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Synthetic Battery Cycling

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SYNTHETIC BATTERY CYCLING

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ABSTRACT

The trend in energy storage is toward systems with high-voltage and high-power outputs. These conditions accentuate the cumulative effects of small differences in characteristics from cell to cell in any large multielement battery. These considerations are of particular concern with a number of the emerging electrochemical concepts where convenient overcharge reactions do not exist. The use of interactive computer graphics is suggested as an aid in battery system development. Mathematical representations of simplistic but fully representative functions of many electrochemical concepts of current practical interest will permit battery-level charge and discharge phenomena to be analyzed in a qualitative manner prior to the assembly and testing of actual hardware. This technique will be a useful addition to the variety of tools available to the battery system designer as he bridges the gap between interesting single-cell life test data and reliable energy storage subsystems.

INTRODUCTION

Synthetic battery cycling is intended to be an aid in developing advanced battery systems as well as in evaluating single-cell electrochemical concepts at any stage of their development. It is built around the use of mathematical representations of very elementary electrochemical principles. It is not intended to be a cell or battery modeling technique.

This technique takes advantage of computer solutions to simplistic but fully representative charge and discharge functions of electrodes, cells, batteries, and finally battery systems where charge control, power processing, etc., are taken into account. Coupling this with real-time graphical simulations of the cell capacity, the balance of capacity between the anode and cathode, and the temporary and permanent loss of capacity due to aging phenomena and charging inefficiencies as a function of the number of simulated cycles will provide the required insight into and recognition of the problems that are present at the battery and system levels that may not be present at the single-cell level.

The rechargeable batteries that have found wide acceptance in applications in and out of the aerospace field are based on the lead-acid and nickel-cadmium systems. This acceptance stems from the fact that these cells, when connected together into a battery, perform for satisfactory lengths of time. For the most part this service duration is limited by the morphological wear-out of the mechanical features of the cells and not deterioration of the electrochemical features of the cells. The somewhat unique characteristics of these two systems permit them to be maintained in what might be called an electrochemically balanced condition. When in electrochemical balance a cell has its maximum capacity per unit of weight. Because of slight differences in the charging efficiency of the anode and cathode material within a cell, there is a gradual departure from the degree of electrochemical balance that existed at the beginning of life. If uncorrected, this would result in a gradual loss of capacity at the single-cell level or a gradual divergence of cell capacities at the battery level, where this difference in efficiency varies in a random manner from cell to cell. These types of problems are of no particular concern in the two aforementioned battery types since a simple overcharge each cycle or an occasional equalization charge restores this electrochemical balance at the cell level.

Not all cell concepts can be restored to electrochemical balance by this type of procedure. The battery-level restoration of balance would represent an even more difficult situation. Various battery-level and single-cell-level charge control techniques can be envisioned that would circumvent the loss of useful capacity at the battery level that results from these problems. This situation can be viewed from the opposite direction as well; that is, what single-cell characteristics would be required to give a certain overall battery capacity loss rate?

Synthetic battery cycling should be helpful in three different but interrelated aspects of battery system development:

(1) Identification of the possible shortcomings of certain electrochemical storage systems that are being considered for development on the basis of their very attractive single-cell performance characteristics

(2) Identification of possible battery charge control techniques that may prove useful in circumventing the shortcomings of certain single-cell concepts

(3) Identification of the most significant areas of research at the single-cell research and technology level that will have the greatest effect on the downstream battery-level problems

The technique of synthetic battery cycling will, of course, be very inexpensive and rapid as compared with real hardware run in real time. The initial outputs of this technique are only intended to be qualitative and general in nature, but the trends should be helpful. With the aid of much real-time test data that has been gathered over the years on cells and battery packs, a measure of quantitativeness can be added to this technique as it applies to certain more fully characterized electrochemical systems.

This report first describes in detail several important cell, battery, and battery system concepts and features. The actual technique of synthetic battery cycling is then described and some examples given.

BACKGROUND

Over the past several decades a number of new electrochemical systems have received considerable developmental attention. Furthermore, aerospace as well as terrestrial applications require not only higher energy density systems, but higher voltage assemblies of cells than is the current state of the art. The difficulties associated with the reliability of large
battery packs has in part resulted in the rapid emergence of what are referred to as fluid batteries, such as the perchlorine, zinc-bromine, and the iron-chromium redox systems, where the commonality of reactive material among the grouping of individual cells permits a degree of leveling out of slight differences between the individual cells. As attractive as the fluid batteries are for certain applications, they tend to be most attractive in multikilowatt or larger systems since in smaller systems the pumps and associated controls reduce the system's overall efficiency. However, it should be obvious that with the more traditional cell and series-connected battery construction, wherein the reactive materials are placed into a container and for the most part sealed, the functionality of the grouping of such cells is very such a function of the "weakest" of them.

Of the electrochemical systems that have found acceptance in multicell arrangements are those based on some rather unique electrochemical features that are described later. Some of the newer electrochemical systems are presently undergoing testing and evaluation at the single-cell level. These systems have many attractive features in terms of energy density, power density, and potential for low-cost production. These technologies are currently addressing the problems associated with the grouping of single cells into batteries with the required energy, power, and voltage. Some of these advanced systems are currently undergoing testing and evaluation at the single-cell level and then at the battery level, which will be the same. The case of the redox couples being 100 percent in balance and present in the same ampere-hour capacities, a cell voltage of 1.50 volts under open-circuit conditions would be expected at 50 percent depth of discharge. By using simple Nernstian corrections a plot such as that shown in Figure 3 (curve A) can be generated. As one of the redox couples becomes out of balance with respect to the other, there is a loss of usable capacity.

What is meant by being 10 percent out of balance can be illustrated by Figure 4. Here two redox half-cell relationships are plotted. One electrode is out of phase relative to the other by 10 percent in terms of the depth of discharge. Another way of stating this is to note that one electrode becomes fully charged while the other is only 90 percent fully charged.

This loss of capacity results from the fact that, as the first of the two redox couples approaches full charge, its half-cell potential will increase very rapidly and charging will cease. Likewise, during discharge as the first redox couple approaches full discharge, its half-cell potential will decrease very rapidly and discharge will be terminated. Figure 3 illustrates the case of being fully in balance (curve A) and the cases of being 10, 20, and 50 percent out of balance (curves B, C, and D). The voltage-capacity curves are symmetrical about the point of 1.5 volts at 50 percent depth of discharge. The span in cell voltage over the range from the point where the first couple reaches 98 percent of full charge to the point where the first couple is 98 percent fully discharged is about the same. The case of the redox couples being 100 percent out of balance results in a point of 1.3 volts at 50 percent depth of discharge with no available capacity. Out-of-balance conditions and the resultant loss of cell capacity occur to varying degrees in most of the electrochemical cells of practical interest. It is not the intent of this paper to list and quantize the side reactions that result in capacity loss at the cell level but only to illustrate in larger systems of the report the effect of this type of capacity loss - first at the single-cell level and then at the battery level, where this phenomenon may well have a distribution from cell to cell, and finally at the battery system level, where attempts are made to optimize certain undesirable single-cell characteristics.

Problems related to out-of-balance conditions need not lead to a permanent loss of usable capacity. By adjusting charging conditions an "overcharge" can
be impressed on the cell, and this causes the electrode that has reached the fully charged condition to unbalance to a secondary electrochemical reaction. The electrode that was in an undercharged condition can now be more fully charged, and under certain circumstances electrochemical balance between the two electrodes can be restored. This rebalancing technique can be carried out each cycle by employing a recharge that results in a greater number of ampere-hours of capacity back into the cell than were withdrawn during the discharge portion of the cycle. Alternately, the rebalance procedure can be performed after a certain amount of imbalanced charge has built up. The various cell technologies that employ these techniques have acquired their own terminology to describe these processes, and they will not be described in detail here. Note that these secondary reactions can present problems of their own. In nonvented cells the products of these secondary reactions must be made to recombine so as not to create a continuously divergent situation. In vented cells the products of these secondary reactions (usually hydrogen and oxygen in the case of aqueous electrolytes) simply are gradually lost from the cell and occasionally water must be added. Not all cells are as simple to rebalance as others. In fact, some electrochemical systems cannot be rebalanced at all because of the disastrous consequences of an overcharge. The capacity loss due to an out-of-balance condition will be only a temporary loss if suitable rebalancing techniques are available, or it may be permanent in the case where there is an absence of suitable rebalancing techniques. Permanent capacity loss at the single-cell level can also result from a number of phenomena that are morphological in nature. To be sure, a cell operated at very high current densities reaches its cutoff voltage earlier, but the losses under discussion here would include loss of active material and/or loss of crystallite surface area caused by the cumulative effects of many charge and discharge cycles.

In summary then, the capacity losses that build up during the course of cycle tests can roughly be divided between those that are related to morphological phenomena and those that are related to electrochemical out-of-balance systems. These latter problems may or may not result in permanent capacity losses, depending on whether suitable rebalancing techniques are available for the restoration of electrochemical balance. Note that a technique fully suitable at the single-cell level, such as a high-voltage cutoff, may not be of use at the battery level. For the most part, charge control techniques for the more advanced battery concepts must include some form of single-cell monitoring and control.

The charging techniques that have found acceptance at the single-cell level are varied depending on the electrochemical system. In general, cells that are at a low state of charge can be charged at a more rapid rate than those that are close to being fully charged. On the other hand, the procedure used for terminating the charge portion of a cycle are peculiar to a particular system. Some cells have a distinctive rise in voltage at the end of charge, and thus a signal voltage is available to terminate the charge process. Other systems use an arbitrary cutoff voltage in order to minimize the charge inefficiencies since they increase rapidly as the state of charge increases. Still other systems use a cutoff voltage that will preclude any possibility of overcharge since no suitable overcharge reactions are available.

The cutoff at the end of discharge is usually fixed by an ampere-hour withdrawal if only a partial discharge is carried out. Otherwise, a low-voltage cutoff is used that takes into account such things as rate of discharge, temperature, and the lowest permissible voltage level. The problems that can occur if the low-voltage cutoff is exceeded depend on the system. Although certain systems can be safely driven in reverse, others would suffer catastrophic failure.

Although a spectrum of cell characteristics is available that covers all the electrochemical systems currently in various stages of development and although within any one system there are situations where overcharge is safe and others where overcharge is unsafe, for the sake of the mathematical representation to be developed in later sections, overcharge and overdischarge will simply be assumed to be either permissible or nonpermissible.

**SINGLE-CELL LEVEL EXAMPLE**

The preceding sections covering rebalance techniques, permanent capacity loss, etc., can now be incorporated into the mathematical representations as outlined earlier. This discussion is not intended to be either exhaustive or final. It is intended to stimulate those in various technology areas to adapt this concept to their own particular interest. At that time the framework used here, called a mathematical representation, will take on more of the form of an electrochemical model. The illustration presented earlier was for the case of purely hypothetical and perfect electrodes. The easiest phenomenon to introduce is that of ampere-hour efficiency. The capacity remaining in an electrode after a certain number of cycles can be very simply calculated once the particulars of the cycle are known and the charge and discharge efficiencies have been set.

As an example, an electrode has 100 ampere-hours of usable capacity. In other words, a 99 percent, a charge efficiency of 99 percent, a 60-ampere-hour discharge, and a 60-ampere-hour charge. Since the charge efficiency is only 99 percent, 99.4 ampere-hours are replaced each cycle. The difference between the 60 ampere-hours of capacity that is withdrawn each cycle and the 100 ampere-hours that is initially available gradually shrinks by a constant 0.6 ampere-hour each cycle. On the 67th cycle this reserve capacity will be exhausted and the electrode will undergo reversal. If the accompanying electrode had an assigned ampere-hour efficiency of 100 percent, the representation of this situation would appear as in Figure 5, after 66 discharge and charge cycles. The "lost" capacity of the anode in the case in point is distributed between might be classed as permanent and temporary losses caused by the existence of a parallel electrochemical reaction that does not result in the charging of the active material. If the assumption is made that one percent of the 1 percent electrode inefficiency represented a permanent loss, then the situation in Figure 3 would appear as in Figure 6. The capacity loss referred to as temporary is recoverable, provided the cathode can be safely overcharged in the amount of 39.2 ampere-hours. Alternatively, if 0.594 ampere-hour of overcharge had been used each cycle, the overall result would have been the same. Of course, with the use of a small overcharge each cycle, the cell would always have the maximum amount of reserve capacity. By assuming various values for the different parameters that are present, a wide variety of synthetic cell cycling tests can be carried out. The tedium of these simple algebraic exercises can be removed with the help of a small computer coupled to a color video tube where the computer-generated graphics are continually displayed and updated as the charge-discharge "cycles" are carried out.

In this manner the effects of certain assumptions and conditions can be quickly seen. It is left to the reader to adapt these techniques to his own interests. It should be noted, however, that the foregoing exam-
ple, where there was an inefficiency of only 1 percent, led to capacity problems after only 66 cycles at the single-cell level. Future cell and battery requirements are geared by cycle lives in the thousands or tens of thousands. This will necessitate either single-cell properties that are currently not known or, alternatively, addressing the energy storage portion of a device from a more system-oriented perspective.

MULTICELL BATTERY-LEVEL EXAMPLE

In the preceding section single-cell synthetic cycling techniques were outlined. Although it is not required, the cycling was based on ampere-hour calculations. Single cells are usually not cycled on this basis. Usually cycling regimes are devised that take advantage of some useful characteristic of the particular system such as a cutoff voltage, a temperature change, or a pressure rise. Besides being the most simple way of “cycling” cells, ampere-hour charging is also one of the most used methods for cycling complete battery packs. It is at the battery level where this technique becomes more than just an interesting exercise in computer graphics. It should be evident that, when a group of cells is electrically connected in series, the same current flows through each and every cell. The problems associated with battery strings are in part related to the variation of parameters that exist within any group of single cells. Small differences in the anode charge efficiency, cathode charge efficiency, rates of permanent capacity loss, etc., result in the gradual spreading of the important cell property of state of charge.

The rapid solution and simultaneous display of the results of the voluminous algebraic calculations that are possible with this technique allow the cumulative effects of phenomena that from cycle to cycle are insignificant to be seen in all their fullness as they develop. This technique is much like time-lapse photography in being able to speed up slow processes, but it has the added benefit of illustrating how these processes, which take place at the single-cell level, have a significant effect at the multicell battery level. A simple illustration of this situation can be shown for a two-cell battery. The cathodes of both cells are assigned efficiencies of 100 percent; or a node of cell 1 is assigned an overall efficiency of 99.9 percent and the node of -11 2, 99.5 percent. It is assumed that the cells cannot be safely overdischarged or overcharged. The matched electrodes (100 Ah) start out in a balanced condition. A cut-off voltage of 5V is introduced and illustrated in the following section. A cutoff condition of 5V is represented by V1, V2, or V3 exceeds or drops below a present value the cell is switched out of the circuit, and adjustments are made in the power processor to compensate for the loss cell in the circuit. If the current can be momentarily brought essentially to zero by electronic means, small relays can be used for the circuit rewiring. If this is not the case, large circuitbreaker equipment must be used. The 5-percent buffer used in the previous case is no longer needed since a “safe” cutoff signal is assumed.

Table 1 lists the assumptions and conditions for “cycling” this battery system. In this example cells 2 and 3 begin by cycling between 0 and 60 percent depth of discharge. The 60 percent cutoff is set by the control electronics of the battery system (ampere-hour) and the 0 percent cutoff is set by a safe high-voltage cutoff. Cell 1 on the other hand will terminate its discharge at 60 percent depth of discharge, as the others, but will reach full charge as signaled by the high-voltage cutoff after only 99.9 percent of the 60 ampere-hours of capacity has been replaced. The missing 0.005 ampere-hour represents a permanent capacity loss since the cutoff voltage cannot be safely exceeded. In cycle 2 then, cell 1 cycles between 0.006 percent depth of discharge between 0.006 percent depth of discharge down to 60.006 percent and then back to 0.012 percent; another 0.006 ampere-hour is again lost. The battery system will maintain its ability to supply 60 ampere-hours until the reserve capacity is initially 40 ampere-hours and cell 1 now cycles between the upper and lower cut-off voltages and cells 2 and 3 will con-
condition of one cell being out at the tail end of the charge if the power-processing equipment can maintain proper power and voltage to user loads under the condition of one cell being out at the tail end of the discharge. If not, these two cells will undergo progressively shallower discharges until the remaining capacity characteristics of cell 1 fall below some minimum acceptable value. Figure 10 depicts cell 1 in the wired-out condition.

Thus far this technique has suggested itself as an aid in predicting cell and battery cycling characteristics based on certain assumed cell parameters. And, in fact, a wide spectrum of cell parameters and their interactions can be evaluated in a short time. However, the problem can be worked in reverse also. Very often a particular application requires a certain cycle life at the battery level. By using this technique the required single-cell characteristics or the single-cell charge control technique can be fixed prior to the actual hardware development and testing. If this is possible, much needless expense can be avoided during the development phases of the overall effort.

CONCLUDING REMARKS

The general topic of synthetic battery cycling has been introduced. It is meant to be a versatile tool in the very important field of battery system development. The differences between single cell, battery, and battery system considerations have been emphasized since they are very important in helping to judge the potential usefulness of various electrochemical concepts that are under development. The development of this technique, which will be built around the use of interactive computer graphics, has just begun. It is not currently viewed as a model of any particular system, although the reader may find this type of technique useful for his particular area of interest and adapt these ideas and principles to a more specific model rather than the general mathematical representation presented here. Only the essence of the full utility of this technique was addressed in this brief report. Much has been left to the skill, imagination, and special areas of interest of the many groups of technologists that are currently pursuing the development of any number of new and different electrochemical systems. Only the most simple cases were used as illustrations of the ways to use this general method. Besides the utility that the technologist may gain in addressing the most important developmental problems, computer interactive graphics will also be very useful in illustrating rather subtle aspects of battery-level electrochemical considerations to those that might be considered nonspecialists.

When more fully developed, this method of cell, battery, and battery system analysis will be able to simulate

1. Cell and battery state of charge (anode and cathode)
2. Cell and battery capacity loss mechanisms
3. Cell and battery overcharge and reversal characteristics
4. Cell and battery rebalance and capacity maintenance techniques
5. Single-cell control techniques used in battery systems during charge and discharge
6. Battery and battery system-level performance and life expectations for various distributions of critical cell parameters

This, of course, is only a partial list, and much is left to the reader to adapt synthetic battery cycling to his own particular needs. The parameters that will be varied as this method is further developed include

(1) Anode and cathode charge and discharge efficiencies
(2) Relative active mass (capacity) of the anode and cathode
(3) Depth of discharge
(4) Percent of overcharge (if permissible)
(5) Rate of permanent capacity loss

The resultant outputs then will be able to illustrate in principle the following situations:

1. The cumulative effects of small cell-to-cell differences
2. Safe or unsafe overcharge conditions
3. Safe or unsafe overdischarge conditions
4. Rates of recoverable and nonrecoverable capacity loss
5. Reconditioning cycles and charge equalization cycles
6. The divergence of cell-to-cell capacities within a battery or battery system during the life of the "test" article
7. The relative merits of various single-cell charge control techniques

Note that these lists are more generic in nature than specific. The effects of various recombination rates, temperature rise, or pressure rise on overcharge; the significance of "soft" shorts; and capacity-rate effects are more specific to certain technologies and can, of course, be incorporated into synthetic battery cycling when the mathematical representation is converted into more of a model for nickel-cadmium, nickel-hydrogen, or lithium aluminum - metal sulfides batteries, or whatever is of interest.

REFERENCES


TABLE I. - ASSUMPTIONS AND CONDITIONS FOR THREE-CELL BATTERY PACK

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Figure 1. - Simplistic diagrams for single-cell, battery string, and battery system test equipment.

(a) Single-cell test apparatus.  
(b) Battery string test apparatus.  
(c) Battery system test apparatus.

Figure 2. - Mathematical representation of a single cell.

ASSUMPTIONS

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CAPACITY CURRENTLY IN USE

CAPACITY AS YET UNCYLED
Figure 3. Voltage as a function of depth-of-discharge characteristics of a cell at several degrees out of balance.

Figure 4. Out-of-balance half-cell and resultant full-cell potential as a function of depth-of-discharge relationships.
**Figure 5.** - Mathematical representation of a single cell illustrating development of out-of-balance situation.

**Figure 6.** - Mathematical representation of a single cell illustrating partial restoration of balance using a rebalance technique.
Figure 7. - Mathematical representation of a two-cell battery at beginning of life.
ASSUMPTIONS

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Figure 8. - Mathematical representation of a two-cell battery illustrating development of divergent, out-of-balance conditions.
Figure 9. - Mathematical and schematic representation of a three-cell battery system featuring cells that may be switched in or out of the battery string. (Illustrated - all cells in; all cells at zero percent depth of discharge.)

Figure 10. - Mathematical and schematic representation of a three-cell battery system featuring cells that may be switched in or out of the battery string. (Illustrated - cell 1 switched out; 6667 cycles.)