

## A FAILURE MODEL FOR SEALED NICKEL-CADMIUM BATTERIES

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### Summary

A model has been developed to describe failure in electrochemical batteries. The model is based on the concept of the existence and subsequent growth of flaws which ultimately lead to battery failure. This model provides, in a natural way, for the statistical variability of lifetime data. The model as applied to the Crane data indicates that when the effects of temperature and depth of discharge are taken into account, the observed variability in lifetime data is due almost entirely to statistical variability inherent in the battery itself.

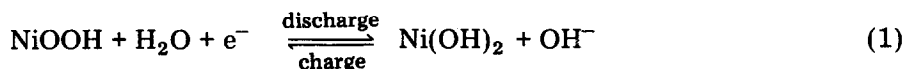
### 1. Introduction

#### A. Cell description

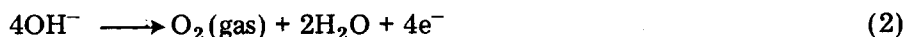
The current nickel-cadmium battery for aerospace use is an hermetically sealed system which consists of alternately interleaved positive and negative sintered plates which are separated by a porous separator and wetted by a conductive electrolyte. Non-woven nylon cloth is commonly used as a separator, although sometimes polypropylene is used instead, and the electrolyte is a 33% solution of potassium hydroxide.

#### B. Electrode reactions

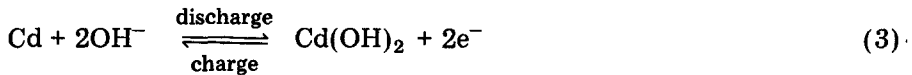
The charge-discharge reactions taking place at the nickel positive electrode can be written as [1 - 3]:



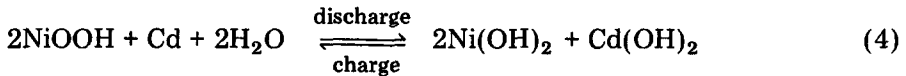
The above reaction occurs in the solid state because no soluble intermediates are apparently formed. During overcharge, oxygen is evolved at the charged positive electrode according to the following reaction:



The charge-discharge reactions at the cadmium negative electrode are:



In contrast to the solid state reactions at the nickel positive electrode, the reactions at the cadmium negative electrode are solution reactions because soluble  $\text{Cd}^{2+}$  and  $\text{Cd}(\text{OH})_3^-$  are formed as intermediates. The main overall reaction in a Ni-Cd cell can be written as:



Equation (4) is only an approximate chemical representation for the overall cell reaction.

### C. Causes of failure

The lifetime reliability of a cell is closely related to the cell design and the manufacturing processes. A cell design is a compromise of many requirements, such as charge/discharge capability, overcharge capability, storage capability, energy density, low and high temperature performance, cycle life and cost [4]. At the present time, the most highly developed electrical energy storage system for aerospace applications is the nickel-cadmium battery, but several problems have been of major concern in its application [4].

The failure of a battery may be defined as the inability of a battery to deliver on discharge or accept on charge, a prescribed quantity of electrical energy within a prescribed set of limits [5]. The causes of failure in general, and those of the nickel-cadmium batteries in particular, have not yet been established. Certain changes which occur in failed nickel-cadmium batteries have been observed and studied. However, the exact cause or causes of battery failure are still to be determined.

Among the changes which occur in nickel-cadmium batteries are:

#### (i) Positive electrode

The studies have shown that the positive electrode expands — referred to as swelling — and microcracks are formed as the cell ages [6 - 8]. This changes the interelectrode spacing in the cell by compressing the separator. The electrolyte is forced out from the separator and is redistributed into the positive electrode. This has been referred to as *electrolyte redistribution*.

The electrolyte is trapped in the electrode and cannot diffuse rapidly enough through the compressed separator at the reaction rates required. This gives rise to an increase in the internal resistance of the cell. Consequently, the discharge voltage and the capacity of the cell are lowered, and the cell appears to be degraded.

It has also been shown that the loss of active material is a cause of capacity loss of the positive electrode. This can occur visibly as shedding and blistering, or under the microscope as a detachment of small particles which can cause electrical shorts. It has been concluded that the loss of active material on the positive electrode is related to the evolution of oxygen gas during charge and overcharge as well as to the electrode design and manufacturing processes [9].

### (ii) Negative electrode

A possible cause of failure associated with the cadmium negative electrode is *cadmium migration*. During discharge, cadmium hydroxide is produced which subsequently reacts with hydroxide ions to form a soluble intermediate  $\text{Cd}(\text{OH})_3^-$  [10]. The  $\text{Cd}(\text{OH})_3^-$  may precipitate in the pores of the electrode, thus restricting the diffusion of the electrolyte into the interior of the plate [11]. This results in the apparent loss in capacity at a given discharge rate. In addition to the migration factor, it has also been found that the cadmium tends to agglomerate and form large crystals. The size and the rate of formation of these crystals are a function of temperature and the rates of charge/discharge of the cell.

### (iii) Separators

The most widely used separator materials in current Ni-Cd batteries are non-woven nylon and polypropylene.

A problem with the non-woven nylon separator is its oxidation, which results in the formation of  $\text{CO}_2$  which reacts with KOH to form  $\text{CO}_3^{2-}$ . The carbonate contamination in the cell not only reduces the electrolytic conductance of the electrolyte and thus interferes with the electrochemical reactions but also harms the cadmium negative electrode. Small amounts of carbonate will increase cadmium solubility in KOH significantly, resulting in cadmium migration through the separator as well as reducing the negative plate efficiency. In addition, carbonates accelerate the corrosion of positive plates and increase  $\text{H}_2$  generation, thus reducing the charge acceptance of the nickel positive electrodes [12].

In addition to oxidation, the nylon separator, being a polyamide, is subject to hydrolysis. The low molecular weight fragments obtained during hydrolysis can migrate to the positive electrode, thereby decreasing the overcharge protection [13].

As far as the polypropylene is concerned, it is found to be more stable than nylon. However, its wettability and gas permeability are poorer than those of nylon, and since it is hydrophobic, it does not retain as much electrolyte as nylon. It has been found that a cell made with polypropylene separators has 5% less capacity than the cell made with non-woven nylon separators [14]. In addition, when using polypropylene, more electrolyte is added, resulting in greater difficulty with oxygen recombination.

*(iv) Electrolyte*

Sealed nickel-cadmium batteries operate with a minimum amount of electrolyte, which is often referred to as a "semi-dry" or "starved" condition. This is necessary for the mobility and the recombination of oxygen evolved during overcharge. In other words, a small increase (even a few milliliters) in the quantity of electrolyte has a substantial effect on the oxygen recombination rate and cell performance [15]. On the other hand, too little electrolyte results in poor electrical and thermal performance, voltage variability, lower capacity and a greater memory effect.

The other major problem associated with electrolyte is so-called electrolyte redistribution. As mentioned earlier, this is caused by the swelling of the nickel positive electrode, which compresses the separators. As the separators are compressed, their porosity and, consequently, the quantity of electrolyte that they can retain is reduced. When this occurs, it increases the internal resistance and lowers the discharge voltage of the battery, and as a result the battery appears to be degraded.

## 2. Failure model

As pointed out previously, the exact cause or causes of failure of nickel-cadmium batteries is, at the present time, unknown. Some or all of the factors discussed above may contribute to battery failure. The hope is that once the failure mechanisms are understood, this will lead to the development of methods to predict battery lifetime.

For aerospace and other applications, the expected lifetime of a battery under a given set of operating conditions is probably its most important characteristic. Hence, even in the absence of a proper understanding of failure mechanisms, a considerable amount of work has been devoted to the subject of battery lifetime. The present work is an attempt to develop a model which can be used to predict battery lifetime. An especially comprehensive series of experimental studies of factors affecting the lifetime of nickel-cadmium batteries is being carried out at the Naval Weapons Support Center, Crane, Indiana [16]. In these studies the effects of variations in environmental factors (test temperature, depth of discharge, charge rate, discharge rate, and percent recharged) and in design factors (concentration of electrolyte, quantity of electrolyte, and ampere hours of precharge) on cell lifetime were assessed.

Basically, there are two general ways of treating data for battery lifetimes. On the one hand, one can attempt to describe the data using empirical linear or nonlinear mathematical functions. The fit of the data then provides numerical values of the coefficients appearing in the function. Once the coefficients are known, the function can be used to obtain interpolated values for the variables of interest. This approach has been applied to lifetime data by several groups [16 - 20]. A drawback to this approach is that while a given set of data can be fitted given a sufficient number of terms, the

use of the fit to estimated lifetimes outside the range of the actual data may not be appropriate. In addition, it is very difficult to take into account the fact that the lifetime of a battery is a statistical variable.

Another approach is to attempt to develop a model which reasonably describes the system. The model can be derived either from a detailed knowledge of the behavior of the system or, more commonly, from intuitive arguments. The advantages of the model approach over the first approach mentioned above is that the possibilities exist for (1) the prediction of the behavior of the system outside the range of the measured variables, and (2) the rationalization of the statistical nature of lifetimes which can, in addition, lead in a natural way to the assessment of battery reliability.

In the model suggested here, it is assumed that a battery fails by the growth of a pre-existing flaw or defect. When the flaw size reaches a critical value, failure occurs. It is interesting to note that in this treatment the exact mechanism of failure need not be known. The flaw postulate is not new and has a long history. It has been invoked to explain why the strength of a material is so much less than that calculated for a perfect specimen. This difference is rationalized by assuming the presence of flaws in the specimen, which weaken it. The flaw concept, in addition to providing a ready explanation for lifetime data, predicts the other well-known characteristic of such data, *viz.*, statistical variability.

In the model developed for cell lifetimes, it is assumed that flaws or defects exist in all cells. It is assumed that only one type of flaw exists. The relationship developed below can be generalized to the case where two or more types of flaws exist. The flaw is characterized by three important quantities: (1) the rate of growth of the flaw; (2) the distribution of flaw sizes; and (3) the total number of flaws present.

#### A. Rate of flaw growth

The first factor to be considered is the rate of growth of an individual flaw. The reasonable assumption is made that the movement of electrons in the battery interacts with a flaw, leading to a transformation which results in the growth of the flaw. The case of the cyclic charge-discharge test to failure as described in the Crane report [16] is treated here. It is assumed that the rate of change in flaw size,  $c$ , with cycle number,  $n$ , is given by:

$$\frac{dc}{dn} = kf^m c^s \quad (5)$$

where  $k$  is a reaction rate or transformation rate constant,  $f$  is the number of faradays of electricity per unit surface area of electrode passing through the cell per cycle, and  $m$  and  $s$  are constants. This expression is the analog of a general bimolecular reaction or transformation with both flaws and electrons considered as reactants or participants.

Equation (5) can be recast into the form:

$$c_0^{1-s} \frac{d(\Delta c/c_0)}{dn} = kf^m \left(1 + \frac{\Delta c}{c_0}\right)^s \quad (6)$$

where  $\Delta c = c - c_0$ . Direct integration yields:

$$(n - n_0) = \Delta n = \frac{1}{kf^m c_0^{s-1}} \left[ \frac{\Delta c}{c_0} - \frac{s}{2} \left(\frac{\Delta c}{c_0}\right)^2 + \frac{s(s+1)}{6} \left(\frac{\Delta c}{c_0}\right)^3 - \dots \right]. \quad (7)$$

In these expressions,  $c_0$  is the flaw size when the cycle number is  $n_0$  and  $c$  is the flaw size when the cycle number is  $n$ .

Equation (7) is the basic relationship connecting the growth of a flaw to the number of cycles which have elapsed. As such, the equation contains several parameters whose values need to be estimated. These parameters are:  $m$ ,  $s$ , the initial flaw size  $c_0$ , and the reaction rate constant  $k$ .

The parameter  $m$  appears only as a scaling parameter, *i.e.*, in the form  $kf^m$  as a multiplier for the denominator of the right hand side of the equation. On the other hand, the second parameter  $s$  determines the form of the relationship between cycle number and flaw size. For example, with  $s = 0$ , the growth of the flaw is independent of the flaw size; with  $s = 1$ , the growth depends on the logarithm of the flaw size, etc. It will be shown later that the assumption that  $s = 0$  fits the experimental lifetime data. In what follows, we wish to show how the values of some of the parameters can be expressed in terms of measured variables.

First of all, in accordance with common practice, we assume that the reaction rate or transformation rate constant  $k$  depends only on temperature and is given by an expression of the Arrhenius form,

$$k = k_0 \exp\left(-\frac{\Delta E}{RT}\right) \quad (8)$$

where  $k_0$  is a parameter independent of the temperature whose value depends only on the nature of the reaction or transformation involving the growth of the flaw,  $\Delta E$  is the energy associated with the reaction or transformation,  $R$  is the gas constant in the appropriate units and  $T$  is the temperature in degrees Kelvin.

Next, the quantity,  $f$ , the number of faradays of electricity passing through the cell per cycle can be expressed as

$$f = 2(\text{DOD})C \quad (9)$$

where DOD is the depth of discharge and  $C$  is the capacity of the battery expressed in faradays. This apparent capacity of the battery depends on the test conditions such as temperature, charge rate, discharge rate, etc. Hence, we express  $C$  as

$$C = C_0 g(T, \alpha_1, \alpha_2, \dots) \quad (10)$$

where  $C_0$  is the intrinsic or electrochemical capacity of the cell, and  $g$  is a function which depends on the test variables of temperature and others,  $\alpha_1, \alpha_2, \dots$ , which represent the effects of charge rate, discharge rate, etc. It is apparent that the value of  $g$  is always less than or equal to unity.

Using these results, the scaling parameter term  $kf^m$  can now be expressed as

$$kf^m = k_0 \exp\left(-\frac{\Delta E}{RT}\right) (\text{DOD})^m (2C_0 g)^m. \quad (11)$$

If this result is combined with eqn. (7) there is obtained,

$$\Delta n = \frac{\exp\left(\frac{\Delta E}{RT}\right)}{k_0 (\text{DOD})^m (2C_0 g)^m c_0^{s-1}} \left[ \frac{\Delta c}{c_0} - \frac{s}{2} \left(\frac{\Delta c}{c_0}\right)^2 + \frac{s(s+1)}{6} \left(\frac{\Delta c}{c_0}\right)^3 - \dots \right]. \quad (12)$$

Equation (12) represents the general expression relating the growth of a single flaw of initial size  $c_0$  to cycle number. As such, it should be applicable to any battery where failure is controlled by the growth of a flaw. The specific values of  $k_0, \Delta E, m$  and  $s$  and the functional form of  $g$  will, however, depend on the specific nature of the chemical reactions taking place in the battery of interest.

### B. Distribution of flaws

So far, we have been concerned with the growth of a single flaw of initial size  $c_0$  and we now inquire about the distribution of  $c_0$  values.

It is assumed that each battery contains a large number,  $N$ , of flaws, and further that each battery can be characterized by a distribution of initial flaw sizes. Intuitively, it is expected that in a given battery, the largest initial flaw will determine the lifetime of a battery. One is then interested in the distribution of the largest value of  $c_0$  in a population  $N$ . This type of problem is treated using a branch of statistics called extreme value statistics [21].

In order to proceed further, some form must be assumed for the distribution of flaws within a battery. A convenient form is the limited power law probability density function given by,

$$h(c_0) = (c_f - c_0)^{\beta-1} \quad \beta > 1, \quad c_0 < c_f \quad (13)$$

where  $\beta$  is a parameter whose value is independent of test conditions and  $c_f$  is the size of the flaw at battery failure. It is assumed that  $c_f$  is a constant for a given battery type and geometry.

Gumbel has shown that the asymptotic probability for large  $N$  and conforming to eqn. (13) is given by

$$\phi(c_0) = 1 - \exp \left\{ - \left( \frac{c_f - c_0}{c_f - c_0^*} \right)^\beta \right\} \quad (14)$$

where  $c_0^*$  is the characteristic value of  $c_0$ . This functional form is referred to as the "third asymptote" [21] and is otherwise known as the Weibull distribution.

Although the form of eqn. (13) may seem arbitrary, Gumbel has shown that for physically reasonable situations, and again for large  $N$ , all flaw size distributions fall into one of only two possible categories; the bounded distribution, eqn. (13), or an unbounded distribution expressible in exponential form. In the unbounded distribution, the flaw size  $c$  can take any value up to infinity.

The bounded distribution leads to the "third asymptote" eqn. (14), while the unbounded exponential distribution leads to another distribution function referred to as the "first asymptote" or Gumbel distribution. We have tested the Gumbel distribution and have found that it does not appear to represent the data nearly as well as the "third asymptote" or Weibull distribution. In other words, once a limited distribution is chosen to represent the distribution of initial flaw sizes, then eqn. (14) automatically follows. It is reasonable to choose a limited distribution because the initial flaw size  $c_0$  cannot exceed  $c_f$ , the size of the flaw at failure, and this assumption is embodied in eqn. (13).

Returning to eqn. (12), we assume as a first approximation that  $s = 0$  (an assumption about the value of  $s$  is unavoidable since we have no way to estimate its value) so that all but the first term in the expansion can be neglected and with some rearrangement this leads to the following

$$c_f - c_0 = n_f k_0 (\text{DOD})^m (2C_0 g)^m \exp \left( - \frac{\Delta E}{RT} \right) \quad (15)$$

where now  $n_f$  is the number of cycles to failure (assuming  $n_0 = 0$ ). When this expression is substituted into eqn. (14) the following cumulative distribution of lifetimes,  $\phi(n_f)$ , is obtained:

$$\phi(n_f) = 1 - \left\{ \exp - \left( \frac{n_{f, \text{red}}}{n_{f, \text{red}}^*} \right)^\beta \right\} \quad (16)$$

where  $n_{f, \text{red}}$  is the reduced lifetime defined by

$$n_{f, \text{red}} = n_f k_0 (\text{DOD})^m (2C_0 g)^m \exp \left( - \frac{\Delta E}{RT} \right) \quad (17)$$

and  $n_{f, \text{red}}^*$  is the characteristic value of the reduced lifetime.



### 3. Application of the model

The model was applied to the sets of data on the lifetime of nickel-cadmium batteries obtained from the NASA Accelerated Test Program carried out by Naval Weapons Support Center, Crane, Indiana, for sealed nickel-cadmium spacecraft batteries [16]. The discussion of this test program is not within the scope of this paper; however, a brief summary of the test will be given here. The objectives of the test were to determine the lifetime of nickel-cadmium batteries, and to evaluate the effects of design and component changes on the lifetime. The test was designed statistically using 8 stress factors: five are environmental and three are physical. These test variables are: (1) depth of discharge, DOD; (2) temperature,  $T$ ; (3) charge rate, CR; (4) discharge rate, DR; (5) percent recharge, %RC; (6) concentration of electrolyte, %KOH; (7) amount of electrolyte,  $\text{cm}^3$ ; and (8) ampere hours of precharge, Ah.

On applying the model to the failure data from Crane, eqn. (16) is re-written as follows:

$$[1 - \phi(n_f)] = \exp \left\{ - \left( \frac{n_{f, \text{red}}}{n_{f, \text{red}}^*} \right)^\beta \right\} \quad (18)$$

by taking the natural logarithm of both sides of eqn. (18), one obtains

$$\begin{aligned} \ln[-\ln(1 - \phi(n_f))] = & \beta \ln n_f + \beta \ln k_0 + \beta m \ln(\text{DOD}) + \beta m \ln(2C_0 g) - \\ & - \beta \frac{\Delta E}{RT} - \beta \ln n_{f, \text{red}}^*. \end{aligned} \quad (19)$$

According to eqn. (19) for fixed values of DOD,  $C_0$ ,  $g$  and  $T$  a plot of  $\ln n_f$  vs.  $\ln[-\ln(1 - \phi(n_f))]$  should be linear with a slope equal to  $1/\beta$ . In order to prepare such a plot, the cumulative frequency,  $\phi(n_f)$ , has to be estimated, and this estimation was done as follows [21]. The values of  $n_f$  are listed sequentially with the lowest value at the top of the list and the highest value at the bottom. Each value in the list is given an integer label starting with unity for the smallest value and ending with an integer denoted by  $l$ . The value of  $\phi(n_f)$  for the  $i$ -th entry in the Table is taken as  $i/l + 1$ .

The data from the Crane test have been normalized for temperature and depth of discharge (DOD), by using values for the parameters  $\Delta E$  and  $m$  determined as described below. The variability of the lifetime due to other test variables used in the Crane test program, such as percent recharge, concentration and amount of electrolyte, and ampere hours precharge was ignored since it has been shown that these variables have only a slight effect on lifetime [1, 16]. However, it is known that the charge/discharge rates have a significant effect on lifetime of a cell, so the data obtained at different rates were kept segregated. Altogether four charge/discharge rate (CR/DR) combinations are included in the Crane data.

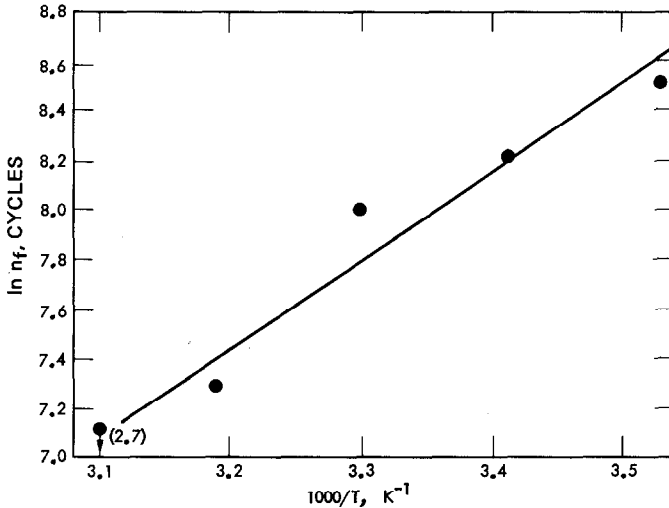


Fig. 1. Dependence of lifetime on reciprocal absolute temperature. Data from ref. 16.

#### A. Estimation of rate parameters $E$ and $m$

The value of  $\Delta E$  was calculated according to eqn. (12) by plotting  $\ln n_f$  vs.  $1/T$ . The graph should be linear with a slope equal to  $\Delta E/R$  provided that DOD and  $g$  are fixed. Figure 1 shows such a plot using data from the Crane report [16]. Although there are only five data points, the best-fitting straight line was drawn as shown, which represents a  $\Delta E$  value of 5.5 kcal/mole.

The data point representing 50 °C fell so far below the other data points that it was ignored in fitting the data. A value of 5.5 kcal/mole for  $E$  is a low value for a chemical reaction, but it is of an appropriate magnitude for a physical or transport process. However, more temperature data are needed before making a strong statement about whether the process is chemical or physical in nature.

The value of parameter  $m$  was also estimated by using eqn. (12). If the temperature as well as the charge/discharge rates are kept constant, then eqn. (12) predicts that a plot of  $\log \text{DOD}$  vs.  $\log n_f$  should be linear with a slope of  $1/m$ . The variation in the initial flaw size,  $c_0$ , from cell to cell is expected to introduce some scatter in the data; this is also true of the data in Fig. 1. Figure 2 is a plot of  $\log \text{DOD}$  vs.  $\log n_f$  obtained from both the Crane report and ref. 1. Five sets of data were available for use and were shifted horizontally to effect superposition. This was done because only the value of the slope is of interest. As seen in Fig. 2, the graph is linear; and from the slope, the value of  $m$  is found to be 1.5.

With  $m$  and  $\Delta E$  both evaluated, the Crane data [16] were segregated into four groups according to the charge/discharge rate imposed; these rates were  $C/0.5C$ ,  $C/2C$ ,  $4C/0.5C$ , and  $4C/2C$ . Within each group, the lifetime data were reduced according to eqn. (17) in the form

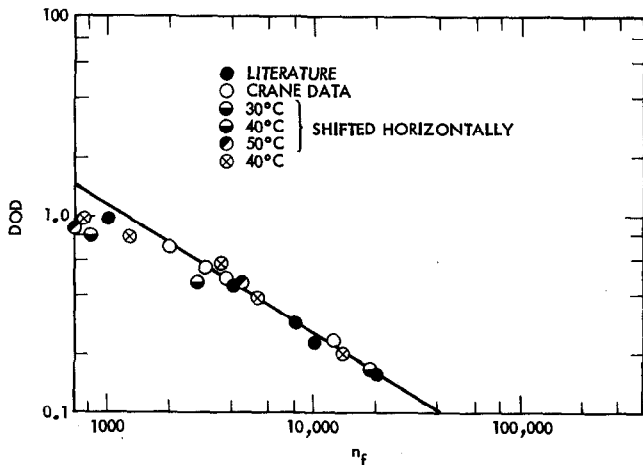


Fig. 2. Dependence of lifetime on DOD. Data from refs. 1 and 16.

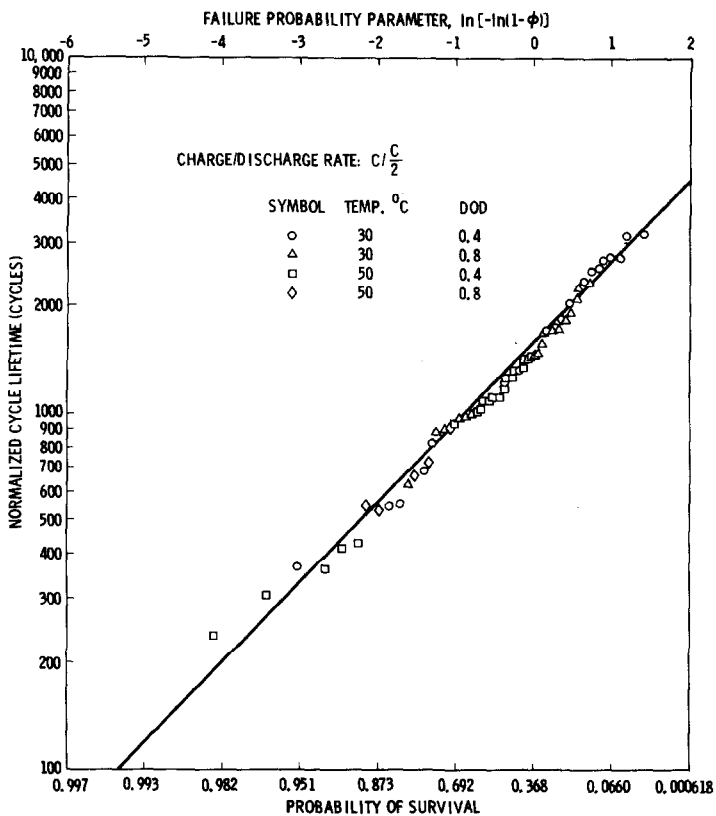


Fig. 3. Dependence of  $N_{f, \text{norm.}}$  on  $\ln[-\ln(1-\phi)]$  for charge/discharge rate  $C/\frac{C}{2}$ .  $\phi$  is the probability of failure at a cycle life of  $N_{f, \text{norm.}}$ . Data from ref. 16.

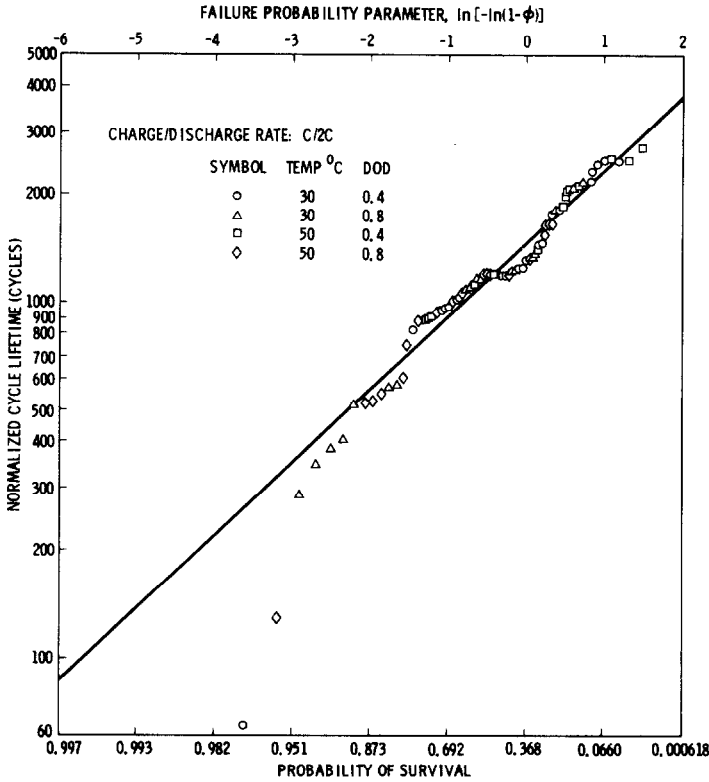


Fig. 4. Dependence of  $N_{f, \text{norm.}}$  on  $\ln[-\ln(1-\phi)]$  for charge/discharge rate  $C/2C$ .  $\phi$  is the probability of failure at a cycle life of  $N_{f, \text{norm.}}$ . Data from ref. 16.

$$N_{f, \text{norm}} = n_f(\text{DOD})^{1.5} \exp \left[ \frac{\Delta E}{R} \left( \frac{1}{303} - \frac{1}{T} \right) \right] \quad (20)$$

where  $N_{f, \text{norm}}$  is the lifetime of a cell normalized with respect to temperature and DOD. That is, at a DOD of 100% and a temperature of 303 K,  $N_{f, \text{norm}} = n_f$ , the actual lifetime of the cell. This definition of  $N_{f, \text{norm}}$  as a relative lifetime is advantageous since it permits the use of the formalization of eqn. (17), even though the values of terms such as  $2C_0g$ , etc., are, in general, unknown.

By substituting eqn. (20) for  $n_f$  in eqn. (19), one obtains the following expression:

$$\begin{aligned} \ln[-\ln(1-\phi)] &= \beta [\ln N_{f, \text{norm}} + \ln k_0 + \\ &+ m \ln(2C_0g) - \frac{\Delta E}{303R} - \ln n_{f, \text{red}}^*] \\ &= \beta [\ln N_{f, \text{norm}} + \text{constant}]. \end{aligned} \quad (21)$$

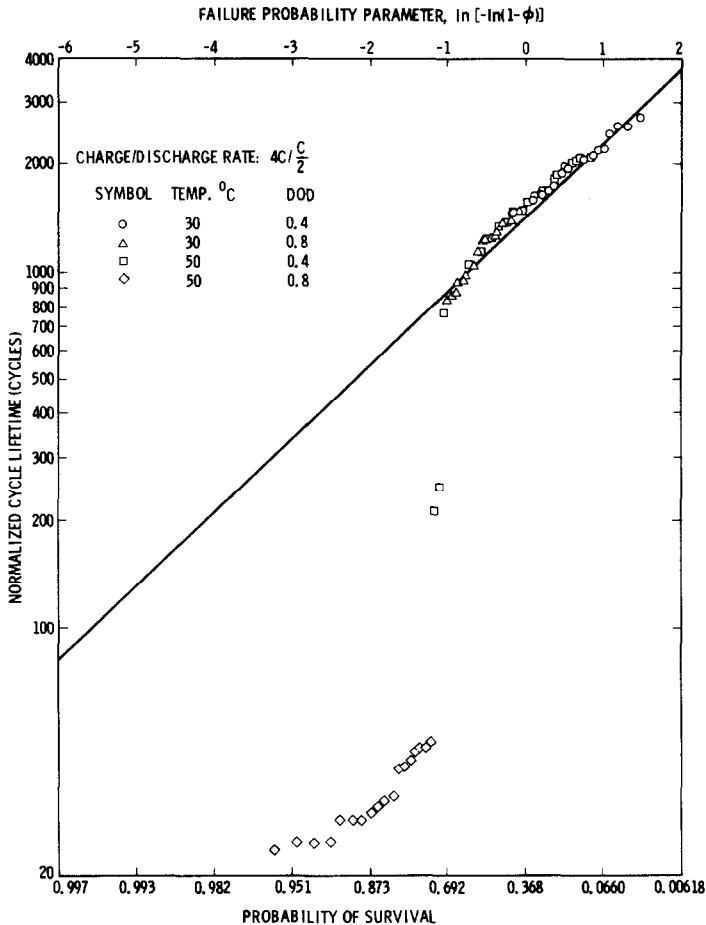


Fig. 5. Dependence of  $N_{f, \text{norm.}}$  on  $\ln[-\ln(1-\phi)]$  for charge/discharge rate  $4C/0.5C$ .  $\phi$  is the probability of failure at a cycle life of  $N_{f, \text{norm.}}$ . Data from ref. 16.

Thus a plot of  $\ln[-\ln(1-\phi)]$  against  $\ln N_{f, \text{norm.}}$  should be linear with a slope equal to  $\beta$ . The value of the constant appearing in eqn. (21) may depend on variables such as battery construction, processing conditions, and other parameters, *i.e.*, charge and discharge rates, etc. However, even in this situation if DOD and temperature are the dominant variables, the linear relationship between  $\ln[-\ln(1-\phi)]$  and  $\ln N_{f, \text{norm.}}$  should still hold.

Application of eqn. (21) to the four groups of data are shown in Figs. 3 - 6. In each Figure, the data for both temperatures, 30 °C and 50 °C, and for the two DOD values of 0.4 and 0.8 are shown separately. These data should be distributed more or less randomly along the line and as may be seen, this is the case. The only exception appears in Fig. 5 which shows the data for CR/DR of  $4C/0.5C$ . In this case, all the data obtained at 50 °C show a marked deviation from the remaining data obtained at 30 °C. It is believed

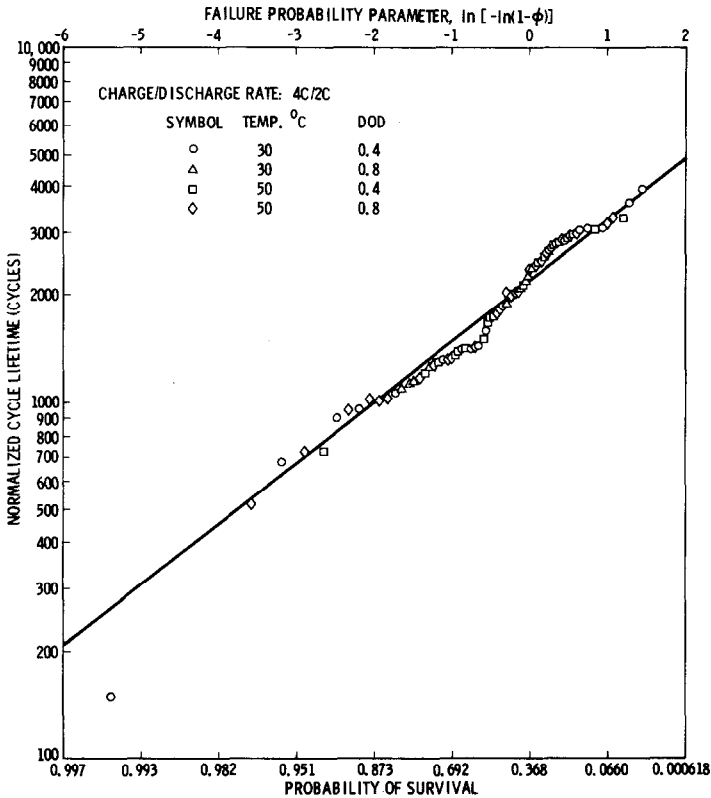


Fig. 6. Dependence of  $N_{f, norm.}$  on  $\ln[-\ln(1-\phi)]$  for charge/discharge rate 4C/2C.  $\phi$  is the probability of failure, at a cycle life of  $N_{f, norm.}$ . Data from ref. 16.

that this discrepancy may be due, in part, to a temperature excursion, *i.e.*, that the actual test temperature of these batteries was higher than the nominal test temperature of 50 °C. This is supported by the fact that the one data point in Fig. 1 which differed so widely from the other four also came from this deviant group of data. Another possible factor is that these particular batteries represent a different population from the others. That some peculiarity of this sort is present in these deviant data is supported also by further work on other data sources which produce good fits of the experimental data to the prediction of eqn. (21). This supports the use of eqn. (21) to calculate normalized lifetimes.

The  $\beta$  values as well as the characteristic value of the normalized lifetime,  $N_{f, norm}^*$  are listed in Table 1. The  $\beta$  values vary somewhat from a low 1.94 to a high of 2.50, while theory requires that the values be constant. Actually, the variation is small and may be related to the small sample size. The characteristic value of the normalized lifetime varies from 1340 to about 2160 for the different rates. Again, this is a small difference. Hence, the data would indicate that the charge/discharge rate groups of data do not differ much and all the data might be combined.

TABLE 1

Parameters of the fit of data to the Weibull distribution function

Charge/discharge rate	$\beta$	$N_{f, \text{norm}}^{**}$
C/	1.94	1590
C/2C	2.10	1480
4C/	2.10	1340
4C/2C	2.50	2160

\*\*Value of  $N_{f, \text{norm}}$  for which probability of failure is  $1/e$ .

Two features of this model are of interest if one attempts to determine the nature of the rate limiting process involved in degradation or growth of flaws leading to failure. The first is that the calculated value of activation energy is appropriate for a diffusive or a transport process but is probably too low for a chemical reaction. The second feature is that the change in flaw size is almost exclusively a function of the number of charge/discharge cycles experienced by the cell, and is not a function of cycling time, as is evident from the fit of the experimental data to the model. This result indicates that the rate of interaction of the flaw with the electron is fast compared with the transport of one of the reactants; in other words, the rate limiting step is some kind of a transport process.

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