Computer aided design of a bipolar lead/acid battery*

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Abstract

Statistical design of experiments, coupled with the proprietary mathematical lead/acid model of Johnson Controls, Inc., were used to derive the design of a very high power bipolar lead/acid battery for the Jet Propulsion Laboratory. The effects of some battery component factors and discharge rate on the battery performance, predicted by the lead/acid model, were evaluated. The strategy to derive the optimum battery design, the roles of each battery component, limitations of the system, and the directions to improve the battery performance are discussed.

Introduction

Johnson Controls, Inc. (JCI) was contracted by Jet Propulsion Laboratory (JPL) in 1988 to develop a very high power bipolar lead/acid battery. The battery should deliver 50 kW total power at a 30 s rate for 100 cycles. The desired specific power was 4.4 kW/kg. The dimensions of the battery, however, were not defined. A conventional automobile lead/acid battery of a monopolar design would give a specific power about 0.2–0.5 kW/kg when discharged at a 30 s rate at room temperature. An improvement in specific power by about an order of magnitude over the conventional design was needed to reach the contract goal. This was a new challenge to the present lead/acid battery technology.

In a bipolar battery, the positive electrode is on one side of a substrate while the negative electrode is on the other side. Each individual cell is constructed by pairing the electrodes with a separator. The battery is assembled by joining the substrates, which also serve as intercell connections, and the battery case or frames. The number of cells in the stack can be adjusted for the required battery voltage. Current collectors are attached to the end plates. Two end blocks may be needed to press the battery. With this configuration one can eliminate non-active components such as straps, intercell connections, and the reservoir found in a conventional lead/acid battery of a monopolar configuration. Ohmic losses can be reduced because current

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travels through the thin substrate instead of running through the grids and straps. The specific power can thus be improved. LaFollette and Bennion reported a specific power as high as 800 kW/kg for up to 500 μs for a bipolar lead/acid battery [1]. They also reported that current densities up to 40 A/cm^2 were achievable for lead/acid batteries [1].

The limit in specific power of a lead/acid system was evaluated. Attia and Rowlette reported [2] that the current density equivalent to a 30 s rate of a bipolar lead/acid battery using a lead foil substrate and conventional active materials was less than 0.6 A/cm^2. The utilization of the positive active material at this rate was about 11.5% [2]. Assuming an average discharge voltage of 1.8 V per cell, this system would deliver the maximum power of 1.08 W/cm^2 at the 30 s rate.

The reaction in the lead/acid system is assumed to follow the double sulfate theory [3]

$$PbO_2 + Pb + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$
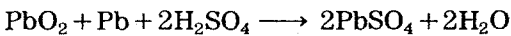
The theoretical capacity of the active materials PbO_2, Pb, and 50% H_2SO_4, calculated using Faraday's law, are 0.2241, 0.2587, and 0.1368 A h/g, respectively. If one aggressively assumes the utilization of these materials at a 30 s rate to be 15%, 30% and 100%, respectively, the total weight of the three active materials required is 0.2497 g/cm^2. The specific power would be 1.08 W/cm^2 divided by 0.2497 g/cm^2, or 4.32 kW/kg, which is 2% lower than the contract goal. In reality, the acid would not be 100% used and there exist non-active components such as battery case, substrate, and end blocks which contribute to the battery weight. Also, 1.8 V average discharge voltage at a 30 s rate may be somewhat optimistic. The specific power would be even lower if the discharge voltage were lower than 1.8 V, the desired utilization of active materials were not achieved, or the weights of other battery components were included.

There are ways to improve the total power of a bipolar battery. Since the dimensions of the battery are not specified by JPL, one can improve the total power of the battery by adding cells to increase the system voltage or by using a large electrode to obtain higher discharge current. Nevertheless, the specific power and discharge time are governed by the performance of individual cells. To improve the specific power output of a cell, the rule of thumb is to increase the discharge current density at the expense of capacity until the polarization effect becomes overwhelming. In other words, the rate at the power maximum needs to be defined. To reach the goal, the battery must be discharged at a current density higher than 0.6 A/cm^2. The capacity at high discharge rates has to be improved in order to sustain the desired discharge time. Major improvement in the utilization of the positive active materials at high rates must be achieved. The compromise between the material utilization and cycle life needs to be understood. Also, inclusion of non-active components must be minimized.

For a sealed bipolar battery, the advantages of using a large electrode include less weight fraction of the frame or battery case and less joining of

cells. However, the difficulty of manufacturing increases with the electrode size. The risk of performance failure increases with decreasing number of cells. For individual cells, the layout of active materials, thickness of the electrodes and separator, weight fraction of non-active components, and discharge current density would determine the performance. The impacts, applicable ranges, and available options of these important factors need to be fully understood before the dimensions of the product can be defined.

In this work, statistical design of experiments [4], coupled with the JCI proprietary lead/acid model modified by Tiedemann and Newman [5] for a bipolar configuration, were used to screen several battery component factors. Based on the results of the screening experiment, a second experiment was then designed to derive the response surfaces, i.e., statistical models, for the performance responses. Optimum battery designs which compromised the performance targets were then derived from the statistical models. Limitations of the system and opportunities to improve the performance are discussed.

Experimental

Two statistical designs of experiments were performed to study the effects of battery component factors on the performance and to derive an optimum design of a bipolar lead/acid battery. The lead/acid model developed by Tiedemann and Newman [5] was used to simulate the battery discharge. Results from the simulation were then used in the statistical analysis. The objective of the initial screening experiment was to find the most important factors, including battery components and discharge rate. The subsequent response surface modelling (RSM) experiment was done to establish statistical models of response surface for optimization of the battery design. A VAX computer (Digital Equipment Corporation) equipped with RS/Discover softwares (BBN Software Products Corp., Cambridge, MA) was used for statistical analysis. Simulation of the lead/acid model was performed using the same computer.

Eight factors — substrate weight, substrate thickness, separator thickness, separator porosity, weight of positive active material, weight ratio of negative to positive active material, acid gravity, and discharge current density — were screened. The substrate resistivity was fixed at 0.5 Ω cm. The electrode area and number of cells were arbitrarily assigned because no quantitative analysis of these two factors was needed in the screening experiment. Weight of the battery case was ignored in this experiment. The responses monitored were system weight, discharge time, total power, and specific power. A two-level, resolution **V** fractional factorial design, which required sixty-four runs of simulation, was adopted. The values of each factor were chosen such that they covered a very broad practical range. The responses calculated from outputs of simulation were used for statistical analysis.

A central composite circumference (CCC) design was used in the RSM experiment to develop quadratic models for prediction of the battery per-

formance. The four factors determined to be important in the screening experiment were explored in the RSM experiment. They were area density of positive active material, electrode area, number of cells and discharge current density. The other factor settings were either the same as those in the screening experiment or were assigned a reasonable value. The total number of simulation runs in this experiment was 25.

Results

Figure 1 shows the main effects of the eight factors screened, determined using the RS/Discover softwares, on the four responses, i.e. battery weight, total power, specific power, and discharge time. The line at 0 of the X axis represents the grand average of the response when all the factors are at their low values. The bar position reflects the effect of each factor when its value changes from the low level to the high level. In other words, it gives the average increase or decrease of a given response as one corresponding factor increases its value while the rest of the factors remain constant. The bar width covers the 95% confidence interval. The greater the distance
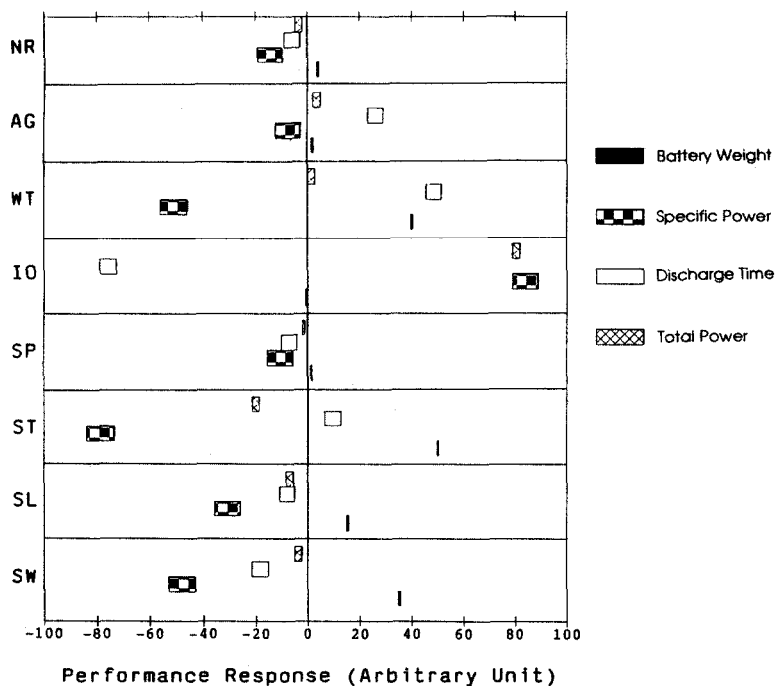

Performance Response (Arbitrary Unit)

Fig. 1. Main effects of substrate weight (SW), substrate thickness (SL), separator thickness (ST), separator porosity (SP), discharge current density (IO), weight of positive active material (WT), acid gravity (AG), and weight ratio of negative to positive active material (NR) on battery weight, specific power, discharge time, and total power.
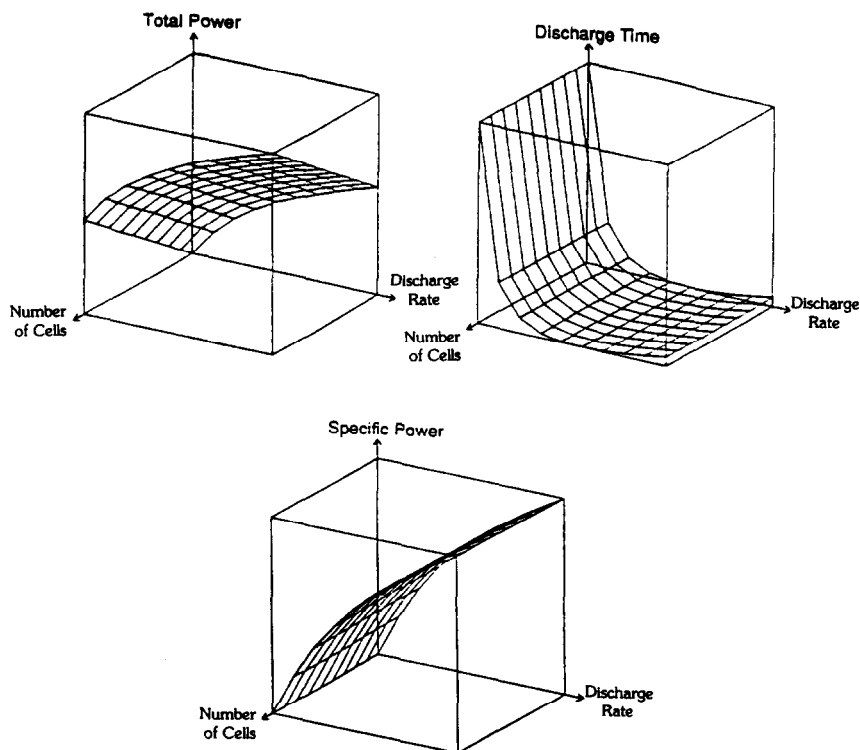
Fig. 2. Three-dimensional plots of response surfaces as functions of number of cells and discharge rate. The weight of positive active material and electrode area are fixed.

between the zero line and the center of the bar, the bigger the effect. No significant effects from interactions of any two factors were observed in this experiment.

Figure 2 shows three-dimensional graphs of a quadratic model for the bipolar system. This statistical model, which represents the best fit of the data, is an equation derived from multiple regression of data in the RSM experiment. In this Figure, responses of total power, specific power and discharge time, as a function of the number of cells and discharge rate for a given area density of active material and electrode area, are displayed. For other values of area density of active material and electrode area, the general shape of the response surfaces is unchanged. In all cases, the battery performance is limited by the positive electrode.

Discussion

The discussion below about the screening experiment is confined within the ranges of the factor settings studied. It is clear from Fig. 1 that every factor except discharge rate has a contribution to the system weight. The

major contributors are weight of active materials, substrate weight and thickness, and separator thickness that determines the amount of acid in a cell. For total power and specific power, the only positive contributor is the discharge current. Acid gravity has a slight contribution to the total power because of improvement in cell voltage. Separator thickness has a negative effect on both total power and specific power, attributable to increasing ohmic loss through the electrolyte and extra weight of acid to fill the separator. Increasing substrate weight, substrate thickness, and weight of positive active material reduces specific power because of the contribution of these factors to the system weight and to ohmic losses through the thicker electrodes and substrate. These factors have no significant contribution to the total power of the system. Increasing the amount of positive active material and acid, as reflected by higher acid gravity or thicker separator, results in higher capacity or longer discharge time. Thicker separator has little contribution to the capacity but significantly reduces the specific power. Obviously, a thin separator is favorable to gain power. The ratio of negative to positive active material does not have a significant effect because the system is positive limiting. Two factors, weight of positive active material and discharge current density, have opposing effects on capacity and specific power.

It is clear from this experiment that one would use the thinnest and lightest substrate, the thinnest separator, and just enough negative active material to provide highest specific power. Higher acid gravity would improve capacity. Discharge rate and weight of positive active material must be compromised due to their opposite effects on specific power and capacity. These two factors along with number of cells and electrode area, which provide adjustment to the total power of a battery, are the factors used in the RSM experiment for derivation of the optimum battery design.

In Fig. 2, the total power increases linearly with number of cells, as expected. The total power, however, gradually levels off at high discharge rates and approaches the maximum. This behavior is believed to be due to compensation of increasing ohmic drop and activation polarization. Although not shown in Fig. 2, the total power starts to decline when the discharge current becomes 3 A/cm^2 or higher. Discharge time is independent of number of cells but decreases dramatically with increasing discharge current. If the curve of discharge time versus current is fitted with a Peukert equation [6], $I^n t = C$, where I and t are the discharge current and time, respectively, n and C are constants, an equivalent n value obtained is 1.26. The specific power increases with discharge current in a similar way to the total power. The specific power is independent of the number of cells. In other words, the power density per cell is unchanged. Considering the bipolar design, the outstanding components which are inactive but contribute to the system weight are the end blocks and current collectors on the end plates. The dead weight from these components has to be shared by each cell when the specific power is calculated. For a large number of cells, the share of the dead weight by each cell becomes minimal. Therefore, the specific power of a battery becomes insensitive to the number of cells. This result again

confirms the statement that discharge rate at a given weight of active material is the most important factor determining the specific power and discharge time of the battery.

The RSM experiment leads to the conclusion that 4.4 kW/kg specific power and 30 s discharge time could not be simultaneously achieved with one single design using conventional active materials. An optimum design which contained less than 40% by weight of inert materials and more than 60% conventional active materials was derived from the statistical model. When discharged at a current density of about 1 A/cm^2 with 20% utilization of the positive active material, the battery could satisfy both total power and specific power. But the discharge time was only 53% of the target.

Some factors which were fixed in these two experiments, such as substrate resistivity and plate porosity, may have a significant contribution to the battery performance at a given discharge rate. Also, the roles of each component in the battery need to be studied in order to understand their working ranges and limits. The following discussion will focus on a quantitative analysis of these factors and their impacts on the battery performance predicted by the lead/acid model. The battery design used for the following discussion contains, typically, 10 mA h/cm^2 solid active materials, and the weight of non-active components except the substrate is limited to 2% of the overall system weight. The thickness and porosity of a conventional separator are used in the simulation.
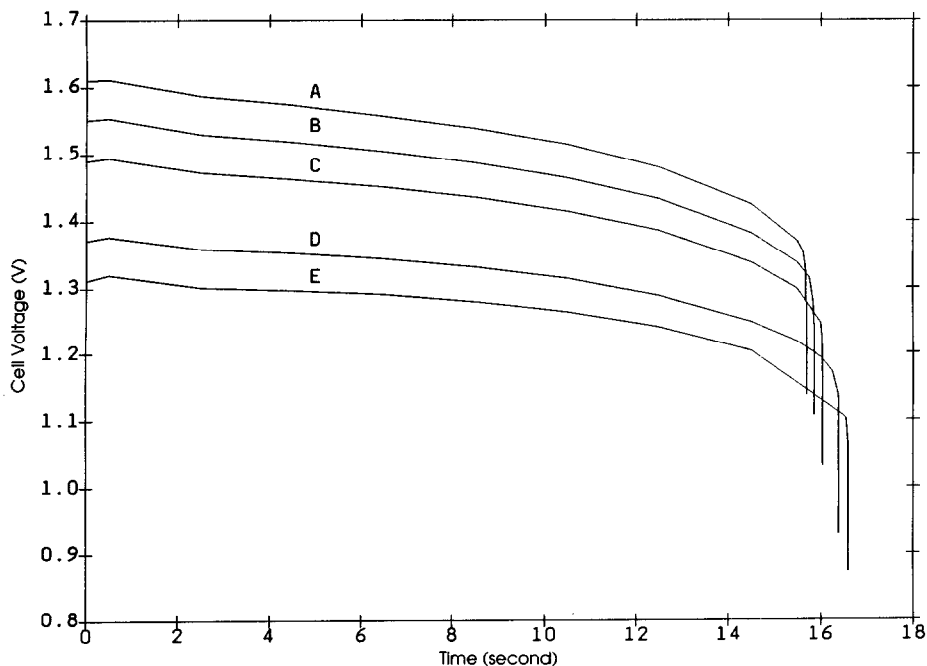

Fig. 3. Effect of substrate resistivity: A, 0; B, 1; C, 2; D, 4; E, 5 Ω cm on discharge curve. Discharge rate is 0.934 A/cm^2.

The contribution of the substrate to the battery performance is manyfold. In a bipolar battery, the substrate serves as the intercell connection, a current collector and the support of active material. It must be conductive, light and stable in the lead/acid environment. Considering light weight and conductivity, one prefers to use the thinnest substrate that can be handled. For the purpose of this study, however, the substrate thickness has been limited to 0.063 cm. A substrate this thick is convenient to manufacture and yet mechanically strong enough to go through battery assembly.

The effect of substrate resistivity on discharge time at a discharge rate of 0.934 A/cm² is shown in Fig. 3. Increasing substrate resistivity from 0 to 5 Ω cm results in about 20% power loss. The discharge time, however, increases by about 5% as a result of faster acid diffusion due to higher cell temperature caused by resistive power loss through the substrate. The specific power and final cell temperature as predicted by the lead/acid model are linear functions of the substrate resistivity, as shown in Fig. 4. The slopes are about -0.137 kW/kg Ω cm, and 1.87 °C/Ω cm for specific power and cell temperature, respectively. A battery containing one pair of the same size plates as those in a monopolar configuration, with the other components the same as those in a bipolar design, would give a specific power around 2.65 kW/kg at the same discharge rate. The substrate resistivity at this specific power, extrapolated from line A in Fig. 4, is about 9.4 Ω cm. The equivalent area resistance is 0.59 Ω cm². In other words, with the substrate resistivity greater than 9.4 Ω cm, the bipolar design loses its advantage over the monopolar design.
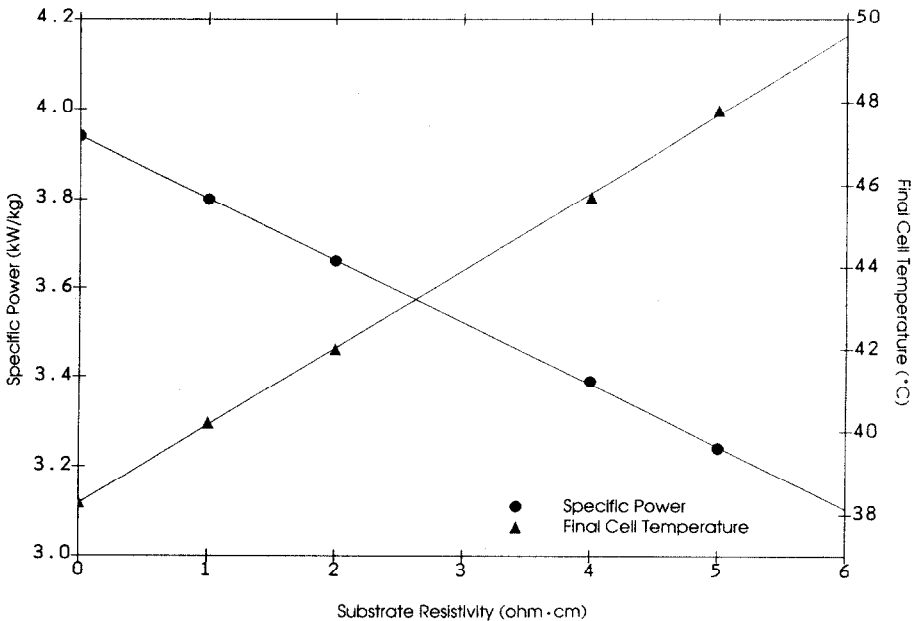

Fig. 4. Effect of substrate resistivity on specific power and cell temperature after discharge.

To maintain a constant total power of the system, the number of cells has to be increased if the substrate resistivity increases. As shown in Fig. 5, the number of cells needed to obtain a constant total power of 50 kW is a linear function of substrate resistivity with a slope of about 1.7. In other words, per unit increase in substrate resistivity, about two more cells are needed to maintain a constant total power. There is a slight penalty in specific power due to the increasing number of cells and substrate resistivity. The substrate weight has a negative effect on specific power. For the battery described above, the specific power decreases linearly with the weight fraction of substrate at a 50 kW rate. the equivalent weight fraction of the substrate to 4.4 kW/kg specific power, extrapolated from the linear function, is 23%. This maximum weight fraction of the substrate, however, may change as the design changes.

As previously discussed, at the present level of technology, the lead/acid system does not provide the desired specific power at a 30 s rate of discharge. In order to preserve the desired specific power, according to Fig. 1 one has to discharge the battery at a higher rate. Discharge at a higher rate reduces battery capacity. The following discussion will focus on approaches to improve the high-rate-discharge capacity with the desired specific power output.

Figure 6 shows typical acid distribution in the discharged system as predicted by the lead/acid model. For this particular design, the overall
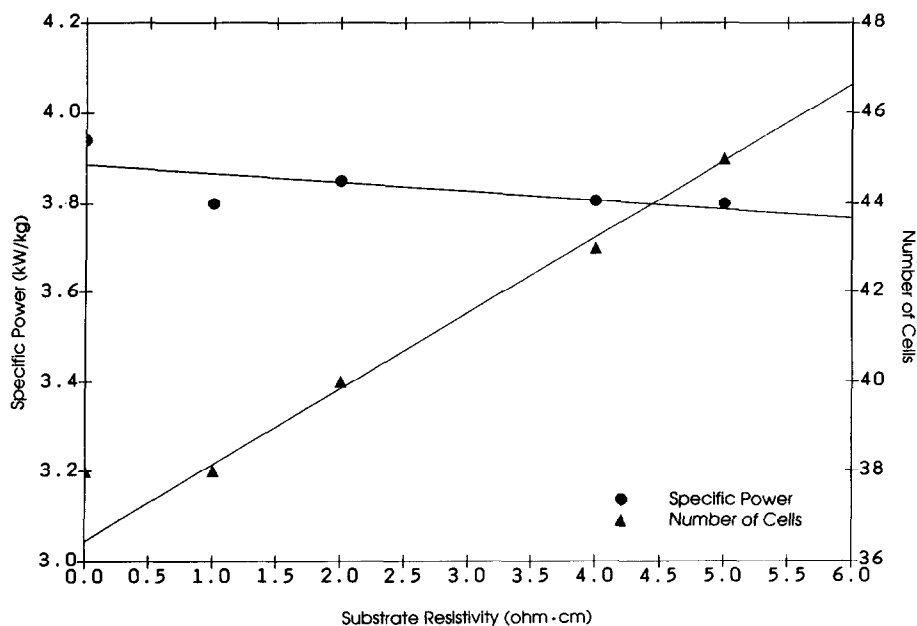

Fig. 5. Effect of substrate resistivity on specific power and the number of cells required to sustain a constant 50 kW output.
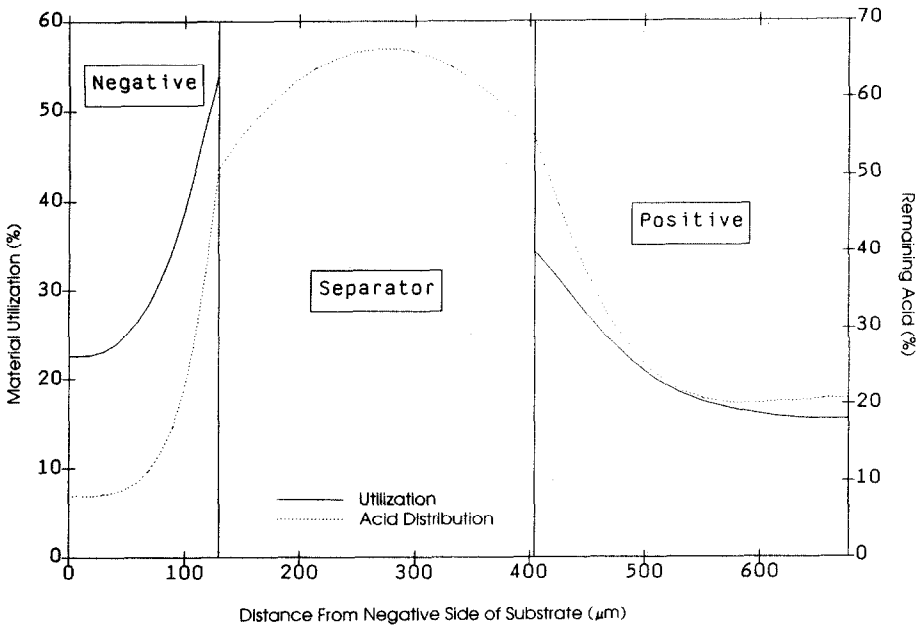
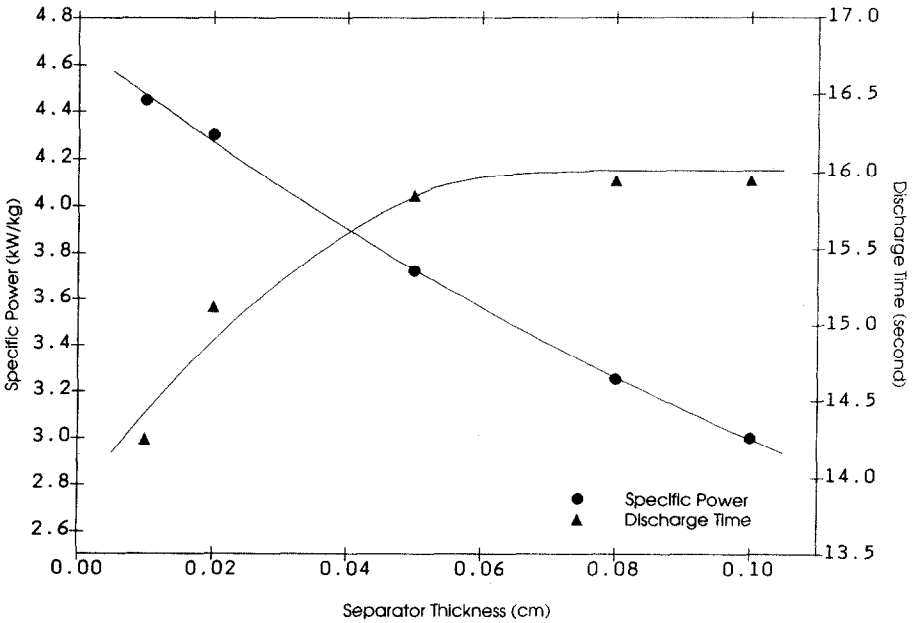Fig. 6. Acid distribution and material utilization in a cell after discharge.

Fig. 7. Effect of separator thickness on specific power and discharge time.

TABLE 1

Effect of plate porosity on performance of a 100 V, 10 A h module

Porosity (%)		Discharge time (s)	Specific power (kW/kg)
Positive plate	Negative plate		
58	64	18.0	4.59
70	64	24.5	4.44
75	64	26.1	4.36
70	70	26.0	4.40
76	76	32.5	4.21
80	80	37.0	4.06

utilization of acid in the separator and the positive plate is about 40% and 75%, respectively. The acid concentration profile in the positive plate shows a minimum at about one third of the plate thickness from the solution side. The acid concentration beyond the minimum gradually increases. This suggests limited acid diffusion from the bulk during discharge and there may be acid diffusion from the interior pores to the surface of the positive electrode. Similar prediction of the acid profile under high rate discharge has been reported in the literature [7]. Limited acid diffusion from the separator restricts the utilization of the interior active material, as is also shown in Fig. 6. Insufficient utilization of the interior material results in low capacity. The interior active material can be better used only if more acid is in the plate initially. Increasing separator thickness, as shown in Fig. 7, would reduce specific power with little improvement in discharge time due to higher ohmic drop through the thicker layer of electrolyte, higher battery weight, and limited diffusion of acid.

One way to increase the amount of acid in the plate is to increase the plate porosity. By putting acid in the plate, one can reduce the thickness of the separator for better specific power. When the weight fraction of non-active components plus substrate is limited to 30% of the system, the effect of plate porosity on discharge time and specific power predicted by the lead/acid model is shown in Table 1. In this study, the weight of active materials and separator thickness were held constant as additional acid was added to the more porous plates. Comparing rows 1 and 3 in Table 1, a 29% increase in positive plate porosity improves the discharge time by 45% with only a 5% penalty in specific power. The penalty is due to increasing thickness of plate at higher porosity and more acid needed to fill the pores. The impact of increasing porosity of the negative plate alone is much less significant. Nevertheless, under given conditions, both 4.4 kW/kg specific power and 30 s discharge time are achievable with this particular battery design if the plate porosity is higher than 70%, as suggested by the lead/acid model. In reality, it is very difficult to make a plate of 70% porosity which gives desired cycle life. It is a challenge to make a highly porous and yet strong plate.

Negative plates are known to be more efficient than positive plates. For the system studied in this work, the utilization of a negative plate at a 30 s rate is about 30%, about twice that of a positive plate. The balance between the positive and the negative active material depends on the utilization of the positive active material as well as on the identity of the limiting electrode. The balance may be slightly in favor of the negative to preserve oxygen recombination during recharge and to make the positive electrode the limiting electrode.

Conclusions

To improve the specific power of a bipolar lead/acid battery, one would discharge the battery at the highest current density until ohmic losses and polarization limit the power output. The high specific power, however, can only be obtained at the cost of discharge capacity. A proper design of a bipolar lead/acid battery would be a compromise of these two characteristics depending on customers' needs. One way to increase the specific power is to reduce the weight fraction of non-active components and the unused fraction of active materials. Increasing material utilization by increasing the plate porosity is the only way to improve capacity at a given high discharge rate. To manufacture a highly porous and yet strong plate, however, is a challenge to the lead/acid technology.

Acknowledgements

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