RELIABILITY EVALUATION OF PRIMARY CELLS

Anyaka Boniface Onyemaechi
Dept. of Electrical Engineering,
University of Nigeria, Nsukka.

ABSTRACT
Evaluation of the reliability of a primary cell took place in three stages: 192 cells went through a slow-discharged test. A designed experiment was conducted on 144 cells; there were three factors in the experiment: Storage temperature (three levels), thermal shock (two levels) and date code (two levels). 16 cells experienced a cycled temperature and humidity environment. All tested cells showed acceptable performance. Results of the designed experiment showed the factor most affecting cell performance was the date code. A long- term capacity test on a sample of primary cells can provide information on their quality and reliability. The example shows a very tight capacity distribution. The cell employed a lithium anode. The capacity of many lithium-system is, by design, limited by the quantity of lithium in the anode. Controls on the quantity may permit the manufacturer to control, with considerable precision the capacity of the cells. From the designed experiment, we infer that the factor most affecting the performance of the cell is the time when it was made. Long term storage, perhaps up to 10 years, in a “normal” environment of 20°C will not appreciably affect it, nor will thermal shock or 2-way combinations of factors.

Key words - *Primary cell, Life test, Environmental stress*

NOMENCLATURE
CCV - Closed Circuit Voltage, the voltage at the terminals of a battery when it is under an electrical load.
SS - Sum of squares.
MS - mean Square.

BASIC DEFINITIONS

Primary Cells*:* A cell that is designed to be discharged one time, and not recharged.

Capacity*:* The total amount of charge available in a cell for delivery to an electrical load before the load voltage drops bellow some defined limit. It varies with the load, usually decreasing with heavier loads, e.g., higher current drains. It is commonly expressed in ampere-hours or milli-ampere hours.

1 INTRODUCTION

There are many types of primary cells, representing a bewildering array of chemistries, currently in the market. They range from the common "flashlight cell," based on the Zn-$Mn0_2$ couple in an NH_4CI electrolyte, to long-lived, high energy-density systems using lithium anodes and one of several cathodic materials. Table 1 describes the characteristics of a few widely available cell systems.

Electronic systems have been using

lithium-based cell in rapidly increasing numbers. These systems commonly require high reliability for periods of 5 to 10 years. Consequently, the question arises: How can one evaluate the reliability and quality of a cell over such a time? This paper describes a case history of the evaluation of reliability and quality of a primary cell. It has a lithium anode, a carbonmonofluoride cathode, and an organic liquid electrolyte. The cell reliability question has three parts

- **QA**: Does the cell posses sufficient capacity to perform its function?
- **QB**: Does the cell have a long enough shelf life for its intended application?
- **QC**: Will environmental factors like humidity or thermal cycling affect the cell?

Table 1. Some Common Cells

Anode	Cathode	Operating Voltage (V)	Energy Density (watt-hour/kg)	Shelf Life (yrs)
Zn	$Mn0_2$	1.5	32	1-2
Zn	Ag_20	1.5	135	2
Zn	HgO	1.35	92	3-4
Li	$Mn0_2$	2.8	275	5-10
Li	$SOCl_2$	3.4	300	5-10
Li	CFx	2.7	300	5-10
Li	I	2.7	200	5-10

Sources [1-3]

2. LIFE TESTING.

A long term life test was used to address question 1 of section 1. In this test, each one out of the number of cells used for the test was discharged through its own load resistor of 180kilohms, and all cells test were done at the same time. The CCV at which the cell is considered discharged is shown in table 2. The resistor used for the test was large enough so as to avoid the cell from being drained with a higher current than is appropriate for its design and application. Cylindrical spirally wound cells have the ability to supply higher current than coin or button types. Most Lithium cells have a relatively high internal resistance. Depending on the chemistry, this internal resistance is anywhere from tens to thousands of ohms.

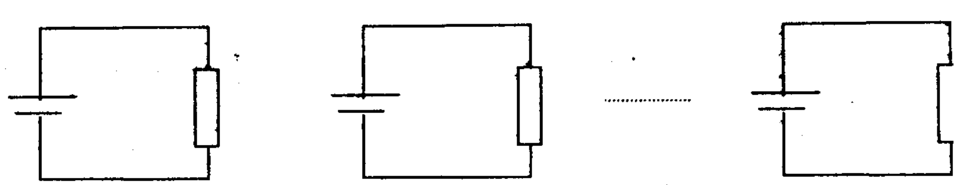

Fig. 1. Cells on Life Test.

Life testing demonstrates that the cell has sufficient capacity to perform its assigned task. A manufacturer's interpretation of "assigned task" may be the cell's having its specified capacity. A user may think of it as having capacity to power his devices for the required time. The cells were assumed to have maximum current rating as most lithium-based cells have, the test was conducted for 95 days.

Through the early weeks of the test, the CCV, was measured, every week. Later on, as the batteries become exhausted, measurements of the CCV were taken more frequently. The objective is to locate, as precisely as possible, the point in time when the cell voltage dropped below some minimum, which defines a failure.

3. SAMPLE SIZE

The sample size was based on 99% good cell at an 80% statistical confidence. Zero failure was taken as the acceptance criterion. Where a failure is the inability of a cell to deliver its specified capacity. The capacity test ended when some fraction of the cells became exhausted.

4 CAPACITY TEST

Table 2 contains an example of capacity-test date. The test consisted of discharging 192 cells through a load, such that they would fail within about 90 days if all had the rated capacity. CCV measurements were taken once a day. However, during the period from day 89 to day 92, there was power outage and power to the circuit was shut down. No date could be collected in that interval. The obtained values were fitted to a Weibull distribution

Fitting the table 2 data to a Weibull distribution leads to a shape parameter of 37.2, with 99% statistical-confidence bounds of 24.0 and 48.0. The Weibull characteristic life is 96.4, with 99% percent statistical-confidence bounds of 94.8 and 99.4. The program WEIREG from the statistical package STATLIBI for the IBM Personal Computer performed the curve fitting operation. The shape parameter of 37.2 indicates a sharply peaked distribution. A shape parameter of 5 is characteristic of a normal (Gaussian) distribution [5].

Table 2 life test date

Days test	Cumulative failure	Failure criterion
82	0	
83	0	
84	1	
85	1	Close circuit voltage of 2.5 volts into a 180 kilohms resistor.
86	1	
87	4	
88	12	
93	14	
94	65	
95	148*	

* Test terminated at failure number (148)

5. THERMAL SHOCK, DATE OF MANUFACTURE, AND ELEVATED TEMPERATURE STORAGE.

The purpose of the experiment is to:

- Determine if a particular cell design capacities was susceptible to damage by thermal shock.
- See if there was any difference in capacity of the cell as a result of lot-to -lot variations.
- Investigate the effects of storage temperatures on the device, with a view to determining shelf life.
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6. INTERPRETATION OF HIGH TEMPERATURE STORAGE

A rule of thumb states that the self-discharge cells double with every 10^oC rise- in temperature. Although there is no rigorous proof of the rule, some evidence suggest it is not unreasonable [4]. Manufacturers claimed that the capacity of cells stored for one month at 80^oC was comparable to that of cells stored for 60 months at 20°C. The apparent loss of capacity was about 5%. This apparent loss was said to be due to escape of electrolyte; that escape impaired the cells' ability to deliver the relatively high current called for when it was discharged. Supposedly, at lower discharge currents, the cell's capacity would be closer to its rated value.

These observations lent some credence to the rule of thumb, since 60^oC temperature difference would imply an acceleration factor of 2^6= 64, which is close to the factor of 60 the vendor described. The activation energy, in the Arrhenius relation, would be approximately 0.61 eV, for capacity loss over the 20^oC to 80^oC range, [5].

Diffusion of water vapor through the polypropylene seal would lead to some capacity loss, as water would react with lithium metal in the anode. The diffusion rate would increase with temperature, since the diffusion coefficient would follow an Arrhenius relation [6]. Work of Jeschke and Stuart [7] revealed that the activation energy for the diffusion coefficient of water in polypropylene is 16.4 kcal/mole, which is approximately 0.71 eV. Barrie [8] reports that absorption of water vapour into polyolefines, like polypropylene, follows Henry's law, which says that concentration of a gas in solid at its surfaces is proportional to partial pressure. These date suggest that lithium consumption due to water ingress would be accelerated by a factor of more than two with a 10^0C rise in temperature.

Loss of electrolyte would raise the internal impedance of a cell, and make it appear to have lost capacity as the voltage output would be lowered as opposed to a cell with a full charge of the liquid. There are some recent accounts of diffusion of organic materials in polypropylene. Diffusion of straight-chained octadecane in polypropylene is reported by Chang [9], which indicates that the activation energy is 0.65eV. Hori, et al, [10] studied the decay of the electron spin resonance spectrum of mobile peroxy radical in isotactic polypropelene, finding that the square root of the diffusion coefficient of mobile species is 1.86 times larger at 309K than it is at 294K. Hence, the diffusion coefficient itself increases by a factor of 3.27 over that 15K range. In an Arrhhenium relation, such an increase implies an activation energy of 0.62 eV. These diffusion studies furnish some additional evidence to support the industry's rule of thumb. Ref [4] reports two capacity- loss mechanisms for a similar cell: evaporation of electrolyte and consumption of lithium. The first degradation mechanism has an activation energy of 0.8eV; the second has an activation energy of 0.3eV. The activation energy for the first mechanism implies that the capacity loss is accelerated by much more than a factor of two for a $10^{o}C$ storage rise in temperature; that for the second mechanism means that the accelerated factor is much less than two for a $10^{0}C$ temperature rise

7 EXPERIMENTAL DESIGN.

Table 3 shows how the 12 test entries were formed. Eight cells went into each entry.

The number eight was chosen because it represented a reasonable number of replications in each test entry. It is also a convenient number, since the date acquisition equipment has 16 input channels, and date could be collected on two entries at the same time. These two entries represent cells that were from the same date code and had experienced the same temperature storage condition. They differed in that one entry had gone through a thermal shock stress, while the other had not.

Table 3. Distribution of 96 Batteries in 12 Test Cells.

Date code/temperature	$20^{0}C$		$68^{0}C$		$80^{0}C$	
I	TS	NTS	TS	NTS	TS	NTS
II	TS	NTS	TS	NTS	TS	NTS

- TS - Thermal Shock
- NTS - No Thermal Shock
- Each entry in table has 8 cells.

The 48 batteries came from each of two date codes. Each set of 48 was then broken down into two subsets of 24, and one of the subsets was put through a thermal shock stress according to Mil-Std-202F, method 107F, for 25 cycles. Finally, three groups of 8 parts were formed from each subset of 24 (those thermal shocked and not thermal shocked). One of these three groups of 8 went into an oven for storage at $80^{o}C$ for 1200 hours, approximately 50 days. According to the rule of thumb, this storage should represent approximately 10 years storage at 20°C. The other two groups of eight were stored for 1200 hours at $68^{o}C$ and 10°C. In all, 96 batteries were tested.

Ideally, we would discharge all cells and determine their capacities. The type of cell examined here has a very sharp downturn in its voltage as it nears exhaustion. Figure 2 is an example of the discharge curve for the cell. It was not feasible to measure precisely the capacity of each of the sample of cell under test. Using the capacity of the cells as the parameter of interest could present another, less obvious problem. The usual analysis of variance assumes that the observed parameter is normally (Gaussian) distributed. Earlier, we saw a capacity distribution during the life test that did not seem to be normal (Gaussian). Instead of capacity, the parameter of interest was the voltage, under the discharging load, each of the cells after the voltage has started its downward turn. The reasonableness of fitting these voltage data to a normal (Gaussian) distribution is discussed below:

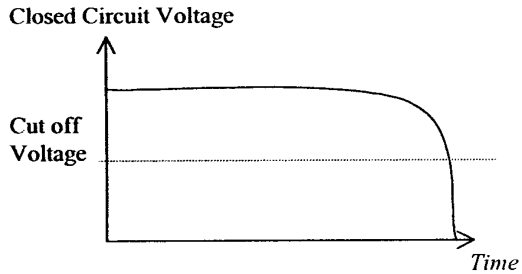

Fig. 2: Cell Discharge Curve of CCV against Time

8. TEST RESULTS

Table 4 shows the voltage of the cells in the various test entries, as they demonstrated the drop indicating their end of life was approaching. These voltages were measured with a date acquisition board. The data acquisition board has a resolution of lightly less than five millivolts. The two different date codes are denoted by I and II. The headings of each of the sub-tables indicate the environmental stress conditions.

In II of the 12 test entries, the eight voltage measurements in the entry appear to be normal (Gaussian) distributed at 10% statistical significance according to the W-test [12]. The distribution of voltage measurements of the eight cells in the entry composed of lot 2, not thermally shocked cells, that had been stored at 80°C did not appear to be normal (Gaussian) according to the W -test. Overall, the distribution of CCV for the cells stored at 80°C did not seem to be as normal (Gaussian) as those of cells stored at lower temperatures. Date from the cell vendor suggested that when the cells are first made, the distribution of internal impedance appears to be normal (Gaussian). Storage of cells at 80°C led to internal resistance distribution that did not appear normal (Gaussian) at all. CCV is linearly related to internal resistance. These observations, along with the recognition that the boiling temperature of one component of the electrolyte is approximately 83°C, suggests that the cell temperature should be kept somewhat below 80°C if one wants to be more certain that the cell is not being damaged by the test.

Table 4: voltage of cells at end of stress test [V]

SAMPLE A					
TS 20°C	NTS 68°C	NTS 80°C	TS 20°C	TS 68°C	TS 80°C
2.70	2.715	2.70	2.70	2.71	2.71
2.72	2.69	2.71	2.72	2.68	2.68
2.71	2.73	2.70	2.70	2.70	2.72
2.73	2.70	2.70	2.71	2.70	2.69
2.69	2.71	2.71	2.71	2.71	2.72
2.73	2.70	2.70	2.73	2.72	2.70
2.68	2.70	2.71	2.71	2.72	2.72
2.71	2.70	2.68	2.73	2.70	2.70

SAMPLE B					
NTS 20°C	NTS 68°C	NTS 80°C	TS 20°C	TS 68°C	TS 80°C
2.70	2.72	2.73	2.69	2.71	2.62
2.71	2.69	2.68	2.69	2.69	2.68
2.67	2.70	2.70	2.69	2.72	2.72
2.71	2.68	2.68	2.71	2.68	2.68
2.67	2.68	2.67	2.67	2.71	2.68
2.67	2.67	2.68	2.73	2.70	2.68
2.66	2.72	2.70	2.70	2.72	2.72
2.69	2.71	2.69	2.65	2.69	2.68

9. ANALYSIS OF VARIANCE

Table 5 summarizes the analysis of variance calculations. The model for this experiment is

$$V_{ijkl} = V + S_i + D_j + T_K + ST_{ik} + SD_{ij} + DT_{jk}^{ijkl} + E_{1(ijk)}$$

V_{ijkl}. Voltage of cell *I* in the entry with thermal shock stress level *i*, date code j and temperature *k*. V = average of all cells in the population. Thermal shock has two stress levels: *done or not done* to an individual cell. Temperature has three levels: three temperatures. Date code has level: two date codes, ST, SD, DT, with their subscripts, represent 2-way interactions of the thermal shock, temperature, and date code factors, $E_{1(ijk)}$ is the uncertainty associated with the measured voltage. The analysis is for a randomized block design, with the S factor treated as fixed, and the D and T factors treated as random.

Table 5 Analysis of Variance Results

Factor	SS	DF	MS	F
S	0.0000	1	0.0000	No Test
D	0.0057	1	0.0057	10.27*
T	0.0010	2	0.0005	0.89
SD	0.0000	1	0.0000	0.0000
ST	0.0001	2	0.0001	189
DT	0.0011	2	0.0006	1.712
E	0.0281	86	.0003	
Total	0.0361	95		

* Statistically significant at 10% level
SS = sum of squares
DF = degree of freedom
MS = Mean square.

10 CONCLUSIONS

The numerical values in table 5 are generated during the analysis of variance. However, the MS column is 0, so we see immediately that the thermal shock (as done here) had no discernible effect on the cells. F tests for the effects of temperature and date code take the ratio of the T and D mean square MS column entries, respectively, to the interaction of temperature and date code MS, from the line for DT. Finally, *F* test for the interaction of factors (SD, ST, DT) take the ratio of the MS for these factors to the MS for the 'error', from the line labelled *E*.

The only statistically significant factor (at the 10% level) is date code. Temperature does not appreciably affect the cell for the temperatures and times we are considering. The interaction of date code and temperature is not statistically significant. The other combinations, date code interacting with thermal shock, and thermal shock interacting with temperature do not appreciably affect the cell.

Although the cells from different date codes show statistically significant differences in their voltages when they are nearly discharged, those differences are not of engineering importance. For practical purposes, both date codes meet the requirements of the application.

REFERENCES

[1] C. L. Mantel., *Batteries and energy System,* McGraw -Hill, 1983.

[2] J P. Gabano, *Lithium Batteries,* Academy Press, 1983.

[3] T. R. Crompton, *Small Batteries: Primary Cells*, Halsted Press, 1983.

[4] F. Sigmund, J. Rea, D. Huffman., J. Lautzenhiser, S, Megahead, "Predicting the date retention life time of a Lithium-carbonmonofluoride battery connected to a zero power RAM," 1986 Proc. Intern. Reliability Physics Symp. pp.68-73.

[5] J. R. King, *Probability Charts for Decision Making* TEAM, 1971

[6] R. E. Treybal, *Mass-Transfer Operation*, McGraw-Hili, 1980.

[7] D. Jeschke, H. A Stuart, Z. *N Naturf* , vo1.l6a, 1961, p.37.

[8] J. A. Barrie, "Water in polymers," *Diffusion in polymers,* Academy Press, 1968

[9] S. S. Chang, "Migration of low polymers: I. Methodology and diffusion of straight chain octadecane polyolefins," *Polymer*, vol. 25, 1984 Feb. pp.209-217.

[10] Y. Hori, S. Shimada, H. Kashiwabara, "ESR study of the decay reaction of isostatic polypropylene peroxy radicals in air," J of *Polymer* Science, vol. 22, 1984 pp.I407-1415.

[11] H. V. Venkatasetry, *Lithium Battery Technology,* John Wiley & Sons, 1984.

[12] G. J. Hahn, S. S. Shapiro, *Statistical Models in Engineering.* John Wiley & Sons, 1967

[13] C. R. Hicks, *Fundamental Concepts in the Design of Experiments,* Holt, Rinchart Winston, 1982.

[14] R. L. Winkler, W. L. Hays, *Statistics: Probability, Inference, and Decision,* Holt, Rinchart, Winston, 1975.

[15] S. L. Basin, W. Spindler, *Using Statistically Designed Experiments in Development of Advanced Battery Systems,* Electric Power Research *Institute, 1.980.*

[16] P. R. Devington, date reduction and error analysis for the physical science ,McGraw-Hill, 1969.