Thermal and Cycle-Life Behavior of Commercial Li-ion and Li-Polymer Cells

Albert H. Zimmerman and M. V. Quinzio
Electronics and Photonics Laboratory
The Aerospace Corporation
El Segundo, California 20245

Abstract

Accelerated and real-time LEO cycle-life test data will be presented for a range of commercial Li-ion and Li-polymer (gel type) cells indicating the ranges of performance that can be obtained, and the performance screening tests that must be done to assure long life. The data show large performance variability between cells, as well as a highly variable degradation signature during non-cycling periods within the life tests. High-resolution Dynamic Calorimetry data will be presented showing the complex series of reactions occurring within these Li cells as they are cycled. Data will also be presented for cells being tested using an Adaptive Charge Control Algorithm (ACCA) that continuously adapts itself to changes in cell performance, operation, or environment to both find and maintain the optimum recharge over life. The ACCA has been used to prevent all unneeded overcharge for Li cells, NiCd cells and NiH_2 cells. While this is important for all these cell types, it is most critical for Li-ion cells, which are not designed with electrochemical tolerance for overcharge.

Introduction

The development of lithium-ion battery cells that are capable of long cycle-life for commercial applications has tempted satellite power-system engineers for years with the promise of smaller and lower weight battery systems. However, the accumulation of the performance history and databases necessary to assure high reliability over long-term space missions as well as the needed optimization of lithium-ion power systems, have made the anticipated transition to lithium-ion batteries in satellite systems quite slow. One of the leading satellite types expected to advantageously utilize lithium-ion technology is nanosatellites and picosatellites. These satellites are very small, typically in the 100g to 10 kg range. Because of their small size, very compact and lightweight batteries offer compelling advantages. Because of their relatively low cost and generally limited life requirements (1-3 years in low earth orbit is typical), commercial lithium-ion battery technology provides a promising power system option for these classes of satellites.

Here we will present performance data and thermal characteristics of selected commercial lithium-ion battery cells to illustrate some of the key advantages of these batteries for small satellites, as well as some of the issues that must be handled to reliably integrate these batteries into a successful power system.

Cycle-Life Measurements

The cycle life of a lithium-ion battery must be adequate to support worst-case mission needs with sufficient margin to assure high reliability when cell performance variability is considered. One issue that has been noted for lithium-ion battery cells is that cycle life performance can be highly variable, depending on the details of how cells are built and how they are tested. It should be pointed out that this experience matches that obtained early in the use of nickel cadmium and nickel hydrogen cells, where large variability in performance taught many lessons related to cell design and charge management practices. Given this situation, it is key to the use of lithium-ion batteries that appropriate test and screening regimens be developed to assure that all cells selected for satellite use will perform well with the anticipated charge control system. To this end we have developed an accelerated cycling test that will rapidly indicate the cycle-life capability of lithium-ion battery cells.

A key difficulty in assessing the cycle-life capability of lithium-ion cells is the strong coupling between cycle life and both charge-management and operational temperature. This kind of coupling is not really surprising, since it has also been found to be the rule for other kinds of battery cells, most notably nickel cadmium and nickel hydrogen. As for these other types of battery cells, databases must be developed that show precisely how temperature and different charge management variations affect cycle-life. To help gather such data we have developed a simple accelerated life test protocol that is based on a simple doubling of the cycle-times normally associated with low-earth-orbits. This test employs a 45-minute cycle consisting of 15 minutes for discharge and 30 minutes for recharge, and operates the cells at 20% depth-of-discharge (DOD). Recharge is at a C/2 rate, with a constant voltage limit of 4.0 or 4.1 volts, and test temperature is 20 deg C. Thus, this test applies the currents normally anticipated at 40% DOD in a standard 90-minute LEO cycle. The test is therefore very sensitive to the increases in resistance that have often been seen to accompany or forewarn premature cell degradation, while allowing a x2 acceleration factor in cycle numbers. Whether this acceleration factor of 2 applies to standard LEO orbital usage remains to be debated, and ultimately will be established based on the test data.

This accelerated life test has been applied to a range of commercial Li-ion cells to determine anticipated performance. Figure 1 shows the relative cycle life performance of two types of SONY 18650 cells. Cell type A was acquired in 1994 and remained stored in the laboratory until 1999, when the cells were put on test. Cell type B was acquired in 1999 and immediately put on test. These two types of cells reflect the changes in cell design over a 5-year period for SONY. It should be noted that the type B cells had at least a 10% greater beginning-of-life capacity relative to the type A cells. These cells are being tested at a 1.5 Ah nameplate capacity and recharge is to a 4.1-volt limit.

There are several noteworthy results in Figure 1. First, after about 16,000 cycles of testing, it has become clear that both the type A and the type B cells are capable of a very long cycle life. Extrapolation of the observed degradation slopes yields a cycle life in excess of 50,000 for all these cells. The other noteworthy result is that the degradation rate for the newer type B cells is about twice that of the older Type A cells, in spite of the greater capacity in the newer cells. This was expected, and is at least partially a result of the utilization of a graphitic carbon in the anodes of the newer cell design, thus providing higher voltage and capacity at the cost of more rapid degradation of the highly ordered graphite structure. These results, however, clearly demonstrate that it is important to routinely screen the performance of each lot of commercial cells acquired for space use so that such changes in design or performance will be detected prior to flight.

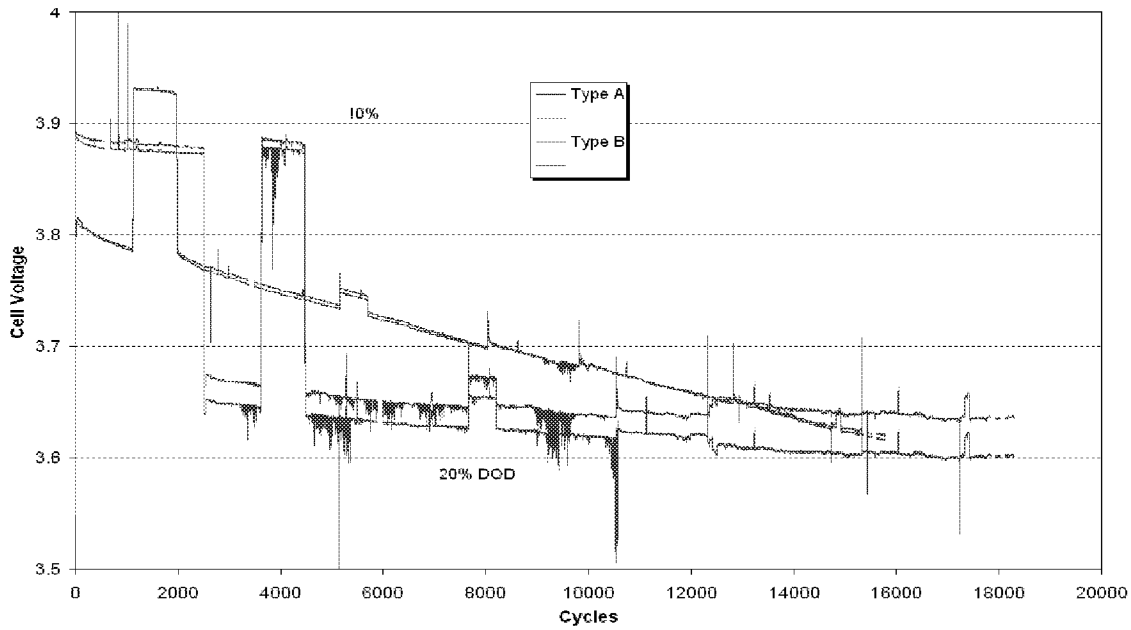

Figure 1. Comparison of Accelerated Cycling Performance for Type A and Type B SONY 18650 Cells.

The need for cell screening can be made dramatically clear by the results in Figure 2, which shows the relative performance obtained for cells from two different lots of cells that were built about 2 months apart. These are lithium-polymer cells, which are of significant interest in nanosatellites because they can be sandwiched into the satellite

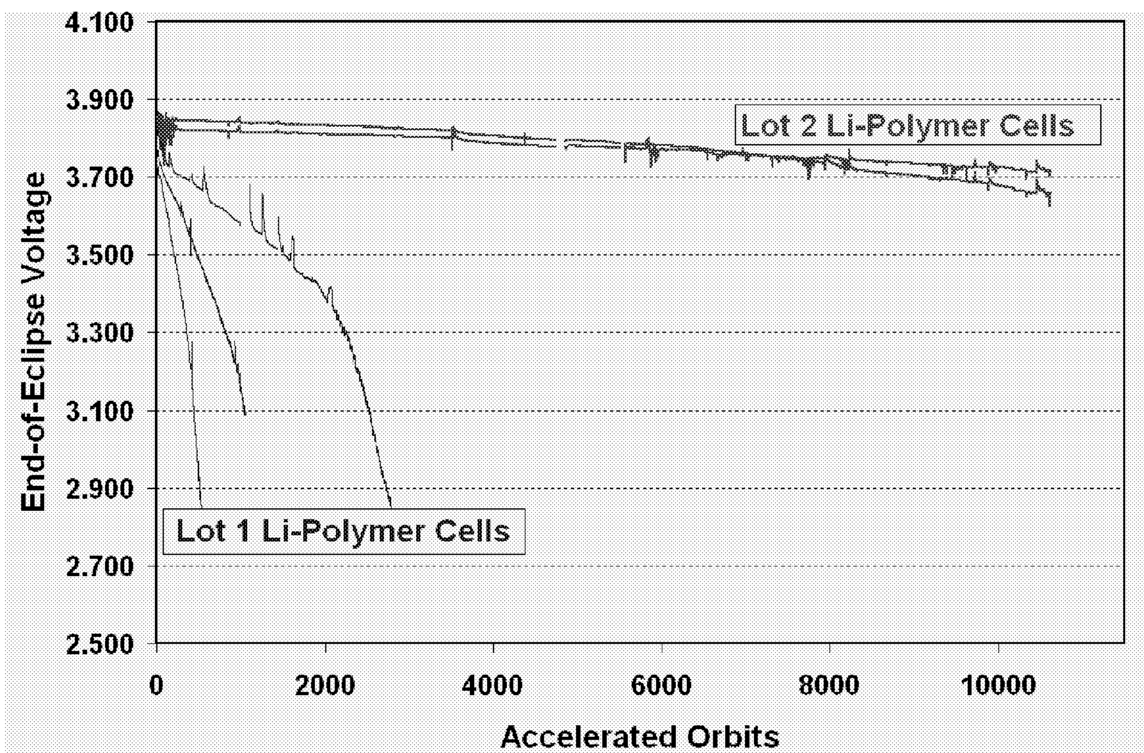

Figure 2. Relative Accelerated Test Performance of Two Lots of Li-Polymer Cells.

structure much more easily than the cylindrical 18650 cells. As noted in Figure 2, cells from the first lot operated only 1000 to 3000 cycles before failing, while cells from the second lot operated 15,000 cycles.

The issue of optimum charge control for lithium-ion cells is an area that has not been fully resolved. As indicated in Figure 1, simple recharge to 4.1 volts each cycle, then allowing the current to taper at the 4.1-volt limit can be very effective. However, the optimum recharge voltage level may not always be 4.1 volts. It may vary with the cell design, temperature, electrode degradation over life, recharge rates, or a variety of other parameters. One indication that this is indeed the case is shown in Figure 3, where the performance of four 1.5 Ah lithium polymer cells from the same build lot is indicated. Two of these cells were cycled with a 4.1-volt recharge limit and the other two were cycled with a 4.0-volt limit. The cells cycled to 4.1 volts started out with a much higher discharge voltage, however they did settle in on a more rapidly dropping voltage as cycling progressed. The cells cycled to 4.1 volts also developed a downwards curve to their end-of-discharge voltage that ultimately made them fail long before the cells that were only being recharged to 4.0 volts. It is noteworthy that the cells cycled to 4.0 volts have degraded with a slow linear slope to the end-of-discharge voltage, thus not displaying any tendency to develop a curving down drop-off.

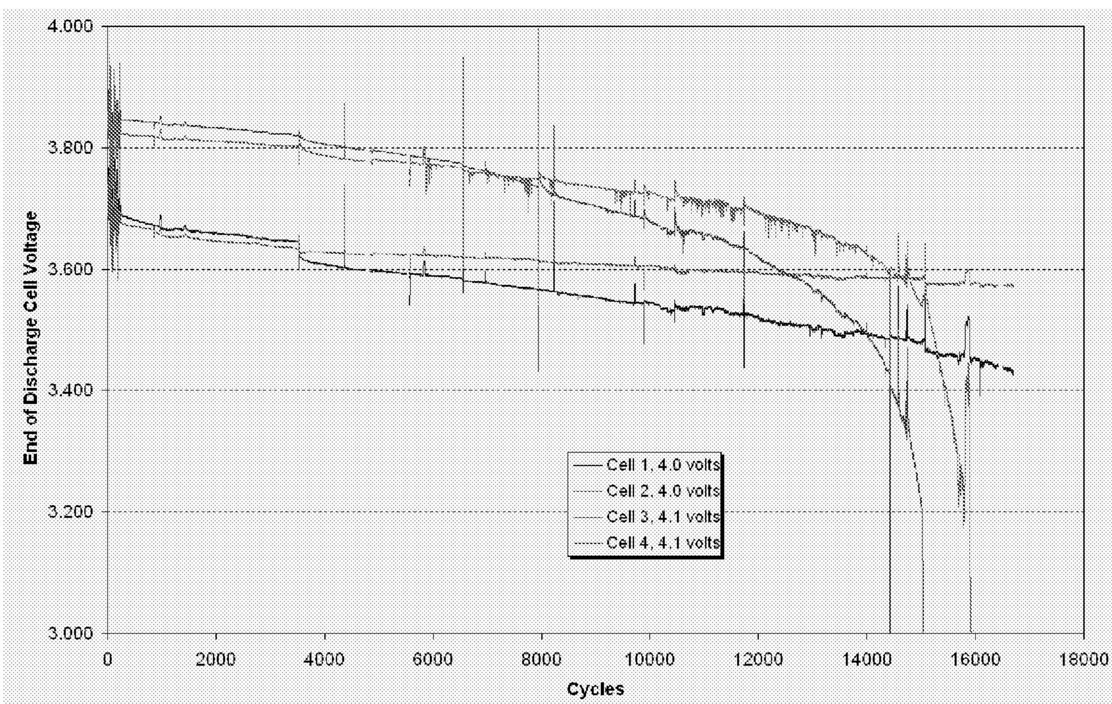

Figure 3. Relative Performance of Lithium-Polymer Cells Charged to Different Voltage Limits.

The results in Figure 3 can be interpreted to suggest a different failure mode coming into play when these cells were cycled to 4.1 volts, which was not the main degradation mode at a recharge limit of 4.0 volts. One suggestion is that the rapid and curving drop-off in end-of-discharge voltage is due to capacity loss, which was significantly accelerated by recharge to the higher voltage. This rapid and curving drop-off is superimposed on a more linear drop-off that is due to increases in the impedance of the electrodes and electrolyte as the cells are cycled. For the cells cycled to 4.0 volts, the increasing impedance of the cells appears to be the dominant degradation mode, explaining why no tendency has yet been seen for the end-of-discharge voltage to curve downwards. These results clearly suggest that limiting the added degradation mode at the higher voltages for these cells can significantly increase their expected performance life and reliability in a satellite power system, at the cost of some lesser performance at beginning of life.

The data in Figure 3 also show another potential issue with lithium ion cells. At about cycle 3500, a two-week test shutdown occurred due to the failure of some test equipment. During these two weeks the cells were left in the fully charged state (either at 4.0 or 4.1 volts). When the cycling resumed, all the cells adopted an increased degradation rate, except one of the cells being charged to 4.0 volts. In addition several of the cells displayed a step decrease in the end-of-discharge voltage in response to simply standing open circuited for two weeks in the fully charged state. Both the variability in how this stand period impacted the cells, as well as the performance loss itself are a significant concern. These results indicate that cells should be maintained at a less than fully charged state during known periods where no cycling or very shallow cycling is required. This is a charge management capability that must be built into the satellite power system, since in many low-earth-orbits there are sometimes periods of up to several weeks when no battery cycling is required.

The accelerated testing that has been done on a wide range of lithium-ion and lithium polymer cells suggests that the initial downward slope in the end-of-discharge voltage is a good relative indication of degradation rate and ultimate cycle life. If we examine the slope over the first 2500 cycles of test, those cells that failed most rapidly always had a higher slope. While simple extrapolation of slopes to a failure point could be deceiving due to the accelerating drop-off for some cells, in all cases these cells had a higher early slope than did cells that did not exhibit downwards curvature towards end-of-life. Thus, we propose a 2500-cycle accelerated screening test be performed on a sampling of commercial cells from each lot intended for use in satellites. While this test can be performed at any temperature, we recommend 20 deg C as a good standard temperature. The charge voltage limit for this test should be based on that anticipated in the power system, but based on our data a 4.0-volt limit is recommended.

Dynamic Calorimetry Results

The heat generation from lithium-ion cells is important both for designing a thermal control system that can adequately handle the end-of-life thermal environment, and for observing the electrochemical processes within an operating cell. The voltage of a lithium-ion cell typically does not clearly show steps and plateaus corresponding to the changing processes in the cell. However, the thermal behavior of a cell is capable of separating quite subtle changes in the cell reaction processes. Heat generation from lithium cells was measured here using dynamic calorimetry. This technique provides accurate heat generation rates or rapidly changing systems, and thus is applicable during high rate charge or discharge. Heat generation is sensed by the response of tiny thermistors attached to the sides of a cell. The cell is immersed in a fluid bath that is held at a constant temperature (to $\pm$0.0002 deg C), and heat generation is determined from the response of the thermistors which respond to the small region of the cell wall to which they are attached. Typical maximum thermal excursions for these thermistors are about 0.1 deg C for 1.5 Ah lithium-ion cells. This heat measurement system is calibrated by balancing electrical and thermal energy over a complete stabilized charge/discharge cycle, and typically has a thermal time constant of only several seconds.

Figure 4 shows a typical charge and discharge voltage, which has a number of subtle inflections during recharge and discharge, but no clear indication of changing electrochemistry as the cell is cycled. Figure 5 shows how the heat generation from a 1.5 Ah lithium-polymer cell varies during charge and discharge at 20 deg C, and compares

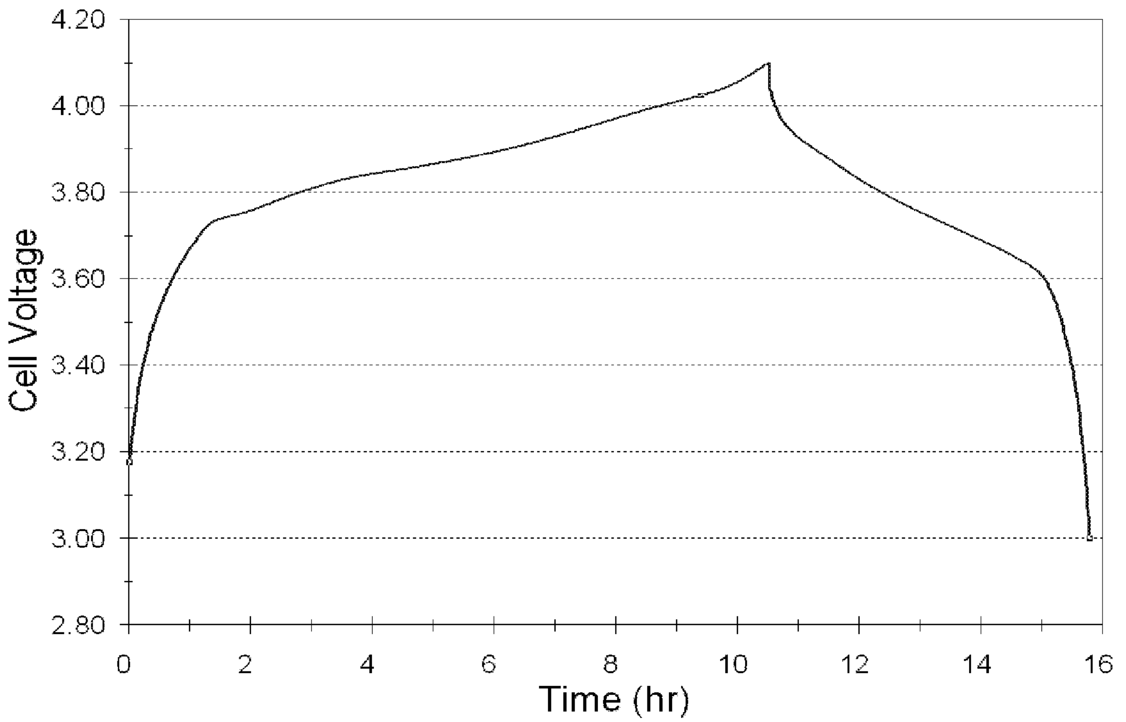

Figure 4. Typical Charge and Discharge Voltage for a Lithium-Polymer Cell.

the heat generation to the voltage profile. There are clearly a number of step changes in the heat production by this cell as it goes through several endothermic processes at the start of recharge, followed by several exothermic processes. All of these processes appear to be fully reversible, i.e. they appear during discharge as well as during recharge with the exception of the exothermic spike seen at the start of recharge. This exothermic spike is always seen for this particular type of cell, suggesting that some reactive material has been formed during recharge that is initially discharged. While this raises some concern regarding cycle life for this cell design, cells that are on test appear to be capable of about a 20,000 cycle life at 20% DOD.

The thermoneutral voltage of the cell may be determined during charge and discharge from the heat generation data. The thermoneutral voltage is the voltage at which no heat is generated during charge or discharge. Figure 6 indicates the thermoneutral voltage along with the cell voltage for a 1.5 Ah lithium-polymer cell. There are clearly a number of staging processes taking place during intercalation as the cell charges and discharges, and which correspond to the changes in heat generation seen in Figure 5.

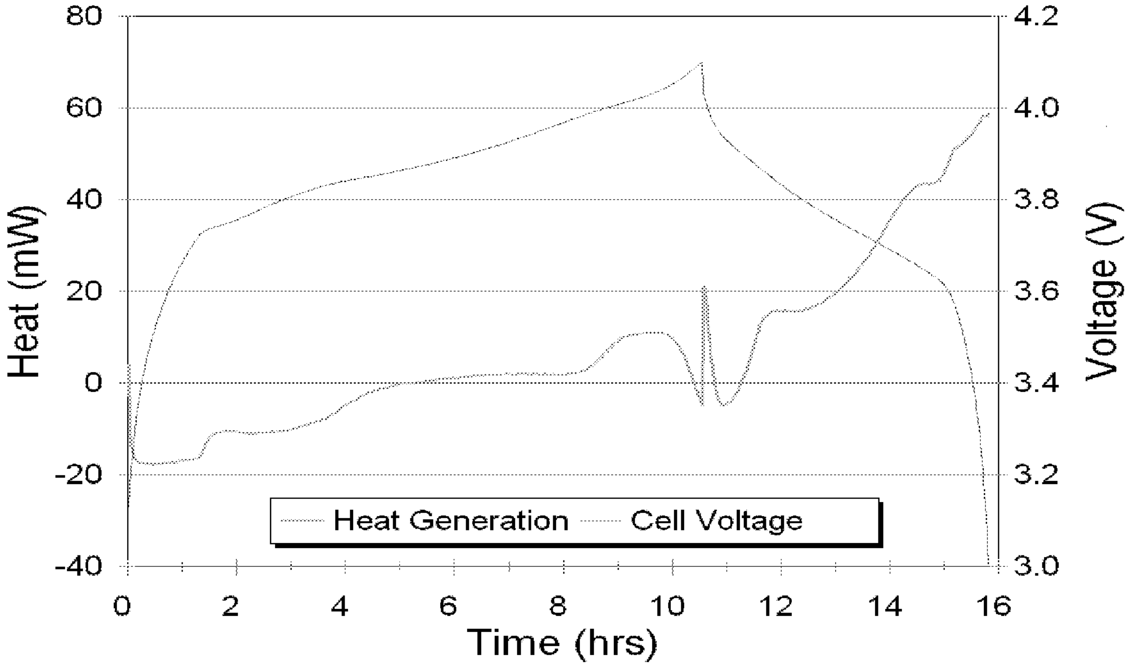

Figure 5. Lithium-Polymer Cell Heat Production during Charge and Discharge.

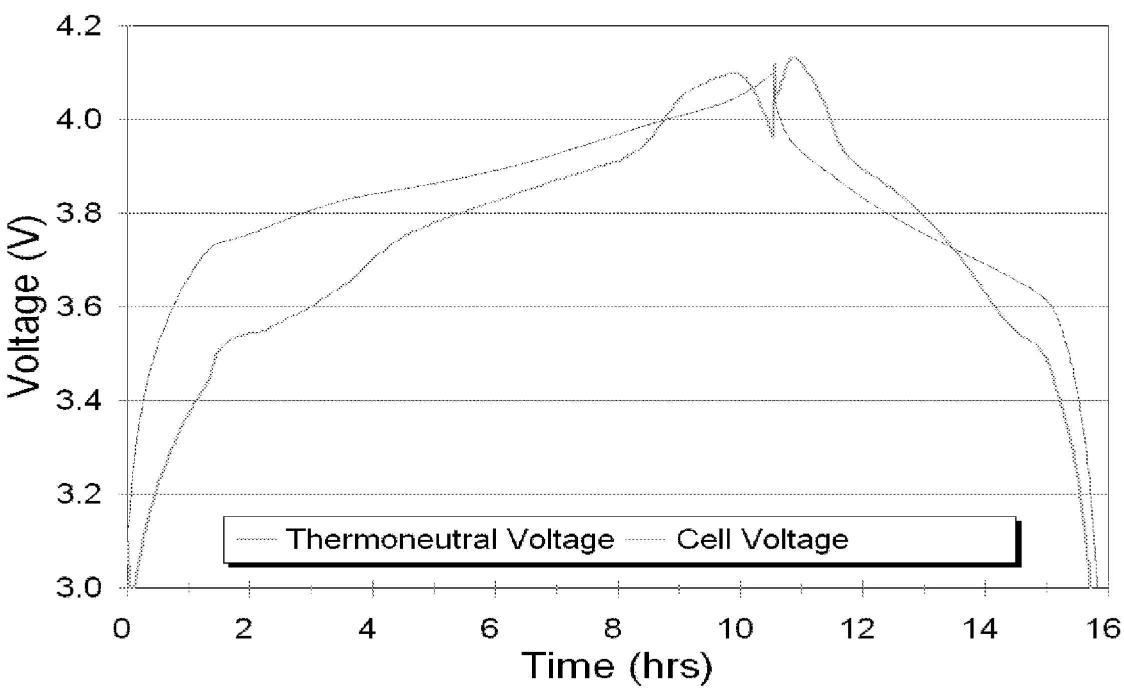

Figure 6. Lithium Polymer Cell Voltage and Thermoneutral Potential during Charge and Discharge.

Adaptive Charge Control Algorithm

The long-term performance of most rechargeable batteries is degraded by unnecessary overcharge. While nickel cadmium and nickel hydrogen cells can tolerate overcharge, any overcharge that is not needed to maintain the state-of-charge does indeed tend to diminish cycle life. Lithium-ion cells have no internal mechanism to allow them to tolerate overcharge, thus any overcharge not needed to keep them charged adequately should be avoided if long cycle life is required. We have developed an adaptive charge control algorithm that applies recharge based on keeping track of recharge ratio, and which continuously adjusts the applied recharge ratio to prevent any overcharge that is not needed to maintain the state of charge. This algorithm automatically adjusts for inaccuracies in the recharge ratio measurement, for temperature variations, electrode or cell degradation, as well as current or DOD changes. In this way this algorithm seeks to prevent any unneeded overcharge over cycle life, which should optimize the cycle life from a given lithium-ion cell design.

Figure 7 indicates a test of this algorithm on a pair of NiCd cells. The algorithm required about 550 cycles to adapt itself to the needs of a NiCd cell, settling out with a recharge ratio of about 101% in this 20% DOD test. Figure 8 indicates another test of this algorithm for a 0.75 Ah commercial lithium-ion cell pair operated in a thermal vacuum environment that simulated low-earth orbit operation at 20% DOD. These cells operated for over 2200 cycles with little evidence of significant degradation. The dithering of the voltages in Figure 8 is due to the continuous adjustments in the cell recharge as the adaptive algorithm verifies that it is maintaining the optimum recharge conditions. Figure 9 shows a similar simulated low-earth orbit test of two 1.5 Ah lithium-polymer cells in a nanosatellite mass simulator operated in a thermal vacuum chamber. In Figure 9 we again see the dithering as the algorithm continuously adjusts the amount of recharge applied to the cells, which is controlled on an independent cell basis. These two cells do show some evidence of degradation after about 3000 cycles, which is recognized by the gradual decrease in the average end-of-discharge voltage and increase in the end-of-charge voltage. In this test the end of life will occur when the average end of discharge voltage reaches 3.0 volts and the peak recharge voltage reaches 4.1 volts.

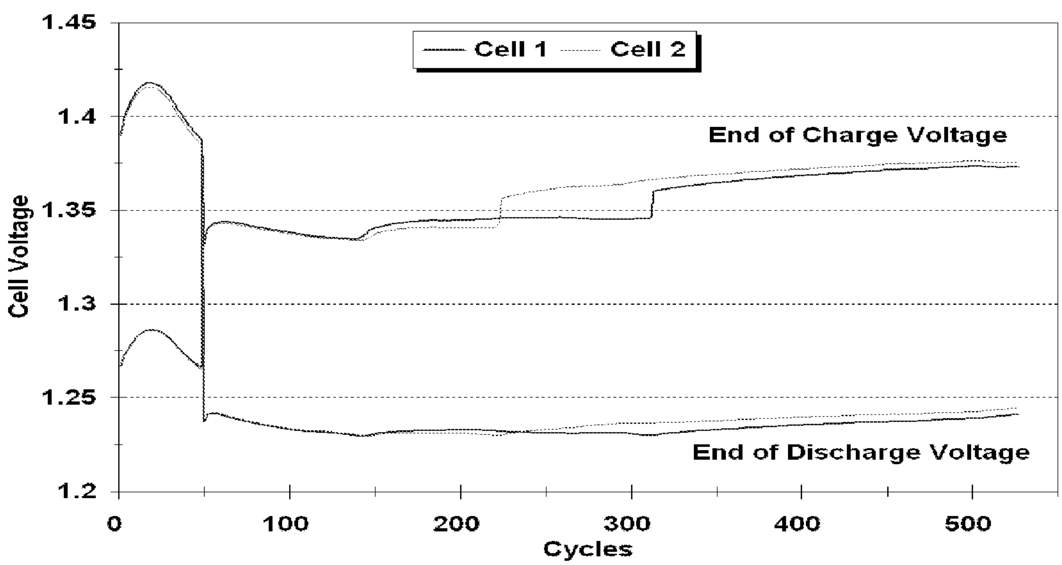

Figure 7. Adaptive Charge Control Test for 2 NiCd Cells.

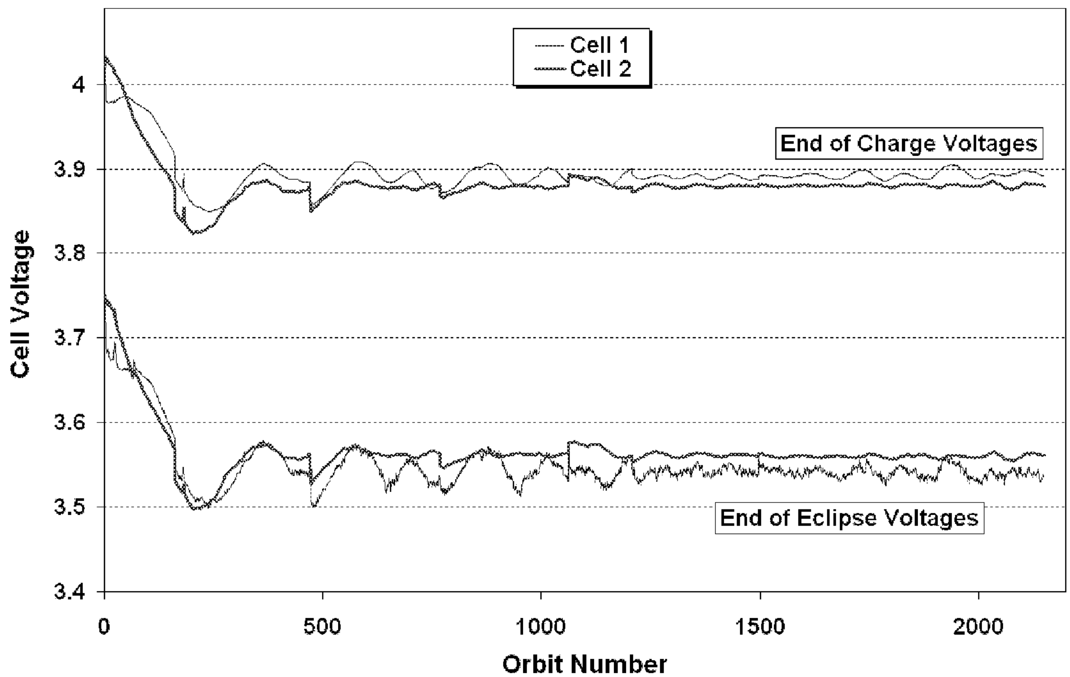

Figure 8. Adaptive Charge Control Test for Two Lithium-ion Cells.

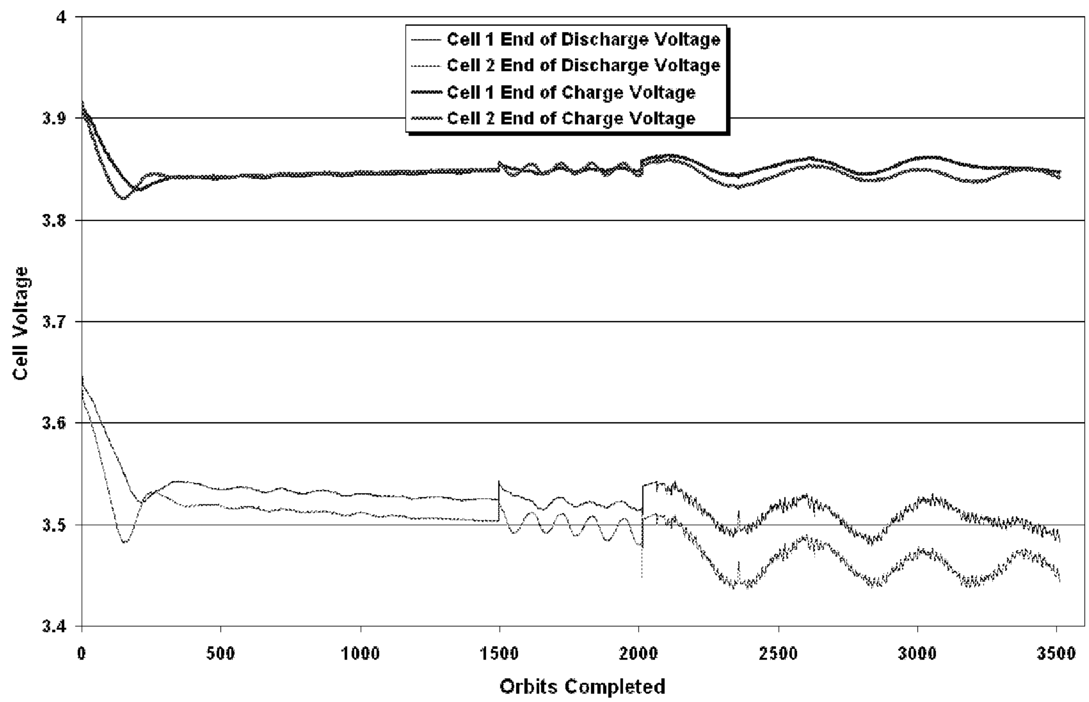

Figure 9. Adaptive Charge Control Test for Two Lithium-polymer Cells.

The Adaptive Charge Control Algorithm method for the charge management of lithium ion batteries can offer a minimum stress cycling regime that will change in response to changes in the cell electrodes, resistance, or environment to maintain minimum stress. This approach is capable of actually optimizing the cycle life of a lithium-ion battery. Additional testing of this algorithm with spacecraft type lithium-ion cells is expected to begin shortly.

Conclusions

An accelerated cycling test has been developed that can screen lithium-ion test cells from a given lot in 2-3 months of test time, and is based on the degradation seen in cell voltages over the first 2500 cycles. Evidence has also been seen suggesting that some lithium-ion cells do not respond well to periods of stand in a highly charged state. Calorimetry measurements on a wide range of lithium-ion and lithium polymer cells invariably show a rich chemistry of staging processes as lithium ions undergo stepwise intercalation into the electrodes. Calorimetry can also provide an extremely sensitive method for detecting changes in cell design or chemistry over time, as well as verifying the thermal design of a satellite for a given type of cell at end of life.

An Adaptive Charge Control Algorithm has been discussed that is capable of automatically adapting to the charge needs of a battery cell so as to maintain an optimized recharge protocol for minimizing stress due to cycling. Data have been presented demonstrating the functioning of this algorithm for NiCd, lithium-ion, and lithium-polymer batteries.