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Modeling the impact of paste additives and pellet geometry on paste utilization within lead acid batteries during low rate discharges

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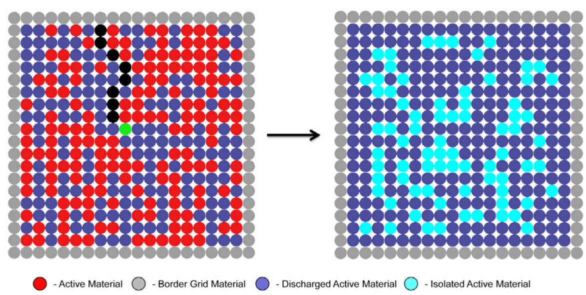
HIGHLIGHTS

- We model the active material of a single pellet within typical lead acid battery.
- The maximum utilization of the active material is modeled successfully.
- Utilization is increased/decreased with the addition of additives.
- Utilization is largely unaffected by aspect ratio of the surrounding grid.
- Utilization is mainly affected by the shortest edge length of the surrounding grid.

GRAPHICAL ABSTRACT



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ABSTRACT

When designing a lead acid battery, there are many factors to consider in order to obtain the best compromise of cost, performance, and ease of manufacturability. We use a modeling approach to study some of the key factors which affect the amount of active material which can be utilized during a low rate discharge. We investigate the effects of pellet size, pellet geometry, disconnected grid mesh borders, and inert paste additives. Furthermore, we look at how the internal path length resistance within a pellet is dependent on those features. Our findings correlate well with earlier works, and help to explain some of the previously observed phenomenon. It is observed that utilization is indeed affected by pellet size, but small grid mesh sizes on the order of ~4 mm edge lengths are necessary in order to realize a significant benefit. Utilization is presented as a function of pellet size, aspect ratio of the pellets, and the loading level of the inert additives in the pellets up to ten percent by volume.

1. Introduction

Since the invention and production of the Planté cell, the lead-acid battery system has been an influential energy storage device on many peoples' lives. Despite being invented in the mid 1800's, lead-acid batteries continue to serve as an economical approach for storing electrical energy in the form of chemical bonds. Lead-acid batteries exhibit good rechargeability, high energy density, and high reaction voltage. Furthermore, the lead-acid secondary battery system can be used in a variety of applications ranging from high-power automobile starting to low-power telecom systems. Depending on the application, a certain amount of current is drawn from the battery and the magnitude of the load can significantly impact its performance. Peukert showed how a battery's available capacity is dependent on the rate at which it is discharged [1]. This effect is generally attributed to the formation of sulfate crystals that will inhibit electrolyte diffusion into the active material [2,3]. At high rates, this generally seems to be true; at low rates, diffusion is not the limiting factor for the reaction, and so another mechanism inhibits the reaction and that is electrical isolation by sulfate crystals [4].

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Based on experiments and percolation theory, as the active material utilization approaches ~60% during a low rate discharge, the pellet will undergo a rapid transformation to a state of conductivity very near that of lead sulfate, which is on the order of 10^{-8} S cm^{-1} [5]. This is due to the material reaching its percolation threshold, which will cause the tortuosity to rise significantly for the electrically conductive pathways within the still non-discharged active material. When the percolation threshold is reached, the pellet becomes mainly sulfate, with a minority of active material that is mostly contained within electrically isolated pockets that cannot discharge. Because there is a certain amount of active material that is not able to react and discharge, the utilization usually does not reach much higher than 60%. This work presented here seeks to investigate the factors that can affect the utilization for the motivation of implementing economical design changes in order to get the best utilization possible.

Several researchers have developed numerical electrochemical battery models to study and to simulate the performance of lead acid batteries under various conditions [6–8]. While many of them have seen good success, it has been proven to be very difficult to fully capture the complex physical and chemical workings of a lead acid battery during charge and discharge. Because the electrochemical models tend to be complex and time consuming, we are not convinced that they are appropriate for a first principles look into the effect of additives on pellet geometry. Modeling the effect of additives and pellet characteristics requires a simulation on a much smaller scale in order to capture the interaction of the paste with the additives.

Here, we take a two-dimensional (2-d) modeling approach with a focus on conductivity, similar to the work of Dayton and Edwards [9]. Their model has been used several times in both a 2-d and a 3-d form to investigate the effects of additives and lattice structure on the active material utilization within a single pellet under a simulated low rate discharge [10,11]. The Dayton and Edwards model considers the active material as an array of conductive nodes, with each node being roughly the size of one fundamental unit of active material on the order of 10 μm that would discharge at a particular time [11]. On the border of the array of "active" nodes lies the "grid" nodes; these nodes represent the conductive border of the pellet, generally represented by the grid wires. Their model randomly selects active nodes and attempts to find a conductive pathway via other active nodes to the border. If the path-finding attempt is successful, then that node is marked as discharged and transformed into lead sulfate, which is considered an electrical barrier that will inhibit conduction for subsequent nodes to discharge. Furthermore, some nodes within the active region can have their properties changed to simulate additives. A node can be set to always be conducting, which would simulate a conductive paste additive, or always be electrically insulating, which would simulate an inert paste additive. Chemically, the additives are considered to be un-reactive.

The modeling work done by Edwards et al. incorporated the effect of paste additives including conducting and non-conducting additives as well as general cases for additives of various aspect ratios and conductive properties. This investigation is also focused on additives, but in addition, we look at the effect of pellet size and pellet geometry. Also, we simulate pellets with some edges disconnected, representing a scenario in which the active material has lost contact with one or more of the mesh wires, in order to determine the effects of this phenomenon from a utilization standpoint. Using the well-known Dijkstra algorithm [12], we are able to measure the path length of each discharge during the simulation by finding the shortest path length possible to the conductive border, analogous to electricity taking the shortest path, or the path of least resistance. This allows us to gain insight into the inner workings of the pellet and to more fully understand the observed effects of changing aspect ratio, paste additives and detached pellet borders windows.

2. Simulation details

The simulation procedure and system properties used for this investigation were based on a previous model developed by Dayton and Edwards [9]. While the algorithms are similar, the code we used was created entirely in-house and was written in the C++ computer language.

2.1. Simulation setup

This model uses an array of nodes in order to simulate a low rate discharge that is non-diffusion limited with an abundance of available electrolyte. Nodes are all of regular size and shape, and connected to each other in an eight neighbor coordination system as depicted in Fig. 1. The model uses a random number generator to perform Monte Carlo simulations that ensure each simulation will be completely random.

The algorithm for performing the simulations takes place in three basic steps as follows:

- Step 1 – System Setup
  - A user specified grid of nodes is created. Each node is programmed to specific characteristics (see Fig. 2).
    - The inner nodes are set to active material.
    - The outer nodes are set to border/grid material.
    - If desired, "additive" nodes are chosen randomly based on a desired volume percentage and given special properties (conducting or non-conducting) to simulate the desired material.
- Step 2 – Discharge Process
  - The program randomly chooses a charged active material node and attempts to find the shortest conductive pathway to any point on the border, in a manner akin to solving a maze.
    - If a pathway exists, that node is marked as discharged and converted to a wall which will obstruct the pathways of future discharges. This represents active material converting into sulfate crystals, which are electrically insulating. Lastly, the path-length is recorded for the discharge that has just occurred.
    - If no pathway exists, that node is marked as isolated and non-discharged.
  - Repeat from beginning of Step 2 until all active material nodes have been attempted.

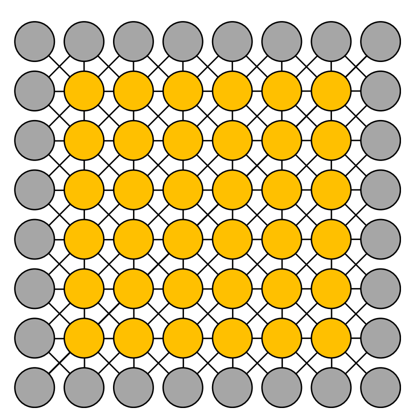

Fig. 1. Depiction of the coordination of each node, indicating the possible conductive pathways that are available.

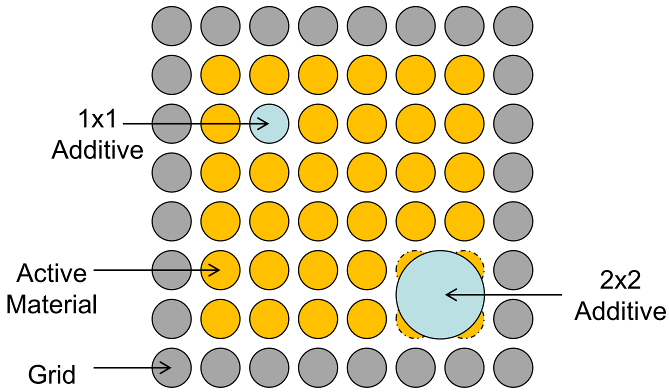

Fig. 2. The system setup is shown with each node having specific characteristics. Additives are represented as 1 × 1 or 2 × 2 blocks of nodes.

- Step 3 – Analysis and Output

– The program counts all charged and discharged nodes and reports utilization percentage. Utilization is defined as: (total discharged nodes)/(total initial active nodes)

The nodes themselves are considered to be a series of hard spheres, with an inherent porosity near 50%, a length scale on the order of 10 μm, and a coordination number of eight [11]. This process is designed to model a conductivity-limited discharge within a single pellet of active material, but because of the geometrical differences of positive and negative active material, it should be stated that with this setup, the model is better suited to simulating positive active material. Lastly, when we measure utilization, we are looking at the situation when all of the available active material is discharged. In practice, a voltage cut-off is used to stop the battery from discharging to such a degree in order to prevent damage due to deep discharging [13]. If such a cutoff were implemented, it might shift the reported utilization down by several percentage points to account for the non-total discharge. For a demonstration of the model's discharge process, see the supplementary video available online.

2.2. Pellet size

Using a length scale of roughly 10 μm per node, we can correlate the size of the arrays of nodes to different pellet sizes [11]. Considering standard industrial practices, we focused on rectilinear pellets up to 1.6 cm. First, a square geometry was chosen in order to isolate the size effect for these particular trials and to remove any geometrical effects due to aspect ratios. Several runs were performed at successively increasing pellet sizes and the simulations were run until all of the active material that had a conductive pathway was discharged.

2.3. Pellet geometry

To investigate the effect of geometry and aspect ratio on the pellet utilization, 3 arrays of nodes were chosen with one dimension becoming successively larger. We ran regular simulations on 300 × 300, 300 × 600 and 300 × 900 node systems with no additives and measured the path length and utilization of each system. These systems correlate to pellet dimensions of roughly 3 × 3(mm), 3 × 6(mm) and 3 × 9(mm) respectively.

2.4. Detached mesh borders

Similar to the pellet size trials, we also ran three additional trials with one, two, and three conducting and connecting borders with the grid mesh detached. This allowed us to see the effect of damage and defects such as cracks and pellet disconnections. Simulations were run over the same range of pellet sizes as the initial trial, up to 1.6 cm.

2.5. Paste additives

This model focused on additives that were microscopic in nature, and chemically inert. While different aspect ratios of additives are possible, they were outside of the scope of this study, and will not be reported here. As our length scale is roughly 10 μm per node, it was decided to represent the additives as 10–20 μm objects (see Figs. 1 and 2). The additives were translated into 1 × 1 and 2 × 2 blocks of nodes as shown in Fig. 2. We simulated samples over a range of 1–10 volume percent of inert paste additives at the 1 × 1 and 2 × 2 node sizes respectively. Both conducting and non-conducting additives were simulated.

3. Results and discussion

3.1. Mesh size

Percolation theory predicts that the total utilization should be ~60% for a sufficiently large system [14,15], and our model showed good correlation as we obtained values that approached ~60% as the system size was increased.

Fig. 3 shows the impact of mesh size on paste utilization. It appears that a clear inverse root relationship is established with increasing mesh size. It's interesting to note the size of the mesh that one has to reduce to in order to see a tangible utilization benefit. Not including other factors which were not simulated (like a battery's total internal resistance), our model shows that any pellet above 4 mm will have a very similar utilization at low rate discharges. Looking at Fig. 4 the path length during discharge is shown for several different sized pellets. If internal resistance within a pellet is considered proportional to the tortuosity of the conductive path (represented by the path length here) then it is clear that larger pellets, while not only having lower utilizations, also suffer from increased internal resistance within the pellets themselves. Depending on the conditions, this may or may not be significant until the end of the discharge where we see the path length rise considerably as it takes longer to find a pathway out of the pellet.

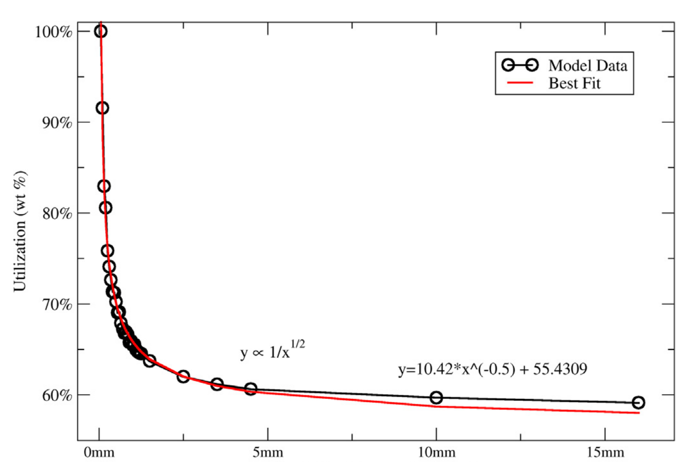

Fig. 3. Paste utilization as a function of mesh size. The red line indicates the best fit to the simulated data in black. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

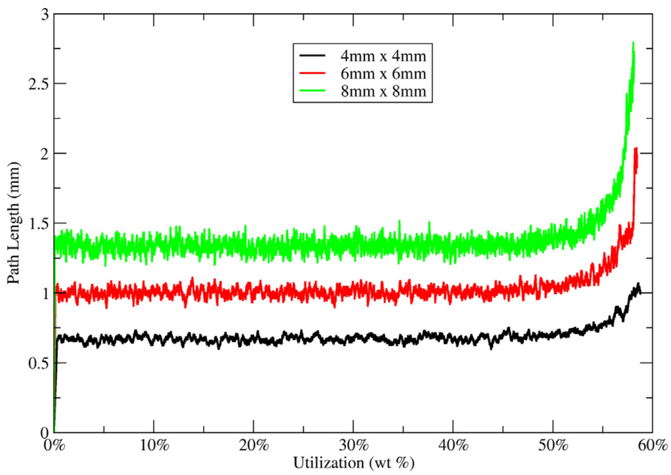

Fig. 4. The path-length for nodes that successfully discharge is shown for increasingly large pellets. Path length is shown here as a running average of 500 node-discharges to enhance viewability.

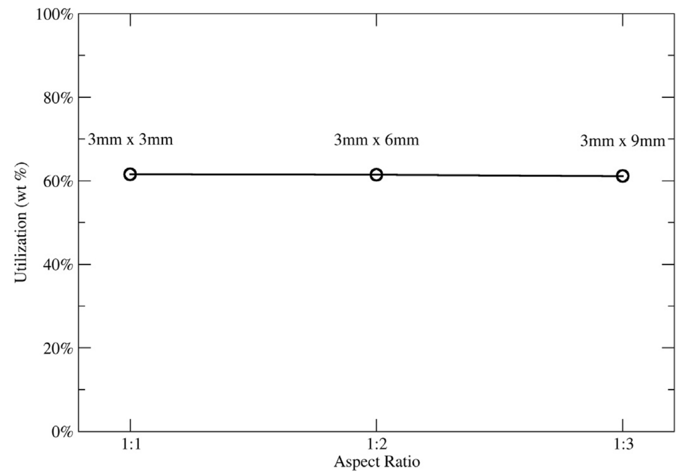

Fig. 5. Utilization as a function of aspect ratio is shown for 3 mm wide pellets that have an increasing length. Changing the aspect ratio appears to have virtually no effect on the overall utilization.

In order to see a tangible benefit from pellet size reduction, one has to decrease the mesh size to below ~4 mm, upon which an increasing amount of paste will be utilized for each unit of length that the mesh is reduced. This correlates well to previously reported work [16,17] which showed a similar trend and length scale for the size-dependent behavior. This gives further validation to some of the well-established battery design principles: generally speaking, a smaller mesh size will tend to be more efficient at paste utilization, with much smaller meshes being substantially more efficient. Furthermore, the internal resistance will tend to decrease as the pellet size is decreased. Note also that reducing the mesh size has the effect of increasing the proportional amount of lead that goes into the grid wires. Therefore, there needs to be a balance in any design between the contact area relating the paste and the grid wires, and the bulk amount of lead in the wires. This is referred to as the gamma-factor by Pavlov [18].

3.2. Pellet aspect ratio

Looking at Fig. 5 we can see the result of the aspect ratio trials. The 3 mm × 3 mm, 3 mm × 6 mm and 3 mm × 9 mm systems all showed a very similar resulting utilization with a corresponding path length increase of only ~30% as shown in Fig. 6. The average path length was taken from the linear portion of the path-length vs. utilization curves (up to 40% utilization by our definition). The results are summarized in Table 1. The utilizations only differed by 0.40%, which was not an expected finding. This is an important observation because it implies that within a pellet, the dominant geometrical factor is the shortest edge length (where edge length is defined as the length along the edge from corner to corner of a rectilinear pellet). Two pellets of similar width but different heights will still perform rather similarly, with the taller pellets being only marginally less efficient due to the increased path length resistances.

3.3. Detached mesh borders

Fig. 7 shows the resulting pellet size vs. utilization curves for pellets with zero, one, two, or three sides of the grid mesh detached. Surprisingly, even with three detached edges, the utilization does not decrease very dramatically. The only real change is the pellet size at which the utilization decreases to its minimum value. Comparing the plots for the zero and three detached edges,

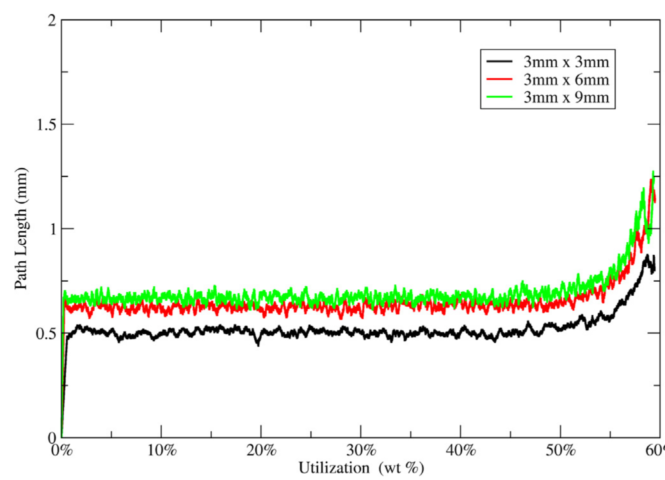

Fig. 6. Path length as a function of aspect ratio is shown for pellets with three different lengths and a constant width. Shown is the 500 node running average.

we see that they both approach ~60% utilization, with the lower curve decreasing much earlier than the upper curve. Looking at the path-length for a particular system size in Fig. 8 we can see that although the utilization is not very different, the path length certainly is. For the systems with one and two edges detached, the path length has not changed much, but for the system with three detached edges, the path length has increased by a substantial amount.

This data is well correlated and explained by our previous observation on different aspect ratios: the dominant geometrical factor for this type of case is the shortest edge length of the system. For the first two cases with detached edges, the system still has a minimum edge length similar to that of a system with all of its

Table 1
The results of the simulations performed on pellets with different aspect ratios.

System	Aspect ratio	Average path length (mm)	Utilization	Total nodes
3 mm × 3 mm	1:1	0.521	61.51%	90,000
3 mm × 6 mm	1:2	0.651	61.42%	180,000
3 mm × 9 mm	1:3	0.694	61.11%	270,000

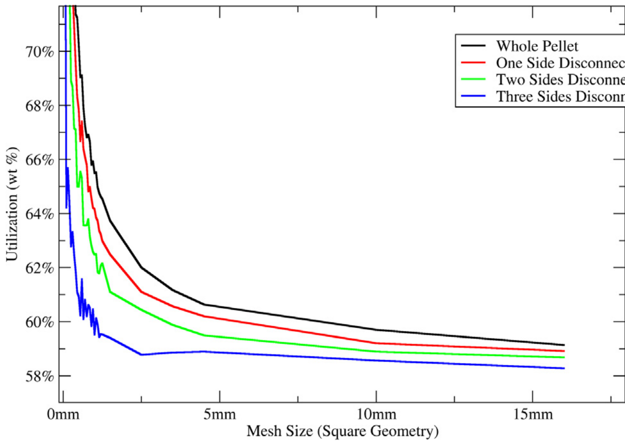

Fig. 7. The relationship between pellet size and utilization is shown for systems that have edges which have become disconnected from the grid.

edges intact and hence the path length does not increase substantially. For the last case however, three of the four surrounding edges have been detached; this is now similar to simulating a single part of a much larger system, one with a much larger edge length. Thus, because the shortest path length has now become suddenly much larger, the path length increases substantially.

Our findings tell us that in theory, two of the edges of a pellet could be replaced with a cheap and possibly inert material, without much performance penalty. In a standard lead acid battery grid, if one were to find an economical way to replace the horizontal wires with some kind of plastic (as has been attempted in the past [19]) a substantial savings could be realized with minimal penalty to product performance. In practice, the vertical grid wires which provide most of the conductive pathway to the lugs/tabs are made much thicker than the horizontal wires which tend to have much shorter conducting path lengths and which serve generally to constrain the active mass.

3.4. Additives

3.4.1. Non-conducting additives

Our results show that within 1–10% non-conducting additive content by volume, the overall paste utilization tends to decrease linearly with increasing amounts of additives, regardless of the pellet size. Our focus was on inert additives that were used in low concentrations. Fig. 9 summarizes our results for both the 1×1 (10 μm) and 2×2 (20 μm) non-conducting additives over a range of system sizes. Both types of additives performed quite similarly, with the 2×2 additives having slightly less influence than the 1×1 additives. Regardless of the size of the system, the impact of the inert additives on utilization tended to be very low and well behaved within the range of this study. Our results show that concentrations of up to 5% by volume would inhibit total utilization by ~1.0%, which is generally much less than the build variation of production cells. This implies that adding inert additives in small percentages would likely have very little if any effect at all on performance on a per unit weight basis. For example, substituting 5% of the active material in a given volume with additives would result in a total of 5% less capacity due to the removed active material plus an additional ~1.0% capacity loss due to the decreased utilization effects.

To understand the mechanism by which the utilization is lowered, we can look at the path-lengths for the low-rate discharges over a range of different additive contents in Fig. 10. Note that the average path length does not increase for the samples with more additives. Instead, the percolation threshold is shifted lower, which is indicated by the sharp rise in the path length after a particular utilization is achieved. As the amount of inert additives increases, the percolation threshold is shifted to the left on the graph, and that correlates to a lower utilization. However, looking at the path length up to and just before the percolation threshold rise, we can

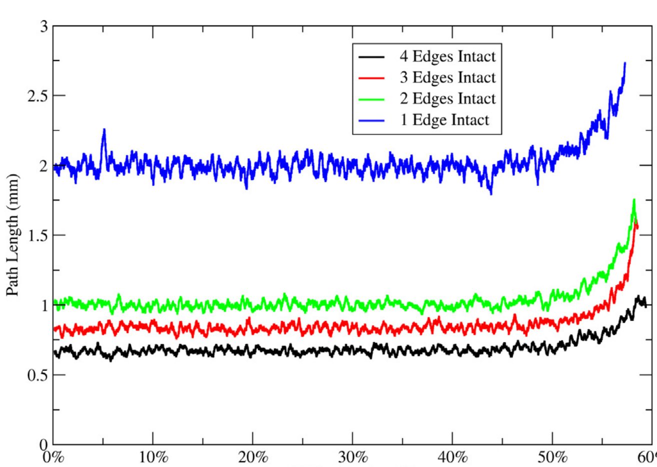

Fig. 8. The path length for discharged nodes during the simulation is shown for a 400×400 node system (4 mm square) with zero, one, two and three conducting edges removed. In order to find a conductive pathway, nodes must navigate to the remaining conductive edges. Shown here is the 1000 node running average.

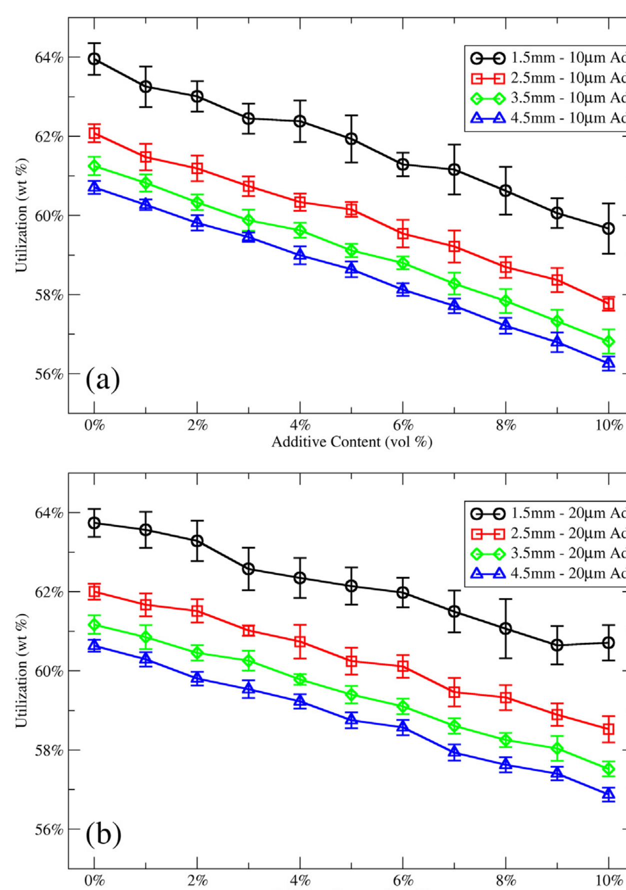

Fig. 9. The effects of inert microspheres are shown for the 10 μm (a) and 20 μm (b) cases. 10 runs per data point.

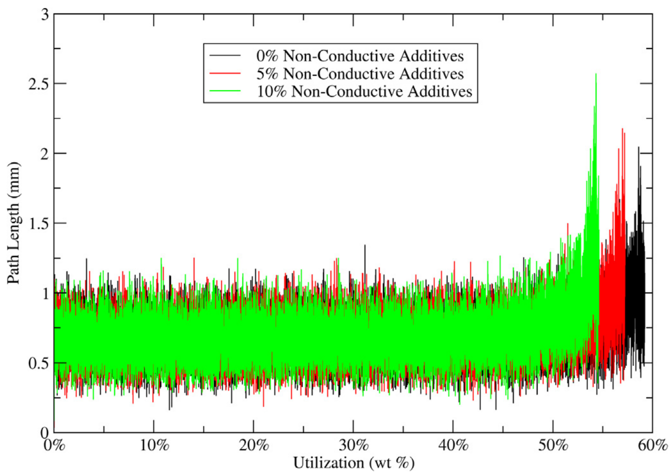

Fig. 10. The path length vs. paste utilization is shown for systems with increasing amounts of non-conductive additives. The addition of non-conductive additives causes the percolation threshold to shift towards the left, indicating a lower utilization. Shown here is the 200 node running average.

see that the battery function itself (via internal path length resistance) is virtually unaffected for the majority of the discharge.

3.4.2. Conductive additives

Similar to the non-conductive additives, the conductive additives showed a well behaved trend within the 1–10% volume percentage range. Utilization is increased in a linear fashion as shown in Fig. 11 for both the 1 × 1 and 2 × 2 cases. One interesting observation is that the utilization increase is less than the volume addition of the conducting additives, resulting in a net decrease of energy density for the pellet as a whole. For example, by replacing 10% of the active material with a theoretical conductive additive, the utilization will increase by ~7%, but the theoretical capacity will decrease by 10% due to the removal of displaced active material. The resulting energy that can be utilized will be 90% of the original capacity multiplied with the original utilization plus 7% (64% + 7% = 71%). Considering that the original amount of energy utilized was ~64% of the active material, the new amount will be 71% of the remaining 90% active material, which is 0.71 × 0.90 = 0.639 or ~99% of the starting value. Therefore, unless the conductive additives are much cheaper or lighter than the active material, or special constraints exist, there does not seem to be a tangible benefit to using the types of conductive additives that we have simulated.

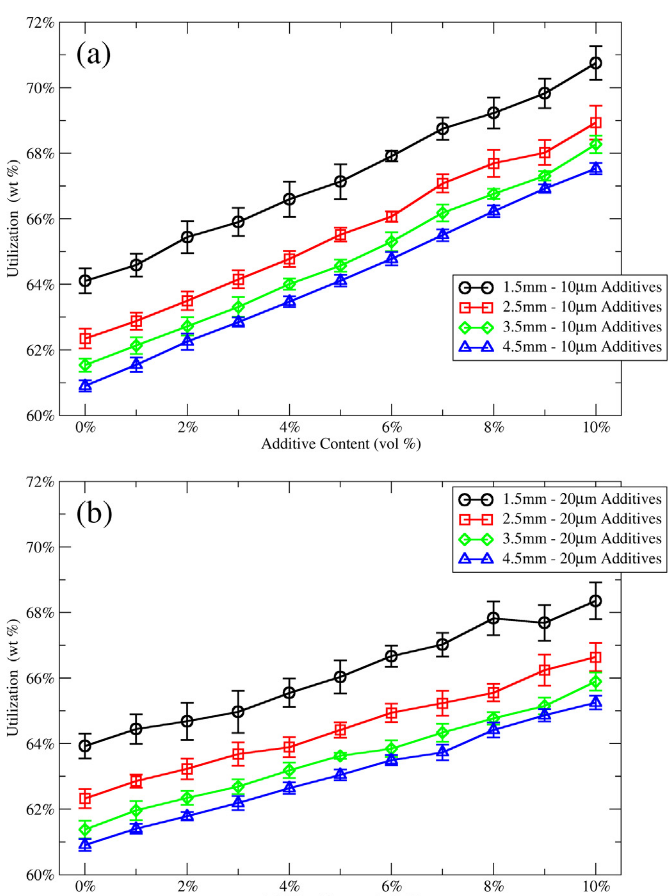

Fig. 11. The effects of conductive additives are shown for the 10 μm (a) and 20 μm (b) cases. 10 runs per data point.

4. Conclusions

This study used a Monte-Carlo based modeling approach to simulate the effects of pellet size, pellet aspect ratio, pellet defects and chemically inert paste additives on the total utilization of the active material during low discharge rates. We found that decreasing the pellet size tends to have a beneficial effect on the paste utilization, but edge lengths on the order of 4 mm or less are required in order to see a significant benefit. The effect of aspect ratio of the pellets was simulated. It was observed that changing the aspect ratio of the mesh only has a minor effect; the dominant geometrical factor was attributed to the shortest edge length of the grid wire mesh surrounding the pellet. The effects of cracks or detached mesh borders were simulated by removing the conductive edges of several samples. It was observed that two parallel edges can be detached without significant penalty to the overall performance of the pellet. However, if three of the four edges of a pellet are detached, a significant internal path length resistance develops. Finally, the effects of microscopic, chemically inert, paste additives were simulated. Non-conducting additives were found to have a small, negative impact on the paste utilization which increased linearly with additive loading up to 10% by volume (conducting additives had a positive impact). Two sizes of the additives at 10 μm and 20 μm were simulated. Our simulations predict similar performance for both additives, with the 20 μm additives having slightly less of a negative effect for non-conductive additives and less of a positive effect for conductive additives with respect to utilization.

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Appendix A. Supplementary data

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2014.08.134.

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