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Synthetic Battery
Cycling Techniques

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SYNTHETIC BATTERY CYCLING TECHNIQUES

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SUMMARY

Synthetic battery cycling makes use of the fast growing capability of computer graphics to illustrate some of the basic characteristics of operation of individual electrodes within an operating electrochemical cell. It can also simulate the operation of an entire string of cells that are used as the energy storage subsystem of a power system. The group of techniques that as a class have been referred to as Synthetic Battery Cycling (Ref. 1) is being developed in part to try to bridge the gap of understanding that exists between single cell characteristics and battery system behavior.

1. BACKGROUND

For many years the nickel-cadmium system has been used for aerospace applications. Typical battery packs are assembled so as to deliver about 28 volts DC. Twenty ampere hours has been a popular cell capacity. There has been an ever-present desire to have the energy storage subsystem weigh less and last longer. Battery systems based on other electrochemical couples have been proposed and now nickel-hydrogen batteries are beginning to be used in space applications (Ref. 2). These promise to be lighter in weight and more forgiving in operation than the more traditional nickel-cadmium systems. Even with nickel-cadmium battery packs, deeper depths of discharge have resulted in an increase in the energy density. Reconditioning or rebalancing procedures (Ref. 3) requiring a certain degree of single cell monitoring and cell switching have also been introduced to aid in the extension of the useful lives of the battery pack. Future missions will require increasingly higher energy densities. One future mission related to a permanent manned space station may require powers in the tens of kilowatts with the suggestion that the voltage level should be 100 volts DC or higher. The possible introduction of new electrochemical couples, the trend toward higher battery voltage levels and the practice of employing deeper depths of discharge all tend to accentuate the problems related to the in-

creased divergence of the individual cell capacities with cycling, to the point where the storage subsystem no longer performs adequately.

The electrochemical out-of-balance that can exist within an individual cell between the anode and cathode material, or the divergence of cell capacities within a battery, results from the cumulative effects of slight differences in the overall electrode efficiencies. It is not the intent of this short paper to address the various failure modes, decay rates, etc. of the various electrochemical couples that are currently under investigation. To be presented here is a methodology for examining the effects of slight variations in electrode properties on a single cell, groups of individual cells selected from a particular population of cells, batteries made from cells selected from a particular population of cells, etc.

Once the causes and effects of certain cell properties and characteristics are more fully understood, cells then can be selected that will result in increased battery lifetimes. Additionally, the use of sophisticated charge control techniques will be required to take advantage of the potentially higher energy density systems that are being considered for applications where high energy density battery packs are required.

2. DESCRIPTION OF THE TECHNIQUE

A full description of synthetic battery cycling has been presented elsewhere (Ref. 1) and will only be covered briefly here. Figure 1 uses two vertical bars to represent the capacity of the two electrodes of a single cell. The electrodes are illustrated here as matched in capacity but that need not be the case. They are also shown to have no excess capacity over and above their rated capacity and that also can be varied. The capacity of an electrode that has undergone cycling can roughly be divided into the following categories: a) a portion that has been permanently lost for a variety of reasons that are peculiar to the system under considerations; b) a second portion that may be lost because the electrodes have become "out of balance", and which could be recovered if the electrodes can be overcharged, c) a third portion is that
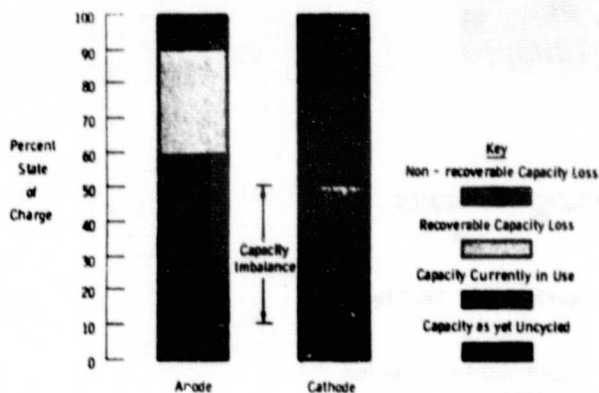
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Figure 1 Graphical representation of an electro-
chemical cell as used in the Synthetic
Battery Cycling studies.

capacity that is currently in use, that is,
undergoing charge and discharge; and d) lastly,
a portion that is currently not in use. This
last category may be looked upon as the reserve
capacity.

The simulated cycling of a cell is done using
computer-generated color graphics (Hewlett
Packard Model 9845-C). The program is set up in
such a manner that a wide spectrum of types of
cells can be examined. The operator has avail-
able a number of options for describing the
cell. The anode capacity and cathode capacity
are selected separately. At this point cathode-
limited or anode-limited features can be intro-
duced. The discharge and charge efficiencies of
the anode and cathode are selected, as well as
the actual ampere hours of discharge and
charge. Another selection permits the specifi-
cation of whether the cell may be safely over-
charged or overdischarged. If not, one must se-
lect whether or not a signal voltage is avail-
able to safely terminate potentially dangerous
overcharge or overdischarge situations. This
entire process of setting up a cycling process
is completed very quickly and easily. Once the
cell type and cycling conditions are selected,
the simulated cycling proceeds until the cell
can no longer deliver the required number of
ampere hours. Depending on the selected condi-
tions, the cycling will simply cease or the cell
will graphically "explode". An option is avail-
able in which a cell that can be overcharged
(Ni/Cd, Ni/H_2) will "recondition" itself when
there is no remaining reserve capacity. That
is, it will recover that portion of capacity de-
fined as recoverable. Cycling will then resume
until that situation is reached again. This is
repeated until the buildup of permanent capacity
loss no longer permits the cell to deliver the
required number of ampere hours. The video for-
matting of this is such that the number of
cycles is updated as cycling takes place.

The model behind the display logic is of course
very important to this technique. The cycling,
as noted earlier, is carried out based on an
ampere hour in and ampere hour out basis. It is
recognized that, particularly at the single cell
level, a wide variety of charging regimes could
be used. However, it is felt that when a cell
is placed in among others in a battery, the
ampere hour counting approach represents the

most reasonable situation. The simple model
used here does not allow for random massive
failures, but rather is a simple wear-out type
of model. Various adaptations and modifi-
cations to the simple basic model could be se-
lected, but only use of the basic model will be
described here in detail.

An electrode will have associated with it a cer-
tain charge efficiency and discharge efficien-
cy. The cell will have a nominal capacity of C
ampere hours and be discharged to a fractional
depth of discharge D. F will represent the
fractional excess capacity at the beginning of
life. The reserve capacity at the beginning of
life will be (1 + F - D)C Ah. The net loss of
capacity per cycle is related to the the frac-
tional depth of discharge D, the efficiency of
the discharge and charge reactions and the
amount of overcharge that is employed to
compensate for any recoverable capacity loss.
In the simplest case, where the same number of
ampere hours are taken from and returned to a
cell, the loss per cycle would be (1 - Eff) x D
x C Ah, where Eff is the cycle efficiency. The
(1 - Eff) term is defined as A. The cycle life
is thus equal to the reserve capacity divided by
the loss per cycle, or to the ratio of (1 + F -
D) x C and A x D x C. The value for A will be
shown to be the most important of all the above
cell model parameters, as it relates to cycle
life. As an example, the case may be considered
where a cell has a nominal capacity, C, of 100
Ah, an actual capacity, (1 + F)C, of 150 Ah at
the beginning of life and a cycle efficiency of
0.99 (A = .01). The cycle life is related to
the depth of discharge as follows:

$$L = \frac{1.0 + 0.5 - D}{0.01 D} = \frac{150 - 100 D}{D}$$

Figure 2 includes a plot of this relationship
showing a life of only 200 cycles at 50 percent
DOD. For an A value of 0.001 the cycle life
would be 1400, for an A value of 0.0001 the
cycle life would be 14,900 and so on.

The graphic displays using two bars are very in-
structive for introducing the concepts of elec-
trochemical imbalance, the use of a signal vol-
tage to terminate the charge or discharge por-
tion of the cycle and the use of reconditioning
or overcharge procedures to extend the cycle
life of a cell. With only a minimum knowledge
of electrochemical theory, the basic principles
of cell life for a single cell can be more fully
appreciated. Once the program has been set up,
little computer knowledge is required to inves-
tigate any number of cases. The program is in-
teractive and provides for prompting of the
user. The simple model for the capacity loss
can be modified by investigators who are speci-
fically interested in a particular cell electro-
chemistry. Specific models of varying degrees
of sophistication have been developed and these
could be substituted for the one used here.
Such changes would increase the power of this
technique as an interpretive tool. The single
cell case then may be viewed as somewhat of an
instructional aid for understanding some of the
fine points of single cell electrochemistry.
The Fall Meeting of the Electrochemical Society
(Ref. 4) will include a paper related to an ex-
tension of the simple model to the actual pre-

$$L = \frac{1.0 + F - D}{AD}$$

$$F = 0.5$$

A = 0.0001

A = 0.0005

A = 0.001

A = 0.005

A = 0.01

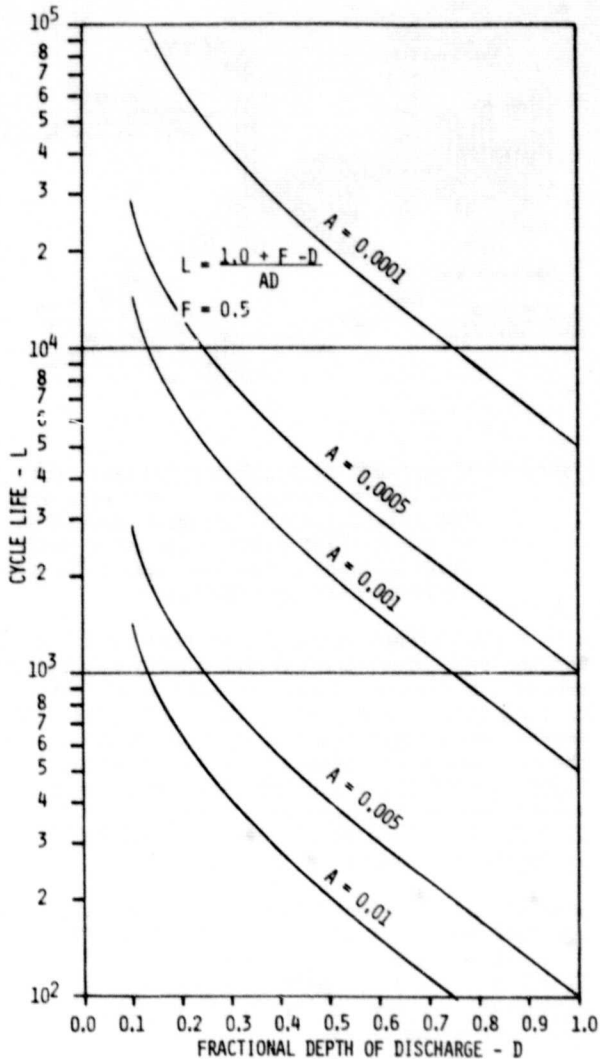CYCLE LIFE - L

FRACTIONAL DEPTH OF DISCHARGE - D

Figure 2 Predicted cycle life vs depth of discharge relationships as effected by the loss factor.

diction of cycle life trends in the form of cycle life vs. depth of discharge relationships. These of course will depend on a number of assumptions related to cell capacity loss rates.

3. MULTI-CELL TECHNIQUES

The multi-cell, or battery case is much more instructive for giving the battery design engineer an appreciation of the cause and effect relationships that are inherent in large electrochemical devices. In battery packs or cell strings or whatever name is used for the grouping of individual cells to provide the voltage, power, and capacity requirements of a particular mission, certain elementary concepts, rules and principles must be appreciated before the battery-level problems can be fully understood. Faraday's Law must be obeyed among cells that are connected in series. The main difficulties which give rise to problems at the battery level

are caused by the fact that each cell is a little bit different from the others. This is caused by a certain degree of randomness that is always present among populations of articles that are intended to be alike in every way. Among cells, for example, there could be a variation in the amount of reactive material within each cell, or the utilization of the reactive material, or the electrode efficiency, etc. What may be an almost imperceptible difference from one cell to the next can very often result in an increasing divergence among cells following repeated cycling. The following covers some of the topics that are currently being investigated under the general heading of Multi-Cell Techniques.

Aerospace applications of energy storage for the most part involve multi-cell strings. As noted earlier single cell monitoring, recondition cycles (Ref. 3), charge control logic, etc. are being used with nickel-cadmium batteries in current use. The tendency for the individual cell capacities to gradually diverge is countered primarily by the careful initial selection of cells to be assembled into the battery pack. The ability to overcharge nickel-cadmium cells as a way of compensating for the randomness of the tendency to evolve oxygen during the charge portion of the cycle has resulted in acceptable cycle lives of batteries based on this system. The use of charge control circuits and reconditiong procedures has extended the cycle lives even further. Although the cycle lives of battery packs that have employed these techniques have been satisfactory, they have resulted in rather low values of energy density. Typically 5 to 10 watt hour/Kg are associated with nickel-cadmium systems cycled to 20 to 30 percent DOD.

Other cell electrochemistries present problems that are more difficult. That is why the modelling techniques to be described in this section should prove to be useful, first in outlining the extent of the problems, and then in suggesting methods of coping with them.

An added level of utility for the modelling approach arises from the use of a subroutine that permits the random selection of the cells for the battery string from a population of mean, m, and standard deviation, σ. The factors that can be randomized are the cell capacities, the individual electrode efficiencies, etc. The variations of characteristics within populations of cells is, of course, an inescapable phenomenon. There is only a question of how large the variation is and what cell selection procedures may be available to minimize it.

Three approaches can be taken to analyze multi-cell groupings. In the first, up to 50 cells are assumed to be in a series string, and all undergo simulated cycling, as described above for single cells. The bar chart indicating the status of each electrode in the string of cells is continually updated until one of the cells exhausts its reserve capacity. The second approach is to switch out the failed cell and continue the simulated cycling of the remaining cells until all the cells in the group have failed. A histogram is then presented on the graphics display, showing the variation of cycle life among the cells due to stochastic consider-

ations. The third approach is used for cells that are connected in parallel. The modelling for this instance requires the use of a main-frame computer to generate and solve the descriptive simultaneous equations. The graphics output has not yet been implemented, but it is intended that the display will show the distribution of the total current between the cells.

3.1 Sets of Series-Connected Cells

As stated above, since the performance of a series string of cells is governed by the weakest cell, graphics simulation of cycling for this case terminates when the first cell "fails." Modelling of this type would have value in making trade-off comparisons between various life-extending techniques such as single-cell switching, bypassing, etc. Such studies will emphasize the importance of power conditioning and will establish the bounds within which it must perform.

3.2 Groupings of Individual Cells

In this approach, each cell is cycled until failure and then a histogram is generated showing the variation of the cycle life that results from the stochastic aspects of the cell set. Using the central laboratory computer (IBM 370) to generate the numerical results and the computer graphics to display the histograms, a range of standard deviations can be evaluated as a family of histograms. Figure 3 shows such a family of histograms in which cycle efficiency is randomized. As would be expected among a
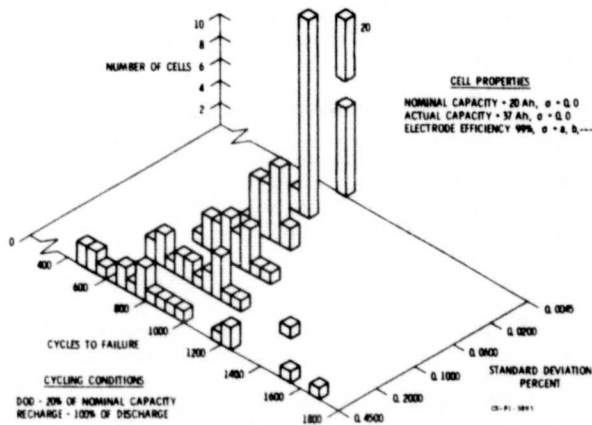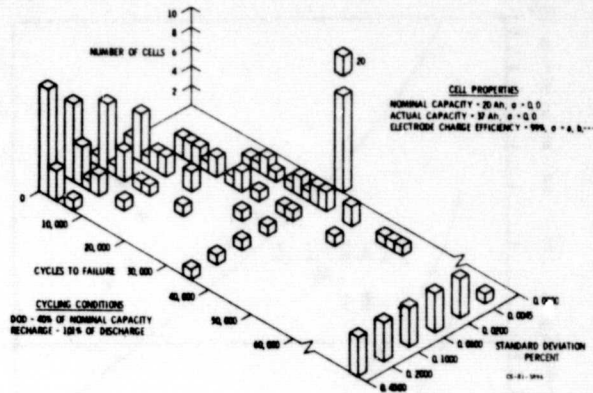
Figure 4 Histograms of Synthetic Battery Cycling results for twenty-cell sets with varying values for the standard deviation of the cycling efficiency under conditions of high dispersion among the individual cell cycle lives.

with a 100 percent recharge, whereas Figure 4 is for the case where the cycling efficiency varied around the mean of 99 percent with a 101 percent recharge. Considering this cell effiency and recharge ratio the A will equal 0.0001. For the case where the standard deviation equals 0.005 percent (2σ = 0.01 percent), the range of values over which A can vary is between 0.0 and 0.0002. For the case where A is equal to 0.0, the cycle life would be infinite.

Statistical variations in the cell capacities do not have such a drastic effect on cycle life since it would take the form of
$(1 + F + 2\sigma - D)$. Figure 5 is a family of histograms for the variation of the amount of reactant in the cells.

Figure 3 Histograms of Synthetic Battery Cycling results for twenty-cell sets with varying values for the standard deviation of the cycling efficiency under conditions of low dispersion among the individual cell cycle lives.

group of cells where there is very little standard deviation, all the cells complete the same number of cycles. As the standard deviation for efficiency becomes progressively larger the histograms at first more or less assume a bell shape. This is followed by a gradual flattening out. This flattening out and progressive splitting as shown in Figure 4 is caused by the standard deviation in the cycling efficiency.
Figure 3 was for the case where the cycling efficiency varied around the mean of 99 percent
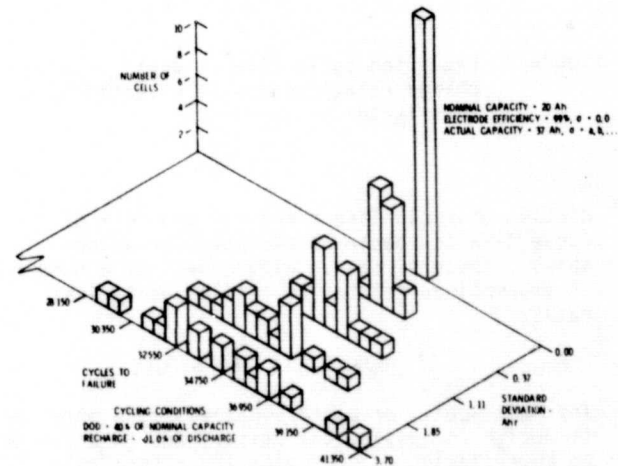
Figure 5 Histograms of Synthetic Battery Cycling results for twenty-cell sets with varying values for the standard deviation of the amount of reactive material within the cell at the beginning of life.

3.3 Cells Connected in Parallel

Such cell assemblies are presently used for the high temperature sodium-sulfur and lithium-

aluminum-iron sulfide batteries. Actually, in the strictest sense, even nickel-cadmium, nickel-hydrogen and other conventional prismatic cells consist of parallel anode and cathode arrays, which are then series-connected to other similar cells. The purpose of paralleling the high temperature cells is to prevent overcharging or overdischarging, by allowing "strong" cells to relieve "weaker" ones of some of their load.

This problem is depicted in Figure 6. The stochastic aspects of interest are the variations in cell resistance and quantity of reactive ingredients for the case of the high temperature cells noted above, and in the plate connector resistance and the reactive material in the plates of the more conventional cells. The solution of the simultaneous loop equations at selected depths of discharge for the individual electrode currents takes a large computer, with the results depicted at the graphics terminal. It is planned to monitor the individual loop currents during the course of the cycling.
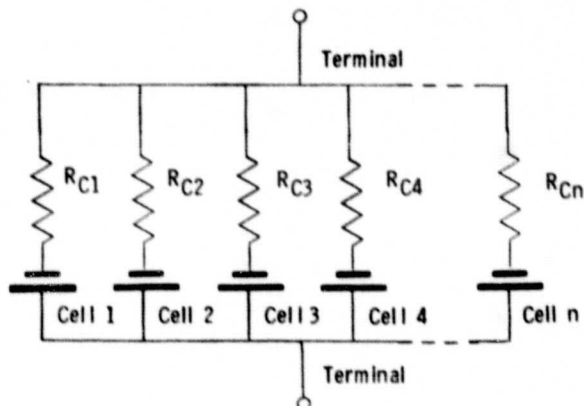

Figure 6   Schematic diagram for a group of cells or electrode pairs connected in parallel.

4.   BATTERY SYSTEMS

Going beyond the cell, set, string, and network problems of the preceeding sections, the ideas of a battery system will be briefly explored. Here, as in the preceeding sections, it is not intended that a complete, final conclusion be presented. But selected examples are presented to stimulate the thinking of others on this topic. Figure 7 illustrates the addition of one
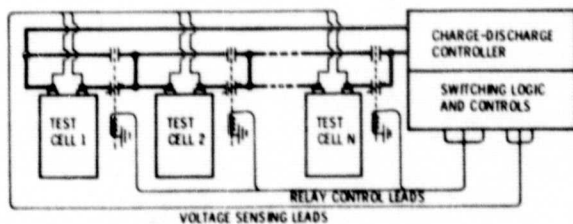

Figure 7   Schematic diagram of a form of single cell charge control that permits individual cell switching.

form of switching logic to the previous example of series-connected cells. This is not considered to be very practical, due to the switching problems for direct current circuits where high voltages and large currents may be present. Power conditioning circuitry could possibly be used to momentarily reduce the current flow using electronic rather than electromechanical means. If that were the case, then smaller switches could be used. In any case, a variety of switching circuits and logic networks can be "designed" into the computer graphics and explored in a preliminary manner prior to the actual construction and test of any actual hardware. As before, different cell populations may be tested using several control logics to see what might be the best way to build a battery system.

Using these techniques, such things as the frequency of switch closures can be counted, and average battery voltage level can be monitored as an aid in assessing the relative merits of several switching networks and control logics. The simplicity, speed and flexibility of these techniques more than compensate for the fact that their accuracy is somewhat limited.

5.   CONCLUDING REMARKS

The techniques of Synthetic Battery Cycling have been used to illustrate the effect of the stochastic aspects that are associated with populations of cells. The results are not intended to be based on an exact model of any particular cell type, but are primarily intended to depict general trends that might be expected from a variety of genetic types of cell electrochemistries. Based on the results presented here, long cycle lives can be expected from groupings of cells that have not only very low loss rates but have a very small standard deviation in the value for the cycling effiency.

Cells that can withstand overcharge can be maintained in closer balance than other cell types

unless the latter have a very low value of loss rate associated with them. Charge control techniques, switching networks and charging logics will become increasingly important as new electrochemical systems or higher voltage systems are considered. These can be explored in a preliminary manner using the general procedures described here.

At the option of those using these techniques, a more formal and exact representation of a particular system can be developed and exercised to predict cycling characteristics based on cell population parameters. This could be used to guide selection of cells from within a particular lot, or, going further, may be used to adjust the manufacturing procedures so as to produce acceptable cell populations.

An illustration of using this technique might give consideration to the cycling efficiency of cells which employ nickel electrodes. Laboratory data may indicate that any percentage overcharge that exceeds a certain value will decrease cycle life. This value could be introduced into the model, which would then be used to evaluate the impact of mean cycling efficiency, and various standard deviations about these means, on cycle life. The graphical representa-

tion of these calculations would help define the cell selection procedures or the cell population characteristics necessary to assure acceptable battery life. The many ways in which these techniques might be of use for any particular battery application is left to the imagination of the reader.

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