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CORRELATION OF DATA FROM TESTS ON NICKEL-CADMIUM BATTERIES

by Irwin M. Schulman

Prepared by
RADIO CORPORATION OF AMERICA
Princeton, N. J.
for Goddard Space Flight Center

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ABSTRACT

This is the final report on the Correlation of Data from Tests on Nickel-Cadmium Batteries, an investigation performed by the Astro-Electronics Division of the Radio Corporation of America for the National Aeronautics and Space Administration, under Contract No. NASW-1001.

This report is divided into five sections. Section I, the Introduction, presents the background of the problem, the philosophy of the technical approach, and a summary of the findings. Section II deals with the problems encountered in data preparation and handling. (These problems ultimately dissolve into the development of a highly effective means of data preparation and handling.) The Theoretical Analysis is presented in Section III. Section IV, an Empirical Analysis, reports the development of an effective means of detecting defective cells and possible early prediction of failure. A possible method of discriminating among failure modes is determined and described. Conclusions and recommendations are presented in Section V.

PREFACE

This is the final report on the Correlation of Data from Tests on Nickel-Cadmium Batteries. This work was performed for the National Aeronautics and Space Administration, Washington, D. C., by the Astro-Electronics Division of the Radio Corporation of America, Princeton, New Jersey, under Contract No. NASW-1001. The performance period covered by this report is from November 1964 to May 1965.

The purpose of the program described in this report was to study test data of nickel-cadmium cells to discern variabilities and patterns in the data that could be used as a basis for developing statistical and phenomenological mathematical models for predicting the life expectancy of a cell.

The "statement of work," as it appeared in the contract document, is reprinted in the paragraphs that follow.

"A. The Contractor shall examine the available data on single Ni-Cd cells statistically and by computer methods to determine:

(1) The initial variability of cells, with respect to a variety of parameters;
(2) Time-dependence of cell parameters;
(3) Time-dependence of the variability of cell parameters;
(4) The effect of cell history upon the evolution of the values of the cell parameters and their variability; and
(5) Whether the data obey a probability law.

This portion of the study should lead to information about the optimum size of a cycling experiment and to validate sampling procedures based on cell statistics. Statistical laws of cell degradation and initial variability, to be derived by the above procedure, shall be used to formulate models of battery degradation.

"B. The Contractor shall develop two or more mathematical models to relate known inputs with measurable outputs through a limited number of parameters. These compatible models must provide such capabilities as:

(1) Definition of selection (rejection) procedures for cells on a rational basis,
(2) Prediction of battery performance and life, under prescribed conditions of use,
(3) Implication of which variables should be measured in a test, leading to the design of the test,

(4) Characterization of the "state" of the cell as a power source and circuit element, in terms of measurable quantities,

(5) Provision of relations among the "state" parameters which allow the establishment and evaluation of operational procedures,

(6) Prediction of the effects of changing the conditions of use.

"C. The Contractor shall devise an almost purely statistical model or models, based on one or more performance parameters (say, end-of-charge voltage) to correlate initial variability of Ni-Cd cells with changes occurring during repeated cycling so as to arrive at a rational acceptance-rejection capability. Correlations shall also be made with various patterns of charge and discharge as well as conditions of use, such as temperature. The information thus developed will be used to predict battery life from single-cell test data, and to gain useful knowledge of cell operation."

"D. The Contractor shall also devise a phenomenological model or models, requiring the definition of a concept of "state", of a phase space the points of which represent the states, of laws relating different points of the phase space, and of laws expressing the effects of inputs and outputs upon the points of the phase space. By the success in the formulation of such a model, the condition of a storage cell or its performance over its useful range will be expressed in terms of a suitable minimal set of variables, other variables being definable in terms of the basic set. Two direct results will be (1) a great reduction in the amount and types of testing necessary, and (2) a systematization of the entire field. This study will involve a search for empirical relations of variables, such as PEUKERT's law.

"E. The Contractor shall establish a basis for standardizing the presentation of test data in a format of broadest possible utility. Cross-plots of battery parameters shall be made to find useful correlations and to determine new and useful parameters, if possible."

The principal investigators in this work were Messrs. Maurice Slud and John Waite. The project manager was Mr. Irwin Schulman.

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SECTION I
INTRODUCTION

A. GENERAL

This is the final report on the correlation of data from tests on nickel-cadmium batteries, and covers the work performed from November 1964 to May 1965. The effort was directed toward developing a rational foundation for future tests of nickel-cadmium batteries that would enable the space power engineers to select cells for space batteries that can be trusted to complete the mission.

B. SUMMARY

This program has shown that battery data obtained by standard procedures can be used to judge the condition of a sealed storage cell under test. For example, analysis of tests on 80 cells for 3000 cycles showed that cells exhibiting random anomalies early in the test cycle failed subsequently; those exhibiting no anomalies did not fail. Computer programs were written and techniques developed for handling large amounts of data. Editing of data into the correct format can now be accomplished by machine coding. FORTRAN or other coding may be applied, as desired. Two types of computer programs are available. One produces empirical data required for formal statistical models. The other consists of statistical subroutines (available at RCA in Subroutine Libraries) with adaptations to specific phenomenological models for purposes of prediction.

An empirical technique has been devised and applied to small samples of data for analyzing families of curves to detect significant deviates. The procedure promises to pinpoint defective cells many cycles before they give detectable signs of impaired function. In some cases, such cells have been identified thousands of cycles before they were declared to have failed. These procedures can be translated into the terms of automatic computers.

The procedures and theory described here provide a possible method of discriminating among failure types. If this can be verified, it would constitute a new tool for battery science and engineering.

C. BACKGROUND

Storage batteries for space applications have been subjected to considerable testing. Typical battery-development programs include qualification and acceptance tests; prolonged cycling tests, in which batteries are subjected to charge-discharge cycles simulating the mission requirements; and, finally, large-scale life-test programs.

However, in spite of the multitude of such tests, certain pertinent basic engineering data concerning the performance of Ni-Cd batteries in space power applications remain difficult to obtain. Indeed, it is often a considerable task merely to determine whether data are, in fact, useful. As a consequence, power systems engineers commonly make judgements and assumptions based to some extent upon subjective experience, and then conduct cycling tests to check the conclusions.

An analysis of storage-battery test programs indicated the necessity for developing better methods of (1) selecting storage cells for space batteries, (2) predicting storage-cell performance, and (3) determining the scope and extent of test programs.

The present effort basically involved:

1. Analysis of curves which were digitalized for machine manipulation,
2. Development of mathematical techniques and models to provide correlations to define variability and establish statistical significance to the prediction technique, and
3. Interpretation by battery experts.

The work followed two approaches: (1) analysis based on visual inspection of analog curves, and characterization of cell behavior on the basis of the variation in the form of the curves, and (2) empirical analysis involving inspection of data to identify critical parameters for analysis.

D. TECHNICAL APPROACH

1. Theoretical Approach

The theoretical approach used mathematical techniques to establish variability and significance of test data. Probability distributions were used to describe cell behavior. Some techniques considered for analysis were (1) principle of least squares, (2) chi-squared test, (3) Kolmogorov-Smirnov test, and (4) Wiener's time-series analysis. The Kolmogorov-Smirnov test was finally selected for use. A determination was initially made as to which parameters were significant and in what way they might be formalized for easier handling.

Early in the program it was found that these theoretical models could not be adapted exclusive of empirical analyses without encountering severe pitfalls, e.g., an oversight of a pertinent critical parameter. However, the theoretical tools provided valuable direction, support, and interpretation of the empirical techniques being investigated.

The contract period expired before full development of the theoretical approach was achieved. However, several courses of research were attempted: Presentation and analysis of Crane data as families of curves, development of phenomenological theory, establishment of distribution laws from small samples, and finally, testing the validity of these distributions and the variability between cells.

2. Empirical Approach

The first problem encountered in the empirical approach was digitalization of the charge-discharge curves. The actual cell voltages were not directly usable because changes in temperature could elevate or depress any specific curve form. * The effects of this temperature variance were greatly reduced by plotting a distribution of the first differences of voltage changes.

A single charge-discharge curve does not contain sufficient information for distribution statistics. The charge-discharge curve of a good or bad cell may in itself be good or bad, i.e., one curve alone may indicate that a good cell is bad, or vice versa. It was therefore felt important to take the distributions on an appropriate number of cycles. If the distributions are based on single voltage changes (ΔV) the "time" variable disappears. However, the time variable may be important, and a variety of techniques can be used to reintroduce it, at least partially. For example, consecutive pairs of voltage differences could be used to produce a histogram, and the larger interval thus considered partly recovers "time". Care must be exercised in applying these techniques so as to keep the data volume to be handled within a reasonable size. Cryptoanalytic techniques** were used, being free of the restrictions imposed by formal mathematical procedures. What is needed initially is any "fingerprint" to differentiate between good and bad cells. Cryptoanalysis not only yields pattern distributions but also periods, which may be useful in selecting sampling procedures.

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* This assumption is based on observation of Crane data.

** Helen Fouché-Gaines, "Cryptoanalysis, A Study of Ciphers and Their Solutions," paper 200, Dover Press (1939).

SECTION II

DATA PREPARATION AND HANDLING

A. GENERAL

The data from the Quality Evaluation Laboratory, U. S. Naval Ammunition Depot, Crane, Indiana, on Ni-Cd cells were remarkably error-free for such a very large volume of material. These data were in digital form and hence could be immediately transcribed onto magnetic-tape; they included considerable supporting documentation, and the test processes were simply designed. However, the very simplicity of the Crane testing program may become a handicap in furtherance of this work because formulation of a generalized theory will require a study of battery data obtained from differing regimes.

B. DATA HANDLING

The Crane data collection is derived from a set of comparative cycling tests continued to cell failure and followed by a post mortem. The criterion of failure is the common one of low end-of-discharge voltage. Thus, time to failure and failure modes are observed.

The Crane Laboratory duplicated all data cards from inception of the test program through September 1964; this included approximately 800,000 punched cards, which constituted the data input to RCA.

To determine just what parameters should be considered for statistical investigation, it was necessary to obtain a display of a large sample of the data for rapid perusal. It was therefore decided to transfer the data to magnetic tape to achieve the advantage of speed and convenience in handling. Various samples were selected for direct plotting by the computer; the resulting curves were expected to provide a basis for determining which parameters were of interest for machine processing. Several hundred such curves were obtained, but the computer cost was too high to be compatible with the scope of the project.

Analysis showed two reasons for the high cost of computer plotting: (1) the time required for retrieving a prescribed data sample, and (2) the inefficiencies of FORTRAN in data editing. Machine coding of the data editing processes, and the preparation of new tapes for the sample curve-plotting programs, would have helped, but there would still have been a large loss of time in data manipulation, so that there would have been no time for productive machine determination of essential variabilities. New prediction capabilities would still have to be demonstrated with additional programs and further computer runs for verification.

After a technique was developed for using the computer effectively, the large quantity of data became entirely manageable. Many times this volume of data can now be handled. For example, near the end of the study, a brief program was written to find information for ten cells, sort it, perform some computations, tally the results, then print them. The time required to perform this variety of tasks on the RCA 301 computer was just one minute.

The format of the data is important in computer manipulation. FORTRAN saves hours of programming and debugging. Unfortunately, it is not economical in non-mathematical operations, such as editing, extracting, sorting, etc., so that data must be provided in both FORTRAN and "compacted" format to realize optimum time and cost advantages. For each application, this results in a system of data tapes which, although simple in concept, is critical in fulfillment of the overall mission. On this program, three sets of data* have been developed for the RCA 301 system. The computer routines associated with retrieval of this data are given in Appendix A.

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* Raw data from the cards, compacted data, and FORTRAN data.

SECTION III

THEORETICAL INVESTIGATIONS

This section contains descriptions of those mathematical approaches for which further development appears desirable and on which most of the effort was concentrated.

A. GRAPHIC PRESENTATION OF CRANE DATA

The types of curves chosen for examination were mentioned in Section II of this report. All of the information acquired in the Crane experiment (excepting, of course, the failure reports) can be expressed in discharge-charge curves, which are common in battery engineering. The most common discharge-charge curves are those for entire batteries, as given in the Crane quarterly reports. However, for the RCA investigation, such curves were plotted for individual cells. Although only end-of-charge and end-of-discharge cell voltages are usually used for such curves (as given in the Crane monthly reports), there are four reasons for wanting to examine these curves in their entirety:

1. The end-of-charge and -discharge voltages are extremely sensitive to conditions which are not necessarily indicative of the state of the cell. Thus, midpoint voltages (measured during both charge and discharge cycles) may be of more value than the end-of-cycle parameters. For example:

   - In repetitive cycling regimes, end-of-discharge voltages are often affected by a "memory" phenomenon which does not affect midpoint voltage;
   - The end-of-charge voltage is often lower than the highest charge voltage because of the inability to keep the cell isothermal, and it is important that the application engineer know the highest cell voltage to determine the working voltage range.

2. The Crane experiment consists of a large number of parallel experiments that can be arranged in pairs differing only by single experiment factors; therefore, these data can be used to determine whether full curves permit discrimination among effects caused by changing test conditions.

3. It is often necessary for the systems engineer to reduce the entire electrical power subsystem of a space vehicle to a computer program in order to study the effects of sun angle, vehicle loads, degradations, etc. In order to do this he must use an average representation of the entire charge/discharge curve.

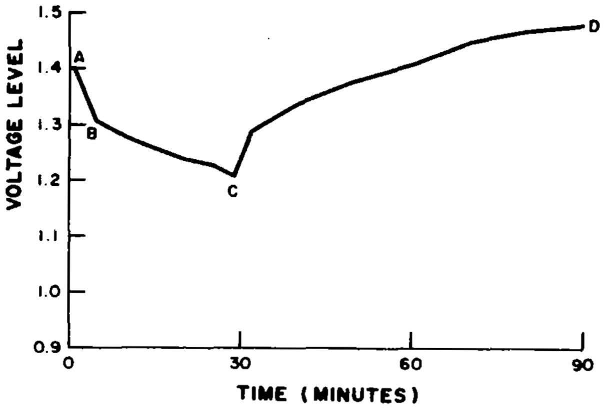
4. A "failure law", inferred from life-test data, would be valuable for reliability engineering. Since failure is due to changes within a cell, perhaps only over a limited area on a single plate, close examination of a performance curve might reveal symptoms long before actual failure, providing an additional indicator for selecting cells for space use. (Cell failures are frequently accompanied by considerable damage due to the effects of failure itself, so that post mortems may be difficult to perform. Hence, early detection should help in identifying causes of failure. Identification of early symptoms of cell failure should also allow more economical use of test time, as cycling could be stopped short.)

B. ANALYSIS OF VOLTAGE TIME CURVES

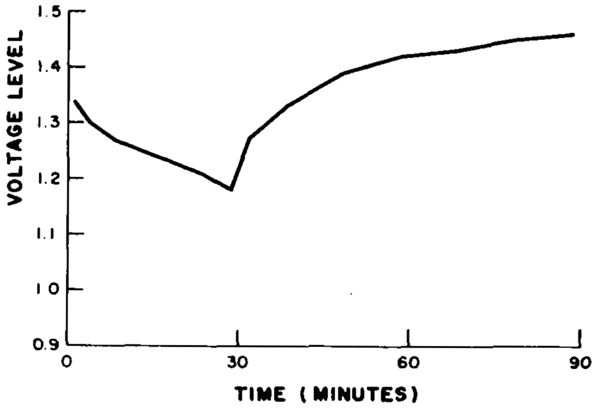
A typical voltage-versus-time curve for a cell in the Crane cycling experiment is shown in Figure 1. Line AB indicates a rapid voltage drop which is of limited interest; BC is generally very nearly a straight line. CD, the charge portion of the curve, may be a parabola (as indicated), a straight line, or a more complicated curve.

The majority of curves selected for examination were for cells known to have failed early, with a few curves for cells that did not fail until several months after the date of the last available data. In general, for cells which did not fail, atypical or irregular curves noted during earlier cycles were not noted during later cycles. Evidently, samples were too small for definitive conclusions. Moreover, curves were evaluated in a gross qualitative way, making comparison and analysis difficult. Also, any single curve may be misleading, since relatively slight irregularities may deform a curve in a way that leads to exaggerations in a qualitative description. One must obtain a family of successive curves and characterize the family, an effort that could not be completed within the time and cost constraints of this contract.

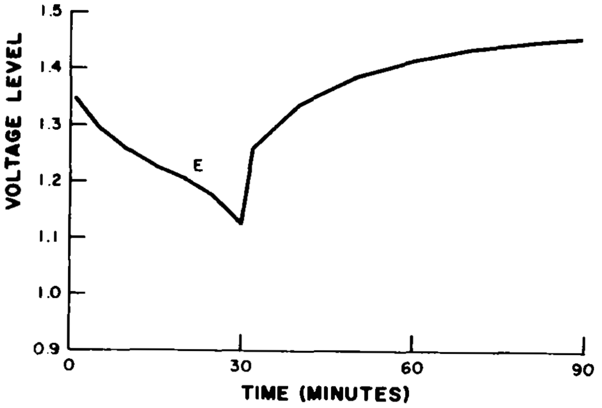
Another suggestive, but inconclusive, point is indicated in Figure 1C. In some cases, the discharge portion of the curve (EC) turned downward as cycling continued. This effect was progressive and was usually associated with a failed cell, perhaps illustrating the "memory effect". A similar effect could be caused by loss of active material from the limiting plate within



A. CYCLE NO. 100

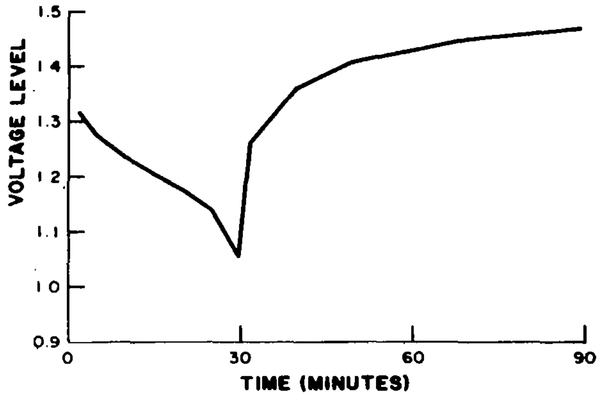


B. CYCLE NO. 1000

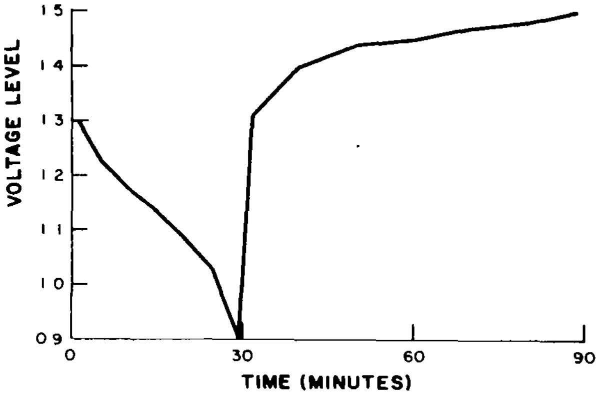


C. CYCLE NO. 2000

Figure 1. Sample Voltage-Time Curves for a Typical Cell in the Crane Cycling Experiment (Sheet 1 of 2)



D. CYCLE NO. 2900



E. CYCLE NO. 4000

Figure 1. Sample Voltage-Time Curves for a Typical Cell in the Crane Cycling Experiment (Sheet 2 of 2)

a cell, which would permanently reduce cell capacity. One way to determine the cause of this effect would be to see whether the dip could be eliminated by altering the cycle to recondition the cell. Such questions could not be resolved from the data available, but might be resolved by tests specifically designed to clarify and define the memory effect.

The empirical analysis of Section IV provides the ingredients lacking in simple visual examination of curves; namely, it combines observations on families of successive voltage-time curves into a single representation, and it does so quantitatively. Results of empirical analysis are often interpretable in terms of the shapes of single curves.

C. DEVELOPMENT OF PHENOMENOLOGICAL THEORY

The apparently simple curves obtained from the Crane measurements immediately suggested similar curves showing the effects of corrosion, formation of protective coatings, and the like — effects which invite formulation in terms of boundary values of differential equations. For intact cells, the dominant phenomena appear to be diffusion and percolation, both of which can be statistically described. Development of such statistical descriptions may lead to an understanding of what happens in working batteries.

Although in a first consideration in the study of batteries the theoretical discussions principally encountered employ the language of electrochemistry and chemical thermodynamics, it has been found that these concepts are not completely adequate for an actual battery. On the contrary, it seemed that the rate-determining processes are transport processes (such as diffusion of heat, ions, and gases) and what have recently come to be called "percolation" processes (such as the migration of ions through the random distribution of crystals constituting the electrode surface). The effects include changes in concentration, temperature, and pressure. Such alterations of conditions tend to mask the phenomena of electrode kinetics, which are revealed externally as polarization.

Searching farther afield, it was discovered that a great deal of work was being done on transport processes in relation to electrical surface phenomena and in relation to such problems as the formation of protective coatings on metals, mass transfer between homogeneous phases, and the like. Unfortunately, most of the work deals with the transport of single quantities and leads to the formulation of the boundary value problem for one or more partial differential equations. When the solution can be obtained, it may be something like a current-density distribution. Unfortunately, the battery problem has three additional complications: (1) there is a system of transport equations, not mutually independent; (2) the boundary conditions are far from simple; and (3) most significant, the boundary conditions are varied according to a scheme external to the dynamics of the battery, with the simplest case being a regular discharge-charge cycle. The observations made outside the battery represent some kind of average of these complex internal relations. It was hoped to start on the problem by discovering what experimental and theoretical data could be obtained about the individual processes involved. Composite models then would be formulated; using appropriate simplifying assumptions, these models might allow at least numerical solutions for simulated cycling conditions. As an aid toward constructing an engineering theory, it was hoped that the detailed analysis of the empirical curves would provide clues as to the dominant transport mechanisms in actual cells being cycled. It would appear that this is an essential if, for example, scaling laws are to be obtained.

D. PREDICTION OF INTERCELL VARIABILITY

Although the cells finally selected for space-battery use are seemingly identical, variability can and does exist, but is not always immediately obvious. Each cell consists of several plates, and a discrepancy within a single plate may be sufficient to cause failure. Although uniformity may be achieved within a particular group of cells through selective testing, there is danger of losing it during the various phases of the test program.

The cells actually used in a cycling test are selected in such a way that they are as much alike as possible. In each individual test in the Crane program, the cells themselves constitute the population of interest, initially either 5 or 10 in number, continually decreasing in size as cells fail in the course of the test. It is interesting to determine how this population changes under cycling, especially what happens to the variability. It would be more interesting still, of course, to be able to determine this in comparative tests at different temperatures, because the results obtained could be combined to make predictions about battery life. The temperatures at which comparative tests are conducted in the Crane program seem to be rather too far apart for this purpose. The effect of prolonged cycling on variability is of great interest and concern; therefore, the fact that the only data available to RCA for this program were measured at the beginning of the Crane cycling program, greatly reduced the effectiveness of this particular investigation. If the growth of variability were so rapid that it became visible in the early part of the cycling program, this would be an interesting finding justifying some alarm, but it was not anticipated that this would happen. It seemed reasonable to suppose that significant changes in variability (excluding defective cells), would be expected in the latter part of the cycling program.

The most reasonable procedure would be to wait until the cycling tests had been run to their conclusion. Then, assume that all cells which were defective for reasons of manufacture or previous treatment had been identified (perhaps by the methods of this report) and that the data for these cells had been excluded from further analysis. The initial cumulative distribution functions would be determined for all packs. They would very likely turn out to be nearly uniformly distributed or truncated normal. At significant intervals, say every 1000 cycles, it would be determined whether the distributions had changed. A measure of significance of the change is provided by the Kolmogorov-Smirnov statistic, which considers the maximum distance between two sample cumulative distribution functions plotted on the same graph.* It has the virtue of being easily computed, but it was planned to do this arithmetic on the computer because it was a calculation which would have to be repeated frequently. Virtues of this statistic are that its probability distribution is known and tabulated, and is independent of the statistics of the populations being sampled. Analogous statements may be made for variants of it. Therefore, it is convenient to use this statistic for testing when sample distributions may be regarded as belonging to the same population, for determining fit to a supposed distribution law, or for determining the relation between sample size and confidence level.

E. DISTRIBUTION LAWS FROM SMALL SAMPLES

It has already been remarked that the main interest of this study program was directed toward the analysis and performance curves, and to the data-processing techniques which would make this analysis feasible on a large scale. Nevertheless, because the reasons for interest in intercell variability continued to remain valid, the study effort was applied to the question of what could be usefully done with samples that were too small to be tested statistically. Obtaining larger samples by compounding data from different tests is not possible at the present time, since cells of the same capacity, but produced by different manufacturers, are not equivalent, and it is not known how to compare cells of different capacities. The following heuristic reasoning was applied:

Suppose that one has a few random values from a probability distribution. Standard methods use these samples as if they were accurate. Yet, nothing would have changed very much if these values were somewhat larger or smaller. Suppose, therefore, that each sample value is replaced by a uniform distribution over some interval containing that value as its center. (The length of this interval is a parameter to be determined.) Suppose, such an interval is assigned and a uniform distribution over it is defined. Now combine all of the uniform

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*Use of the Kolmogorov-Smirnov statistic is explained further in Appendix B of this report.

distributions into a single distribution which is then normalized, at first weighting each value equally. This simple procedure permits the construction of a cumulative distribution function. Note that nothing has been proven; a purely empirical procedure has been defined, on the basis of heuristic reasoning which may or may not be plausible, and it is necessary to test the procedure.

The above procedure was first tested using manual processing techniques. Samples of 5 values were taken from a table of random normal deviates, the procedure was applied, and the results examined. The results seemed good enough to warrant more checking. Because of the tediousness of checking with paper-and-pencil, it was decided to check with the computer. A program was written and debugged, and applied to a set of samples of 5 from a normal distribution. Once more the results seemed so good that it was planned to run a series of rigorous checks, on a number of distributions, in an attempt to determine quantitatively how it compares with the standard methods using the sample distribution function. Unfortunately, this work was interrupted by the ending of the period of study.

SECTION IV
EMPIRICAL ANALYSIS

A. ANALYTICAL PROCEDURES

The purpose of the empirical analysis was to identify statistical regularities by the computer processing of test data. Such regularities or irregularities could be used to construct predictive procedures for use in cell acceptance programs.

The most important result of the empirical work accomplished on this contract is the identification of several statistical techniques involving sophisticated multidimensional tables which provided consistent and correct indications of cell failure long before any of the methods in current use. A most important discovery is that most of the useful indicators of failure seem to appear in the charge portion of the cycling regime. Testing programs have been more concerned with the discharge portion of cycling regime, but evidently the cell is under more strain during charge and therefore deficiencies show earlier and more prominently.

The data pertaining to 80 cells were examined by cryptoanalytical devices. Procedures were devised for manipulating and transforming the data, to obtain criteria useful for distinguishing between time-histories of good and failed cells. Phenomena found by these criteria were compared with known properties of the cells. The cryptoanalytic approach may also point towards effective combinations of voltage behavior which would not be discovered by deduction from theory.

A computer worksheet from this manual analysis, retyped for clarity, is shown in Figure 2. The data are exactly as they appeared on the computer runoff except for the headings, which have been added for convenience, and the voltage differences between successive readings, shown with arrows between the respective readings. The arrows indicate a drop in voltage where pointing downward (discharge), and an increase in voltage where pointing upward (charge). A simple count of frequency of occurrence of a particular value of voltage difference should show the existence and nature of the pattern sought.

DISCHARGE CYCLE

	No. Cells in Pack	Time	Cycle No.	Battery Pack No.	Battery Voltage	Battery Current	Voltage Change for Each Cell										Temperature of Each Cell (°C)										Ambient Temperature (°C)
							1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6	7	8	9	10	
0187 00000	10	000.5	0001	004	14.01	2.90	141	141	141	141	142	142	140	141	140	141	41.6	32.2	32.8	33.3	31.0	31.6	31.9	33.9	51.2	27.6	24.1
							↓ 5	↓ 5	↓ 5	↓ 5	↓ 5	↓ 5	↓ 4	↓ 5	↓ 5	↓ 5											
0188 00000	10	004.0	0001	004	13.54	2.97	136	136	136	136	137	137	136	136	135	136	33.7	34.1	31.7	31.9	31.5	31.0	29.7	31.6	47.5	30.2	25.8
							↓ 5	↓ 5	↓ 5	↓ 5	↓ 6	↓ 6	↓ 6	↓ 6	↓ 5	↓ 6											
0189 00000	10	010.0	0001	004	12.99	2.98	131	131	131	131	131	131	130	130	130	130	34.1	32.2	31.3	32.5	31.8	30.4	30.2	29.6	46.0	32.0	24.2
							↓ 2	↓ 2	↓ 2	↓ 2	↓ 2	↓ 2	↓ 2	↓ 2	↓ 2	↓ 2											
0190 00000	10	014.0	0001	004	12.78	2.98	129	129	129	129	129	129	128	128	128	128	36.0	36.0	33.1	33.9	33.3	34.8	32.0	31.7	45.6	27.9	27.3
							↓ 2	↓ 1	↓ 2	↓ 2	↓ 1	↓ 2	↓ 1	↓ 1	↓ 1	↓ 1											
0191 00000	10	018.0	0001	004	12.63	2.98	127	128	127	127	128	127	127	127	127	127	34.1	33.5	30.7	34.7	31.2	33.2	32.2	34.4	45.6	32.0	25.6
							↓ 1	↓ 2	↓ 1	↓ 1	↓ 2	↓ 1	↓ 1	↓ 2	↓ 1	↓ 1											
0192 00000	10	024.0	0001	004	12.52	2.98	126	126	126	126	126	126	126	126	126	126	33.9	33.9	31.6	34.3	27.9	32.2	31.4	39.6	45.4	29.8	24.5
							↓ 0	↓ 0	↓ 1	↓ 1	↓ 0	↓ 1	↓ 1	↓ 0	↓ 0	↓ 0											
0193 00000	10	028.0	0001	004	12.48	3.08	126	126	125	125	126	125	125	125	126	126	34.1	32.9	34.7	31.9	34.5	36.2	31.1	36.0	46.4	30.3	25.4
CHARGE CYCLE																											
							↑ 6	↑ 6	↑ 7	↑ 7	↑ 7	↑ 8	↑ 7	↑ 8	↑ 8	↑ 7											
0194 00000	10	032.0	0001	004	13.19	1.60	132	132	132	132	133	133	132	133	134	133	34.8	33.1	34.1	33.6	33.9	36.2	33.9	33.3	50.1	31.4	24.2
							↑ 4	↑ 4	↑ 4	↑ 4	↑ 3	↑ 3	↑ 4	↑ 3	↑ 3	↑ 4											
0195 00000	10	040.0	0001	004	13.56	1.59	136	136	136	136	136	136	136	136	137	137	33.4	30.3	33.9	32.9	33.4	34.1	30.2	32.9	35.7	31.6	24.2
							↑ 3	↑ 3	↑ 3	↑ 4	↑ 4	↑ 4	↑ 3	↑ 3	↑ 3	↑ 2											
0196 00000	10	050.0	0001	004	13.88	1.60	139	139	139	140	140	140	139	139	140	139	33.9	31.4	1.1	32.7	33.9	33.9	30.2	32.2	47.0	32.0	25.4
							↑ 3	↑ 3	↑ 3	↑ 2	↑ 3	↑ 3	↑ 3	↑ 4	↑ 2	↑ 3											
0197 00000	10	060.0	0001	004	14.17	1.56	142	142	142	142	143	143	142	143	142	142	35.8	31.0	31.8	31.7	31.9	31.5	30.2	30.2	47.5	32.3	24.6
							↑ 3	↑ 4	↑ 3	↑ 5	↑ 4	↑ 4	↑ 3	↑ 5	↑ 3	↑ 3											
0198 00000	10	070.0	0001	004	14.54	1.40	145	146	145	147	147	147	145	148	145	145	32.9	32.0	32.1	35.9	30.2	30.0	30.0	20.0	48.1	30.2	25.2
							↑ 3	↑ 2	↑ 2	↑ 3	↑ 3	↑ 1	↑ 2	↑ 1	↑ 1	↑ 1											
0199 0000	10	080.0	0001	004	14.74	1.85	148	148	147	150	150	148	147	149	146	146	42.7	1-.7	33.0	77.2	58.7	-2.7	41.6	26.2	33.0	79.1	39.7
							↑ 3	↑ 4	↑ 4	↑ 3	↑ 3	↑ 2	↑ 3	↑ 4	↑ 1	↑ 2											
0200 00000	10	089.0	0001	004	15.03	1.13	151	152	151	153	153	150	150	153	147	148	43.5	23.8	41.6	1-.7	32.7	31.3	29.7	11.4	38.0	28.3	22.3

NOTE: All temperature indications are actual readings; anomalous entries are caused by errors in the monitoring equipment.

Figure 2. Worksheet Developed from Typical Computer Run-Off of Cell Charge and Discharge Data for Battery Pack 004

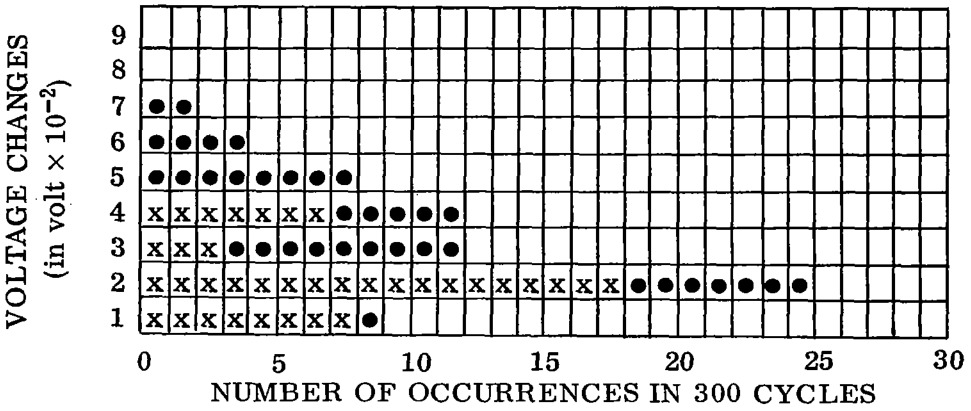
An appropriate number of cycles had to be chosen to yield a significant difference in overall frequencies of occurrences, thereby differentiating good cells from bad. Obviously, voltage fluctuations would not be discernible in only one or two charge-discharge cycles. Conversely, too many cycles might complicate indications of a bad cell because of the possibility of including too many parameters. For example, a cell might start by showing signs of eventual high pressure, but failure may actually occur in another mode which would be reflected in later statistics. The number of charge-discharge cycles selected for initial analysis was 300. This number 300 actually represented only 10 cycles of data, since data were collected by monitoring every 32nd cycle. Larger and smaller numbers of cycles were tried with no observed advantages gained.

Since the voltage differences generally ranged from 0.00 to 0.09 volt, ten levels of change were selected for tabulation. Any larger difference was counted as 0.09 volt, thereby derating large errors.

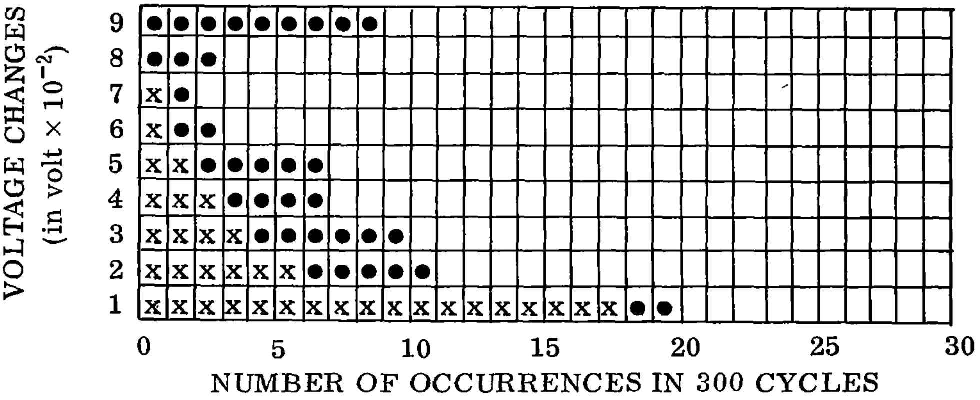
Frequency histograms of voltage differences were made for each of the ten cells in one battery pack for 3000 cycles. For this small sample, characteristics of bad cells were evidenced 1000 cycles before failure. Figure 3 presents data on two cell samples. Data samples for a cell that in 3000 cycles showed no anomalies indicative of early failure are presented in View A of Figure 3. Data samples for an early-failing cell are presented in View B of Figure 3, where the early failure is indicated by the high level of charging. According to the histogram, during the charge portion of the cycle there were nine occurrences of voltage differences of at least 0.09 volt.

A computer run-off of the data in Figure 3 has been retyped and is shown in Figure 4. The ten levels of voltage change, mentioned above, are tabulated in the columns for charge and discharge. There is one column for each of the ten cells, giving the number of occurrences of each of the possible ten levels of voltage change. For example, with respect to cell number 4, discharge cycle, no voltage changes at levels 9 through 5 occurred. However, at change level 4, there were seven occurrences. This means that a 0.04-volt change occurred seven times, for a total voltage change of 0.28 volt. The sums of the total voltage changes ($\Sigma\Delta f$) for each cell are given in the bottom row.

(For example, in column C1 of Figure 4, $\Sigma\Delta f = (10 \times 0.03) + (21 \times 0.02) + (5 \times 0.01) = 0.77$ volt, listed in the table as 0077.) The basis of interest in this particular calculation is the assumption that a normal cell being exercised under the same cycling regime should exhibit similar voltage excursion histories, and that any major total change during consecutive monitoring periods must have physical significance. The problem of determining the physical significance of such variabilities, although valuable in setting direction of effort, was not essential to the statistical identification of experimental facts.



A. CELL NO. 4, NEVER FAILED



B. CELL NO. 10, FAILED ON 502 CYCLES

LEGEND: ● = charge, x = discharge

Figure 3. Positive and Negative Changes in Cell Voltages for Two Cells in Battery Pack 004

DISCHARGE

Voltage Change (Δ)	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
09	0000	0000	0000	0000	0000	0000	0000	0000	0000	0000
08	0000	0000	0000	0000	0000	0000	0000	0000	0000	0000
07	0000	0000	0000	0000	0000	0000	0000	0000	0000	0001
06	0000	0000	0000	0000	0000	0000	0000	0000	0000	0001
05	0000	0000	0000	0000	0000	0000	0000	0001	0000	0002
04	0000	0002	0005	0007	0002	0000	0001	0001	0002	0003
03	0010	0011	0012	0003	0010	0010	0007	0006	0008	0004
02	0021	0013	0011	0018	0019	0021	0021	0019	0021	0006
01	0005	0010	0008	0008	0004	0005	0007	0009	0005	0018
	0077	0077	0086	0081	0080	0077	0074	0074	0079	0077

CHARGE

Voltage Change (Δ)	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
09	0002	0002	0003	0000	0002	0002	0002	0004	0002	0008
08	0000	0001	0002	0000	0001	0000	0000	0001	0000	0003
07	0005	0004	0004	0002	0004	0001	0001	0003	0000	0001
06	0002	0003	0001	0004	0003	0005	0002	0003	0004	0002
05	0006	0005	0004	0008	0001	0001	0004	0006	0003	0005
04	0002	0007	0005	0005	0005	0004	0006	0007	0007	0004
03	0013	0009	0010	0009	0006	0005	0005	0006	0004	0006
02	0006	0005	0010	0007	0010	0010	0008	0006	0015	0015
01	0005	0003	0003	0001	0010	0009	0008	0004	0009	0002
	0159	0165	0170	0140	0145	0120	0120	0175	0136	0186

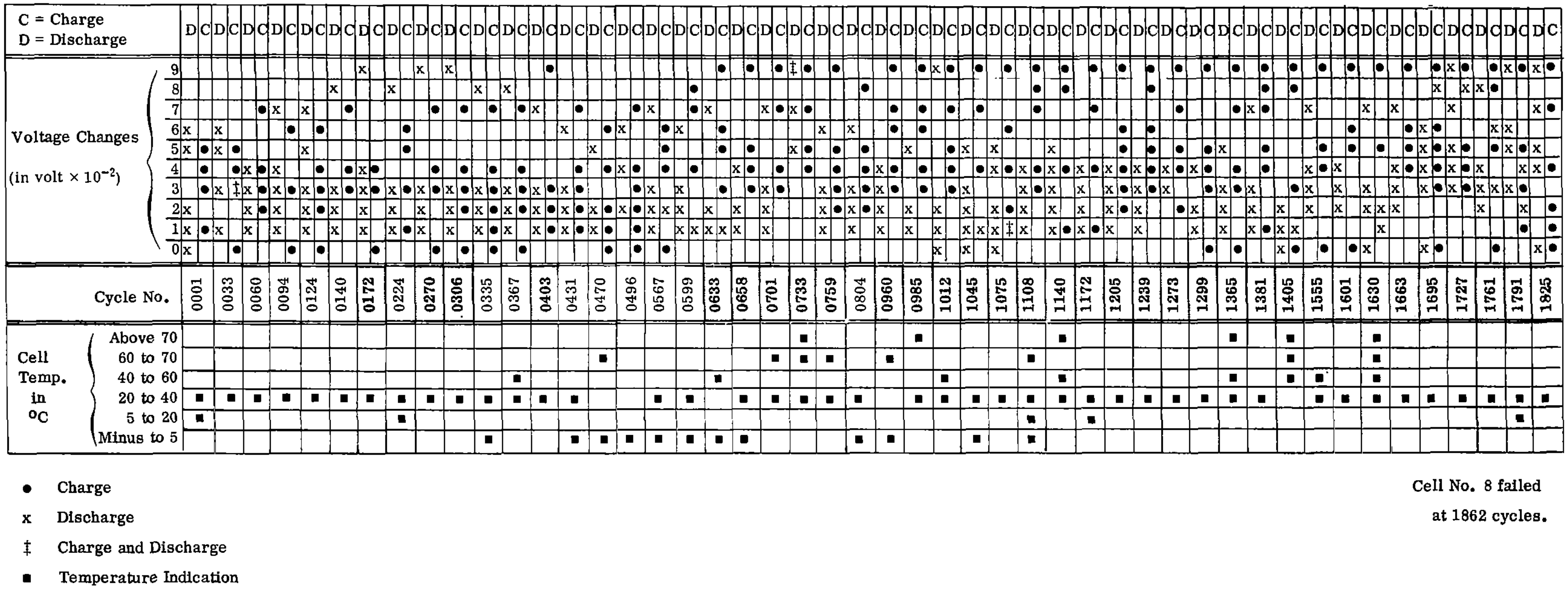
Figure 4. Computer Run-Off Showing Voltage Changes for 10 Cells in Battery Pack 004

For example, it is conceivable that a statistical phenomenon may be discovered to be a reliable indicator of impending failure even though the cause of this phenomenon is not known. In fact, it was the intention of the researchers on this project to spend their major effort on identifying parameters in this phase of the contract, and to consider the physical justification and tests for statistical significance when all the empirical facts were identified and properly structured. Just how far cell trouble can be predicted in advance is shown in Figure 5, which represents the history of one cell to failure. Early failure of this cell is indicated by the large amount of activity at the highest levels of voltage change; where this occurs, the cycle number is shaded to show a preliminary indication of failure in that cycle. However, activity at the highest level of voltage change represents only one criterion for failure, and would not be sufficient for the selection of cells, since some failure modes do not involve such activity. (For example, deteriorated separators appear to be associated with low voltages, as seen in Figure 6 for cell 2, which failed for this reason.)

Figures 6 and 7 illustrate the product sum of voltage differences recorded at 300-cycle intervals for each of the ten cells in battery packs 002 and 004, respectively. These data were obtained from computer run-offs that provide this information at 300-cycle intervals for approximately 5000 cycles. (A sample of this type of computer data, representing cycles 300 to 700 for battery pack 004, was given in Figure 4.) In Figures 6 and 7, the charge sum for each cell is subtracted from the discharge sum and is plotted in the column representing the appropriate cycle interval. A graphic presentation of this type serves as an efficient prediction device. On the basis of Figure 6, it can be predicted very clearly that cells 10, 5, and 2 will fail. Observing Figure 7, it can be seen that cells 7 and 8 drastically deviated from the norm by cycle 700. Cell 7 failed by cycle 1900 and cell 8 failed by cycle 2200. Cell 1 experienced a consistently severe voltage drop and failed by cycle 2500.

A prediction tabulation is given in Table 1 for battery pack 004. This tabulation is based on two different sets of failure criteria. The four surviving cells are tabulated at the top of the list, showing the indications of possible trouble. The tabulation for the failed cells specifically points out the difference in behavior between good cells and bad, using either set of the criteria. Both sets of criteria are defined at the bottom of the table.

Second differences, shown in Table 2, were reviewed to see if they would yield any new information. These are values obtained by subtracting the consecutive differences already obtained, as shown in Figure 2. A review of the values derived as second differences will show that although no new information has been obtained, the previously described prediction techniques are still further confirmed. The information deals with battery pack 002; charge totals for cells 10, 5, and 2 are well over the norm, as shown in Figure 7.



Cell No. 8 failed
at 1862 cycles.

Figure 5. Testing History of One Cell
to Failure

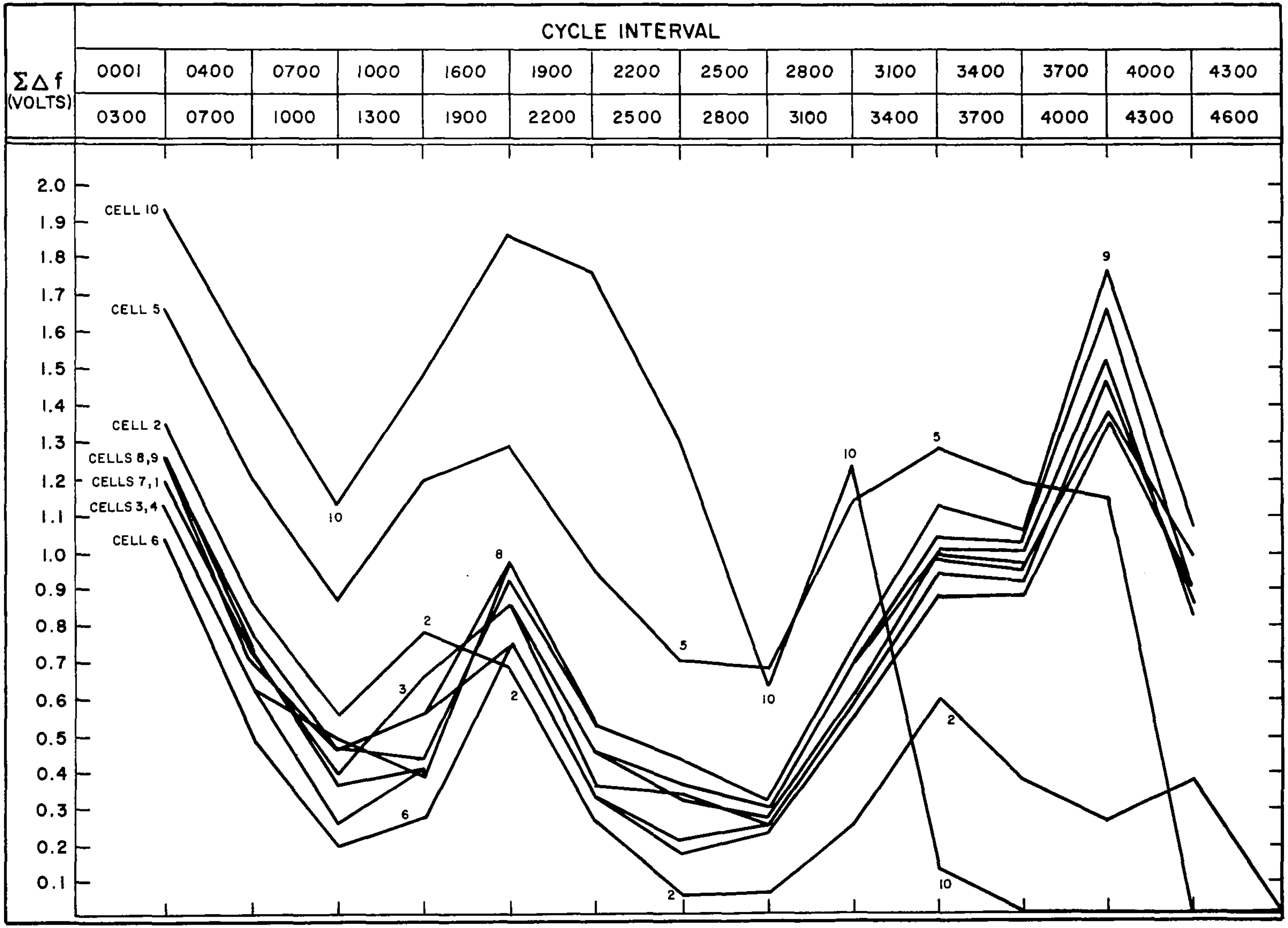


Figure 6. Voltage Differences at 300-Cycle Intervals for Each of the Ten Cells in Battery Pack 002 (Cell numbers are repeated as required to assist in identifying the various plots)

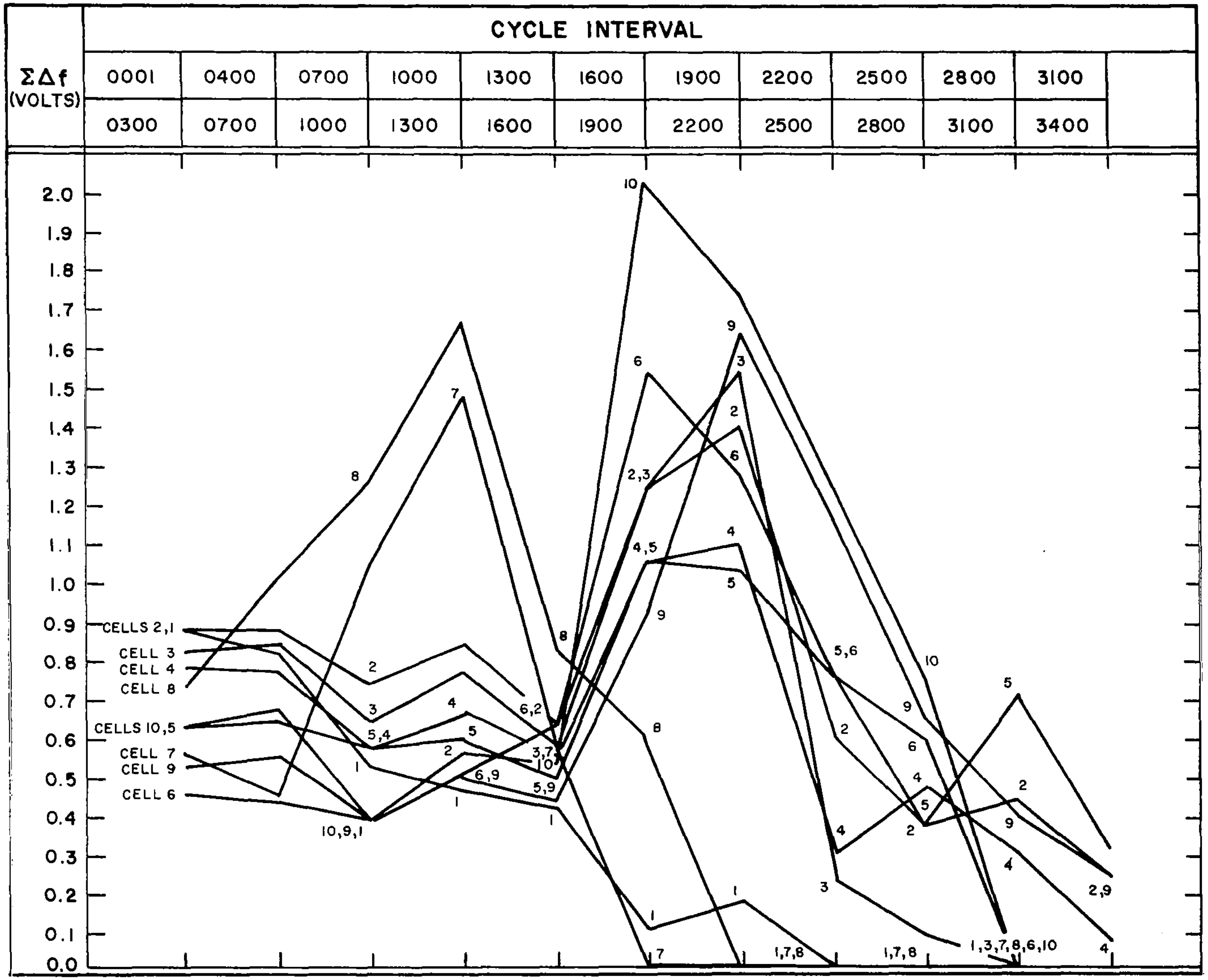


Figure 7. Voltage Differences at 300-Cycle Intervals for Each of the Ten Cells in Battery Pack 004 (Cell numbers are repeated to assist in identifying the various plots)

	Cell No.	FIRST CRITERION							SECOND CRITERION									
		CYCLE NUMBER							CYCLE NUMBER									
		0001 to 0300	0400 to 0700	0700 to 1000	1000 to 1300	1300 to 1600	1600 to 1900	1900 to 2200	0001 to 0300	0700 to 1000	1000 to 1300	1300 to 1600	1600 to 1900	1900 to 2200	2200 to 2500	2500 to 2800	2800 to 3100	3100 to 3400
NON-FAILING CELLS	9		1				5						1	1	2, 1			
	5		1	1	5		5						1	1				
	4		1	1, 4	1, 5		1, 5						1	1	1			
	2		1				5						1	1	1			
FAILED CELLS	10		1				2, 3, 5						2, 3, 1	3, 2, 1	3, 1	3	→	Failed 9
	8	4	1, 2, 3, 5	1, 3, 4, 5	1, 2, 3, 5	3	4, 5 ←	Failed 16	1	3, 1	3, 1	3, 1	1, 4	→	Failed 9			
	7	2	1, 2, 4	1, 2	1, 3, 5	1	2, 4 ←	Failed	2	2, 1	1	3, 1	1, 4	→	Failed 8			
	6	1	1			2	5					2, 1	1	1	1	→		Failed 5
	3	3	1	1, 4	1, 5	1	1, 5		3, 1	1		1	1	1	1			Failed 7
	1		1		2, 4	4	4				2	1, 4	4	4	4 ←	Failed 6		

DEFINITION OF FAILURE CRITERIA

FIRST CRITERION	SECOND CRITERION
1. $\Delta \geq 0.09$	1. $\frac{\sum_{\Delta V = 5}^{9} \Delta V}{\sum_{\Delta V = 0}^{5} \Delta V} < 1$
2. Min $\Sigma \Delta V \cdot f$ on discharge	2. Max $\Sigma \Delta V \cdot f$ on charge
3. Max $\Sigma \Delta V \cdot f$ on charge	3. Max Count for $\Delta V = 0$
4. Max Count for $\Delta V = 0$	4. $\Delta V = 0$ High
5. $\Sigma (\Delta V > 5) > 10$	5. The number of ΔV for 0, 1 > the number of ΔV2, 3, 4

TABLE 1. PREDICTION TABULATION FOR TWO FAILURE CRITERIA

TABLE 2. SECOND VOLTAGE DIFFERENCES FROM CYCLES 0001 TO 0300 FOR THE TEN CELLS IN BATTERY PACK 002

	ΔV	CELL NUMBER									
		1	2	3	4	5	6	7	8	9	10
DISCHARGE	09	-	-	-	-	-	-	-	-	-	-
	08	-	-	-	-	-	-	-	-	-	-
	07	-	-	-	-	-	-	-	-	-	-
	06	-	-	-	1	-	-	-	-	-	-
	05	-	1	2	1	-	-	-	-	-	-
	04	1	1	-	1	3	-	2	3	2	-
	03	3	3	4	3	3	1	5	4	4	6
	02	7	9	7	8	11	5	7	7	9	9
	01	14	19	16	18	14	19	20	18	12	14
	00	19	16	18	13	13	12	14	13	18	10
	ΣΔf	41	55	52	58	57	32	57	56	50	50
CHARGE	09	-	2	-	-	2	-	-	-	1	2
	08	-	-	-	-	1	-	-	1	2	1
	07	-	3	1	-	2	-	1	1	1	1
	06	2	2	1	2	3	3	2	3	-	2
	05	1	1	1	1	4	-	1	-	-	1
	04	1	1	-	2	1	2	1	-	1	7
	03	3	7	2	2	1	3	4	3	3	4
	02	14	3	5	7	4	4	7	6	8	9
	01	19	13	11	15	16	16	12	16	11	9
	00	4	8	13	6	3	5	5	3	6	7
	ΣΔf	77	100	45	60	109	59	66	70	72	117

These examples demonstrate that the actual mode of failure is reflected in the statistical indications. The worst data were those for battery pack 042, which was tested under adverse conditions (ambient temperature 40^{o} and higher throughout the test). However, remarkably good results were obtained, considering the unreliable input data. Four of the cells failed before cycle 484. Even here, however, the indications of failure were initially reliable. Predictions based on the machine results for battery pack 042 were not attempted. Packs 001, 002, 004, 007, 013, 037, 039, and 042 were machine processed, and the tabulations were analyzed to develop the best set of criteria to indicate cell failure. To date, seven statistical indicators have been identified. These indicators are described in the paragraphs that follow, preceded by definitions of employed symbology:

f = frequency count

c_f = frequency count for charge portion of cycle

d_f = frequency count for discharge portion of cycle

f_{ij} = frequency for each ΔV against cell number

where

i = cell number

j = measure of difference between two successive voltage readings.

Therefore, the meaning of the following expression is "look at frequency counts for charge only and for $\Delta V = 9$ only, and select out of all ten cells, the maximum":

$$c_{f_{i9}} \Big/_{i\,=\,1}^{10} = \text{max}$$

B. IDENTIFICATION OF STATISTICAL INDICATORS OF FAILURE

On the basis of machine runs for data on 80 cells, the following indicators of failure have been verified. Although the material presented here was derived from manual analysis of the machine tabulations, a machine program must be developed to test and select the best indicators over a large sample of data. Formulations and verbal descriptions for each indicator are presented in the following. All of the indicators described apply to the analysis of tabulations similar to that presented in Figure 4 of this report.

1. If the frequency of occurrence of a 0.9-volt difference ($\Delta V = 0.9$) is higher for any particular cell than for all the other nine cells for the charge cycle, it is considered a sign of trouble. (Refer to Table 1 and Figures 5, 6, and 7 of this report.) This is represented by the expression:

$$cf_{i9} \Big/_{i=1}^{10} \qquad \text{max.}$$

The voltage differences between the last reading of discharge and the first reading of charge were not tabulated, since there was always a large ΔV increase between these two readings. It is desirable to process these particular differences in a separate tabulation, as it has already been manually observed that these differences behave peculiarly. In the same way, the differences between the last reading of charge and the first reading of discharge were not considered; however, these differences probably never should be considered, since 32 cycles of charge-discharge, or 48 hours, have elapsed between the readings. It does bring up the point, however, that important information may be obtained by requiring the test experiment to include at least two consecutive charge-discharge cycles in their test design, as it would certainly be important to determine if the change from charge to discharge affects the statistical behavior of weak cells.

2. Since only the difference levels $\Delta V = 0$ to $\Delta V = 0.9$ were included in the program, any $\Delta V > 0.9$ was considered to be $\Delta V = 0.9$. However, if these differences of $\Delta V > 0.9$ occurred with the wrong sign (that is minus for charge, or plus for discharge), a tally of $\Delta V = 0$ was recorded. Such reverse voltage difference extremes usually were caused by the failure of the monitoring equipment, or in some cases by a short in the cell. A reverse voltage difference of less than 0.9 occurred often in the charge portion of the cycle as a result of the cut-in of the charge limiter. These values also were programmed to result in an increase in the tally count for $\Delta V = 0$. Although a high tally count for $\Delta V = 0$ is used here as being significant in prediction, there must be much more work done on the various categories of causes for $\Delta V = 0$ in order to improve its reliability. This indicator is represented by the expression:

$$c_{f_{i0}} \Big/_{i=1}^{10} > K$$

where K is a constant fixed by the results of a large sample of data.

3. The first two indicators involved only the consideration of frequencies recurring at single levels for ΔV. Actually, all combinations of levels (n-at-a-time) could be considered with Boolean conditions imposed upon their selection. This type of tabulation procedure may be significant, as is demonstrated in the attached Volume 002. Where the sum of the ΔV's for $\Delta V = 0.9, 0.8, 0.7, 0.6$ is measured against the sum of the ΔV's for $\Delta V = 0.1, 0.2$, and where $\Sigma \Delta V\ 0.9, 0.8, 0.7, 0.6 > \Sigma \Delta V\ 0.1, 0.2$, it is considered a sign of cell defectiveness. In battery pack 002, this particular indicator allowed the defective cells to be selected throughout the data history. A program will be considered for this type of indicator as the most important next step in the program.

This indicator is represented by the expression:

$$\sum_{j=6}^{9} c_{f_{ij}} - \sum_{j=1}^{2} c_{f_{ij}} \Big/_{i=1}^{10} \geqq 0$$

4. Another highly reliable and interesting statistic derived from the cell test data was the sum of the products of the ΔV levels multiplied by the frequency of occurrence of these levels. This product-sum turned out to be quite different for good cells than for defective ones. The results appeared to reflect an attempt by the cell to work harder during charge to make up for losses due to some defect, while still not reflecting any increase in performance during discharge. In other words, this sum-product figure would be higher than normal for charge and often lower than normal for discharge. This meant that the total voltage excursions for charge were 100 percent higher than were normally necessary for a proper operating balance. It would be immediately of interest to consider these figures for all acceptance requirements. It is also possible that the sum-product procedures should be used in the indicators described in indicator No. 3 above, but requirements were not the object in this phase of the program. This indicator is represented by the expression:

$$\sum_{j=1}^{9} \left(j \times {}^{c}f_{ij}\right) \Big/_{i=1}^{10} \rightarrow \max$$

5. The normal behavior of cells during the discharge cycle was to exhibit high frequencies for ΔV = 0.2, 0.3. Even where other signs of cell deterioration appeared, the cell discharge voltage behavior appeared normal (as demonstrated by the data on battery pack 002). In certain instances, however, it was noted that the discharge voltage differences tended to creep up to higher levels and flatten out. It is suspected that cell damage has occurred when this happens. This possibility is mentioned here to emphasize the fact that although cell voltage characteristics during discharge are important, they do appear to change later in the history of the cell and are not a good basis for long-term prediction. Nevertheless, the statistical picture on discharge does change substantially before actual failure. A general indicator to represent this change is the measurement of any frequency distribution which appears greater than ΔV = 0.2, or 0.3 in discharge. This is represented by the expression:

$${}^{d}f_{k_i} \Big/_{\substack{j=1 \\ j \neq 2,\,3}}^{j=10} \rightarrow \max$$

6. Several simple inequalities, such as a high occurrence of $\Delta V = 0.8$ as compared to occurrences of $\Delta V = 0.2$, can be used as indications of failure. In this phase of the program, no attempt has been made to fit all of these relationships into a comprehensive program filter which requires the procedures illustrated in Table 1.

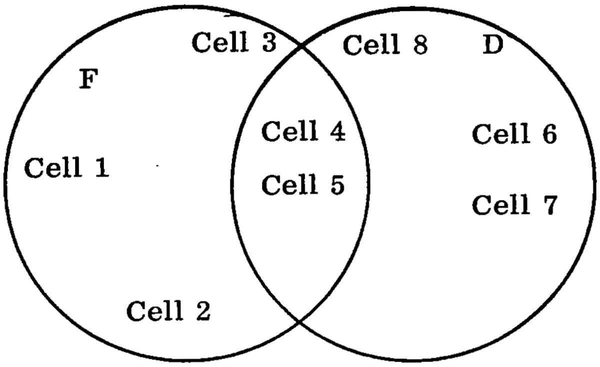
7. As noted in the discussion of indicator No. 4 above, the sum product of the voltage difference levels multiplied by frequency of occurrence on discharge is not the same for all cells. On the results of the test data sampled, it is clear that when this figure is a minimum, there is a high correlation with the defective cell histories. Therefore, this relationship is included as an indicator of failure and it is represented as:

$$\sum_{j=1}^{j=9} \left(\Delta V_j \times {}^{d}f_j \right) \rightarrow \min$$

C. INDICATORS OF CELL FITNESS

Some initial analysis indicates that different failure modes will affect different indicators, so that it is desirable to construct a point system and thresholds for the number of occurrences of each indicator in the development of a reliable prediction filter. Some thought has also been given to a point system for indicators of sound cell behavior and it would also be desirable to indicate means for combining the indicators to obtain an optimum. The advantage of this dual failure-soundness evaluation system is that the output results can be used to adjust the parameters for making the tabulations in accordance with changes in the cycling regime. For example, the Nimbus Battery Test program has two-minute intervals between each point of data, which results in smaller voltage increments with more levels to tabulate. If a given set of indicators is to be used for any battery test program then some method should be divised to normalize the data to fit the filter.

In the same way that indicators for cell defectiveness were developed and described as a result of computer analysis of the Crane test data, it is possible to describe and develop such indicators for cell fitness. The advantage of doing both is clear from this conceptual diagram below:



It is obvious from the set intersection that the ultimate filter desired should have as few common elements as possible. (The symbology used is the same as that used for cell defectiveness.)

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

Means have been devised to measure intercell variability and consider the validity of such measurements through actual use, despite the unavailability of large statistical samples.

On the basis of manual checks of the data for 80 cells, a number of digital procedures were found to be applicable to the test data and appear to enable discrimination between sound and impaired cells in the Crane program.

B. RECOMMENDATIONS FOR FUTURE WORK

Using current programs and having the Crane data on magnetic tape, there are some immediate objectives which may be reached. Some need little additional programming; some need more. The following tasks are recommended:

1. Complete Processing of Crane Data

Utilizing the indicators described in Section IV, processing should be completed for all of the Crane Data now on tape to determine the best indicators of impairment and to record the actual time (in cycles) before failure occurs at which a positive identification can be made. Rather than setting a threshold, a weighting system should be used so that probabilities for successful detection can be plotted against any threshold level.

2. Categorization of Failure Modes

The cell failure modes should be categorized and the indicator statistics correlated with the known failure modes.

3. Comparison of Cell-Selection Techniques

Results obtained from new techniques should be compared with the results of present cell-selection procedures. Presently used indicators of undesirable cells (high end-of-charge, low end-of-discharge, and midpoint-of-discharge voltages) have given us criteria for evaluating new methods of detecting defective cells.

4. Feasible Modifications of the Crane Data

Several obvious changes to the way that Crane takes the data are suggested from the work already done. These suggestions are not intended to improve the Crane data, but rather to provide a means of determining the effects of such changes upon the statistics obtained. For example, Crane monitors each cell at about every 32nd cycle. The data from ten cycles are required in order to obtain sufficient statistics for each cell. At the present time, this means that 300 cycles must be completed before an estimate may be made of cell condition. There is reason to believe that the intervals between monitored cycles need not be so large, so that useful information could be obtained from far fewer than 300 cycles. In order to obtain the data for, say, every second cycle, it appears that the Crane test need not be changed in any essential way, but only interrupted for a short period to get a sufficient sample for each monitoring interval.

5. Determination of Failure Laws

So far, consideration has been given to the problem which is usually of explicit concern to both battery users and manufacturers — namely, to estimating how good a battery is. Systems and reliability engineers also need to know the potentialities of batteries, under the widest possible range of operating conditions. A particularly important problem is that of predicting the useful life of a particular kind of space battery. A major objective of the entire Crane program is to provide this kind of information. Elsewhere in this report, some discussion has been given of the importance of establishing suitable failure laws. Potentially, it would appear, data of the sort provided in a life test like the Crane test should be able to serve as a basis for establishing an appropriate failure law. Three basic difficulties have been mentioned:

- To make use of the data in a life test, it is best for the life test to have been completed, especially when the underlying law of failure is unknown. But Crane data hitherto available have related only to the earliest phase of the test, when the initially defective cells have not yet all been weeded out.

- A failure law presumes that failure has been unambiguously defined, and it has been shown that this has not been done for space batteries in a manner that relates to cell condition rather than to a conventional threshold.

- If there is more than one kind of failure, a separate law is required for each, and an overall omnibus failure law can then be deduced. But it is not easy to see how to proceed in the reverse direction.

However, there is now a technique for the very early detection of a cell which shows defectiveness in its performance curves, and for identifying the characteristics of performance curves associated with different kinds of failures. This observation provides a potential of defining the events needed for a failure law. That is, for each kind of failure, it would become possible to determine the time of the first occurrence of deviation from normal behavior; the time to actual failure from first appearance of defect then could be obtained when all the records are in. On the basis of this data one could hypothesize failure laws in terms of the probability that a failure will occur within a certain range of time (or number of cycles) after the observation of particular kinds of behavior. The verification of these laws will have to be done by statistical techniques applied to large samples of data. Thus, for a given experiment, it may become possible to determine the failure law belonging to each distinguishable type of failure. Moreover, there is the further by-product that after impairment has become evident, and after the failure type has been identified — before engineering failure has actually occurred — it would be possible to remove the cell from the cycling and so dissect it that the detailed mechanism of failure may be traced in a way which is not possible if post mortems are performed after the failure process is very far advanced.

6. Further Development of Statistical Models and Tools

Depending upon the results of using the criteria discussed above, it may be desirable to continue investigating other means of describing performance curves which could be used as criteria in failure laws. Curve shape descriptors or comparisons of values at particular points of the charge-discharge cycle may be useful. Under any circumstance, the statistical tools necessary for evaluation of the validity of the failure laws or for determining probability distributions (based on sampled observations) must be available in usable, computer program form. In many cases this only requires gathering of existing programs. When necessary, some additional programs should be developed.

7. Analysis of the Transport Theory Approach

The preliminary investigation of the transport theory approach was encouraging enough to suggest that a further study of its applicability to the description of cell behavior is desirable.

APPENDIX A

DATA DEVELOPED FOR RCA 301 SYSTEM

I. VOLTAGE DEVIATION COUNTER FOR RCA 301 COMPUTER

PURPOSE: The VDC program generates frequency range counters from the Crane battery data.

DESCRIPTION: Data is manipulated in the following manner:

1. Data is grouped in batches of cycles
2. Data is subgrouped by cell number (from 01 to 10) and by charge or discharge, yielding 200 subgroups
3. The program calculates individual ranges and prepares a frequency chart composed of the 200 counters and a total line of 200 counters. The output is in the form of the frequency-count charts and is displayed on the "on-line-printer".

OPERATING INSTRUCTIONS:

1. Prepare parameter card listing pack number and cycle range
2. Place parameter cards behind "execute" card
3. Place E/F and two blanks after parameter cards
4. Mount first tape on any TK
5. Load PGM with bootstrap - INCLUDE MEMORY DUMP
6. PGM halts at P = 1680
    a. Insert data trunk number in B register
    b. Start

IF TROUBLE

1. If PGM halts with a ⊡ 1 or ⊡ 2 or ⊡ 3
    a. Note register
    b. Save STP
    c. Memory dump
    d. To restart, set P to 2330 and start

2. If PGM halts with an arithmetic alarm
    a. Note P register
    b. Memory dump
    c. Set P to 2330 and start
3. If PGM halts with tape alarm near end of reel
    a. Mount next tape on another drive
    b. Put previous tape in "local"
    c. Set P to 2330 and start
    d. At DDF
        (1) Set P to 0890
        (2) Start
        (3) Halt at 1680, store new TK number in B
        (4) Start

EOR AT ⊡ 0 AT P = 1810

1. If other conditions cause hang
    a. Save registers
    b. Dump
    c. Back up about ten records on input and tape-print selective two pages

II. BATTERY REDUCTION PROGRAM

INPUT: Any or all 301 FORTRAN data tapes, or set of processing cards (each card calls for a particular processing option) to be carried and to contain a

1. Pack number
2. Cell number
3. Cycle number
4. Option code
5. Own coding option code
6. Write save option

DESCRIPTION: The 301 FORTRAN program basically performs the following operations

1. Searches the input data for the particular pack number, cell number, and cycle number called for
2. Stores the information in memory and possibly on tape
3. The information stored is based on the option called for and can be
   a. T vs t
   b. V vs t
   c. Charge T vs t
   d. Charge V vs t
   e. Discharge T vs t
   f. Discharge V vs t
4. The program can simply plot the above curve
5. If an own coding block is called for, it could perform the following on the data stored:
   a. Integration of I vs t
   b. Integration of EI vs t
   c. Plot E/I vs t
   d. Print T's
6. More own coding blocks can easily be added

III. 301 COMPACTION ROUTINE

INPUT: 501 sorted card images in 301 codes (output 1 through 5)

DESCRIPTION: This 301 routine combines voltage and temperature readings for a 10-cell pack into one record

OUTPUT: 301 compacted data tapes

IV. 301 FORTRAN ROUTINE

INPUT: 301 compacted data

DESCRIPTION: The 301 routine produces tapes which can be read by the FORTRAN system. It converts that data into 121 character blocks with control indicators.

OUTPUT: 301 FORTRAN data tapes

APPENDIX B

USE OF KOLMOGOROV-SMIRNOV STATISTIC

The Kolmogorov-Smirnov statistic(1) provides a means of estimating the distribution function of the population from a sample of size n. The advantage of this statistic is that the confidence band can be determined without any prior knowledge of the population distribution function when the size of the sample is large. A statement of the method is as follows:

The sample measurements are $x_1, x_2 \ldots x_n$. For example, this may be a measurement of the change in cell voltage at end of discharge or charge of a single cell in consecutive cycles for n+1 cycles. We define $F_n^*(X)$ that

$$F_n^*(X) = \frac{\text{Number of } x_1, x_2 \ldots x_n \text{ less than or equal to X}}{n}$$

It is hypothesized that in the population of a very large number of cycles (actually infinite), the relative number F(X) of the infinite population lies close to $F_n^*(X)$ and may be approximated by it. Naturally a different sample of size n will lead to another $F_n^*(X)$. However, it is possible to predict, for example, the excursion limits that must be assigned to the estimated F(X) such that 95% of the observed $F_n^*(X)$ will fall within these limits for all X. The main result is that, for large n,

$$g(Z) = \text{probability that } \left| F_n^*(X) - F(X) \right| < \frac{Z}{\sqrt{n}} \quad \text{for all X}$$

g(Z) is a tabulated function of Z. For example, in the case $g(Z) = .95$, $Z = 1.36$. Hence

$$F(X) = F_n^*(X) \pm \frac{1.36}{\sqrt{n}}$$

will guarantee that 95% of the observed $F_n^*(X)$ will fall within those limits.

In cycling a second cell, it is desired to know whether the observed $F_{n2}^*(X)$ are derived from the same F(X) as the observed $F_{n1}^*(X)$ derived from measurements on the first cell. Are the differences significant or not? The main result is,

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(1) "Statistics and Experimental Design in Engineering and the Physical Sciences," Vol. 1, Johnson and Leone, p. 285, John Wiley and Sons, Inc. N. Y.

$$g(Z) = \text{probability that } \left| F_{n_1}^*(X) - F_{n_2}^*(X) \right| < \frac{2Z}{\sqrt{n}} \quad \text{for all } X$$

If the probability of occurrence of the observed differences is small, the difference is significant and may be ascribed to a deficiency in one of the cells.

This test can be used to determine both the variability in the results obtained from cycling a single cell and that from cell to cell.

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