

Performance of SONY 18650-HC Lithium-Ion Cells for Various Cycling Rates

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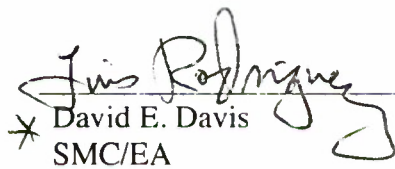
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 * For Mr Dave Davis
* David E. Davis
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Five different life tests of SONY 18650-HC lithium-ion cells have been run for up to 10 years. These tests evaluate the 18650-HC lithium-ion cells under conditions ranging from rapid cycling at 32 cycles per day, to slow cycling at 90 cycles per year, to stand tests that involve no cycling at all. These tests examine the self-discharge of the cells, the divergence between cells in batteries, and their degradation rates as a function of the cycling rate and calendar life for cells manufactured at several points in time.

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1. Introduction

The long-term performance capability of commercial lithium-ion battery cells has been of significant interest since the early 1990s when SONY began producing the 18650 cell size in a version that appeared to demonstrate exceptional stability during long-term cycling applications. Here, we report on the status of tests that have been performed on the SONY cell design that uses a hard carbon anode, generally termed the 18650-HC cell. The cells that have been tested were built either in the 1994 or the 2002 time period. The cells that were built in 1994 were stored at ambient temperature for about 5 years before their testing was begun in early 1999. These 1994 cells had an actual capacity at the start of testing of about 1.2 Ah, and were rated at 1.00 Ah for these tests. The 2002 cells had an actual capacity of about 1.4 Ah, and were rated at 1.20 Ah for these tests. The cells that were built in 2002 began testing very soon after they were manufactured.

The testing described here involves three different cycling regimes, thus allowing the performance of these cells to be evaluated under conditions of no cycling up to very rapid cycling conditions. Test regime 1 involves rapid cycling at about 20% depth of discharge, with 32 cycles being done per day. Test regime 2 involves slow cycling at about 75% depth of discharge, with 90 cycles being done per year. Test regime 3 involves no cycling at all, with batteries or cells being held either on float charge or on open circuit. The details for each of the tests summarized in this report are provided in Table 1.

Table 1. Details of 18650-HC Cells Tests Summarized in This Report

Test #	Cell Date	Name Plate Ah	Pre-Test Storage (yr)	# Cells on Test	Test Temp. (°C)	Avg. Cycles/Day	Charge Control	Depth of Discharge(%)	Cycles Complete
1	1994	1.00	5	2	20	32	Cell, 4.1 V	22.50	109,087
2	2002	1.2	0	2	20	32	Cell, 4.1 V	18.75	73,567
3	2002	1.2	0	8	23	0.25	Battery	75.00	672
4	2002	1.2	0	8	23	0	Battery	0 (float)	0
5	2002	1.2	0	4	23	0	Cell, 3.6–4.1 V	0 (OC)	0

2. Test Profiles

2.1 Test 1

Test 1 operates two cells that were made in 1994, stored at ~3.6 V for 5 years at ambient laboratory temperature, and then began cycling in 1999. These cells are discharged in series at 0.9 A for 15 min each cycle, and then are recharged for 30 min at a peak rate of 0.75 A with a cell voltage limit of 4.1 V for each cell. This gives a 22.5% depth of discharge based on the 1.00-Ah nameplate capacity of this cell type. Cell temperature is controlled at 20°C at the coldest part of the cycle, which is at the end of the recharge period. This test runs 32 repeated cycles per day, and 11,680 cycles per year if there is no test down time. The 109,087 cycles completed to date corresponds to 85.59% test operating time and 14.41% test down time over the nearly 11-year duration of this test. Figure 1 shows the cell voltage and current for a typical cycle.

2.2 Test 2

Test 2 operates with a test profile and temperature identical to that described above for Test 1. The only difference is that Test 2 contains two cells that were made in 2002, and which started test immediately with no storage prior to testing. These 2002 cells had a higher capacity and were rated with a nameplate capacity of 1.20 Ah. This resulted in an 18.75% depth of discharge for the 32 cycle per day test profile described above. The 73,567 cycles completed to date corresponds to 86.62% test

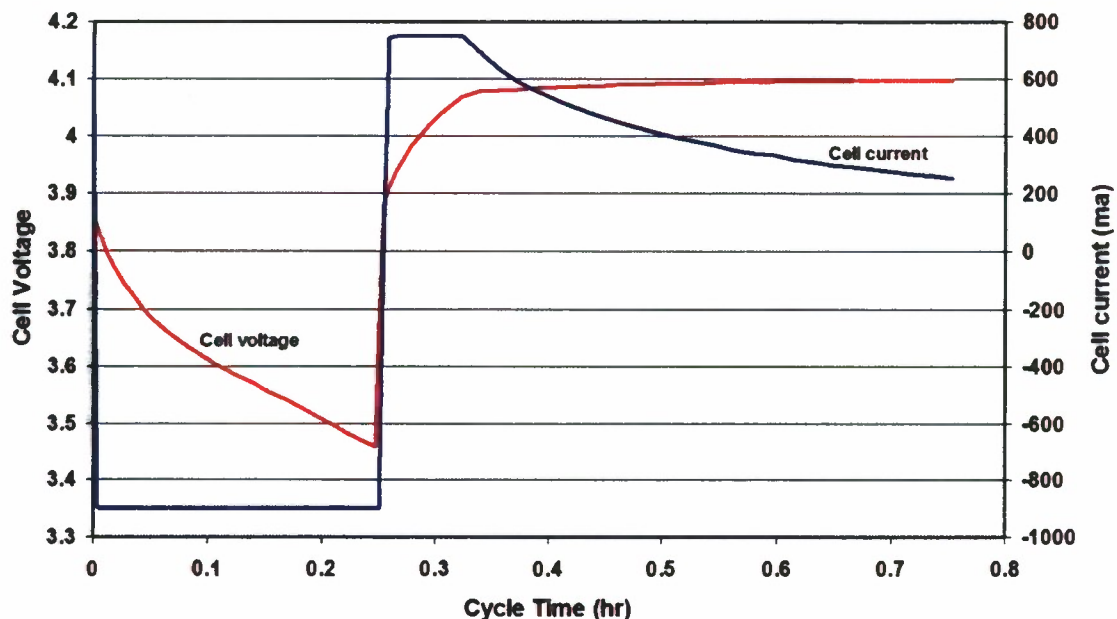


Figure 1. Voltage and current profiles for a typical cell in test 1 during cycle 108,601.

operating time and 13.38% test down time over the 7.27-year duration of this test. The cell voltage and current profiles in this test look very similar to that in Figure 1.

2.3 Test 3

Test 3 cycles a battery of eight series-connected cells. This battery of cells is operated in a repeating sequence of 45 cycles at 75% depth of discharge with one cycle per day, followed by 138 days of float charge at a controlled voltage. The discharge during each 45-day cycling period is done at a current of 0.75 A for 1.2 h. Recharge is then done at 0.131 A until the battery reaches a peak voltage limit, after which the current tapers down to keep the battery voltage at the peak allowed level for the rest of the 22.8-h recharge period. Figure 2 shows a typical voltage and current profile for a cycle in this test.

The peak charge voltage level during the 45-day cycling periods was 32.8 (4.10 V per cell) at the start of the test, and the plan was to increase it to 4.20 V per cell in 0.05 V/cell steps if the average end-of-discharge voltage of the cells fell below 3.00. At cycle 322 (after 7 cycling periods) the peak charge voltage was increased to 4.15 V per cell (33.2 V at the battery) to keep the average end-of-discharge voltage above 3.0 V. It has remained at 33.2 V to the present.

These eight cells were initially very well matched in capacity. However, we exposed the cells to an aging process that was designed to introduce an imbalance of 10% between the capacities of these cells. This procedure involved storing these cells at voltages between 3.4 and 4.2 V at ambient temperature for 220 days. This procedure resulted in nearly a 10% capacity loss in the cells stored at the highest voltages and very little capacity loss in the cells stored at the lowest potentials. The 10% capacity imbalance was targeted as an expected imbalance condition that could develop after 10 years

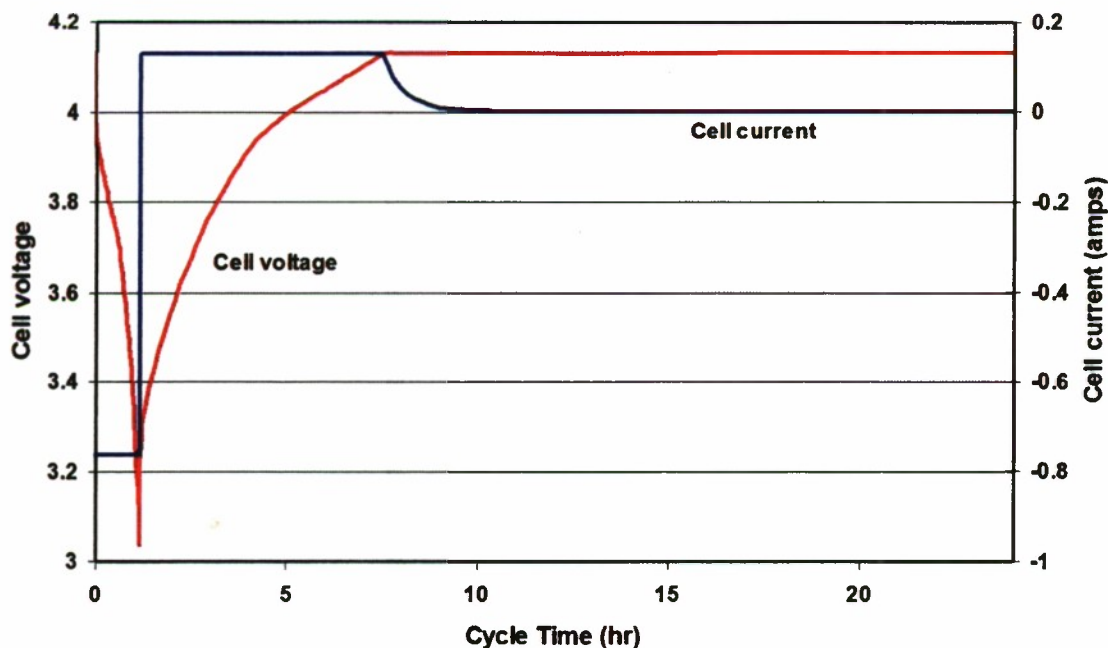


Figure 2. Voltage and current profiles for a typical cell in test 2 during cycle 647.

of operation in this test profile. A key element of this test involved determining whether the imbalance continued to grow with time, or whether processes existed in the cells that could bring them back together during either the cycling or non-cycling periods.

During the 138-day non-cycling period, the battery is discharged to 32.0 V (4.0 V per cell), and held on float charge at that voltage level until the 138 days have elapsed. After completion of the 138-day float period, the battery is recharged at the normal charge rate up to the peak charge voltage in preparation for the next cycling sequence.

The cell temperatures are controlled by mounting them in an aluminum block that is placed in the approximately 23°C ambient room air. A small fan is used to blow ambient air over the aluminum block, thus keeping cell temperatures close to ambient. A temperature rise of several degrees C is typical during discharge.

2.4 Test 4

Test 4 is a battery of eight series-connected cells that has been held at a nominal battery float voltage of 3.95 or 4.05 V per cell since 2002. For the first 265 days of this test, the battery was held at a nominal voltage of 3.95 V per cell, and since then it has been held at 4.05 V/cell. The objective of this test is to evaluate whether cells that have slightly higher self-discharge rates than other cells will continue to drift below the voltage of the other cells, or whether cells that have slightly lower self-discharge rates will continue to drift above the voltage of the other cells. These cells have been held at ambient temperature during this test, and have been mounted in an aluminum block to assure a similar thermal environment for all eight cells.

2.5 Test 5

Test 5 involves four individual cells that were charged to voltages of 3.6, 3.9, 4.0, and 4.1 V at the beginning of life. Thereafter, the cells have been held in the open-circuit state while their voltages have been monitored once every 4 h. The infrequent monitoring is done to minimize slight capacity drain that might arise from the voltmeter that does the monitoring, which has 100-M Ω input impedance. The cells have been maintained at ambient temperature during this test, and have been mounted in an aluminum block to assure a similar thermal environment for all four cells.

3. Test 1 Results

Test 1 has been running for nearly 11 years, and has accumulated nearly 110,000 cycles to date. While the two cells have performed well, they have begun to show signs of wearing out, particularly one of the cells, as is shown in Figure 3. Figure 3 plots the end-of-discharge voltage of the cells as a function of cycle number. The failure point for these cells is defined to be 3.0 V at the end of discharge.

This test ran some of the cycles at approximately 10% depth of discharge early in the cycling due to a programming error. The occasional spikes in the data of Figure 3 occur when there were test interruptions. The voltage discontinuity at about 64,000 cycles corresponds to a 7-week test shutdown, during which the cells were at about 4.0 V, and during which there were six recharges to 4.1 V for troubleshooting the charge control circuits. One of the cells seemed to be affected significantly more than the other cell by this 7-week stand in the nearly fully charged state. After about 50,000 cycles, the cell represented by the magenta line in Figure 3 began to degrade significantly faster than the other cell. The reason for the faster degradation rate is not known; however, at the present degradation rate, this cell will probably fail in the next approximately 10,000 cycles. The degradation in the charge and discharge voltage profiles through this test is shown in Figure 4 for the worst performing of these two cells.

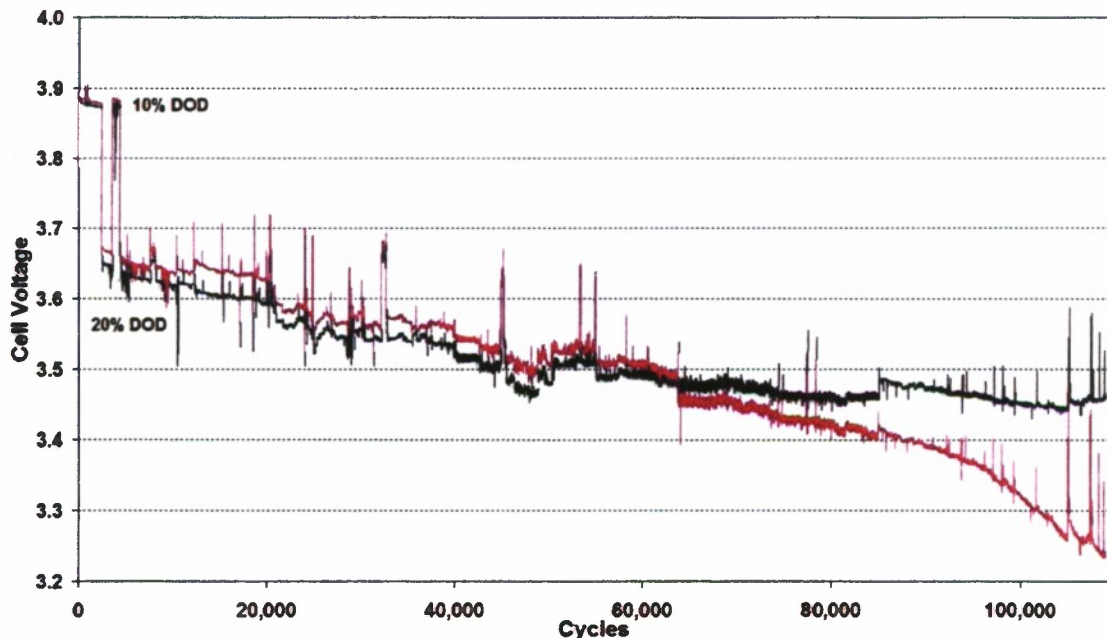


Figure 3. End of discharge voltage for 1994 SONY 18650-HC cells as a function of cycle number.

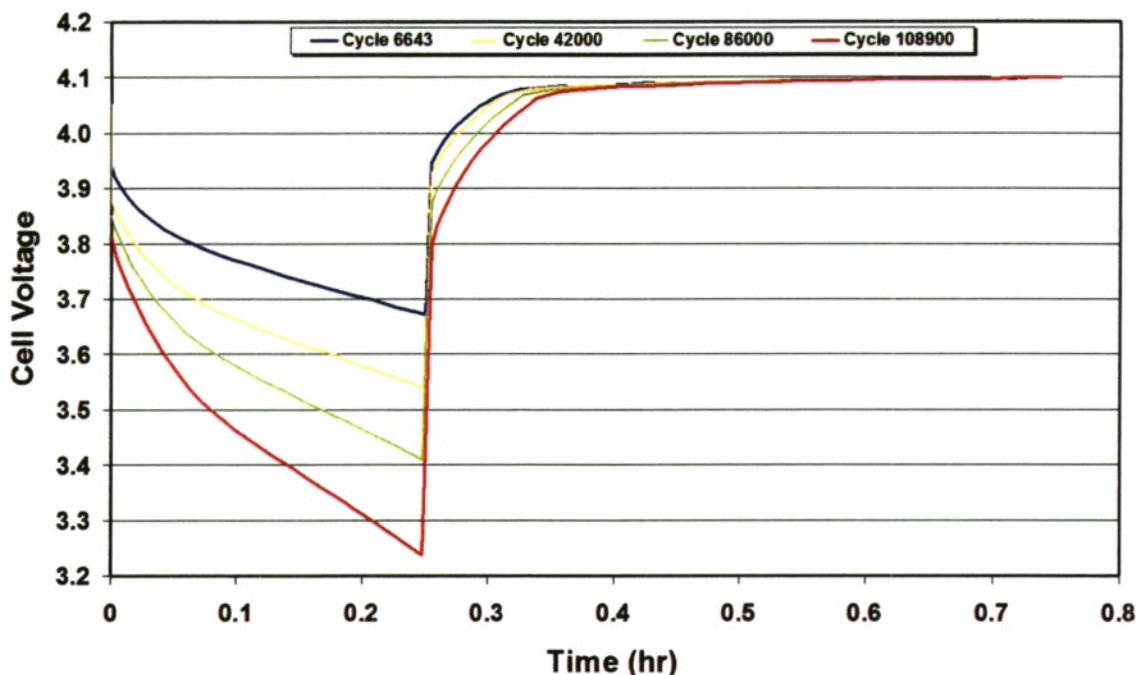


Figure 4. Change in voltage profile for the worst performing SONY cell in Test 1, represented by the magenta line in Figure 3.

The changes in the discharge voltage profiles in Figure 4 indicate that the degradation in this cell results from a combination of capacity loss (as suggested by the increasing slope of the discharge curve) and resistance increase (as suggested by the magnitude of the rapid voltage change from discharge to recharge).

As suggested in Figure 1 for this rapid cycling profile, the current at the end of the taper recharge period is expected to be sensitive to changes in internal cell impedance, which can affect how rapidly the current tapers down once the voltage limit is reached. Figure 5 indicates the changes in the end of charge current for these two SONY 18650-HC cells, using the same color coding for the cell data as used in Figure 3. The cell that experienced more degradation (magenta line) does indeed exhibit the greater drop in its taper current, probably because its internal impedance is greater. Figure 6 shows the details of how the shape of the current profile changed during the life test for this cell. Because the current took longer to start tapering, and then tapered more rapidly after the cell had experienced degradation from extensive cycling, the data suggests that capacity loss has been the dominant degradation process in these cells.

The average temperature of these cells is indicated in Figure 7. The end-of-charge temperature has typically been maintained within 2°C of the 20°C target value, and the end-of-discharge temperature has been consistently about 2°C warmer than the end-of-charge temperature. Careful examination of the voltage data in Figure 3 shows that many of the bumps in the voltage performance data are caused by variations in the test temperature.

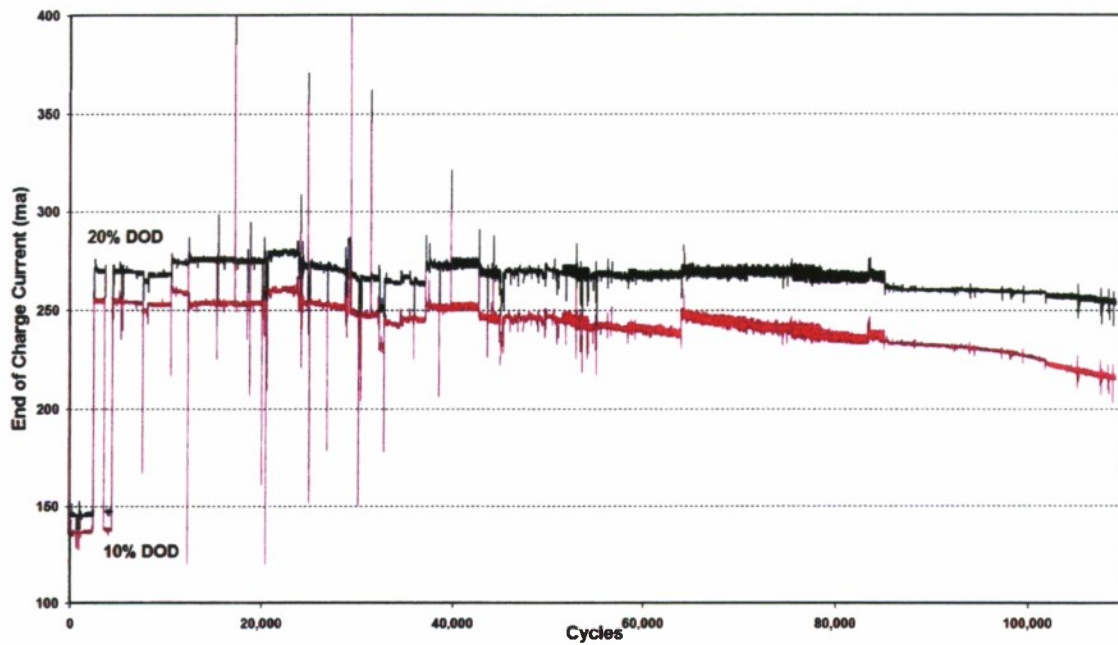


Figure 5. End of charge taper current level as a function of cycle life for 1994 vintage SONY 18650-HC cells in Test 1.

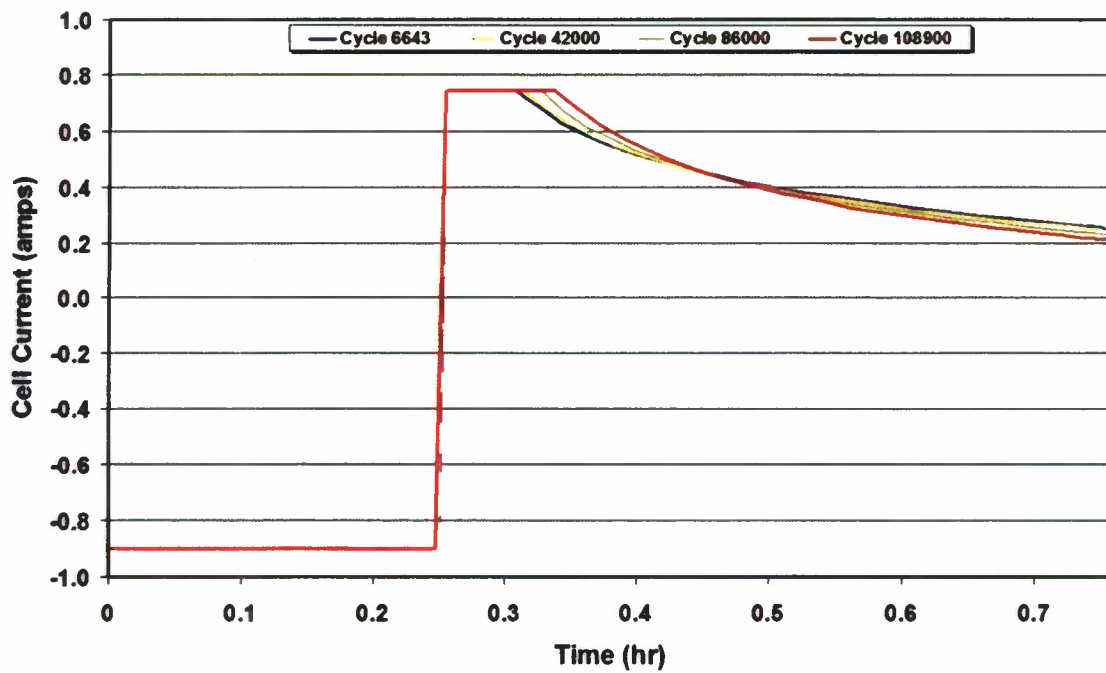


Figure 6. Change in current profile for the worst performing SONY cell in Test 1, represented by the magenta line in Figure 3.

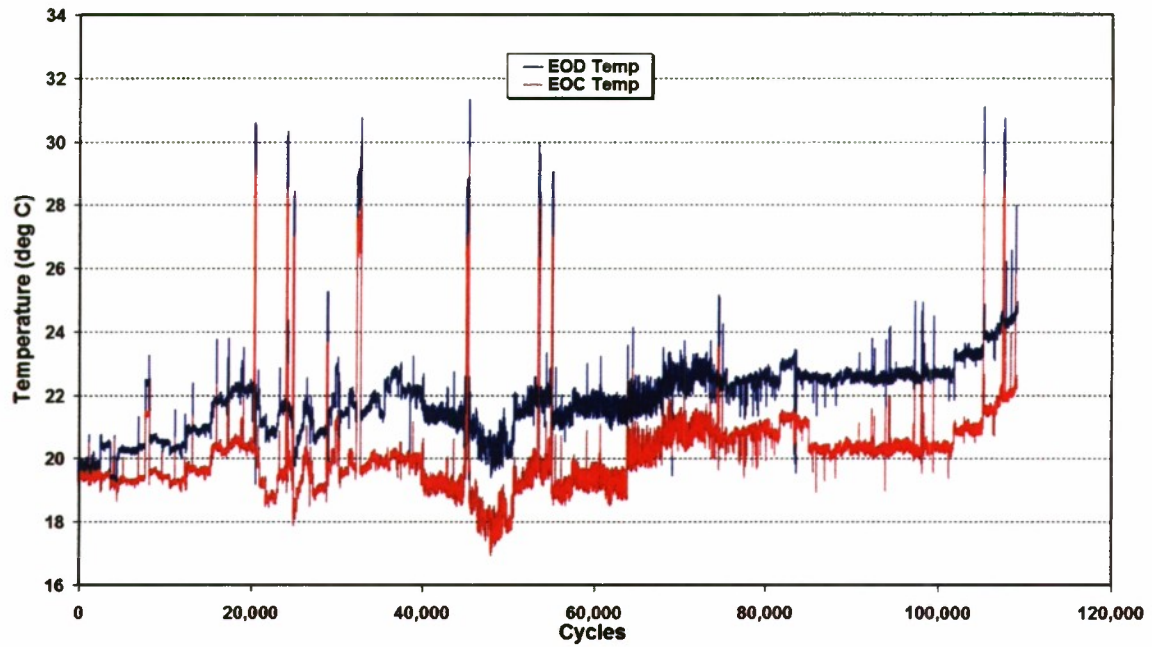


Figure 7. Average temperature for the SONY 18650-HC cells in Test 1 at the end of charge and the end of discharge as a function of cycle number.

4. Test 2 Results

Test 2 started 8/27/2002, and thus has been running for nearly 7.5 years, and has completed over 73,000 cycles. The two 2002 vintage cells in this test have been performing quite well, although it must be remembered that they are running at slightly lower depth of discharge than are the 1994 vintage cells in Test 1. The end-of-discharge voltage for these two cells is shown in Figure 8 for the cycles completed to date.

The end-of-discharge voltages have been dropping for these two cells at a quite regular rate during Test 2 cycling. The cells have remained matched in performance very well. These two cells appear to be performing as well as, or perhaps better than the 1994 vintage cells in Test 1. The degradation in voltages that is seen in Figure 8 can be examined in better detail by plotting the changes in voltage profiles over the course of the test. This is done in Figure 9, where the voltage profiles for cell 1 are plotted for a cycle early in the test, in the middle of the test, and near the end of the cycles completed to date. The voltage profiles appear to be degrading in a way very similar to that seen in Figure 4 for the 1994 vintage cells. The discharge profiles show the greatest change, and it appears to be primarily a downward shift in the discharge plateau accompanied by a slight increase in the slope of the discharge plateau.

The end-of-charge currents for the two cells in test 2 are shown in Figure 10. The currents have been quite stable so far over the course of the cycling. Similarly, when the current profiles are examined for a cycle early in the test, in the middle of the test, and near the end of the cycles completed to date, very little change in the current profile is also seen, as shown in Figure 11. The subtle changes that

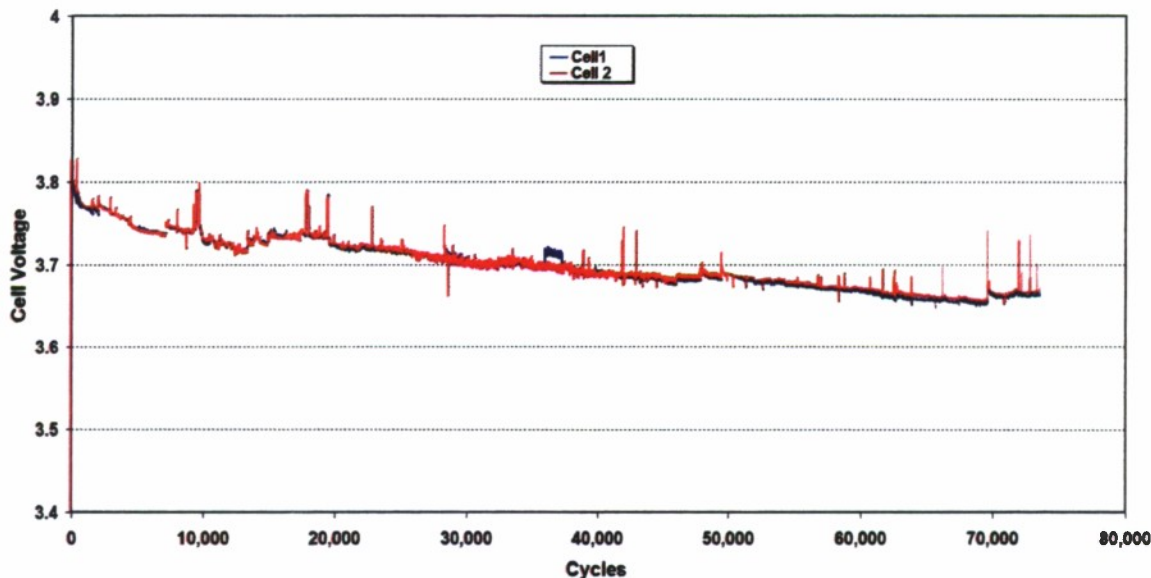


Figure 8. End-of-discharge voltages for 2002 SONY 18650-HC cells in Test 2.

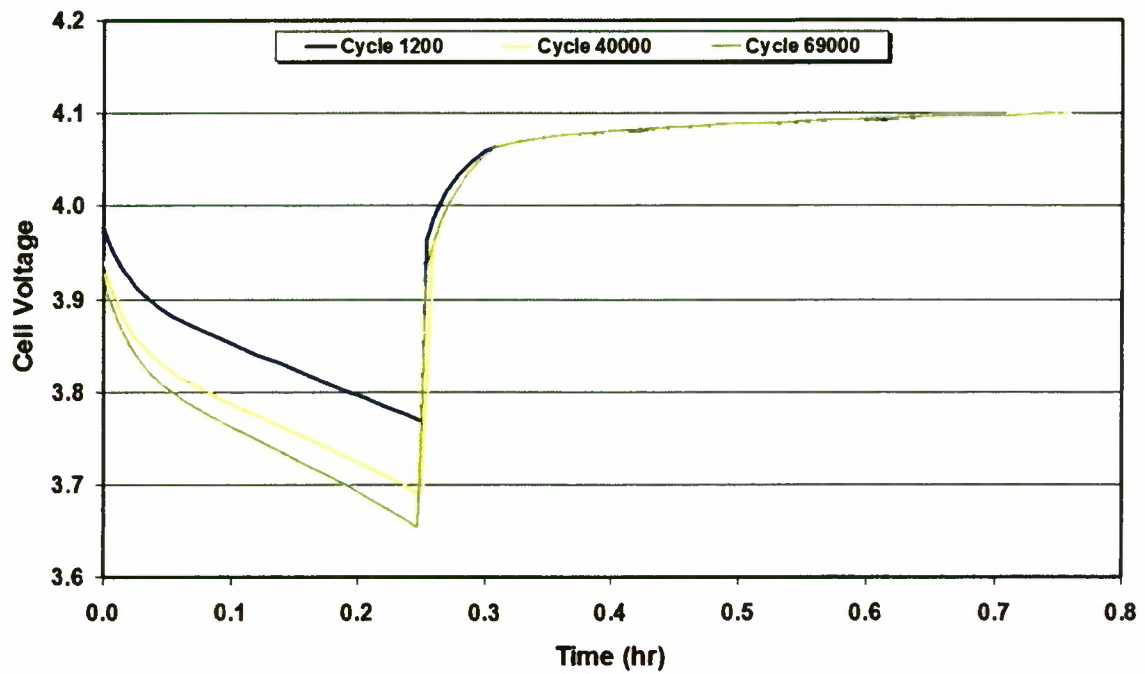


Figure 9. Change in voltage profile for the SONY 18650-HC cell number 1 in Test 2.

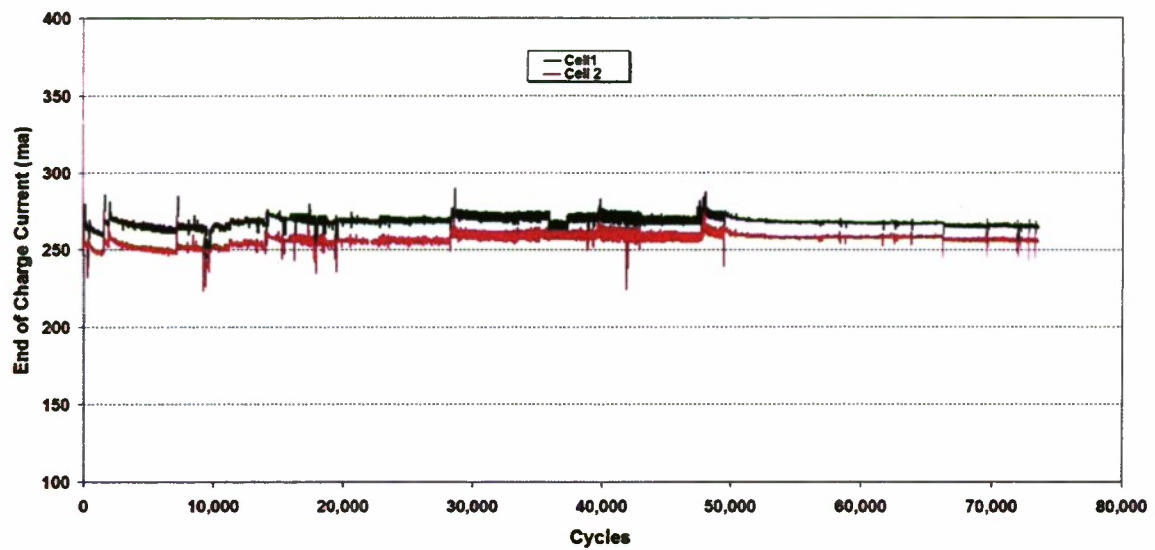


Figure 10. End-of-charge currents for 2002 SONY 18650-HC cells during Test 2.

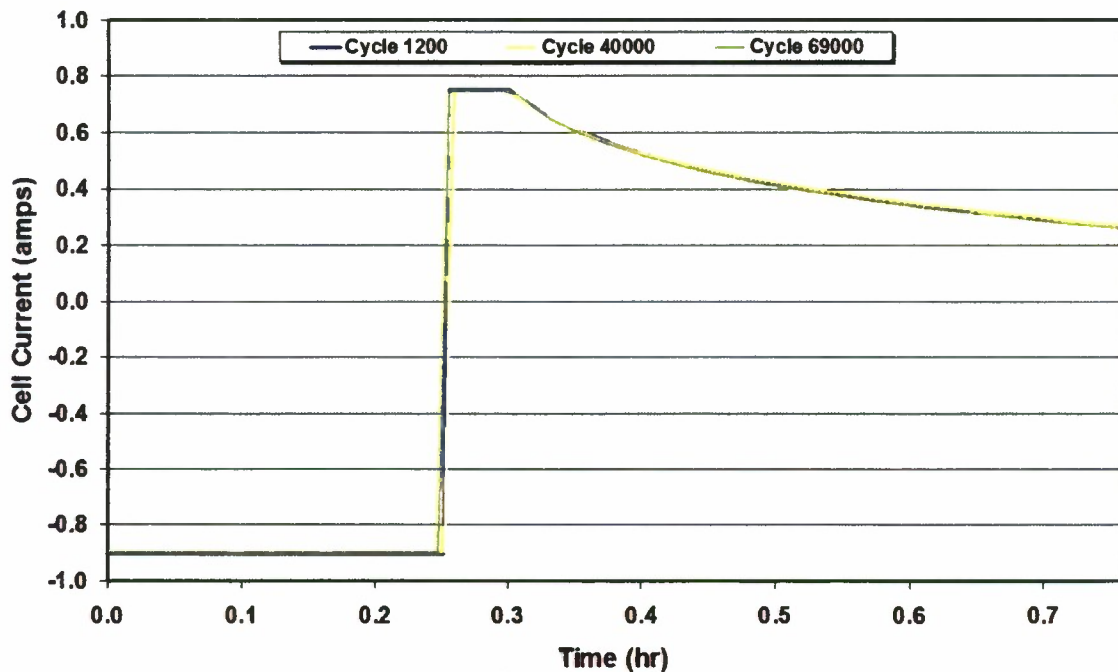


Figure 11. Change in current profile for the SONY 18650-HC cell 1 during Test 2.

are seen in the current profiles of Figure 11 are consistent with the degradation trends seen in Figure 6 for the 1994 cells, but are not very great at this point in the cell lifetime. The voltage degradation seen at 40,000 cycles (comparison of Figure 9 to Figure 4) is only about 75% of that seen for the 1994 vintage cell, which is probably a reasonable difference considering the lower depth of discharge for the 2002 cells.

The average temperature of the cells in Test 2 is indicated in Figure 12. The end-of-charge temperature has typically been maintained within 2°C of the 20°C target value, and the end-of-discharge temperature has been consistently about 2°C warmer than the end-of-charge temperature. Careful examination of the voltage data in Figure 8 shows that many of the bumps in the voltage performance data for these cells are caused by variations in the test temperature.

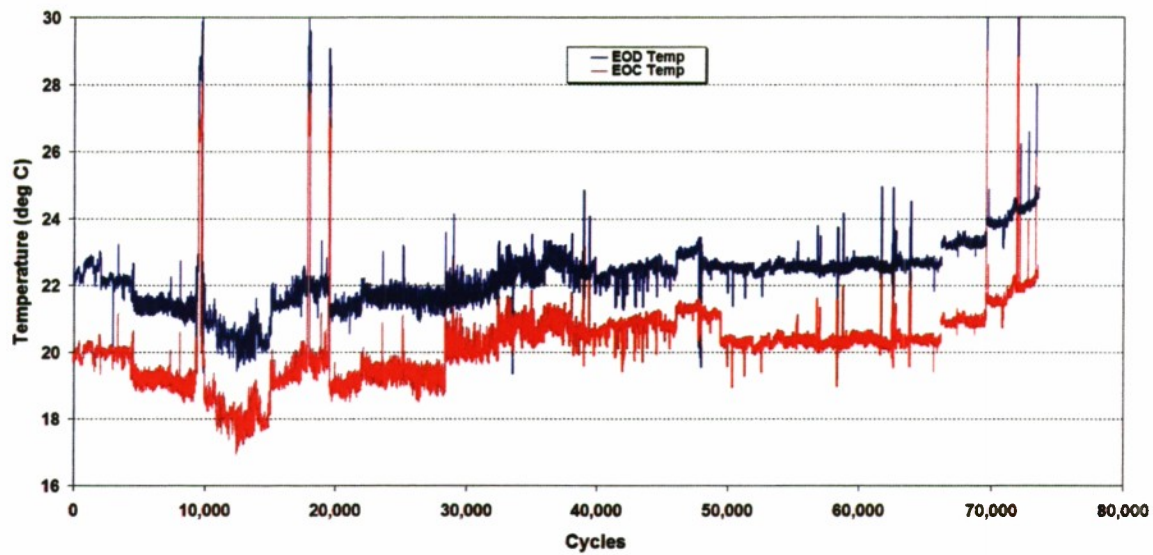


Figure 12. Average temperature for the 2002 vintage SONY 18650-HC cells in Test 2 at the end of charge and the end of discharge as a function of cycle number.

5. Test 3 Results

Test 3 started 3/18/2003, and thus has been running for over 6.5 years and has completed 671 cycles. This is a test that involves slow cycling of an 8-cell battery of 2002 vintage SONY 18650-HC cells, and nominally performs 90 cycles per year at 75% depth of discharge. Figure 13 shows the changes in end-of-discharge voltages for the eight cells in the battery. As discussed in the description of this test in Section 1, these eight cells started this test with imbalanced capacity before they were assembled into the 8-cell battery. Since the beginning of the test, the eight cells have always been operated in series. Thus, the divergence between the cells is of interest since the lifetime of the battery depends on the cells staying reasonably balanced in capacity.

As shown in Figure 13, the voltage divergence at the end of discharge has increased over the course of this test, but seems to have stabilized after several hundred cycles. The end-of-discharge voltage of all the cells has dropped as the cells have degraded. After 322 cycles, the peak battery recharge voltage was increased from 4.10 V per cell to 4.15 V per cell to keep the average cell voltage above 3.00 V at the end of discharge. This increase had the desired effect, as shown in Figure 13. Another increase in the peak battery charge voltage to 4.20 V per cell is expected to be required after about 900 cycles, based on the current voltage degradation slope. In this test, if any individual cell voltage falls below 2.7 V, the peak charge voltage will also be increased. However, it does not appear that the cell divergence will become great enough that this will occur. This battery will reach its point of

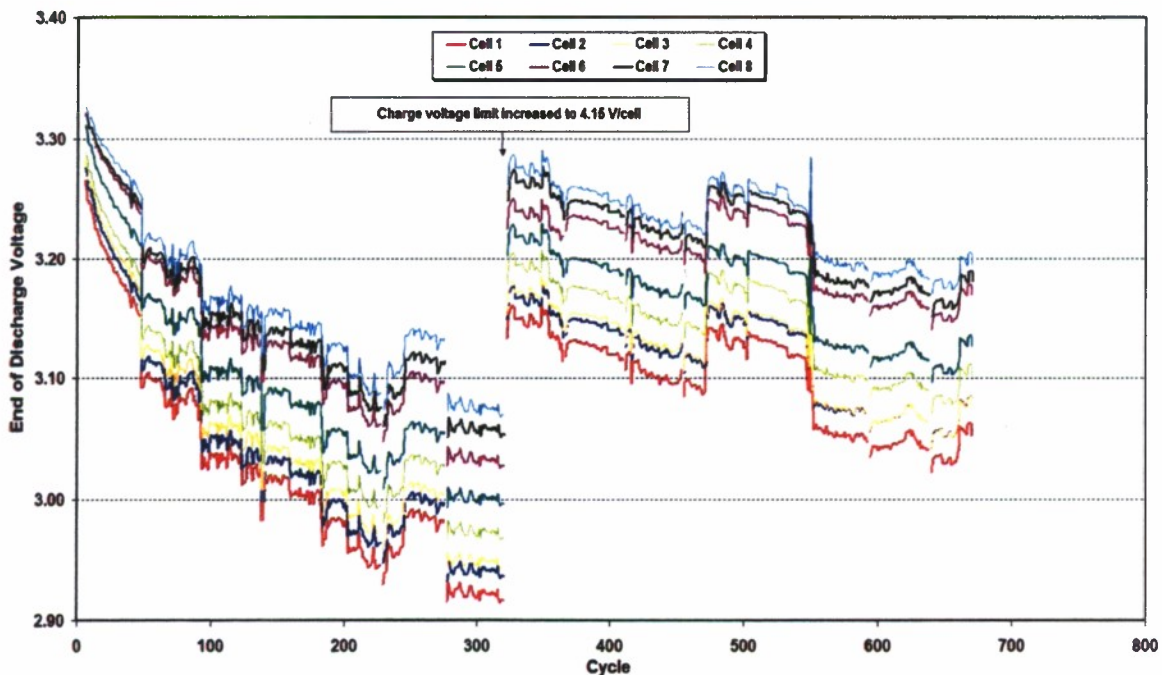


Figure 13. End-of-discharge voltages for eight cells comprising the battery cycling in Test 3.

failure when the peak recharge voltage is 33.6 V (4.20 V per cell) and the average end-of-discharge battery voltage drops below 24 V (3.00 V per cell).

The end-of-charge voltages for the eight cells in the Test 3 battery are shown in Figure 14 as a function of the cycles completed to date. The end-of-charge voltages do not spread as much during the test as do the end-of-discharge voltages. The point where the average end-of-charge voltage for the battery was increased at 322 cycles from 4.10 to 4.15 V per cells is quite clear in Figure 14.

The recharge ratio during the cycling in Test 3 was slightly greater than 1.00. The average recharge ratio over the entire 671 cycles to date was 1.00059. It is unclear how accurate this number is, but if this excess charge is required to compensate for self-discharge, it suggests a self-discharge rate of about 22 μ A.

The actual divergence between the cells at the end of discharge or the end of recharge can be plotted, and is shown in Figure 15. The divergence at end of discharge is greater because the slope of the voltage is steeper as the lowest cells drop toward the depleted condition. The divergence at end of charge was about 30 mV when the peak charge voltage was 4.10 V/cell, but increased to about 45 mV when the peak recharge voltage was increased to 4.15 V per cell. This 45 mV divergence caused the highest cell voltage to increase to about 4.18 V when the average cell in the battery was at 4.15 V. It remains to be seen how much the highest cell goes above 4.2 V when the peak charge voltage is eventually increased to 4.2 V per cell.

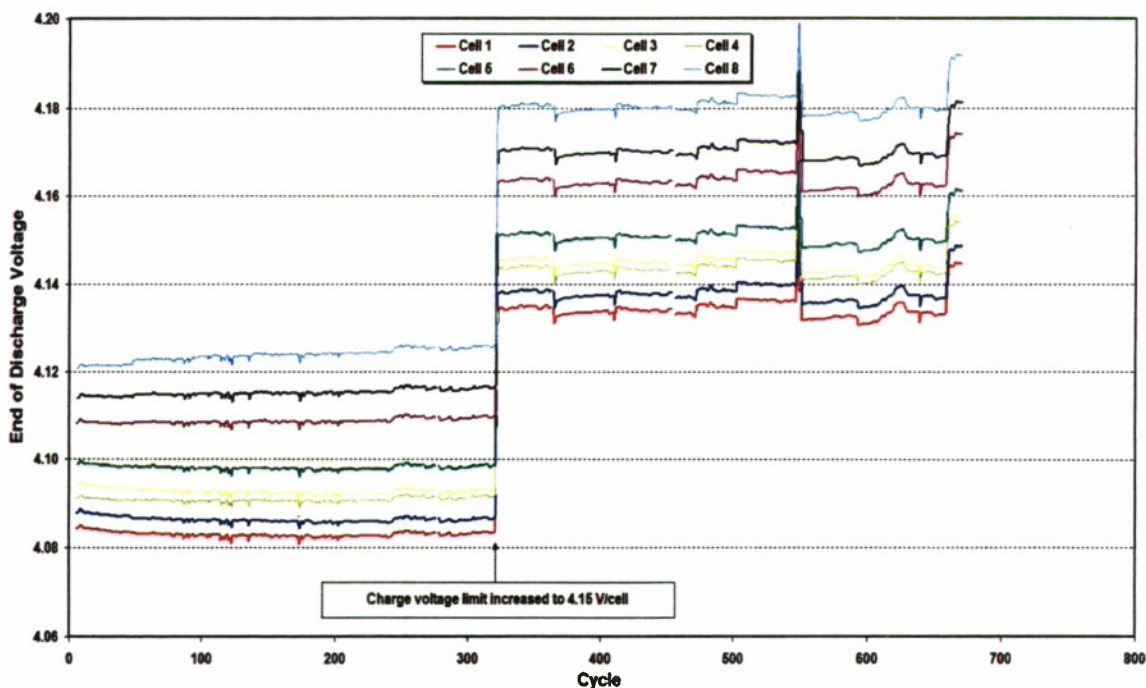


Figure 14. End-of-charge voltages for eight cells comprising the battery cycling in Test 3.

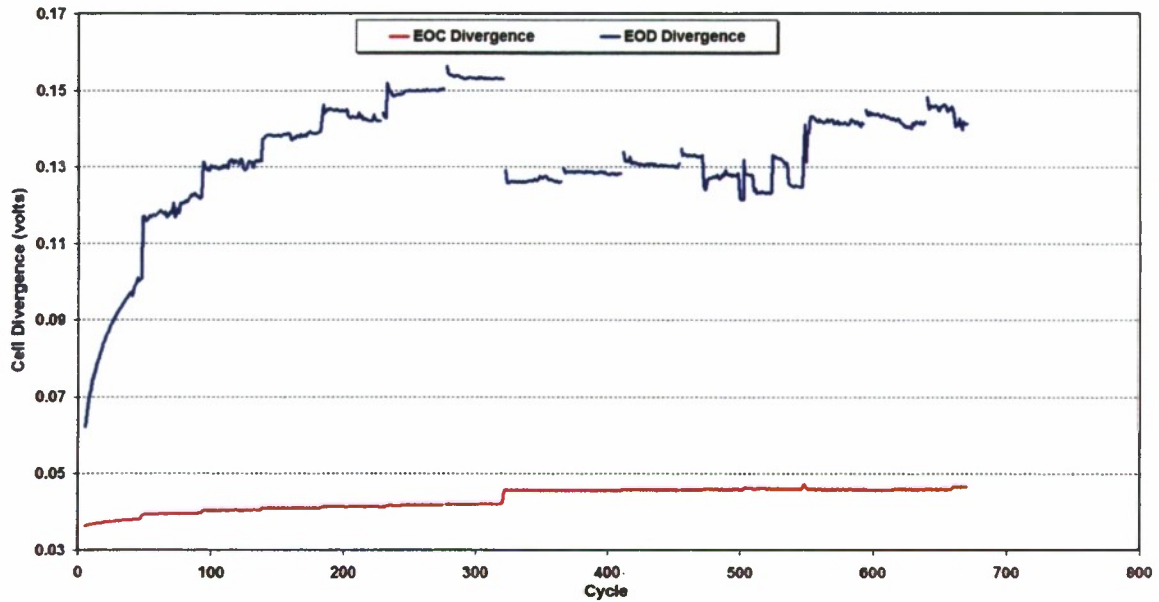


Figure 15. Range of cell voltage divergence seen in Test 3 battery at end of discharge and end of recharge.

The divergence between the cells can also be trended during the 138-day non-cycling periods that occur between the 45-day cycling periods. The changes in cell-to-cell divergence during these non-cycling periods (during which the battery is held at 32 V) are shown in Figure 16. The increases seen earlier in the test have decreased over the years; however, the divergence continues to slowly increase over time.

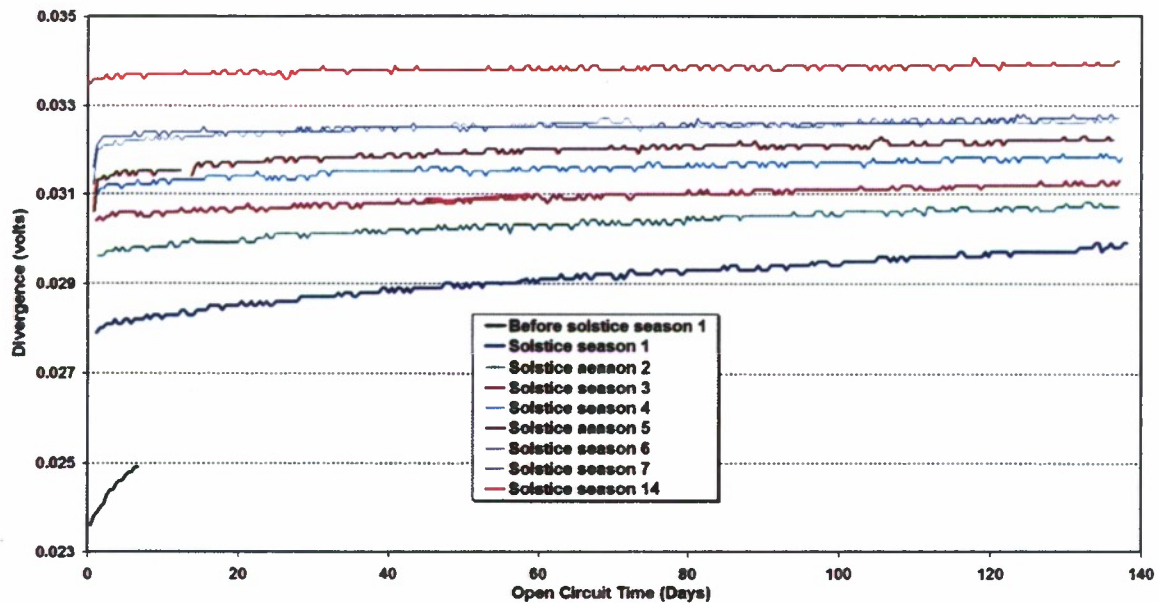


Figure 16. Changes in cell-to-cell divergence during 138-day non-cycling periods.

The amount of current that has to be recharged into the battery during the 138-day non-cycling periods to hold the battery at 32 V has been integrated during each non-cycling period to estimate the average self-discharge rate of the cells. Because the currents are very small, there is significant noise in the average self-discharge rate calculated each day. The daily self-discharge rate appears to start at 10 to 30 μA just after the end of the 45-day cycling period, and then drops to close to zero after about 20 days. The rate determined just after the end of the 45-day cycling period is consistent with the 22 μA self-discharge rate determined from the average recharge ratio during the cycling periods. The average self-discharge rate between days 20 and 138 of the non-cycling periods can be integrated, and is plotted in Figure 17. The curve in Figure 17 is the best logarithmic fit to the data points, and is only included to better illustrate the trend in the data points. Clearly, the average self-discharge rate is decreasing as these cells age in this life test.

The loss of capacity during each cycling period can be estimated from the discharge curves during each non-cycling period. This has been done for cycle 23 in each 45-day cycling period, and the capacity has been normalized to the capacity at the beginning of the test. The results are shown in Figure 18. The capacity loss increased rapidly during the first two seasons, but thereafter it has increased at a lower rate; roughly 0.5% per season. The large decrease in capacity loss after season 7 was due to the peak recharge voltage being increased to 4.15 V per cell at that point, which increased the capacity stored in the cells significantly (about 8% based on Figure 18) relative to the starting capacity.

The resistance of the cells can be determined by the change in cell voltage that occurs each time the battery is switched from charge to discharge. This has also been calculated for cycle 23 in each 45-day cycling period, and the results are plotted in Figure 19. The resistance has continuously increased during the test, but the rate of increase is much less after season 8. The average cell resistance has increased about 65% during the life test to date.

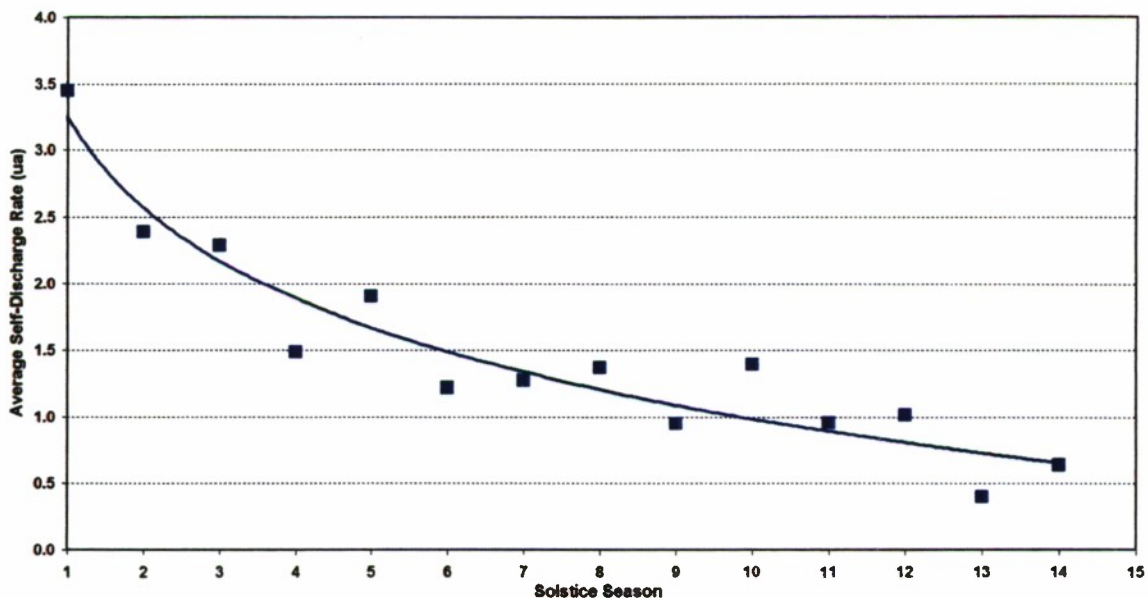


Figure 17. Average self-discharge rate integrated over days 20 to 138 of each non-cycling period.

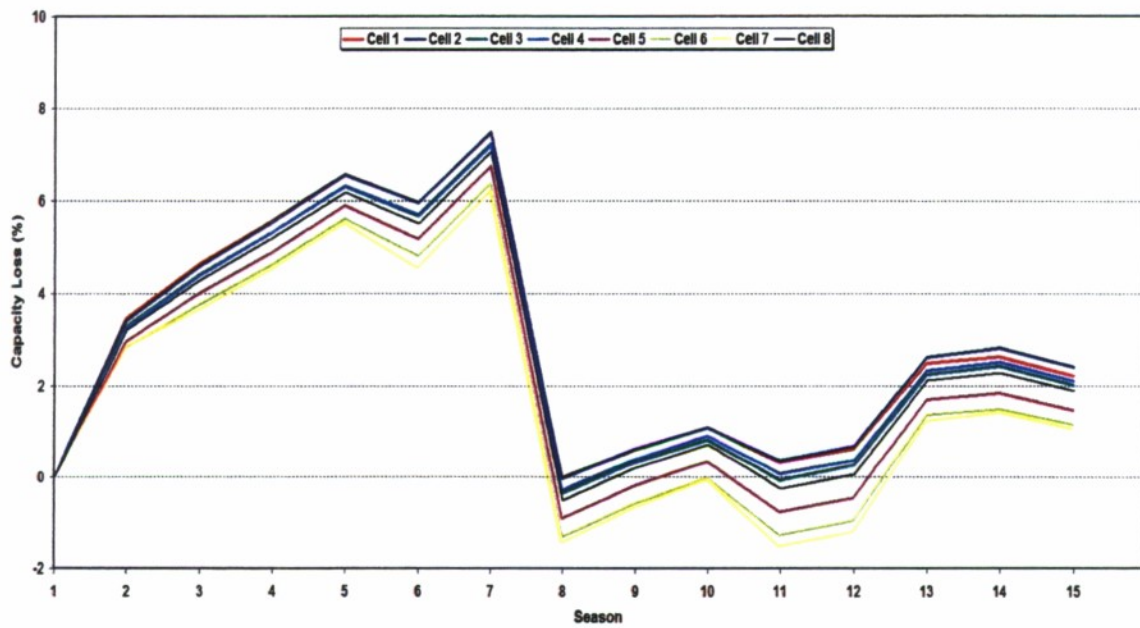


Figure 18. Capacity loss relative to season 1 for each cell in the battery. The large capacity recovery at season 8 is because the peak battery charge voltage was increased to 4.15 V/cell.

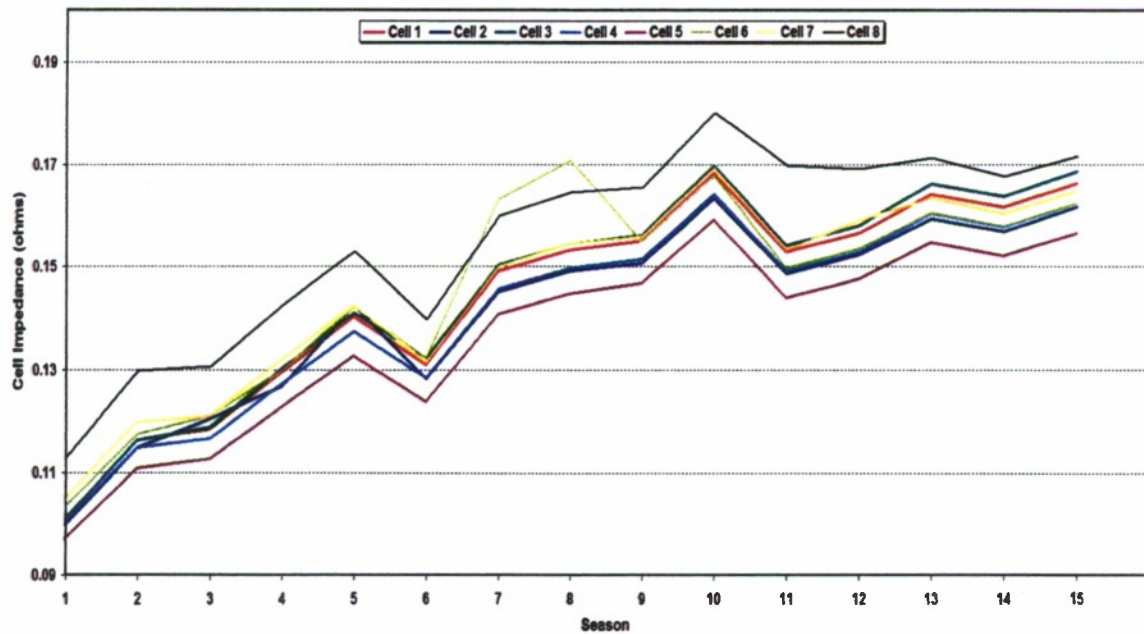


Figure 19. Resistance for each cell in the Test 3 battery as a function of season number.

6. Test 4 Results

Test 4 started 7/11/2002, and thus has been running for nearly 7.5 years. This test simply monitors an 8-cell battery of vintage 2002 SONY 18650-HC cells while the battery is held at a constant voltage. For the first 264 days of this test the battery was held at a nominal voltage of 3.95 V per cell, and for the remainder of the test it has been held at a nominal voltage of 4.05 V per cell. The purpose of the test is to determine whether the cells continuously diverge from each other in voltage, or whether processes exist that keep them from continuously diverging. The results from the test are shown in Figure 20, which shows the cell voltages over 2706 days.

The results in Figure 20 indicate that the cells have continuously increasing divergence from the average, except for cell 6, which is the lowest voltage cell. The divergence is, however, increasing very slowly. It has increased to about 3 mV after 7 years on float. At this rate of continuing divergence, it is unlikely that the divergence between the cells will ever become a problem during stand at a constant float voltage in the 3.95 to 4.05 V per cell range.

It is somewhat suggestive that cells 6, 7, and 8 have all drifted to lower voltages since these three cells are at the high-voltage end of the string relative to ground. This could be a signature for very low rate leakage paths to ground, which could cause the observed behavior with hundreds of

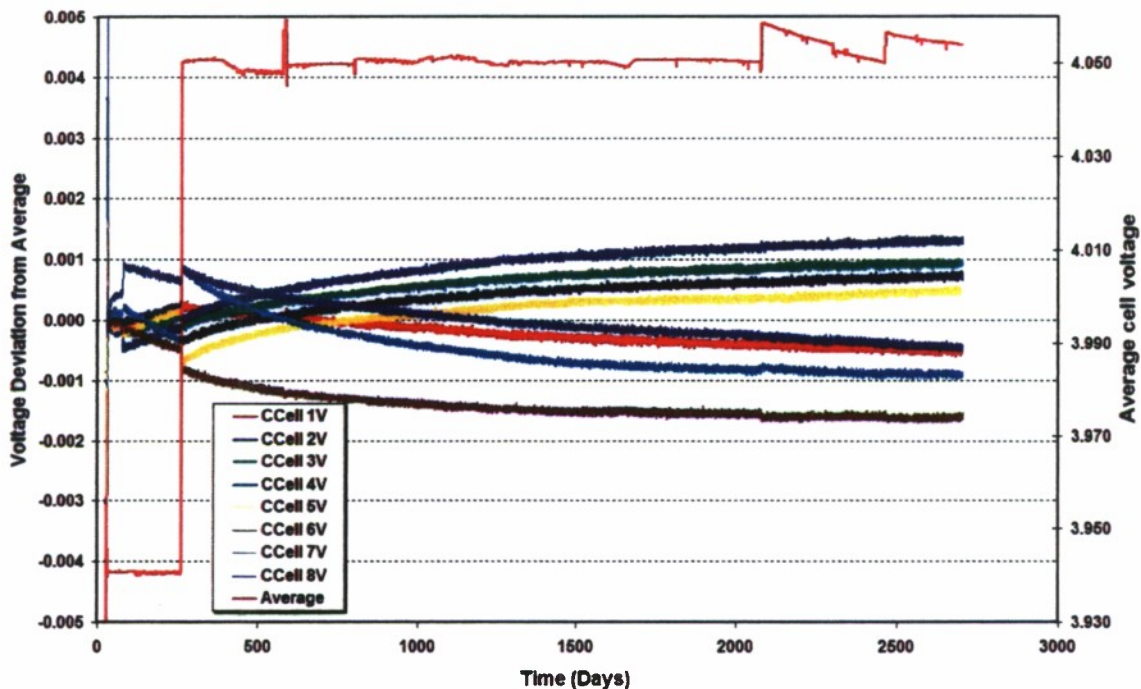


Figure 20. Average cell voltage and divergence of each cell from the average for the Test 4 battery.

megohms of resistance. The fact that cell 1 is also a lower voltage cell potentially refutes this explanation; however, isolation leakage is clearly an issue of real concern.

7. Test 5 Results

Test 5 started 7/11/2002, and thus has been running for nearly 7.5 years. This test simply monitors the open-circuit potential of four vintage 2002 SONY 18650-HC cells. These four cells were initially charged at a C/10 rate to 3.6, 3.9, 4.0, and 4.1 V, respectively, and then were subsequently allowed to stand open-circuited while the voltage droop of each cell was monitored. The results for these cells are shown in Figures 21 to 24.

The rate of voltage droop for these four cells was more rapid initially, then decreased with time up to roughly 1500 days, after which the rate of voltage droop became nearly constant. For these four cells, the rate of voltage droop after 1500 days was determined from the slopes in Figures 21 to 24, and is shown in Table 2.

The self-discharge rates calculated in Table 2 are based on the slope of the voltage vs. capacity curve for these types of 18650 cells at the average cell voltage during the decay period from 1500 days to the end of the data. The first observation from Table 2 is that the self discharge rate seems to increase with increasing state of charge, as is indicated in Figure 25. This may prevent the cells from self-discharging completely to the depleted condition, assuming the self-discharge rate falls to near zero as the cell state of charge becomes very low. The other observation is that the cell that was initially set to 4.0 V appears to have about twice the self-discharge rate of the other cells. It remains to be seen whether this is due to a low-level short circuit in that cell. These data clearly show the importance of matching cell self-discharge rates to enable a battery to be stored without developing major capacity imbalance between the cells.

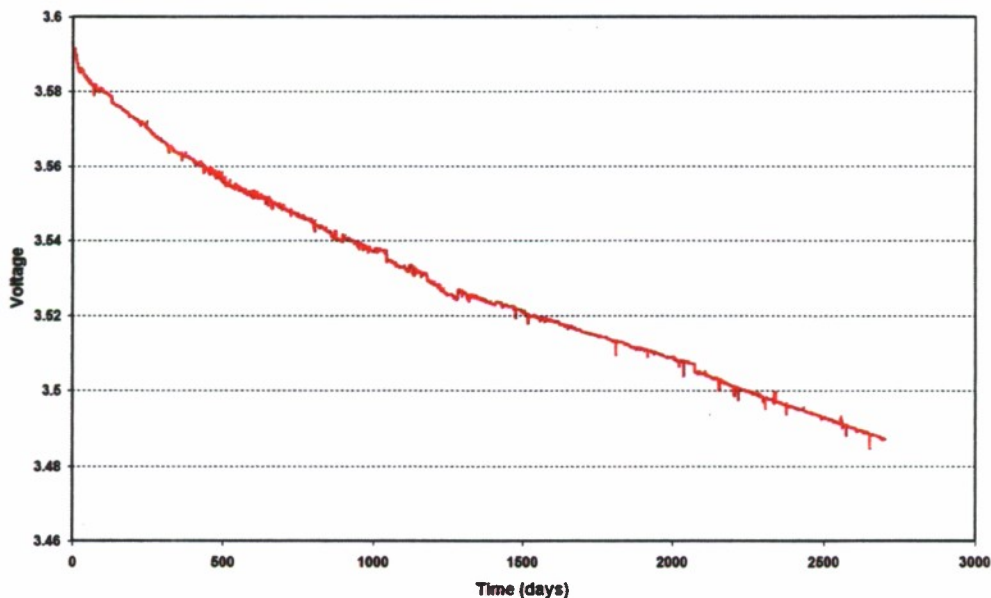


Figure 21. Open-circuit voltage decay for a SONY 18650-HC cell initially charged to 3.6 V.

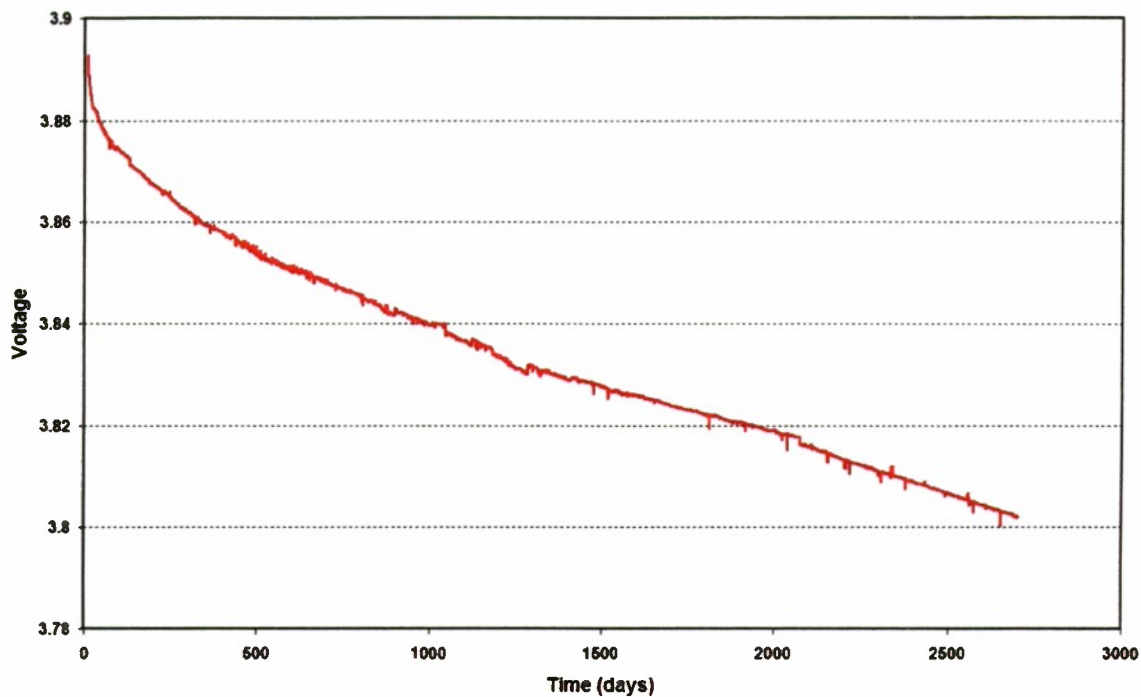


Figure 22. Open-circuit voltage decay for a SONY 18650-HC cell initially charged to 3.9 V.

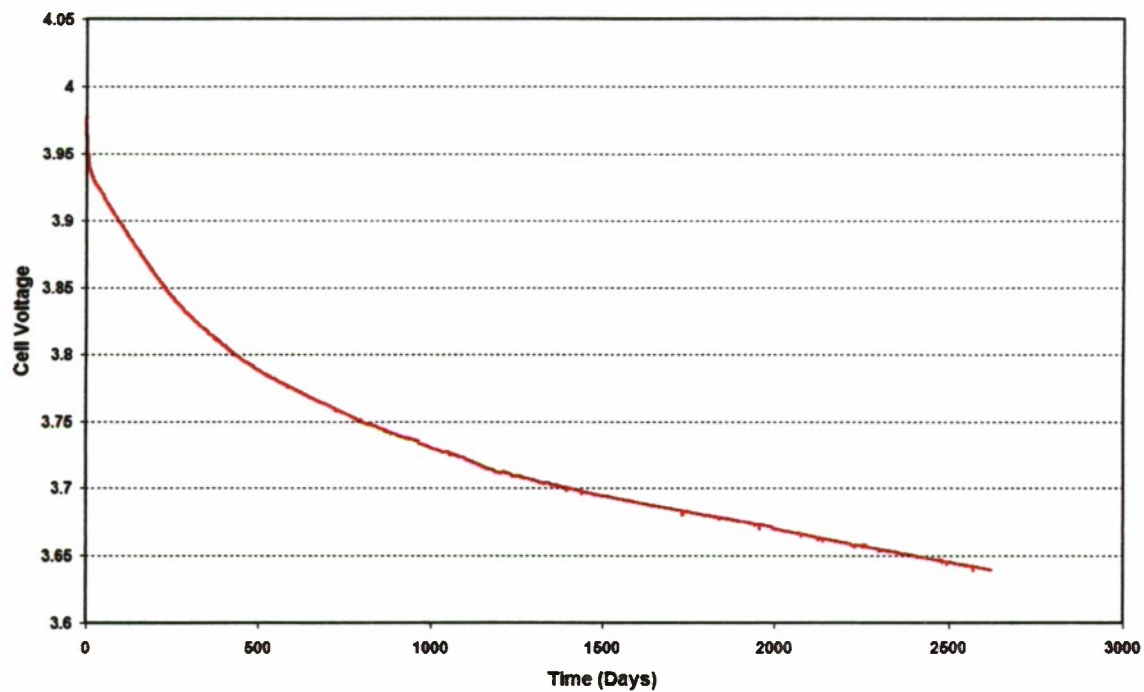


Figure 23. Open-circuit voltage decay for a SONY 18650-HC cell initially charged to 4.0 V.

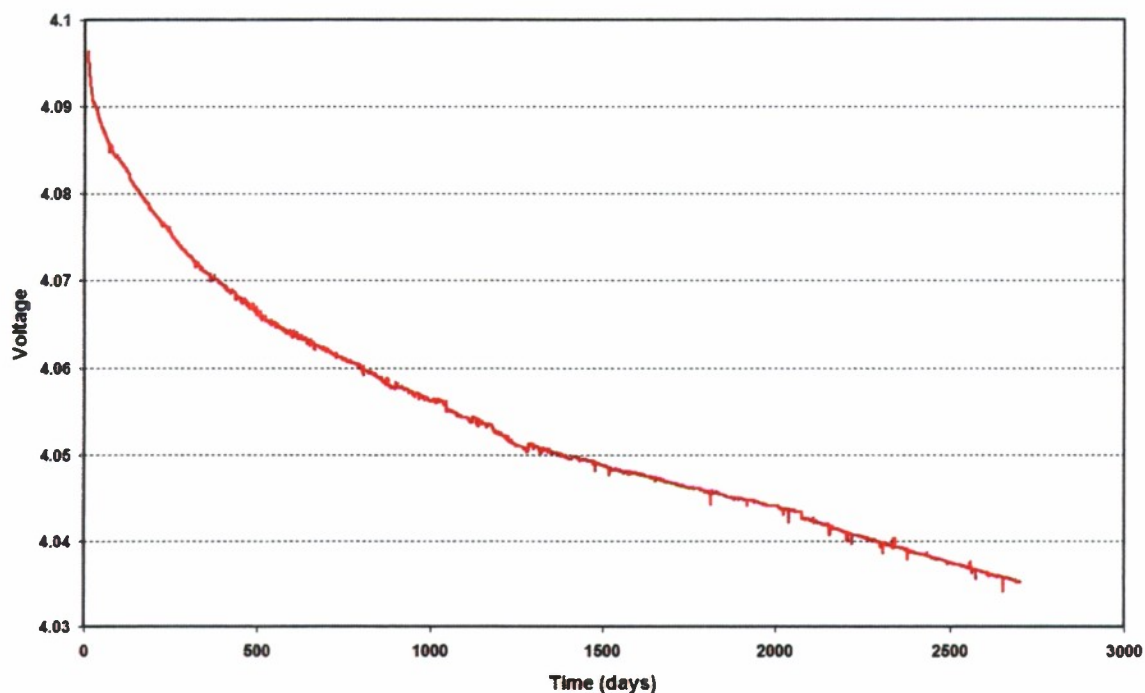


Figure 24. Open-circuit voltage decay for a SONY 18650-HC cell initially charged to 4.1 V.

Table 2. Voltage Decay and Self-Discharge Rates for Test 5 SONY 18650-HC Cells

Initial Cell Voltage	Stable Slope (mV/day)	Average Voltage >1500 days	dC/dmAh (mV/mAh) @ avg V	State of Charge (%)	Loss Rate (μA)
3.6	-0.0289	3.505	1.800	12	4.58
3.9	-0.0217	3.815	0.950	30	5.99
4.0	-0.0497	3.665	1.330	20	10.20
4.1	-0.0116	4.045	0.322	50	8.91

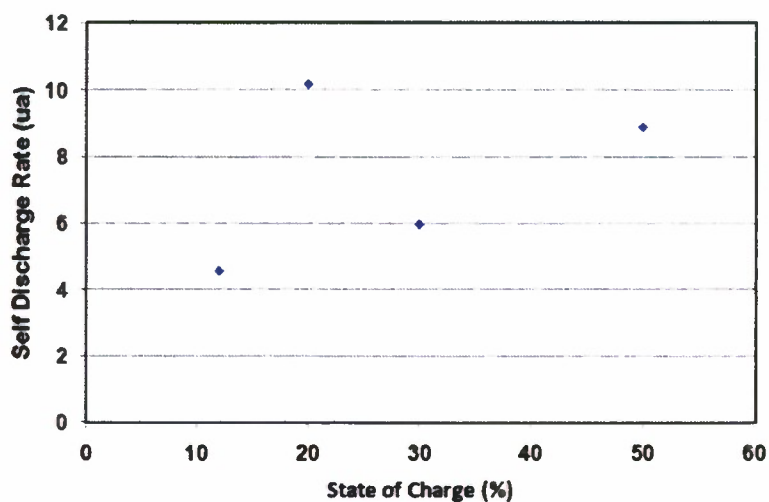


Figure 25. Self-discharge rate as a function of state of charge for 18650-HC cells in Test 5.

8. Conclusions

These tests allow the following conclusions to be drawn regarding the performance behavior of SONY 18650-HC cells:

- These cells are capable of operation in rapid cycling applications for more than 10 years at depths of discharge of about 20% or less.
- Life of more than 7 years in slow cycling applications has been demonstrated at 75% depth of discharge (after an initial 10% capacity degradation), suggesting that performance at this depth of discharge may be possible out to beyond 15 years.
- Cells made in 2002 appear to perform at least as well as those made in 1994; however, there are clearly design changes between these commercial cells made at different times.
- Degradation in both rapid and slow cycling tests indicates that much of the cell degradation occurs as the result of capacity loss, although resistance increases take place and also affect the observed voltage levels.
- Cells assembled into batteries continue to diverge from each other over their lifetime, but this divergence is very slow if the cells are well matched at beginning of life.
- Variability in self-discharge rate can occur, and is best screened by long-term voltage decay rate measurements.
- Self-discharge is relatively high after cycling, but drops to very low levels after months or more of open-circuit stand.
- Self-discharge rates increase with increasing state of charge.
- Maintaining cell isolation resistance in batteries in the $10^9 \Omega$ range and up is critical to keeping cells well balanced.

These tests are continuing for the purpose of determining the lifetimes of the cells, as well as evaluating the performance signatures that accompany the end-of-life condition in the cells when degradation has become quite severe.

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