International Journal of Reliability and Application
Vol.1, No.1, pp.89–104, 2000

A Study on the Accelerated Life Test for Evaluating the Reliability of Nickel–Cadmium Batteries

Soo–Ho Kwon Yang–Hyun Huh
Reliability Team, Q & R Center
LG Electronics, Inc. Seoul, Korea

Tae-Jin Lim
Department of Industrial Engineering
Soong–sil University, Seoul, Korea

Abstract. Accelerated testing consists of a variety of test methods for shortening the life of products or hastening the degradation of their performance. This paper presents practical, modern statistical methods for evaluating the reliability of Nickel-Cadmium batteries at their design temperature of 20°C by accelerated life test.

Batteries have been life tested at three high temperature conditions, 50, 60, 70°C, respectively to yield failures quickly. The failures have been observed and judged by means of charge and discharge current integration. Analyses of life data from those conditions resulted in the Weibull distribution, which has been verified on the ground of the Kolmogorov–Smirnov test and the pairwise t–test. Life data are modeled according to the Arrhenius life–temperature relationship. The mean life of tested batteries is assessed at about 590 cycles, and the activation energy of this chemical reaction is concluded to be 0.39eV as results.

This study provides procedures for estimating the reliability of batteries in a short period, which has little been possible in domestic industries. The results can be applied in many fields such as proof testing, acceptance testing, and estimating assurance periods.
Key Words : *Accelerated testing, reliability of Nickel–Cadmium batteries, Weibull distribution, Kolmogorov–Smirnov test, pairwise t–test, Arrhenius life–temperature relationship* .

1. INTRODUCTION

Products and components reliability contributes much to quality and competitiveness. Many manufacturers yearly spend a lot of money on products and components reliability. Much management and engineering effort goes into evaluating reliability, assessing new designs and design and manufacturing changes, identifying causes of failure, and comparing designs, vendors, materials, manufacturing methods, and the like.

Major decisions are based on life test data, often from a few units. Moreover, many products last so long that life testing at design conditions is impractical. In this case, many products and components can be life tested at high stress conditions to have failures occur as soon as possible. Analyses of data from such an accelerated test yield needed information on product life at design conditions(low stress). That is, the aim of accelerated testing is to quickly obtain data which, properly modeled and analyzed, yield desired information on product life or performance under normal use. Such testing saves much time and money[Nelson, 1990].

Analyses of data from an accelerated life test employ a model. Such a statistical model consists of a life distribution that represents the scatter in product life and a relationship between life and stress. Usually the mean of the life distribution is expressed as a function of the accelerating stress.

A well designed and executed experiment is much easier to analyze and interpret. The design with the best life distribution while overstressed is assumed to have the best life distribution under normal conditions[Lee, 1995].

Concerning cells and batteries, it is well known that they can be accelerated under high temperature, but the specific model with the relationship between the life of batteries and temperature has seldom been reported. Although a model depends on the test method, the accelerating stress, the form of the specimen, and other factors, it is assumed that this experiment will contribute to more efficient accelerated testing methods and to valid and more accurate information of Ni–Cd batteries.

2. Ni–Cd BATTERIES

The rechargeable batteries have driven today's growing numbers of portable electrical applications. With long operating and storage life, Nickel–Cadmium batteries can provide over 500 charge/discharge cycles, making them an economical energy source with a small outlay. Due to their low internal resistance, Ni–Cd batteries offer excellent discharge characteristics through their discharge capability at very stable voltage. And using the appropriate charger, they can be fast charged in times ranging from about 15 minutes to one hour.

Sealed Ni–Cd batteries are electrochemical systems which convert chemical energy into electrical energy in reversible reactions. During charge and discharge, the electrochemical processes are represented by the following reactions: At the positive electrode:

$$2Ni(OH)_2 + 2OH^- \Longleftrightarrow 2NiOOH + 2H_2O + 2e^-$$

At the negative electrode:

$$Cd(OH)_2 + 2e^- \Longleftrightarrow Cd + 2OH^-$$

This gives an overall reaction of:

$$2Ni(OH)_2 + Cd(OH)_2 \Longleftrightarrow 2NiOOH + Cd + 2H_2O$$

Cylindrical cells consist of positive and negative electrodes, a separator, alkaline electrolyte, metal case and sealing plate with a resealable safety vent. All cylindrical cells are constructed with either a sintered or a foam positive electrode and either a sintered or a plastic bonded negative electrode.

The useful life of a Ni–Cd battery can be expressed in number of cycles before end of life [KS C 8515, 1987]. Experience and laboratory test data show that cycle life depends on depth of discharge and temperature. When performing a fast charge, cycle life is also a factor of the way end of charge detection is achieved.

Discharge characteristics are capacity and voltage. Capacity, measured in terms of ampere–hours, depends on several factors, i.e., cell size, cell design and construction, charge effectiveness, temperature, open circuit time, discharge rate, final voltage and cell history. The average discharge voltage depends on size and construction, discharge temperature and cycling history [Saft Communication Department, 1995].

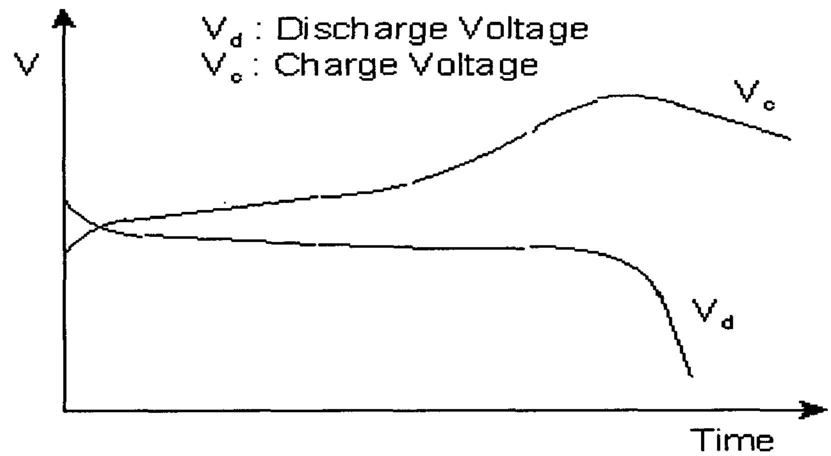

Figure 1: The Voltage in charge and discharge

The charge retention is based on storage at various temperatures. The self–discharge rate is a function of temperature and cell technology. Storage at higher temperatures will reduce charge retention.

Correct charge and discharge are critical to the cycle life of rechargeable cells and batteries. And there are three main types of charge cut–off methods for Ni–Cd batteries; voltage cut–off, temperature cut–off, and detection of positive variation of current[Saft Communication Department, 1995].

3. EXPERIMEMT

3.1 SHIPMENT SIMULATION

Shipping containers where batteries are transported from producing districts are exposed to complex dynamic stresses in the distribution environment. Approximating the actual damage, or lack of damage, experienced in real life may require subjecting the container and its contents to environmental simulation. In this experiment, batteries are tested in the test machine for 72 hours under the specific circumstances shown in Figure 2 and random vibration.

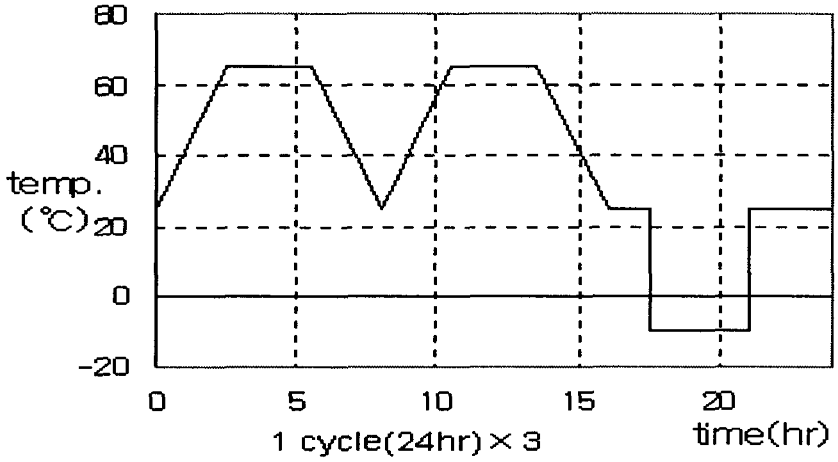

Figure 2: Shipment simulation condition(Matsushita Battery Industrial Co.,Ltd.)

3.2 TEST CONDITIONS

3.2.1 TEST SAMPLES

20 batteries which were random sampled have been tested under three different temperatures each, 70, 60, and 50°C. The batteries apply to cordless telephones made by LG Electronics, Inc., and each of the batteries is assembled with three cells whose rated capacities are 600mAh.

3.2.2 TEST METHODS AND OBSERVATION

Batteries have been charged and discharged at specific constant currents respectively and their capacities can be expressed in ampere hours(Ah or mAh). Continuous monitoring is required for checking whether each sample is in failure. The judgment of failure is based upon KS C 8515, which defines the capacity failure as a state that a battery only has the capacity of 60%. Then a life can be described as the cycles until a battery losing the capacity of 40%.

4. DATA ANALYSES

4.1 LIFE DATA

Table 1. Life data and cumulative distribution function

	70°C		60°C		50°C	
Rank	t(cycles)	$F(t)$	t(cycles)	$F(t)$	t(cycles)	$F(t)$
1	43	0.0476	58	0.0500	91	0.0476
2	47	0.0952	64	0.1000	102	0.0952
3	47	0.1429	67	0.1500	102(+)	–
4	52	0.1905	69	0.2000	102(+)	–
5	54	0.2381	81	0.2500	102(+)	–
6	55	0.2857	82	0.3000	102(+)	–
7	57	0.3333	87	0.3500	102(+)	–
8	59	0.3810	100(+)	–	102(+)	–
9	59	0.4286	100(+)	–	102(+)	–
10	61	0.4762	100(+)	–	102(+)	–
11	64	0.5238	100(+)	–	102(+)	–
12	65	0.5714	100(+)	–	102(+)	–
13	65	0.6190	100(+)	–	102(+)	–
14	68	0.6667	100(+)	–	102(+)	–
15	70	0.7143	100(+)	–	102(+)	–
16	75	0.7619	100(+)	–	102(+)	–
17	75(+)	–	100(+)	–	102(+)	–
18	75(+)	–	100(+)	–	102(+)	–
19	75(+)	–	100(+)	–	102(+)	–
20	75(+)	–			102(+)	–

The life data in Table 1 are cycles to failure of 60 batteries run at 70, 60, and 50°C. For each test temperature, the 20 batteries have been continuously examined for capacity failure.

The n failure cycles at a test stress from smallest to largest are ordered. The theoretical cumulative distribution function is calculated for each failure from its rank i as

$$F_i = \frac{i}{n+1}$$

F_i values appear in Table 1. These *expected plotting positions* approximate the percentage of the population below the ith failure[Lawless, 1982]. One sample at

60°C is censored due to having been judged to be in another failure mode, *safety vent opening.*

4.2 FAILURE RATE FUNCTIONS

From the life data, failure rate functions can be plotted, which is significant to assume the model distribution. Multiple distributions can be considered and distinguished by increasing failure rate(IFR), decreasing failure rate(DFR), or constant failure rate(CFR).

Examining failure rate functions shown in Figure 3 gives the alternative assessable distributions, the *Weibull distribution* and the *lognormal distribution.* (1) The Weibull distribution is worth assuming for the reason why failure rates are in overall increase. (2) The lognormal distribution may be assumed because the failure rate at 70°C has its maximum around the median(50^{th} percentile)[Lee, 1995].

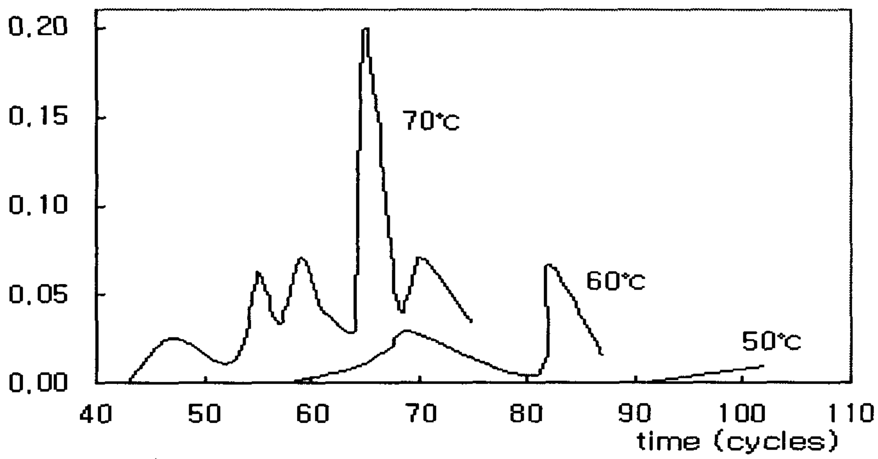

Figure 3: Failure rate functions

4.3 INFERENCE OF ALTERNATIVE DISTRIBUTIONS

4.3.1 WEIBULL DISTRIBUTION

The population fraction failing by age t is

$$F(t) = 1 - \exp\left[-\left(\frac{t}{\theta}\right)^{\beta}\right], \quad t > 0$$

The *shape parameter* β and the *scale parameter* θ are positive. θ is also called the *characteristic life.* It is always the 63.2^{th} percentile. θ has the same units as t, cycles. β is a unitless pure number; it is also called the *β parameter* and *slope parameter* when estimated from a Weibull plot.

4.3.1.1 ESTIMATING PARAMETERS

In order to fit life data according to linear regression, the least squares method is applied for estimating.

$$\ln[-\ln\{1 - F(t)\}] = -\beta\ln\theta + \beta\ln t$$

Figure 4 shows plots of $\ln[-\ln\{1 - F(t)\}]$ as a function of $\ln t$.

The parameters and the determination coefficients(R^2) of each stress level, shown in Table 2, can be obtained through computations of least squares estimates.

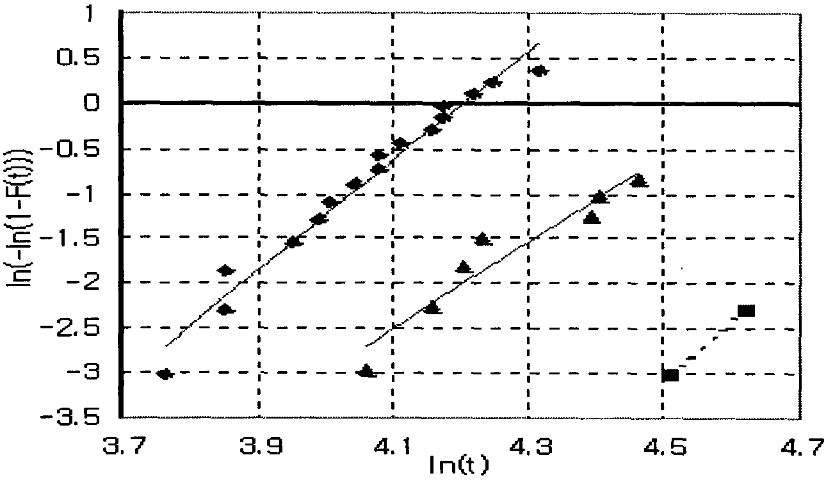

Figure 4: Weibull probability plot

Table 2. Weibull parameters

Level(i)	β_I	θ_i	R_i^2
70°C ($i = 1$)	6.074	66.90	0.970
60°C ($i = 2$)	4.789	101.78	0.918
50°C ($i = 3$)	6.296	147.02	–

4.3.1.2 GOODNESS OF FIT TEST

It is important to check the adequacy of distributions upon which inferences are based. The *Kolmogorov–Smirnov* method provides valuable tools for examining a model's suitability[Lawless, 1982].

The plotted data at each level shown in Figure 4 are tested by means of the Kolmogorov–Smirnov, and distributions(except at 50^{o}C for insufficiency of data) prove to be suitable for the Weibull estimation with 10% significance level(see Figure 5 and 6).

4.3.1.3 TESTING EQUALITIES OF SHAPE PARAMETERS

Assumption that the failure modes at three different stress levels are identical starts with a hypothesis that the slopes of each line are equal. Herein, three shape

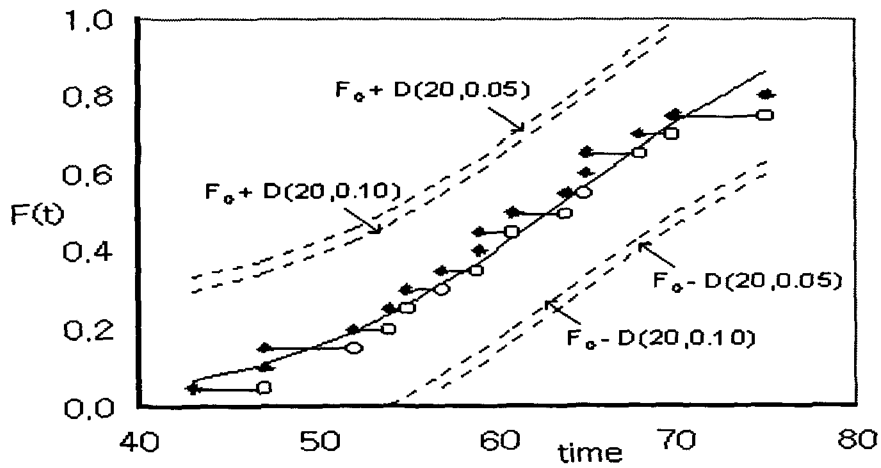

Figure 5: Kolmogorov–Smirnov test at 70°C

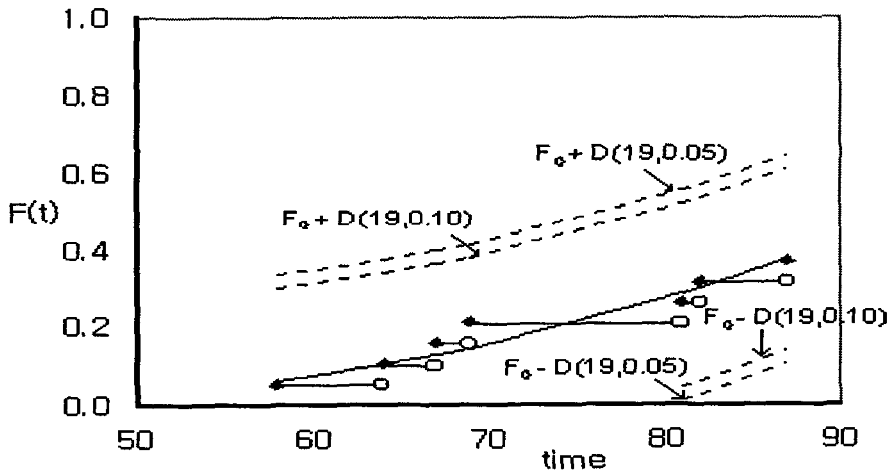

Figure 6: Kolmogorov–Smirnov test at 60°C

parameters are compared in pairs.

$$H_0 \; : \; \beta_1 = \beta_2 = \beta_3$$
$$H_1 \; : \; \text{not} \quad H_0$$

All three equality combinations, $\beta_i = \beta_j$, are verified through *t-test*, and the test statistic can be expressed as

$$|\, t_{ij} \,| \;=\; \frac{|\, \beta_i - \beta_j \,|}{\sqrt{Var(\beta_i) + Var(\beta_j)}} \;<\; t_{\frac{\alpha}{2}}(\phi^*_{ij}) \quad \Longrightarrow \quad \text{Accept} \quad H_0$$

where Var(β_i), the variance of β_i, can be obtained from residual mean square which is the unbiased estimator of σ_i^2 as follows[N. R. Draper & H. Smith, 1981].

$$Var(\beta_i) = \frac{\sigma_i^2}{S_{xx(i)}} = \frac{S_{xx(i)}S_{yy(i)} - S_{xy(i)}^2}{S_{xx(i)}^2(n_i - 2)}$$

And Φ^*, *Satterthwait degree of freedom*, is solved by the function of two unbiased variances and approximates t–distribution[Park, 1991].

$$\phi_{ij}^* = \frac{[Var(\beta_i) + Var(\beta_j)]^2}{\frac{[Var(\beta_i)]^2}{n_i - 1} + \frac{[Var(\beta_j)]^2}{n_j - 1}}$$

However, n_3, the number of failures at 50°C, is two, which cannot allow the data at 50°C to be tested through the t–test. Therefore, the null hypothesis is revised below.

$$H_0 : \beta_1 = \beta_2$$
$$H_1 : \text{not} \quad H_0$$

The parameters for testing the hypothesis are solved as

$$Var(\beta_1) = 0.0809$$
$$Var(\beta_1) = 0.4085$$
$$\phi_{12}^* = 7.077,$$

and $t_{\frac{\alpha}{2}}$ for the significance level of 5% is

$$t_{\frac{0.05}{2}}(7.077) = t_{\frac{0.05}{2}}(7) - (7.077 - 7)\left[t_{\frac{0.05}{2}}(7) - t_{\frac{0.05}{2}}(8)\right]$$
$$= 2.360$$

Accordingly, with the critical region in this case t_{12} is

$$\mid t_{12} \mid = \frac{\mid 6.074 - 4.789 \mid}{\sqrt{0.0809 + 0.4085}} = 1.837 < t_{\frac{0.05}{2}}(\phi_{12}^*)$$

Consequently, the null hypothesis is accepted with 5% significance level. It means that the failure modes at stress levels are identical with the Weibull inference.

4.3.1.4 ESTIMATING COMMON SHAPE PARAMETER

As the slope of each line in Figure 4 are considered to be identical, the common shape parameter from each shape parameters at different levels is solved as follows.

$$\tilde{\beta} = \frac{\sum_{i=1}^{3}\sum_{k=1}^{n_i} x_{ik}y_{ik} - \sum_{i=1}^{3} n_i\bar{x}_i\bar{y}_i}{\sum_{i=1}^{3}\sum_{k=1}^{n_i} x_{ik}^2 - \sum_{i=1}^{3} n_i\bar{x}_i^2} = 5.734$$

4.3.1.5 CORRECTING SCALE PARAMETERS

Estimation of the common slope makes it possible to shift the lines through their linear regression equations which are transformed as

$$\bar{y}_i = -\tilde{\beta}\ln\theta_i + \tilde{\beta}\bar{x}_i$$

That is, scale parameters can be relocated according to

$$\theta_i = \exp\left(-\frac{\bar{y}_i - \tilde{\beta}\bar{x}_i}{\tilde{\beta}}\right)$$

Corrected scale parameters are listed in Table 3, and Figure 7 shows the lines which are modified with common shape parameter and corrected scale parameters.

Table 3. Corrected scale parameters

θ_1(70°C)	67.46
θ_2(60°C)	96.10
θ_3(50°C)	153.23

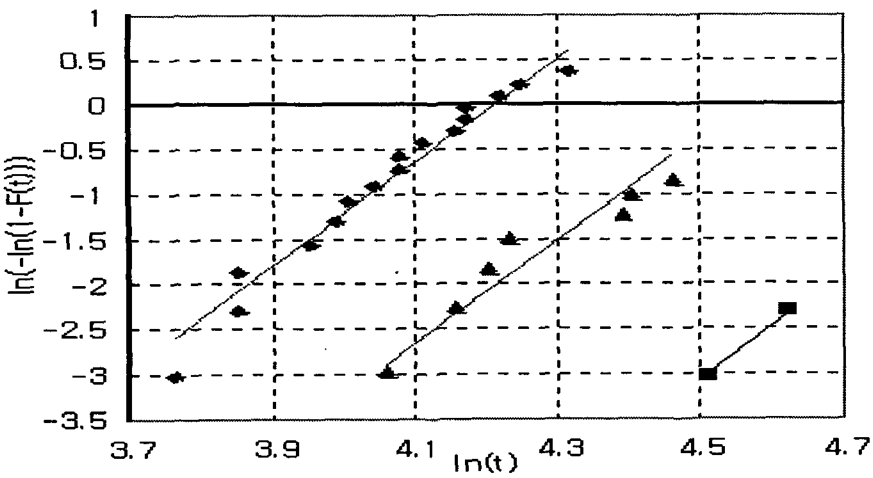

Figure 7: Common shape parameter on Weibull plot

4.3.2 LOGNORMAL DISTRIBUTION

Although the Weibull estimation seems to produce a good solution, it is possible that other distributions may fit the data better. From analysis of failure rate function in Figure 3, the lognormal distribution can be adopted and tested.

In the lognormal distribution, the population fraction failing by age t is

$$F(t) = \Phi\left[\frac{\ln t - \mu}{\sigma}\right], \quad t > 0$$

μ is the mean of the natural log of life and may have any value from $-\infty$ to ∞. σ is the natural log of life standard deviation and must be positive.

4.3.2.1 ESTIMATING PARAMETERS

In order to fit life data according to linear regression, the least squares method is applied for estimating.

$$\ln t = \mu + \sigma \cdot \Phi^{-1}[F(t)]$$

Figure 8 shows plots of lognormal estimation.

The parameters and the determination coefficients(R2) of each stress level, shown in Table 4, can be obtained through computations of least squares estimates.

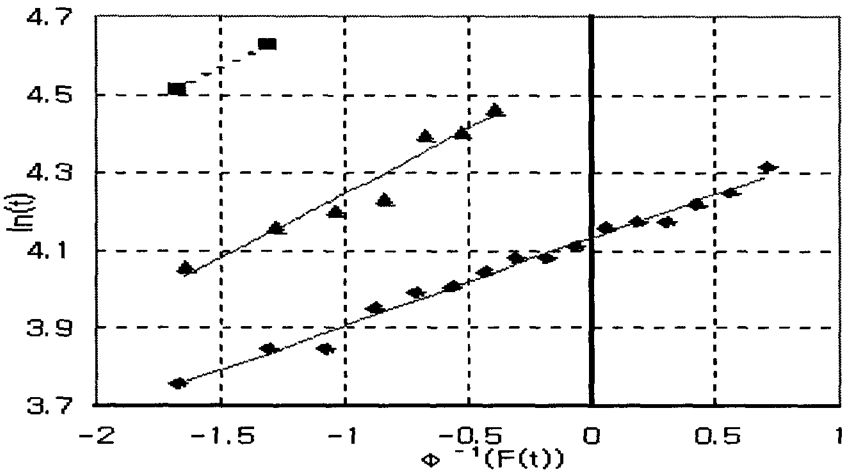

Figure 8: Lognormal probability plot

Table 4. Lognormal parameters

Level(i)	μ_i	σ_i	R_i^2
70°C($i=1$)	4.132	0.224	0.987
60°C($i=2$)	4.574	0.328	0.942
50°C($i=3$)	5.041	0.318	-

4.3.2.2 GOODNESS OF FIT TEST

The plotted data at each level shown in Figure 8 are tested by means of the *Kolmogorov-Smirnov* test, and distributions(except at 50°C for insufficiency of data) prove to be suitable for the lognormal estimation with 10% significance level(see Figure 9 and 10).

4.3.2.3 TESTING EQUALITIES OF SLOPES OF LINES

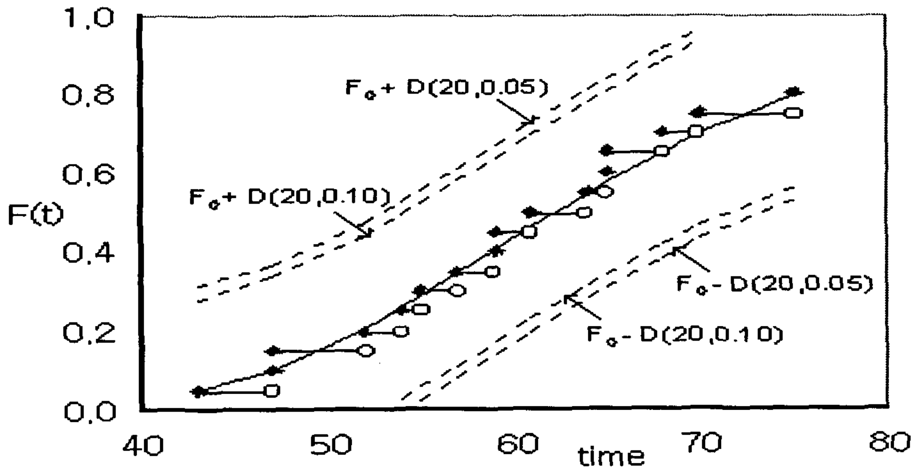

Figure 9: Kolmogorov–Smirnov test at 70°C

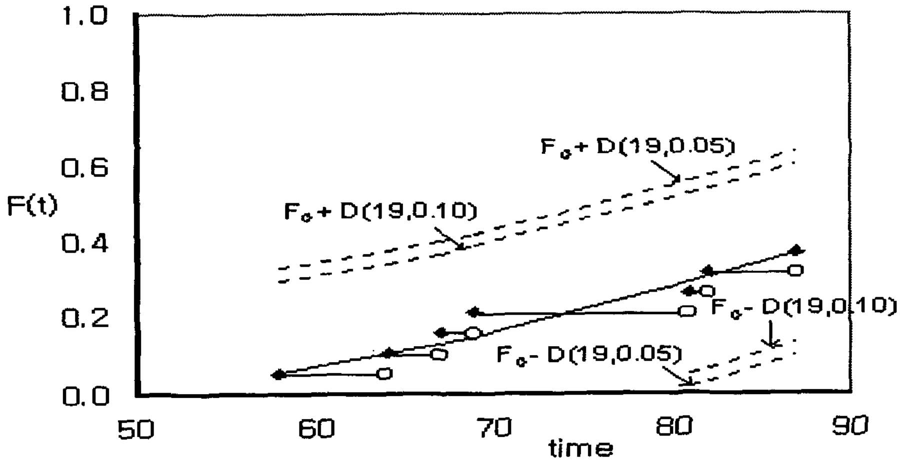

Figure 10: Kolmogorov–Smirnov test at 60°C

In order to verify that the slopes of each line are identical, the hypotheses below are tested.

$$H_0 \ : \ \sigma_1 = \sigma_2$$
$$H_1 \ : \ \text{not} \quad H_0$$

σ_1 is made a paired comparison with σ_2 through *t-test*, and the test statistic can be expressed as follows.

$$|\, t_{12} \,| \;=\; \frac{|\, \sigma_1 - \sigma_2 \,|}{\sqrt{Var(\sigma_1) + Var(\sigma_2)}} \;<\; t_{\frac{\alpha}{2}}(\phi_{12}^*) \quad \Longrightarrow \quad \text{Accept} \quad H_0$$

And the result is;

$$| t_{12} | = \frac{| 0.224 - 0.328 |}{\sqrt{4.651 \times 10^{-5} + 1.313 \times 10^{-3}}} = 2.821 > t_{\frac{0.05}{2}}(\phi^*_{12})$$

Consequently, the null hypothesis is rejected with 5% significance level. It means that the failure modes at each stress level are *NOT* identical with the lognormal inference. The rejection of the equalities of slopes is important because the lognormal distribution is accepted through the *Kolmogorov–Smirnov* test.

5. ARRHENIUS MODELING

5.1 ARRHENIUS LIFE–TEMPERATURE RELATIONSHIP

A simple relationship does not describe the scatter in the life of the test units. For each stress level, the units have some statistical distribution of life. A more refined model employs a statistical distribution to describe the scatter in life[Nelson, 1990].

The Arrhenius life relationship is widely used to model product life as a function of temperature. Based on the *Arrhenius Law* for simple chemical–reaction rates, the relationship is used to describe many products that fail as a result of degradation due to chemical reactions or metal diffusion. The relationship is adequate over some range of temperature.

According to the Arrhenius Law, the rate of a simple chemical reaction depends on temperature as follows

$$\text{rate} = A' \exp\left[\frac{-\Delta H}{kT}\right]$$

ΔH is the *activation energy* of the reaction, usually in electron–volts. k is Boltzmann's constant, 8.617×10^{-5} electron–volts per °C. T is the absolute Kelvin temperature. A' is a constant that is characteristic of the product failure mechanism and test conditions.

The following relationship is based on a simple view of failure due to such a chemical reaction. The product is assumed to fail when some critical amount of the chemical has reacted; a simple view of this is

$$\text{(critical amount)} = \text{(rate)} \times \text{(time to failure)}$$

Equivalently,

$$\text{(time to failure)} = \text{(critical amount)} \;/\; \text{(rate)}$$

This suggests that nominal time τ to failure is inversely proportional to the rate. This yields the *Arrhenius life relationship.*

$$\tau = A \exp\left[\frac{\Delta H}{kT}\right]$$

Here A is a constant that depends on product geometry, specimen size and fabrication, test method, and other factors. Products with more than one failure mode have different A and ΔH values for each mode.

The Arrhenius *acceleration factor* between life τ at temperature T and life τ' at reference temperature T' is

$$AF = \frac{\tau}{\tau'} = \exp\left[\frac{\Delta H}{k}\left(\frac{1}{T} - \frac{1}{T'}\right)\right]$$

5.2 ARRHENIUS-WEIBULL MODEL

The lives of batteries analyzed through the Weibull estimation can be combined with an Arrhenius dependence on temperature.

At absolute temperature T, the lives of batteries have Weibull distributions. The Weibull shape parameter β is a constant. The natural log of the Weibull characteristic life θ is a linear function of the inverse of T:

$$\ln\theta(T) = \ln A + \frac{\Delta H}{k}\cdot\frac{1}{T}$$

Thus the natural log of θ is a linear of inverse absolute temperature $x = \frac{1}{T}$. The corresponding pairs of variables are given in Table 5 and plotted in Figure 11 according to the least squares method.

Table 5. Variables from Weibull analyses

Level(i)	$1/T_i$	$\ln\theta(T_i)$
70°C($i=1$)	1/343.16	$\ln 67.46$
60°C($i=2$)	1/333.16	$\ln 96.10$
50°C($i=3$)	1/323.16	$\ln 153.23$

The fitted regression equation in Figure 11 is thus

$$\ln\theta(T) = -9.704 + 4553.85\frac{1}{T} \quad (\mathrm{R}^2 = 0.996)$$

And ΔH, the *activation energy*, is obtained from the above equation as

$$\Delta H = 4553.85k = \mathbf{0.392}\text{ eV}$$

From the regression, the scale parameter at the design temperature of 20°C can be estimated as follows.

$$\begin{aligned}\theta(20^\circ\mathrm{C}) &= \exp\left(-9.074 + 4553.85 \times \frac{1}{20 + 273.16}\right) \\ &= 638.90\end{aligned}$$

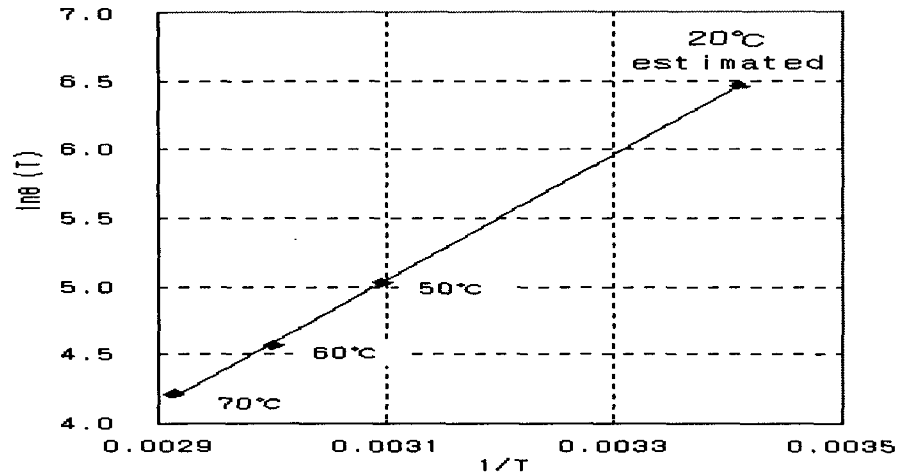

Figure 11: Arrhenius relationship plot

Consequently, the mean *cycles to failure* at 20°C can be computed below according to the Weibull distribution with the scale parameter at 20°C and the common shape parameter.

$$\begin{aligned} \text{MTTF} &= \theta(20^o\text{C}) \cdot \Gamma\left(1 + \frac{1}{\tilde{\beta}}\right) = \left(1 + \frac{1}{5.734}\right) \\ &= 591(\text{cycles}) \end{aligned}$$

6. CONCLUSIONS

This experiment can be significant for the reason why it took much less hours and money to evaluate the mean life of batteries through the accelerated testing. The mean time to failure of the Ni–Cd 600mAh batteries applying to LG's cordless telephones is estimated at about 590 cycles.

The Arrhenius activation energy is assessed at about 0.39 eV, which doesn't appear to be available from MIL–HDBK–217F. With ΔH, the Arrhenius acceleration factors between each temperature are obtained in Table 6.

Table 6. Arrhenius accelation factors

	50°C	60°C	70°C
20°C	4.23	6.46	9.62
50°C		1.53	2.27
60°C			1.49

REFERENCES

J. F. Lawless, *Statistical Models and Methods for Lifetime Data*, John Wiley & Sons, Inc., New York, pp. 277–282, 1982.

KS C 8515, *Sealed Nickel-Cadmium Cylindrical Rechargeable Single Cells*, Korean Industrial Standard, Seoul, pp. 4–6, 1987.

MIL–HDBK–217F, *Reliability Prediction of Electronic Equipment*, Naval Publications and Forms Center, Philadelphia, 1991.

N. R. Draper & H. Smith, *Applied Regression Analysis*, 2nd Edition, John Wiley & Sons, Inc., New York, pp. 59–60, 1981.

Saft Communication Department, *Portable Cells and Batteries Handbook*, Saft, Romainville, 1995.

S. H. Park, *Statistical Quality Control*, 2nd Edition, Minyoung Publication, Inc., Seoul, pp. 133–136, 1991.

S. Y. Lee, *Reliability Engineering*, Hyungsul Publication, Seoul, 1995.

W. Nelson, *Accelerated Testing: statistical models, test plans, and data analyses*, John Wiley & Sons, Inc., New York, pp. 60–65, 1990.