Capacity predictions for lead/acid battery plates having conductive additives

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Abstract

In this paper, we predict the capacity of positive plates having conductive particles mixed into its paste. Computer models previously reported are used to make these predictions. The models use a few physical parameters to predict capacity. The most important of these parameters is the critical volume fraction. This parameter provides the maximum amount of active material that can be discharged before the paste's conductivity limits the reaction. We estimate the critical volume fraction for plates containing different size conductive particles using the conductivity model. These results are then used in the capacity model to predict cell performance. Conductive particles improve low rate capacity and, on a per weight basis, can improve cell capacity at higher rates. The model predicts that the addition of 34% by volume of a conductive particle 20 μm in diameter will increase the capacity from 25 to over 60% of the stoichiometric capacity at 1 h rate. We compare the predicted performance of plates with conductive particles to other plates having no additives or non-conductive additives. A number of conductive particles were tested in an attempt to validate the model, but all proved to be unstable in the positive plate's oxidizing environment.

Keywords: Lead/acid batteries; Capacity; Additives

1. Introduction

As electric vehicles make an entrance into the US market place, the search for the ideal battery continues. One battery that has high specific power and low cost is the sealed lead/acid battery. Ratner et al. of the US Department of Energy [1] reported that sealed lead/acid batteries had the greatest technical merit and lowest development risk for use in electric vehicles. One limitation to using sealed lead/acid batteries is their specific energy (i.e., Wh/kg). If the specific energy could be improved, the range of electric vehicles could be increased, thereby improving the acceptability of electric vehicles in the consumer market.

To address the limited range of electric vehicles, it is important to understand the capacity limiting mechanisms of the lead/acid battery. Electrolyte diffusion plays a dominate role in limiting the capacity of lead/acid batteries, and many researchers [2–9] have developed diffusion models for this battery. Stein [2] studied the electrolyte diffusion using Fick's laws of diffusion and developed empirical values for the boundary conditions at the plate/electrolyte boundary. Horvàth

et al. [3] studied the electrolyte diffusion using Fick's second law of diffusion in combination with an approximate mass balance to give a theoretical approximation of both the electrolyte concentration distribution and the current distribution in the positive active mass. Papazov [4] used mass transport theories to model the movement of all the ion species in a cell during the formation of the positive and negative plates. Ekdunge and Simonsson [5] modeled the kinetics of the electrode, the ionic mass transport, and the effects of structural changes to predict the performance during high discharge rates. Björnbom [6] also developed a model of the diffusion resistance of the electrolyte through the microporous structure using results from Ekdunge et al. [5] and Pavlov and Basthavelova [7,8,].

Other researchers [9–16] modeled the cell resistance and other properties to predict cell performance. For example, Simonsson [9] evaluated the current distribution of the battery during discharge by using a macrohomogeneous model for the porous electrode. Vaaler et al. [10] modeled the battery grid and active mass using Kirchoff's equations to determine the potential and current distribution on the electrode surface. Maja

and Spinelli [11] has modeled the grid, the active material, and the electrolyte as a series of resistors. In a four paper series Nilson and Chaplin [12–15] used a combination of three different models using the dilute-electrolyte theory and an electrical equivalent resistance circuit to model the behavior of the microstructure of active mass. These models are based on relating the discharge capacity to the solution and solid phase volumes, and the charge and discharge surface areas to the charge state. The three models are combined to relate the active mass microstructure to the current, potential, and the acid concentration.

Researchers have also evaluated the change in conductivity of the positive active material during discharge. As the battery discharges, the lead dioxide in the positive plate, which is conductive, becomes lead sulfate, which is an insulator. Metzendorf [16] modeled this behavior using the percolation theory and the effective medium theory. He found that the positive active mass maintains a conductivity that is similar to pure lead dioxide during most of the discharge. When the volume percent of lead sulfate reaches a certain volume percent, however, the conductivity rapidly declines until the conductivity matches that of lead sulfate. At this state of discharge, further reaction of the active material ceases. The change in the active mass's conductivity from conductive to non-conductive mimics a step function. The ratio of conductive material to non-conductive material at which the active material becomes non-conductive was defined as the critical volume fraction.

Pohl and Schendler [17] has experimentally demonstrated this effect. He combined lead dioxide and lead sulfate in various ratios and determined the conductivity of the combined powder. Winsel and co-workers [18–20] continued to modify Metzendorf's model to develop the aggregate-of-spheres model. Winsel correlates the capacity of the active mass to the formation of necks between the active material particles that act as conductive pathways. The model is used to explain the loss of capacity during cycling and other failure mechanisms of the lead/acid battery.

The computer model used in this paper to predict cell capacity combines Fick's laws of diffusion with the critical volume fraction parameter. This combined model, which we will refer to as the capacity model and was presented in Ref. [21], predicts the discharge behavior of the lead/acid battery over a wide range of discharge rates and for various additions of non-conductive particles to the positive paste. In Ref. [22], the capacity model effectively predicted the capacity of plates containing a wide ratio of hollow glass microspheres (a non-conductive particle) to the positive active material. An advantage to the approach used by this model is that most of the properties, with the exception of the critical volume fraction, are directly measured from an existing plate. The critical volume fraction is estimated from a computer model which we will refer to as the conductivity model [23].

In previous work [22], we found that the glass microspheres helped to increase the specific capacity of the active material by eliminating the material that does not react. This effect was most noticeable during high discharge rates where the battery was limited by electrolyte diffusion. Since the microspheres decrease the conductivity of the active material, the cell capacity decreased during low discharge rates. The specific capacity performance of plates having conductive particles will not suffer the same decrease in low rate capacity.

In this paper, the capacity model will be used to predict the behavior of positive plates containing conductive particles. These predictions are plotted and compared with computer results for plates containing non-conductive particles. The capacity model was previously validated for plates having non-conductive particles. We were not able to validate the predictions for plates containing conductive particles due to the oxidizing environment of the positive plate.

Few conductive materials can withstand the anodic oxidation at the positive plate. For example, several authors [24,25] have evaluated graphite as a possible additive to the positive plate and found that it oxidized, resulting in an increase in porosity. The increase in porosity causes an increase in capacity as reported by Baker et al. [24], and Tokunaga et al. [25]. Baker et al. [24] were unable to determine, however, if an increase in electrical conductivity occurred.

We have evaluated several conductive additives without success. The particle types tested were carbon black, graphite, anisotropic graphite, silver-coated glass microspheres, titanium-coated glass microspheres, and titanium powder. In all of the cases, the particles were added in a 34% by volume ratio. The particles all suffered from anodic oxidation and caused the plates to self-discharge during the formation charge.

2. Model parameters

The capacity model requires a number of physical parameters to model the plates. Only a few of these parameters, however, vary with the amount of additives used in the positive paste. Table 1 shows these parameters that are varied for this study. The plates are classified according to the volume percent of additives in the positive active mass, see Ref. [22]. All particles are assumed to be identical except for their conductivity. In this manner the benefits of using conductive particles can be established since all other parameters used in the capacity model will be the same.

The plate and cell parameters that are not listed in Table 1 are the same for all the plates being modeled and are taken from commercially manufactured plates

Table 1
Plate parameters for positive electrodes with conductive particles

Volume % of microspheres in paste	0.0	19.5	34.0	54.0
Critical volume fraction (V_c) (conductive/non-conductive)	60.0%	64.6/58.5	68.5/50.0	80.0/37.0
Stoichiometric capacity (Ah)	19.68	13.87	9.54	3.59

used for verification in Ref. [21]. One of the cell parameters is the electrical resistance, which is 0.026 Ω. The cell's electrical resistance is a combination of the resistance of the electrolyte, active material, plate grids, wire length and size, the connections, and other resistance associated with the testing equipment. The other parameters taken from the commercial plate were the surface area of 35.06 in^2, the plate thickness of 0.096 in, the percent porosity of 34.7%, and the volume of active material of 1.315 in^3. The use of these values make all of the variables in the model the same, with the exception of the percent particle additions and the conductivity of the particle.

The critical volume fraction parameter is the major difference between glass microspheres and conductive particles. The effect that different size non-conductive particles have on the critical volume fraction were modeled in a previous paper [23]. This conductivity model has been extended to include conductive particles. Fig. 1 shows the effect that particle size and conductivity have on the critical volume fraction. A modeled particle size of 10×10, shown in the Figure, corresponds to a particle size of 20–50 μm. The particle size of 20–50 μm is the smallest glass microsphere commercially available by the supplier we used. The critical volume fractions for plates having conductive as well as non-

Fig. 1. Critical volume fraction vs. particle percentage by volume.

conductive particles of this size (i.e., 20–50 μm) are listed in Table 1. In Fig. 1 it can be seen that a smaller particle size would have the greatest effect on the critical volume fraction.

3. Model predictions

In Refs. [21,22], the capacity model's prediction were compared with experimental voltage–time curves as well as capacity curves. Since the comparisons made in this paper are computer generated, only the capacity curves will be reported. These curves, however, will show the improvements in battery capacity that can be expected from paste with conductive additives.

Table 1 lists the three different plate-types evaluated, 19, 34 and 54% by volume of particles. For each plate-type the capacity performance curve is plotted against the experimental capacity curve for a commercially produced plate. This curve is presented to provide a baseline comparison with the projected data. Also presented this Figure are the computer predictions for plates having equivalent amounts of non-conductive particles. The predictions for the non-conductive particles were previously verified by comparing them with test data from plates containing hollow glass microspheres.

Figs. 2–4 show the performance curves for the three different plate-types. In all three Figures, the capacity curves for the non-conductive particles are higher than the standard curve at the higher discharge rates. Despite the improvement at the high rates, the capacity for the non-conductive particles is reduced at the low discharge rates. The capacity curve for plates having conductive particles is higher than the plates not having fillers or plates having non-conductive particles. These curves show that the capacity curves for plates having conductive particles are shifted to the right from the curves for a standard plate, with a cap at the critical volume fraction value. Fig. 5 shows the capacity curves for all three plate-types as well as the curve for a standard plate. This Figure is used to show the improvement achieved when the amount of conductive filler used in the plate design is increased.

The plates with conductive additives have increased capacities over their entire discharge range. As seen in Figs. 2–4, the capacities at the low rate discharges
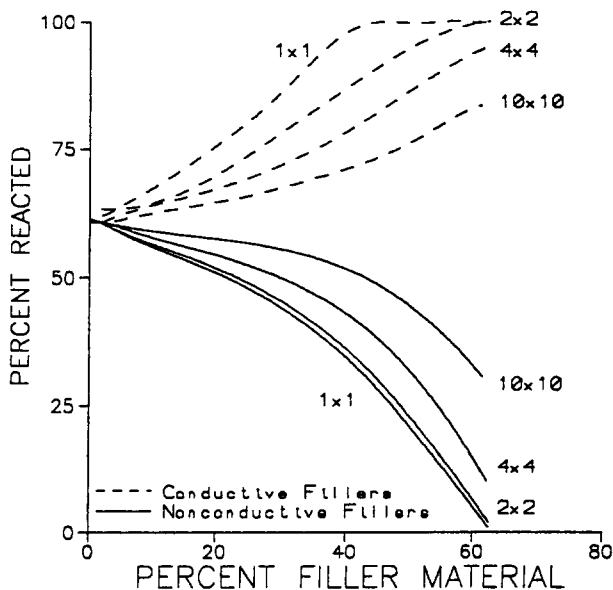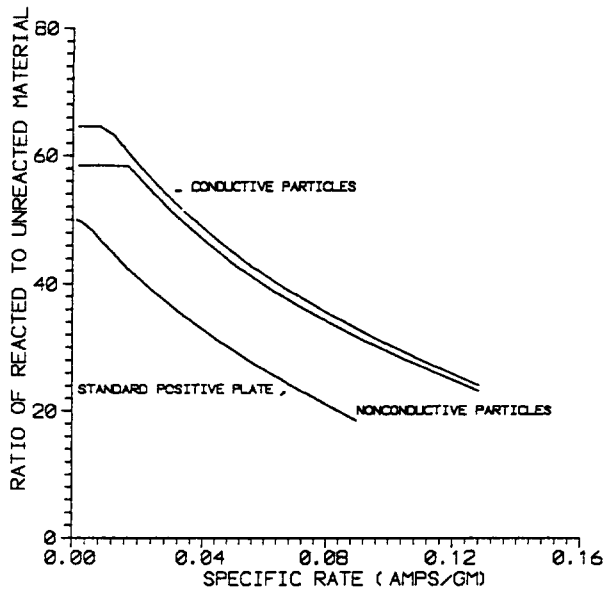
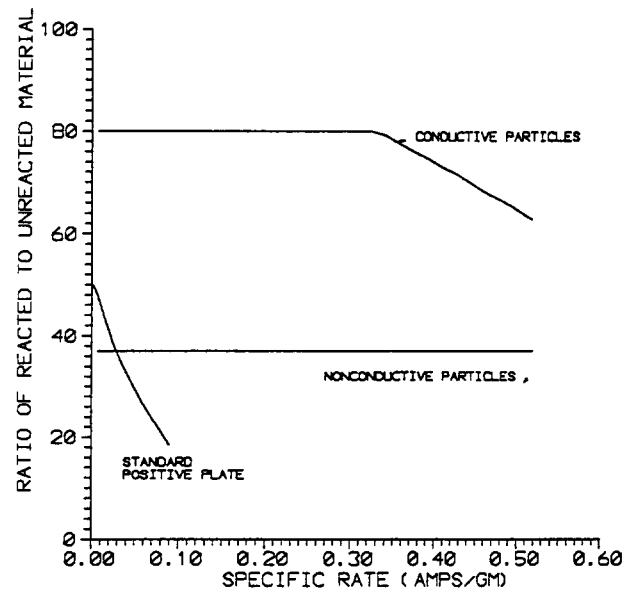Fig. 2. Capacity curves for plates containing 19% particles by volume.

Fig. 4. Capacity curves for plates containing 54% particles by volume.
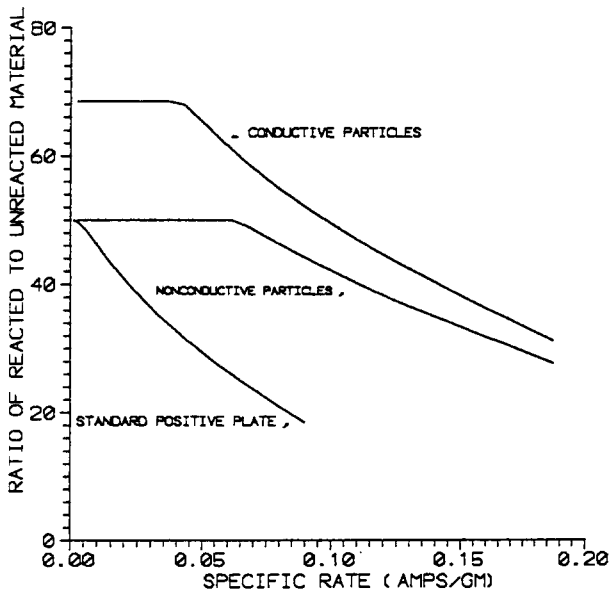

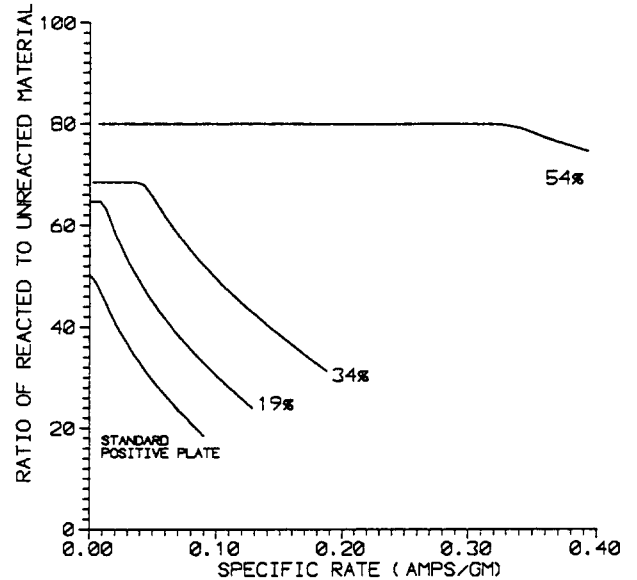Fig. 3. Capacity curves for plates containing 34% particles by volume.

Fig. 5. Comparison of capacity curves for plates containing conductive particles.

are higher than both the standard plate and the plates having an equivalent amount of non-conductive additions. This result shows the effect of improving the critical volume fraction and demonstrates the dominant effect paste conductivity has on the capacity at low rates. Even at medium discharge rates, 0.035–0.075 A/g, there is a significant improvement in the capacity over plates with glass microspheres, and a large improvement over standard plates.

In the Figures, the capacity curves for plates having conductive additives asymptotically approach the capacity curves for plates having non-conductive particles, which is most noticeable in the 34% by volume model. This effect demonstrates the decreasing importance of

conductivity at high discharge rates. At these high rates the diffusion limitation dominants. Even so, plates with a 34% addition of conductive particle can double the capacity at the 1 to 2 h discharge rates. These discharge rates are typical of the average discharge rate experienced by electric vehicles.

One main concern with the addition of any particulate to the lead/acid battery is the effect on battery life. During previous work [26,27] with the glass-particle additions to the positive and negative plates, it was found that low additions of glass particles did not severely decrease the mechanical integrity of the plate. When the particle additions exceeded 30–40% by volume, the mechanical integrity of the plates started to

diminish. Further work is needed to understand the effect particle additions have on plate life.

4. Summary

In previous work [22], it was found that non-conductive glass microspheres could improve cell performance. The microspheres increase the ratio of internally stored electrolyte to active material. By increasing this ratio, less electrolyte has to diffuse to the reaction site from between the plates, since most of the electrolyte needed for the reaction is already in the plate. However, the low rate discharge capacity was decreased with glass microspheres. The glass microspheres, being a non-conductive particle, decreased the critical volume fraction. A conductive particle was therefore desired so that the critical volume fraction could be increased and cell performance could be improved for all discharge rates.

Unfortunately, no conductive particles have been found that will survive the positive plate oxidizing environment. Computer models were therefore used to predict the performance of positive plates having conductive additives. The model found that conductive particles can improve the low rate capacity of the lead/acid battery. The particles also help increase the ratio of stored electrolyte to active material, thereby increasing the high rate discharge capacity. If large amounts of these particles are added, the capacity can be maintained at 80% of the stoichiometric capacity over a wide range of discharge rates, see Fig. 4. Conductive particles, when added to the active material, help overcome the limitations caused by paste conductivity and electrolyte diffusion.

If a conductive particle, 20–50 μm in diameter, can be added to the positive active mass of the lead/acid battery, in a ratio of 34% by volume, its capacity at 1 h rate, approximately 0.07 A/g, will nearly double. This is assuming that the material is stable throughout the life of the battery, and that the mechanical integrity can be maintained. The use of additives will also increases the volume of paste so that some degradation in performance based on volume will occur. Even so, the performance projections of using conductive additives are substantial and the search for a conductive

material that is stable in the positive plate should be pursued.

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