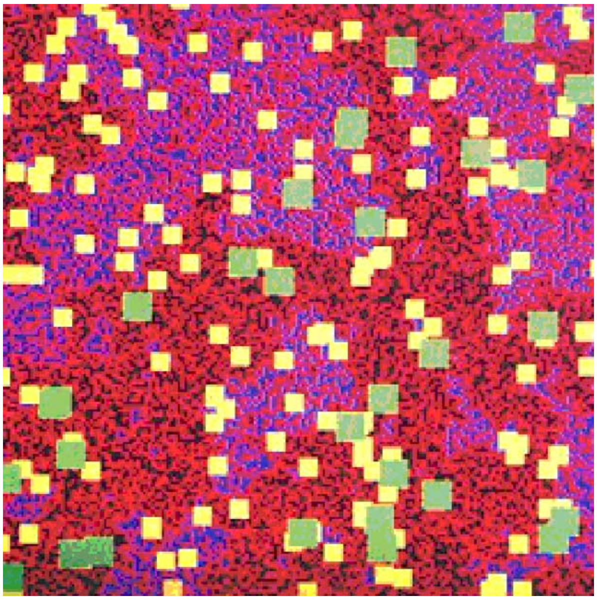

Fig. 3. Computer display of a plate having both conductive and non-conductive additives.

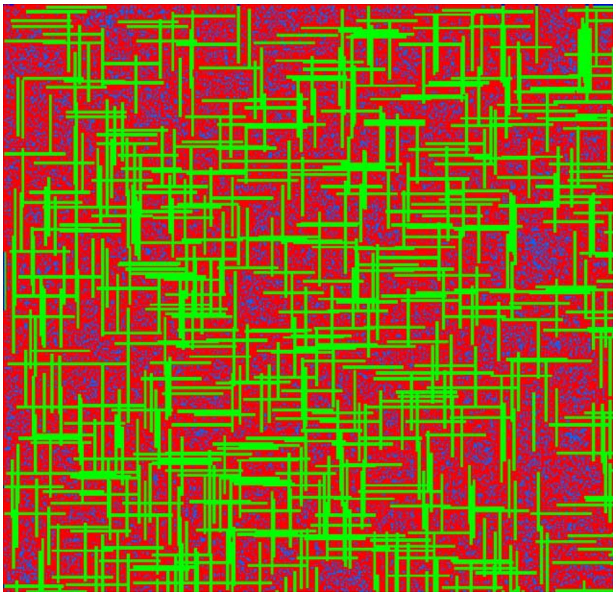

Fig. 4. Computer display of a plate with conductive additives (2 × 40 aspect ratio, 32.4 vol.%).

Fig. 4 shows all the nodes for a completely discharged plate having 2 × 40 node (i.e. additive particle is two nodes wide and forty nodes long) conductive additives. The green vertical and horizontal lines represent the conductive additives. The red areas represent the discharged material and the blue areas represent the isolated material. In Fig. 4, the conductive additives take up about 32.4% of the total volume.

Previous research [5–7,9–11] investigated the use of different types of paste additives to improve the performance of lead–acid batteries. These additives were spherical and were modeled as square in the 2D computer simulation program. Fig. 5 shows the critical volume fraction of pasted plates plotted against the additive volume percentage. The different curves represent different size additives with the higher critical volume fraction curves associated with the conductive additives. This figure demonstrates 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.

However, the larger-sized non-conductive particles are less harmful to utilization than the smaller non-conductive particles. Fig. 5 demonstrates that when 20% of the total volume is non-conductive particles, the plate that was filled with the smallest 1 × 1 particles has the lowest utilization,

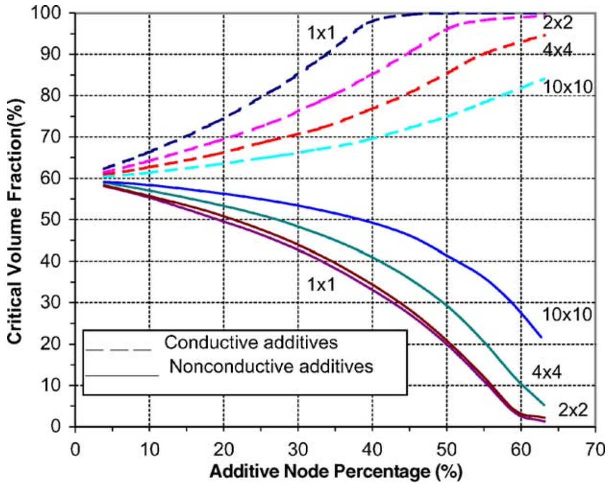

Fig. 5. Critical volume fractions of original spherical additives.

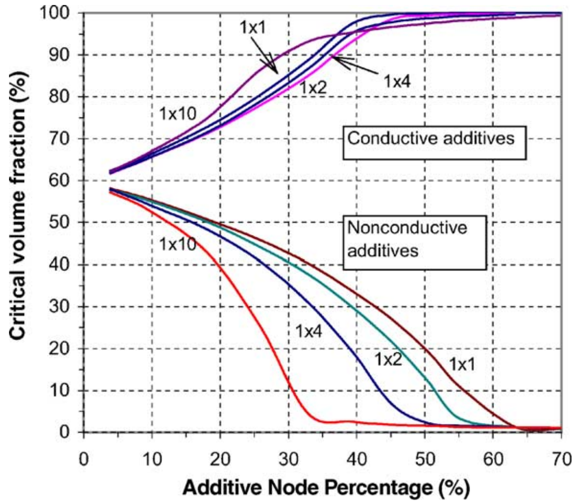

Fig. 6. Critical volume fractions with different aspect ratio additives.

whereas the plate filled with the largest 10 × 10 particles has the highest utilization.

From this graph, we see that the small conductive particles increase utilization and the large non-conductive particles have the minimum negative effect on utilization. For the same volume percentage, the smaller particles are more widely distributed than the larger particles and therefore provide more opportunity to prevent isolation. The large non-conductive particles are more concentrated than an equivalent volume amount of smaller particles and do not block as many conductive pathways.

We present the results of previous computer simulations for spherical additives so that we can contrast them with the results we found for different aspect ratio additives. In the next section, we will present the simulation results we found for different aspect ratio additives, both conductive and non-conductive. Although the results of the different aspect ratio additives are similar to the results obtained for the spherical additives, we were surprised by the results for the very high aspect ratio additives.

3. Simulation results and discussion

In this paper, we have extended our conductivity model so that we can analyze additives with different aspect ratios. Fig. 6 shows the results of different aspect ratios for conductive and non-conductive additives where all the additives are one node wide. For the conductive additives at the lower loadings (i.e. <15%), the additives with the longer aspect ratios give about the same critical volume fraction as the one node spherical additives. At higher loadings, however, the curves cross so that the highest aspect ratio additive (i.e. 1 × 10) provides a higher critical volume fraction than the small spherical additive for some loadings.

Fig. 6 also demonstrates that for the non-conductive additives, the highest 1 × 10 aspect ratio additive is more detrimental to the critical volume fraction than the lower 1 × 2 and 1 × 4 aspect ratio non-conductive additives. For example, when 30% of the total volume of the plate is taken up by non-conductive particles, the plate with the higher 1 × 10 aspect ratio non-conductive particles has the lowest utilization (only about 12%), while those plates filled with lower 1 × 4, 1 × 2 and 1 × 1 aspect ratio non-conductive particles have higher utilizations.

When Fig. 6 is compared with the critical volume fraction for spherical additive, Fig. 5, we see that the higher aspect ratio particles have a greater influence on the critical volume ratio than does the spherical additives. For the same size particle, the higher aspect ratio additives provide better conductivity than the equivalent spherical conductive additives, whereas the reverse is true for the non-conductive additives. Fig. 6 also shows that with the volume percentage ranges from 10 to 35% (which is the range commonly used), plates with the higher 1 × 10 aspect ratio conductive particles provide higher utilization than those plates with lower 1 × 1, 1 × 2 and 1 × 4 aspect ratio particles. As the aspect ratio is increased for the lower aspect ratio particles, the conductive additives begin to bridge what would have been isolated areas. This process helps the formation of the conductive pathway and increases the utilization. For the non-conductive additives, the higher aspect ratio additives are better able to isolate areas of the active material than the spherical additives, thereby reducing the critical volume fraction.

Fig. 7 shows the performance of different aspect ratio additives (both conductive and nonconductive) and compares their performance with the baseline 1 × 1 spherical additive materials. Here, the 2 × 2 and the 1 × 4 additives have the same size, but affect performance differently. For conductive additive materials, the 1 × 4 aspect ratio additive is more effective than the 2 × 2 additive, and its critical volume fraction is higher in all loadings than that of the 2 × 2 additive. For the non-conductive additive materials, the 1 × 4 aspect ratio additive is more detrimental than the 2 × 2 additive and

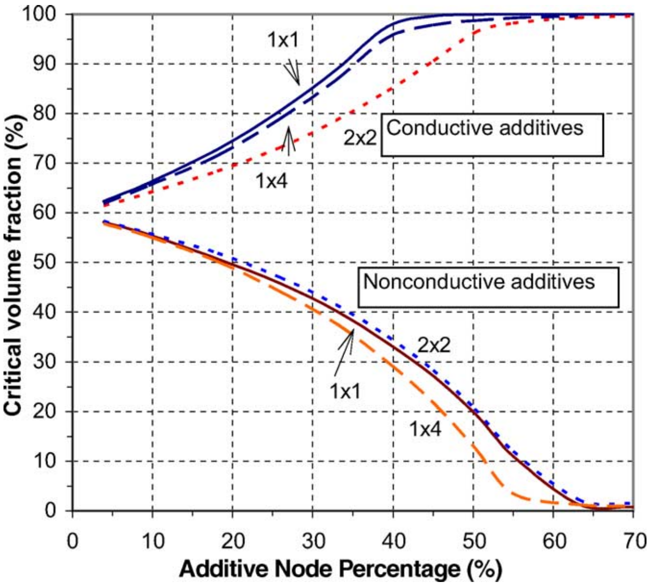

Fig. 7. Critical volume fractions with different aspect ratio additives.

has a critical volume fraction that is always lower than that of the 2 × 2 additive.

This phenomenon occurs because the 2 × 2 particles are more concentrated than the 1 × 4 particles. Thus, the conductive clusters within the plate formed by these 2 × 2 additives are not dispersed as widely as those conductive pathways created by the 1 × 4 particles. The 1 × 4 particles are better able to bridge across areas that have been discharged and are therefore able to improve utilization. Alternatively, the 1 × 4 non-conductive additive blocks more pathways and provides better isolation than the equivalent 2 × 2 particle. The higher aspect ratio non-conductive additive, therefore, causes the active material to have a lower critical volume fraction.

Fig. 7 also demonstrates that while 1 × 4 particles provide higher utilization than the equivalent sized 2 × 2 particles, its utilization is still a little lower than that of the 1 × 1 small spherical particle. The reason is that the 1 × 4 aspect ratio particles are more concentrated and are not distributed as widely as the 1 × 1 spherical particles.

Fig. 8 shows the utilization of paste having very thin, high aspect ratio additives. This graph demonstrates that these thin, high aspect ratio additives provide very high utilization even at very low volume percentages. For example, a plate with the 1 × 20 conductive additives has 85% utilization with only 20% loadings, and a plate with the 1 × 100 conductive additives has 78% of utilization even though only 10% of its volume is taken up with these particles.

Conversely, very thin, high aspect ratio non-conductive additives decrease the utilization much faster than equivalent size spherical particles. From Fig. 8, we can see that when 10% of the total volume is taken up by non-conductive additives, the plate with the 1 × 1 spherical non-conductive particles has about 55% utilization. However, the plate with 1 × 100 aspect ratio non-conductive additives only has 11% utilization. The reason for this result is the same as what we have previously discussed. The thin, high aspect ratio conductive particles provide paths through the discharged active material and increase paste utilization. For the non-conductive additives, the long particles insulate larger areas of the plate much faster than the small spherical particles, and substantially decrease the utilization.

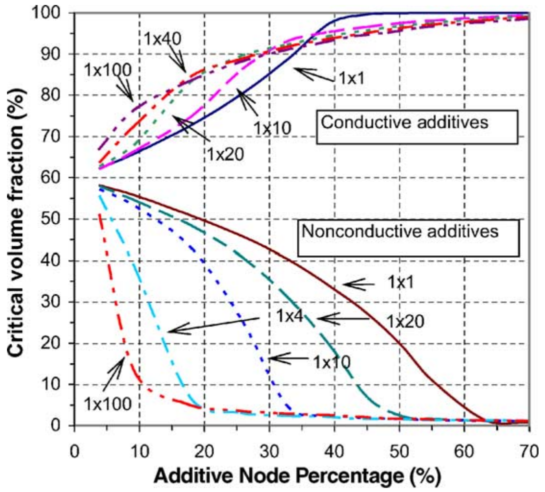

Fig. 8. Critical volume fractions with different aspect ratio additives of one node wide.

Fig. 9 shows the critical volume fraction of plates with different aspect ratios for conductive and non-conductive additives where all the additives are two nodes wide. The utilization of plates with 1 × 1 spherical conductive and non-conductive additives is also shown for comparison. The utilization curves of paste having two-node-wide conductive additives are always lower than that of the 1 × 1 spherical particles except for the very high aspect ratio additives (i. e. 2 × 80 and 2 × 200). The two-node-wide additives are more concentrated than the one-node-wide additives and for the

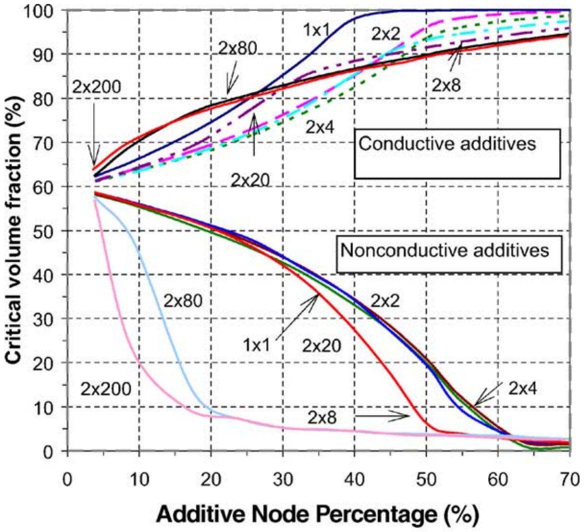

Fig. 9. Critical volume fractions with different aspect ratio additives of two nodes wide.

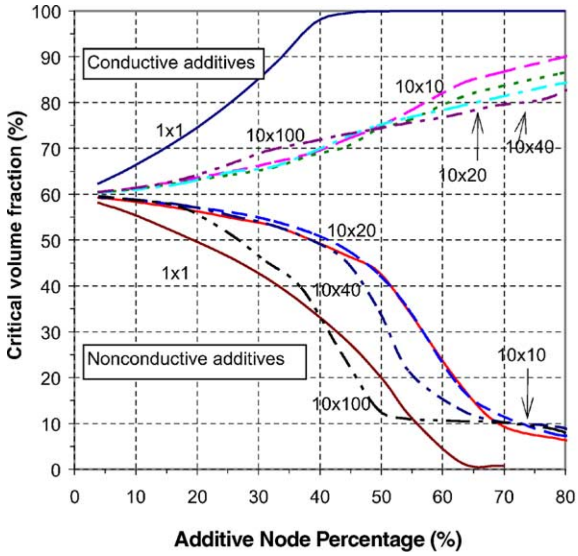

Fig. 10. Critical volume fractions with different aspect ratio additives of 10 nodes wide.

same volume percentage would only have half the number of particles.

Comparing Figs. 8 and 9, we find that although they have the equivalent volume percentage, the 2 × 20 conductive particle is not as effective as the 1 × 40 conductive particles, and by comparison, the 2 × 20 non-conductive particles is not as detrimental to the utilization as the 1 × 40 non-conductive particles. For the same volume percentage of additives, the thin, long particles with a high aspect ratio are preferred to the thick, short particles with low aspect ratio conductive particles.

Fig. 10 shows the utilization of paste with different aspect ratio, 10-node-wide conductive and non-conductive additives. The utilizations of plates having 1 × 1 spherical conductive and non-conductive additives are also shown as the base case for the comparison. From this figure, we can see that the utilizations of paste with the thicker 10-node-wide conductive additives are lower in all loadings than the 1 × 1 particles, and the thinner additives.

Utilization can be improved by increasing the aspect ratio of conductive particles. This method is more effective for thinner, smaller particles than for thicker, larger particles. As the aspect ratio is increased, it is easier for the conductive additives to bridge more of the active material which helps prevent the nodes from being isolated. If the particle is very long and the aspect ratio is very high (1 × 100, for example) the conductive pathway can be formed even at very low volume percentages. Thus, high utilization can be achieved even at very low volume percentages of a plate that is taken up by the conductive additives. On the other hand, if long non-conductive additives are used, a plate's utilization drops dramatically even at very low volume percentages.

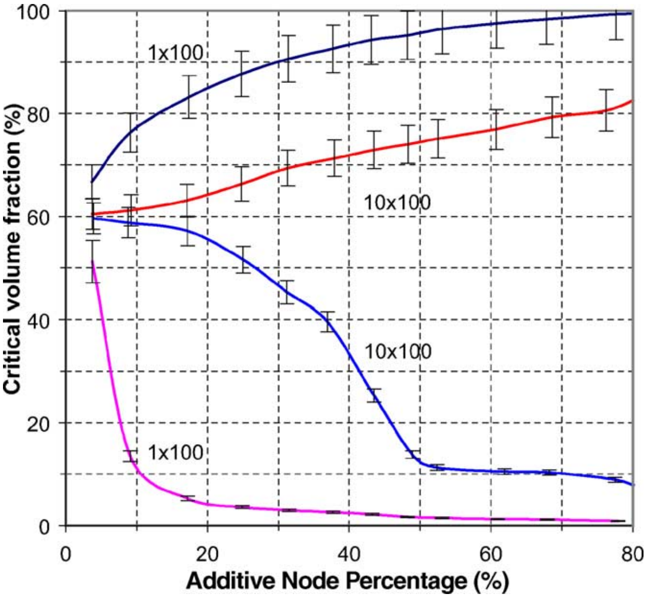

Fig. 11. Critical volume fractions with 5% standard deviation.

Fig. 11 shows the plate's utilization of 1 × 100 and 10 × 100 conductive and non-conductive particles with a 5% error bar spread. We show this figure to emphasize the variability in the data. Although all the data is created with computer simulations and not experimentally, the Monte Carlo method is inherently statistical in nature and causes the variability in the data.

4. Summary and conclusions

For a given volume percentage of additives, the large particles concentrate the nodes so that the additives are not as dispersed as the smaller particles. This causes the larger conductive particles to be less effective than the smaller particles for improving the critical volume fraction or active material utilization. Conversely, the larger non-conductive additives are not as detrimental as the smaller particles to the utilization of the active material. The strategy, therefore, would be to use small, conductive additives to improve utilization and large non-conductive particles for structure and fill so that the reduction in utilization is minimized.

This size effect is also observed with the lower aspect ratio particles. However, as the aspect ratio is increased, the conductive additives begin to bridge what would have been isolated areas. This process increases utilization. In the extreme case, very long particles bridge from one side of the plate to the other. The utilization can become quite high because these long particles afford more paths to the edges.

The inverse is also true in that when long non-conductive particles are used, they can quickly isolate large areas of the plate. Again, if the particles are as long as the plate, then a few particles that block the sides could completely isolate all the material in the plate for this two-dimensional analysis. This phenomenon is observed with the 1 × 100 conductive and non-conductive particles. The utilization quickly climbs to 80% with only about 10% by volume of additives but falls to 10% utilization with the same amount of non-conductive additives.

The models used in this paper are all two dimensional. The actual battery would be better represented by a three-dimensional model, which would allow the electrons to shift planes to find a pathway to the edge. In the future, a more accurate three-dimensional computer model should be developed to better simulate the actual reaction that occurs in the plates.

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