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Expected Cycle Life vs. Depth of Discharge Relationships of Well Behaved Single Cells and Cell Strings

Lawrence H. Thaller
Lewis Research Center
Cleveland, Ohio

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EXPECTED CYCLE LIFE VS. DEPTH OF DISCHARGE RELATONSHIPS OF WELL BEHAVED SINGLE CELLS AND CELL STRINGS

Lawrence H. Thaller

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

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ABSTRACT

The factors that might influence the cycle life vs. depth of discharge relationship are examined. This is done first at the single cell level using a progressively more complex cell life model. This is then extended to multicell battery strings where the stochastic aspects associated with groupings of cells are introduced. These relationships are important when considering the weight, cost, and life of battery packs. The results of this theoretical study are compared with a recent review of actual cell-cycling data. The factors examined are the rate of capacity loss, the amount of excess capacity built into the cells, and the penalty in capacity loss resulting from the use of deep depths of discharge. This study suggests that the relationship between cycle life and depth of discharge is not one that can be varied or significantly improved by cell research. The relationship appears to be determined by certain more or less fixed cell parameters. Among multicell strings, the standard deviation, as expected, plays an important role in determining overall battery life.

INTRODUCTION

Large battery packs for multikilowatt storage, operating at deep depths of discharge, are required for aerospace and terrestrial applications. The desirability of high voltage levels will require a significant number of individual cells to be connected electrically in series. The cycling of such battery packs will be influenced not only by the stochastic variations associated with the grouping of items, but also by the cycle life vs. depth of discharge characteristics of the single cells from which the battery packs are assembled. A recent review (Ref. 1) of this latter subject pointed out the semilogarithmic relationship of cycle life as a function of depth of discharge. Although the actual performance of these single cells and three- or six-cell modules ranged from good to poor, a relationship of the form $L = L_0 e^{\alpha(1-D)}$ could always be fitted to the data. The term, L_0, is the cycle life at 100 percent depth of discharge and D is the fractional depth of discharge. The term, L, is then the cycle life at any fractional depth of discharge. The exponent α is determined by plotting corresponding values of $\ln L$ and D. Reference 1 showed how important the value of α is in determining what the most cost effective depth of discharge would be.

This article examines what factors might influence the cycle life vs. depth of discharge relationship, first at the single cell level and then at the battery level. The factors examined are the rate of loss of cell capacity, the amount of excess capacity built into the cells, and the penalty in capacity loss resulting from the use of deep depths of discharge. What might be called "first principles" have been used to develop a cell life model for somewhat arbitrary conditions. This model is then used to estimate the cycle life vs. depth of discharge relationships (and thereby α) for "well behaved" single cells. The stochastic variations associated with groupings of single cells are then introduced to the battery pack cycle life model.

For the purposes of this paper, a "well behaved" single cell is one that does not suffer any abrupt failure mode during the course of its operation. It gradually loses capacity for any number of the usual reasons at a rate that is the product of the fractional depth of discharge and a factor which is characteristic of the cell under consideration. This approach to be reported here, would suggest that the slope of the semilogarithmic life vs. depth of discharge relationship is fixed by the value of certain cell parameters such as the amount of excess reactive material, or the penalty related to deep depths of discharge, and is not a factor that can be varied or improved over a wide range. What might be improved is the rate of capacity loss once it is fully understood for the particular cell chemistry under consideration. All of this can be done without the necessity to evaluate lengthy life cycle test programs of actual cell hardware.

BACKGROUND

The electric vehicle application has proven to be a very severe and challenging one for near term electrochemical systems. Although cycle life requirements are rather modest (1,000 to 2,000 cycles), the depths of discharge (DOD) to which these batteries will be cycled (up to 80 percent DOD) are not usually associated with long life. A complicating factor associated with this application results from the desirability to use high voltage strings of cells and modules to attain battery pack voltages around 100 volts. The inherent stochastic variations accompanying the grouping of items from a population of certain average properties and the standard deviation thereof, can very easily lead to cell reversal, overcharging, or other undesirable occurrences that would tend to shorten the overall life of the battery pack. A recent review article, Ref. 1, covering the cycle life vs. depth of discharge relationships of near-term single cells and three- or six-cell batteries has been published. Besides being a fine compilation of cycling data and a thorough discussion of failure modes, this article showed how most of this cycling information could be fitted to a semilogarithmic relationship of the form $L = L_0 e^{\alpha(1-D)}$. That is, the cycle life L, at any fractional depth of discharge D, is a function of its cycle life at 100 percent depth of discharge L_0 and an exponent α determined from the slope of semilog plot of the actual cycle life data at various DOD's. An important deduction of this prior review was related to a derivation of an expression for the vehicle miles traveled as a function of the depth of discharge to which the battery is cycled. Since this value is related to the cycle life L and the fractional depth of discharge D, then it appears reasonable that there would be a maximum in that product. This maximum was shown to occur at D equal to $1/\alpha$. The value of α is thus very important in determining the most cost-effective depth of discharge. Although there were some anomalies, the exponents for various lead-acid and nickel-zinc devices from various manufacturers generally fell within the range of 3.0 to 6.0. This would suggest that DOD's of 17 percent to 33 percent would be the most cost effective. Since the value of α was determined from a curve-fitting process and was not assigned any physical significance, it is not immediately obvious whether it is subject to alteration or by how much. The desired end, of course, would be to develop cells which have an α value of 2.0 or less. This would result in the most cost effective DOD being 50 percent or greater.

The objective of this effort is to examine the possibility that indeed α does have some degree of physical significance and can be derived, although ever so crudely, from some pseudo first principles. The Lewis Research Center has been conducting an effort under the title "Synthetic Battery Cycling" (Ref. 2) which has as its objective the prediction of the cycle lives of large battery packs as a function of the stochastic distribution of certain cell characteristics and the rate of capacity loss. In essence, a cycle life vs. DOD relationship is built into a single cell performance model and then the cycle life of a group of such cells subject to random variations of certain characteristics is projected. An equality is established between α, the slope of the semilog plot of the Seiger relationship, and the midrange slope of the similar plot of this paper's single cell performance model. By determining the effect of specific cell characteristics on the latter slope, some inferences are made as to the likelihood of achieving α's smaller than the 3.0-to-6.0 range defined by Seiger for actual cells. Conclusions are then reached concerning how best to approach the development of long-lived battery systems.

THE CELL MODEL AND THE CYCLING MODE

The cells to be described here are hypothetical and are not meant to represent any particular technology. They will be assumed to have a nominal capacity of 100 ampere hours (Ah). Their total capacity will depend on what additional fraction, F, of this nominal capacity is available as reserve capacity at the beginning of life. Figure 1 depicts the significance of the terminology used here. The total capacity at the beginning of life is then $(1+F)\times100$ Ah. In later sections, the parameter F will be assigned a range of values and will also take on a certain degree of variability around each value. Parameters that vary will be taken from populations of normal distributions of mean, m, and standard deviation, σ.

The cells will not be assigned a failure mode as such but it will be assumed that there is a certain capacity loss rate. The parameter, A, multiplied by the fractional DOD to which the cell is cycled, D, will represent the amount of capacity that is lost in each cycle. The parameter A can be assigned any constant small number or be a parameter with a certain mean and standard deviation when considering a string of cells. It will be shown later that variations in A for this capacity-loss model do not lead to changes in the corresponding α's. A third parameter P will be introduced later which will simulate a higher rate of capacity loss at deeper DOD's and will have an effect on the corresponding α's.

The method of cycling these cells requires a certain degree of explanation. It will be assumed that a fixed number of ampere hours are removed from the cell on discharge and replaced on charge. Overcharging is not considered since the rate of capacity loss under consideration is permanent and thus not recoverable using overcharge techniques. Reference 2 contains a fuller explanation of these matters. The capacity loss per cycle in the simplest case will be AxDx100. The cell has a certain degree of reserve capacity, depending on the fractional DOD and the amount of active material put in the cell at the beginning of life. When the number of cycles times the value of AxDx100 equals the reserve capacity, then the cell will no longer be able to deliver 100xD Ah and the cell will be considered "failed." This cycling mode is not the usual one when considering single cells, but is representative of a cell in a cell string where individual cell switching is not used.

The following sections will, in a sequential way examine the cycle lives of single cells and then cell strings, given an increasingly complex format of assumptions and variations of parameters that can be assigned to cells and populations of cells. The effect of these variations on the resultant slope of the semilogarithmic relationship between cycle life and depth of discharge will be examined in an attempt to explore the possibility of reducing the α value of these relationships.

THE SIMPLEST CASE

In this case the actual cell capacity and the nominal capacity will be the same. The F parameter is thus 0.0 and the reserve capacity is (1 - D)x100 Ah. The loss factor A will be assigned a value of 0.001. The capacity lost per cycle will be 0.001xDx100 Ah. Therefore, cell life is defined as reserve capacity divided by the capacity loss per cycle, or, L = 1 - D divided by AD (see Table 1). Figure 2 is a plot of this relationship. Since there are no wet-stand limitations or failure modes hypothesized other than loss of capacity as a function of DOD, very high cycle lives are predicted at low DOD's and very low cycle lives are predicted at deep DOD's. In fact, using this simple model and assumptions, this simplest case would predict a cycle life of 1 at a DOD of 100 percent since failure is defined as the absence of any remaining reserve capacity. Added to the figure is a straight line drawn tangent to the midportion of the curve. This straight line can be expressed by $L = L_0 e^{\alpha(1-D)}$, per Reference 1. The value of α is equal to the whole integer 4.0. This is to be compared to the α values of 3.0 to 6.0 as experimentally observed in commercially available hardware. Thus, the simple model does give a realistic result.

CELLS WITH ADDED CAPACITY

Quite often cells are built with extra active material so that at the beginning of life they would be able to deliver more than their rated or nominal capacity. Figure 3 assumes that 10 percent, 25 percent, and 50 percent excess capacity is available at the beginning of life. The reserve capacity of these cells takes the form of $(1+F-D)x100$, while the capacity loss per cycle remains as in the preceeding case. The cycle lives are again the quotient of the reserve capacity and the loss per cycle. These curves not only show (as one would expect) that the cycle lives are increased by having excess capacity, but the equivalent α value (at 50 percent DOD) is reduced from 4.0 to 3.0 as the F factor is increased from 0 to 0.5 (50 percent excess capacity). The droop at deep DOD's is removed at the higher values of F. For the remainder of the cases to be examined in this paper, it will be assumed that cells have F equal to 0.5. Figure 4 shows the relationship between the equivalent α value at 50 percent DOD as a function of F. The effect diminishes as F increases and it is problematic what benefits could be derived by having cells with very high excess capacities even though α's less than 3.0 can be thus attained.

CELLS OF DIFFERENT LOSS RATES

The preceding figures were constructed assuming cells for which the loss rate was assigned a value of 0.001. Figure 5 is constructed for the cases where the parameter A is varied over several orders of magnitude. The reserve capacities at the beginning of life are all (1+0.5-D)x100 Ah, and the loss rates take on the A values as noted on the curves of Figure 5. These curves are seen to be simple vertical translations of the base case shown in Figure 3. Thus there is no change in the equivalent α value, but the effect on the cycle life of the cell is very significant.

ADDITIONAL PENALTY FOR DEEPER DEPTHS OF DISCHARGE

Deeper depths of discharge are known to introduce an additional rate of loss of cycle life that is above and beyond the loss rate associated with simple charging inefficiencies. This additional penalty at deep DOD's is caused by higher shedding rates and rates of grain growth, more severe mass transport environments, higher mechanical stresses due to differential expansion, etc. This effect is introduced to the model by assigning a value to the penalty factor P. The loss rate becomes Ax(1+PD)xDx100 Ah where P can be assigned various values. In Figure 6, a series of cycle life vs. DOD relationships are plotted where the value of P is varied from 0.0 to 2.0. The equivalent values are seen to increase from 3.0 to 4.0 (see Table 1). The introduction of P into the model shows that real cells are more likely to have α values closer to 6.0 than to the desired value of 2.0.

The above sections cover the most obvious factors that can assume or be assigned various values. The single cell cycle lives are seen to vary over several orders of magnitude, and the values for α range from 3.0 to 4.0. It would appear that the most significant factor in producing long cycle lives is the loss factor, A. Since this does not affect α, it however does not result in a deep DOD value for the most cost-effective one. This modeling exercise suggests that the most cost-effective DOD will remain where it has been found to be using experimental procedures; that is, between 25 percent and 33 percent DOD.

BATTERY STRINGS

Cells are usually connected in series to yield the proper combination of capacity and voltage level. Going from a single cell for which single values of A, F, and P can be assumed to a multicell string where A, F, and P may be assigned distributive functions, introduces a different level of problems. By assuming that these factors are normally distributed about means of A, F, or P with various values of standard deviation, a wide variety of plots could be generated. The factors F and P will be covered first since they only introduce second order effects.

If a string of cells were to be made of ones where there was a variation in the amount of active material, there would be a distribution of the value (1 + F) around its mean. If, for example, this distribution were to have a standard deviation, σ, of 0.05 (1 + F), the cell that would fail first would of course be the one with the smallest amount of capacity. This would be equivalent to a cell where F now takes the new value of F - 0.05x(1 + F)x2, if it is assumed that the selected population is bounded by 2σ on either side of the mean value. For the case of F nominally being 0.5, the equivalent F for the worst cell is 0.35. This of course would result in a slightly lower cycle life of the string. This definition of string failure may be arguable, but all the following comments will use it and will therefore be on a consistent basis.

For the case where the factor P is varied about an average value, the factor $(1 + (P + 2\sigma)D)$ is not too far from $(1 + PD)$, given reasonable values for the standard deviation around the mean. The resultant values of the cycle life and α would not change very much. The A factor is somewhat different since the variation is usually assigned or viewed in terms of the efficiency, (1 - A). For an A value of 0.001, it can be stated that a cell is 99.9 percent efficient in the recovery of the capacity during any one cycle. For the case of an efficiency 99.9 percent ± .1 percent, there would result a distribution of A from 0.002 to 0.000. An A value of 0.000 would result in a cycle life of infinity. For the following examples the cell efficiency will be assumed to be normally distributed about a mean of 1 - A with a standard deviation that will take on a variety of values. For the string life, only the cycle life of the cell with the largest value A need be considered. Furthermore, it will be assumed that cells beyond 2σ can be culled out of any battery pack. Figure 7 is for strings of cells made up from populations of various values of σ. The number of cells in the string is immaterial since its cycle life is fixed by the worst cell in the string (the 2σ cell). The main feature of this figure is that the resultant string lives are simple vertical translations of the single cell relationship. Although there is no change in the equivalent value of α, it is obvious that battery life is strongly affected by the stochastic character of the cell population.

CONCLUDING REMARKS

The subject of cycle life vs. depth of discharge has been explored from a theoretical standpoint first at the single cell level and then the multicell battery level. A technique was illustrated that permits the study of the effect of a number of parameters on the shape of the cycle life vs. depth of discharge relationship of cells. The equivalent values for α were found to vary over only a very narrow range similar to those found in actual life-cycle testing. No potential variable or parameter was found to have a significant influence on the value of α.

The factors that had the greatest influence on the cycle life were the value of the parameter that represented the rate of capacity loss and the standard deviation of value for the cycle efficiency. Even though desirable, finding conditions for an α value of 2.0 does not appear too probable. It would thus appear that battery string cycle lives approaching 1,000 can only be achieved by assembling those strings from a very close population of single cells that would have cycle lives of several thousand if tested as single cells. The ratio of cycle life obtainable at 20 percent DOD to that at 80 percent DOD will remain about five and possibly higher.

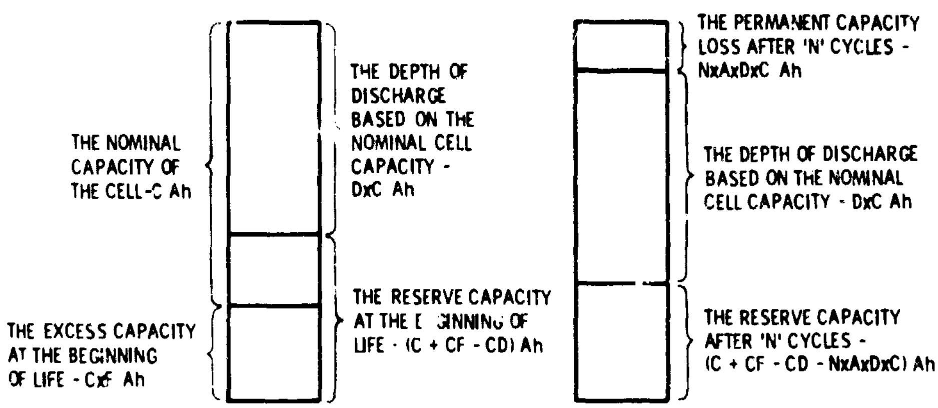
REFERENCES

1. H. N. Seiger, in Proceedings of the 16th Intersociety Energy Conversion Engineering Conference, American Society of Mechanical Engineers, p. 102, (1981).

2. L. H. Thaller, in Proceedings of the 16th Intersociety Energy Conversion Engineering Conference, American Society of Mechanical Engineers, p. 667, (1981).

TABLE I. - EQUATIONS AND SLOPES FOR VARIOUS CASES

Case	Equation	Slope $\frac{(d \ln L)}{dD}$	Slope at D = 0.5	Slope at D = 0.5 F = 0.5	Slope at D = 0.5 F = 5.0 P = 5.0
Seiger (ref. 1)	$L = L_0 e^{\alpha(1-D)}$	$-\alpha$	α	α	α
Simplist	$L = \frac{1 - D}{AD}$	$-\frac{1}{D(1 - D)}$	-4	NA	NA
Excess reactants	$L = \frac{1 + F - D}{AD}$	$-\frac{1 + F}{D(1 + F - D)}$	NA	-3	NA
DOD penalty	$L = \frac{1 + F - D}{A(1 + PD)D}$	$-\frac{1}{D} - \frac{1}{1 + F - D} - \frac{P}{1 + PD}$	NA	NA	-3.66



A. AT THE BEGINNING OF LIFE B. AFTER THE COMPLETION OF 'N' CYCLES

Figure 1. - Schematic diagram of the cycling terms.

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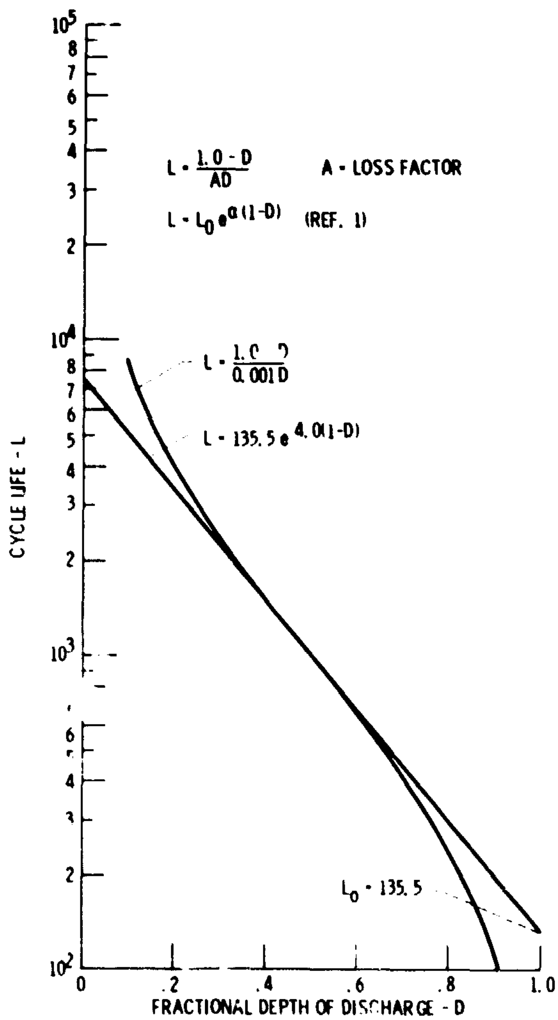

Figure 2. - Cycle life versus depth of discharge relationships predicted by two different models described in the text.

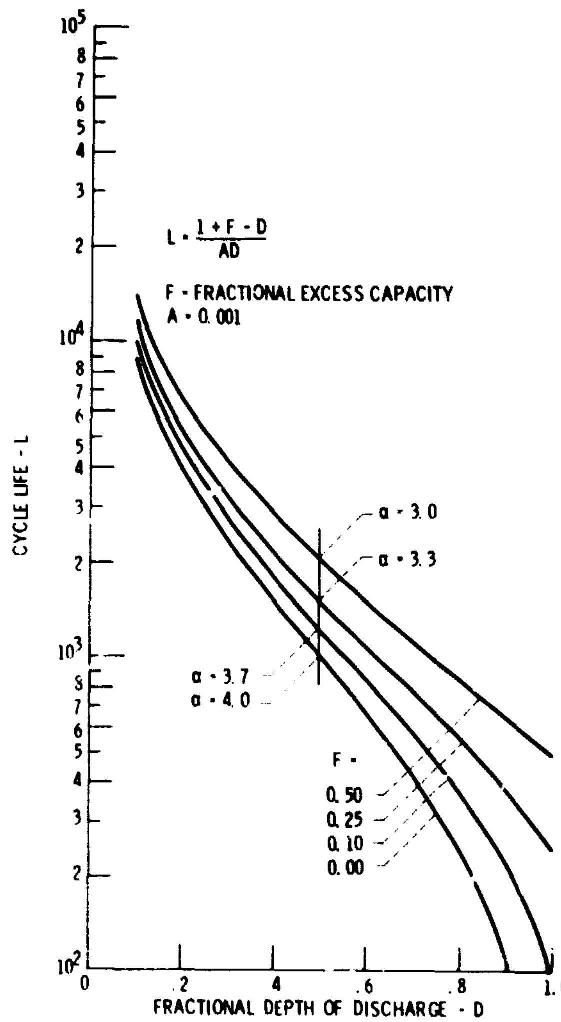

Figure 3. - Cycle life versus depth of discharge as function of the fractional excess capacity, F, defined in the text.

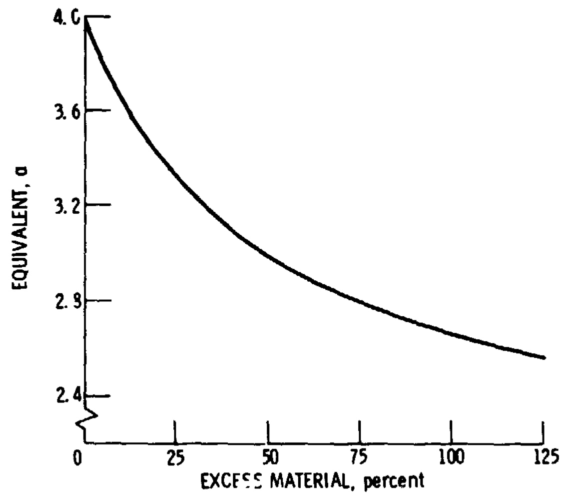

Figure 4. - Equivalent value of α at 50% DOD versus percentage of excess reactive material.

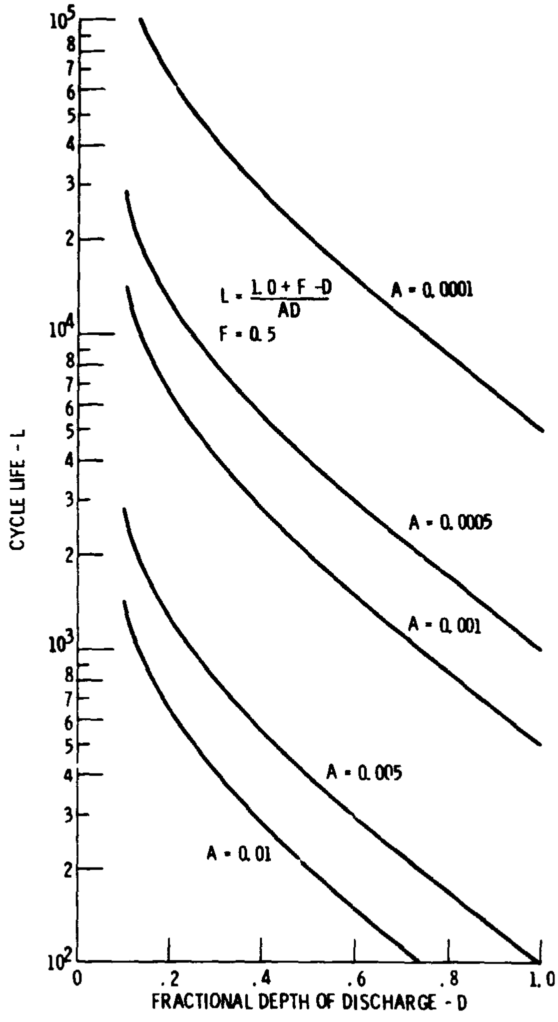

Figure 5. - Cycle life versus depth of discharge as a function of the loss factor, A, defined in the text.

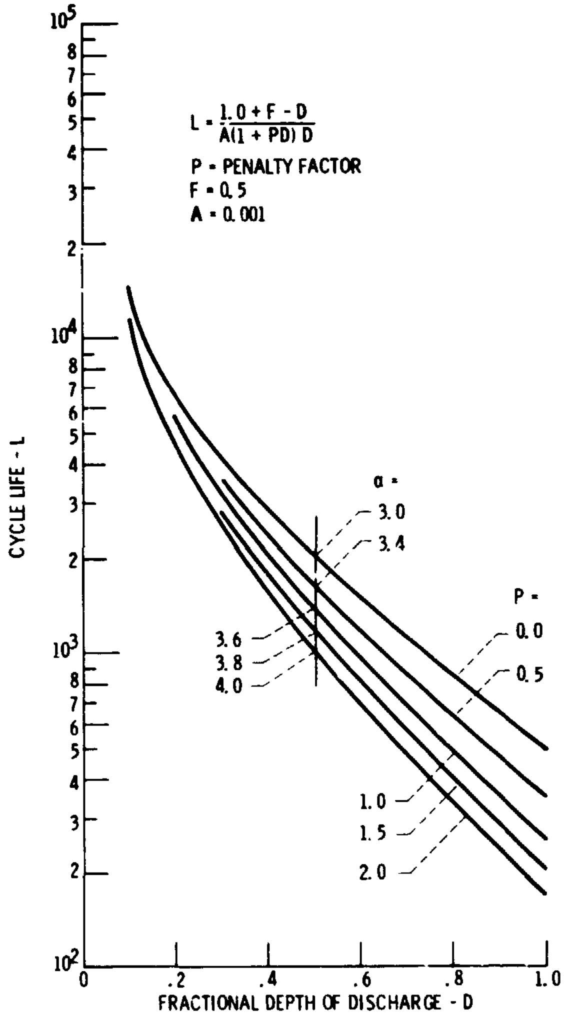

Figure 6. - Cycle life versus depth of discharge as a function of a penalty factor, P, for depth of discharge described in the text.

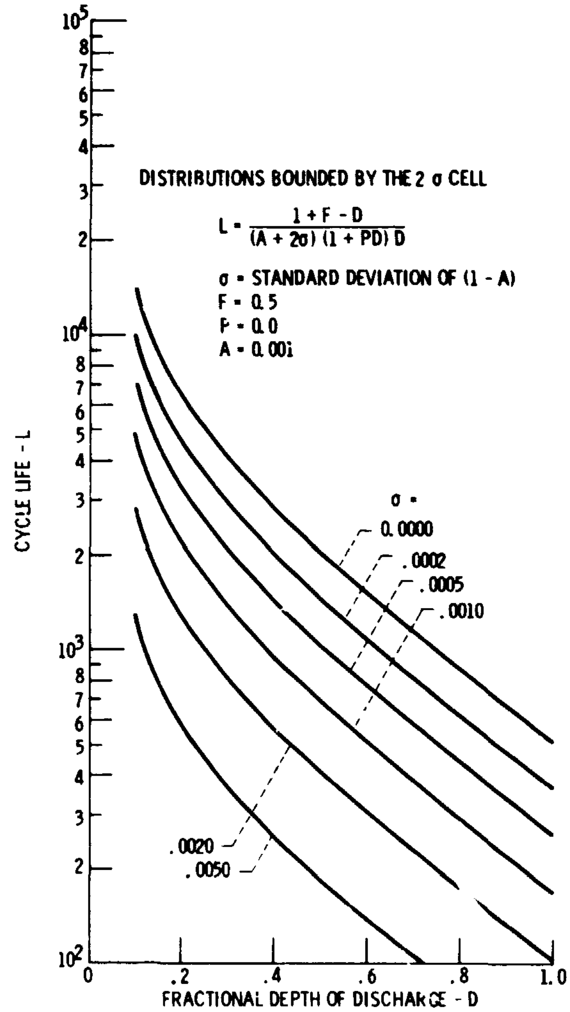

Figure 7. - Cycle life versus depth of discharge in battery strings as a function of the deviation, σ, in the cycling efficiency.