Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Power Sources 119–121 (2003) 865–869
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Power fade and capacity fade resulting from cycle-life testing of Advanced Technology Development Program lithium-ion batteries

R.B. Wright[a,*], J.P. Christophersen[a], C.G. Motloch[a], J.R. Belt[a], C.D. Ho[a], V.S. Battaglia[b], J.A. Barnes[c], T.Q. Duong[c], R.A. Sutula[c]

[a]*Idaho National Engineering and Environmental Laboratory, P.O. Box 1625, MS-3830 Idaho Falls, ID 83415-3830, USA*
[b]*Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA*
[c]*US Department of Energy, 1000 Independence Avenue, S. W., Washington, DC 20858, USA*

Abstract

This paper presents the test results and analysis of the power and capacity fade resulting from the cycle-life testing using PNGV (now referred to as FreedomCAR) test protocols at 25 and 45 °C of 18650-size Li-ion batteries developed by the US Department of Energy sponsored Advanced Technology Development (ATD) Program. Two cell chemistries were studied, a Baseline chemistry that had a cathode composition of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ with binders, that was cycle-life tested at 25 and 45 °C, and a Variant C chemistry with a cathode composition of $LiNi_{0.8}Co_{0.10}Al_{0.10}O_2$ with binders, that was tested only at 45 °C. The 300 Wh power, and % power fade were determined as a function of test time, i.e. the number of test cycles for up to 44 weeks (369,600 test cycles) for the Baseline cells, and for 24 weeks (201,600 test cycles) for the Variant C cells. The *C*/1 and *C*/25 discharge capacity and capacity fade were also determined during the course of these studies. The results of this study indicate that the 300 Wh power for the Baseline cells tested at 25 °C (up to 44 weeks of testing) *decreased* as a *linear* function of test time. The % power fade for these cells *increased* as a *linear* function of test time. The Baseline cells tested at 45 °C (up to 44 weeks of testing) displayed a *decrease* in their power proportional to the *square root* of the test time, with a *faster* rate of *decrease* of the power occurring at ~28 weeks of testing. The % power fade for these cells also *increased* as the *square root* of the test time, and exhibited an increase in the % power fade rate at ~28 weeks of testing. The 45 °C tested Baseline cells' power decreased, and their % power fade increased at a greater rate than the 25 °C tested Baseline cells. The power fade was greater for the Variant C cells. The power of the Variant C cells (tested at 45 °C) *decreased* as the *square root* of the test time, and their % power fade was also found to be a function of the square root of the test time (up to 24 weeks of testing), i.e. the rate of decrease in the power and the increase in the % power fade rate was greater for the Variant C cells than for the Baseline cells also tested at 45 °C. The *C*/1 and *C*/25 Ah capacities of the Baseline cells tested at 25 and 45 °C were determined to be a function of the *square root* of the cycle time (i.e. number of test cycles) for test times up to 44 weeks. The capacity fade was greater at 45 °C than at 25 °C. Similarly, the *C*/1 and *C*/25 charge capacities of the Variant C cells were found to be a function of the *square root* of the test time (up to 24 weeks of testing). The *C*/1 and *C*/25 charge capacities decreased as a function of test time and the rate of decrease was *smaller* for the Variant C cells as compared to the Baseline cells over comparable test times (24 weeks).
Published by Elsevier Science B.V.

Keywords: Lithium-ion batteries; Battery cycle-life; Battery power; Power fade; Battery capacity; Capacity fade

1. Introduction

The US Department of Energy (DOE) Office of Advanced Automotive Technologies (OAAT) initiated the Advanced Technology Development (ATD) Program in 1998 [1] to address the outstanding barriers that limit the commercialization of high-power lithium-ion batteries, specifically for hybrid electric vehicle applications. As part of the Program, 18650-size cells are being designed and manufactured (presently, the second generation of cells, i.e. Gen 2) and are being aged using standardized calendar- and cycle-life tests [2]. This paper presents the 300 Wh power, the % power fade, and the changes in the *C*/1 and *C*/25 Ah charge capacities as a function of cycle-life testing time [2,3], i.e. the number of cycle-life test cycles, for cells designated as Baseline chemistry cells (tested at 25 and 45 °C), and for

* Corresponding author. Tel.: +1-208-526-0959; fax: +1-208-526-0969.
E-mail address: rbw2@inel.gov (R.B. Wright).

0378-7753/03/$ – see front matter. Published by Elsevier Science B.V.
doi:10.1016/S0378-7753(03)00190-3

cells designated as Variant C chemistry cells (tested at 45 °C).

2. Experimental

2.1. Cell chemistry

The 18650-size Gen 2 ATD Program Baseline and Variant C cells were manufactured to the following specifications, as developed by Argonne National Laboratory [4]:

- *Positive electrode (aluminum current collector)*
  - 84 wt.% $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Baseline cells);
  - 84 wt.% $LiNi_{0.8}Co_{0.10}Al_{0.10}O_2$ (Variant C cells);
  - 4 wt.% carbon black (Chevron);
  - 4 wt.% SFG-6 (Timcal);
  - 8 wt.% PVDF binder (Kureha KF-1100).
- *Negative electrode (copper current collector)*
  - 92 wt.% MAG-10 (Hitachi);
  - 8 wt.% PVDF binder (Kureha C).
- *Electrolyte*
  - 1.2 M $LiPF_6$ in EC/EMC (3:7 wt.%).
- *Separator*
  - 25 μm thick PE Celgard.

As can be seen above, the Variant C cell chemistry differs from the Baseline chemistry by an increase to the aluminum dopant from 5 to 10% and a decrease of the cobalt from 15 to 10% in the cathode. This change resulted in a 20% drop in rated capacity (0.8 Ah) at beginning-of-life (BOL) for the Variant C cells compared to the Baseline cells that had a rated capacity of 1.0 Ah at BOL.

2.2. Cell testing

The Idaho National Engineering and Environmental Laboratory (INEEL) is cycle-life testing the Gen 2 cells in two temperature groups (15 Baseline cells at 25 °C and 15 Baseline and Variant C cells each at 45 °C), as described in the cell-specific test plan [2]. Cycle-life testing is performed using the 25 Wh Power Assist profile defined in the *PNGV Battery Test Manual*, Revision 3 [3]. It consists of a constant power discharge and regen pulse with interspersed rest periods centered around 60% state-of-charge (SOC). The cumulative length of a single profile is 72 s and constitutes one test cycle. This cycle is repeated continuously during life testing.

At BOL and every 4 weeks (i.e. 33,600 cycle-life profiles/4-week test period) thereafter, cycle-life testing is interrupted for reference performance testing (RPT) that is used to quantify capacity and power fade. The RPTs consist of a *C*/1 static capacity test, a low-current hybrid pulse power characterization (L-HPPC) test, a *C*/25 static capacity test, and an Electrochemical Impedance Spectroscopy (EIS) test. All RPTs are performed at 25 °C. To minimize temperature fluctuations, the cells remained in environmental chambers during all testing activities.

The *C*/1 static capacity test consists of a complete discharge at a *C*/1 rate (i.e. 1.0 A for the Baseline cells and 0.8 A for the Variant C cells) to the minimum voltage (3.0 V) from a fully charged cell (4.1 V). The *C*/25 capacity test consists of a full discharge and charge at 1/25 of the *C*/1 rate (i.e. 40 mA for the Baseline cells and 32 mA for the Variant C cells). These tests are used to track the capacity fade as a function of time.

The L-HPPC test determines the dynamic power capability over the battery's useable charge and voltage range using a test profile that incorporates both discharge and regen pulses conducted over a depth-of-discharge (DOD) range of 10–90% [3]. From this test, the change in the power capability of the cells at 300 Wh has been determined as a function of aging due to cycle-life testing. From the BOL L-HPPC test [3], the battery size factor was determined to be 553 cells for the Baseline cells, and 651 cells for the Variant C cells.

It should be noted that the EIS studies of the cells as they age have resulted in a correlation of the EIS measurements with the power fade [5].

The Gen 2 end-of-test (EOT) criteria are specified in [2]. The INEEL cycle-life cells are organized in three groups of fifteen, as described above. One cell from each group was sent to a diagnostic lab (either Argonne National Laboratory, Brookhaven National Laboratory, Lawrence Berkeley National Laboratory, or Sandia National Laboratories) for evaluation after the BOL RPT was completed. Following the 4-week RPT, another two cells were removed from test and sent to the diagnostic labs. The EOT criteria for the remaining 12 cells are based on equal power fade increments such that the penultimate pair of cells is sent for diagnostic evaluation when the power fade reaches 30%.

3. Results and discussion

Fig. 1 shows the change in the average power and the average % power fade of the Baseline cells through 44 weeks (369,600 test cycles) of cycle-life testing at 25 °C. The average decrease in the power at 25 °C was observed to be a linear function of the cycle-life test time, i.e. number of test cycles. The % power fade at 25 °C was also found to be a linear function of the test time. The best fits to the two data sets are shown in the figure along with the value of the R^2 correlation coefficient. As can be seen in Fig. 1, the 300 Wh power has decreased ~17.7% after 369,600 cycle-life test cycles.

In Fig. 2 are shown the changes in the power and the % power fade as a function of the test time, i.e. the number of cycle-life test cycles, for a test period of 44 weeks for the group of Baseline cells tested at 45 °C. In this instance, the power was found to decrease as a function of the *square root* of the test time, and the % power fade was also found to have this same time dependence. The power fade rate was ~1.9 times faster at 45 °C than at 25 °C for a test period of 28

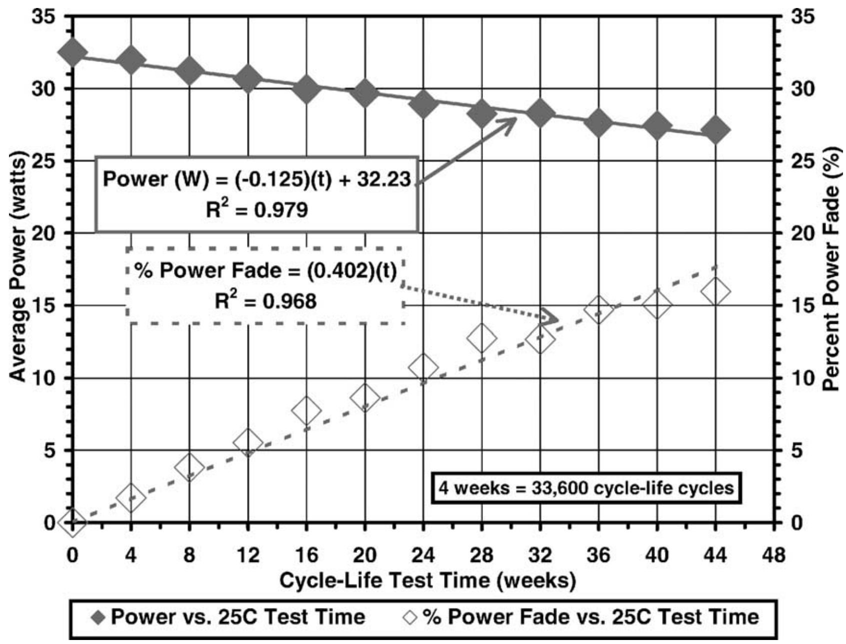

Fig. 1. The average power and the average % power fade as a function of cycle-life test time (i.e. number cycle-life test cycles) for ATD Gen 2 Baseline cells tested at 25 °C. Fits of the data to a linear function of the test time are shown. Test data are shown for a period of 44 weeks.

weeks. It can also be seen that after about 28 weeks of testing the power begins to decrease faster, and the % power fade increases at a faster rate. The % power fade rate at ~28 weeks increases by $100(9.81/4.06) = 242\%$ as calculated from the slopes of the fitting functions. The reason for this increase in the % power fade rate under the test condition of 45 °C and after ~235,000 cycle-life test cycles is not known. The diagnostic laboratories, which are an integral part of the ATD Program, are conducting physical and chemical characterization studies using a wide range of analytical techniques on disassembled cells that have undergone testing. These studies may elucidate the physical/chemical processes responsible for this observed increase in the power fade rate. Thus, there appears to be different mechanisms

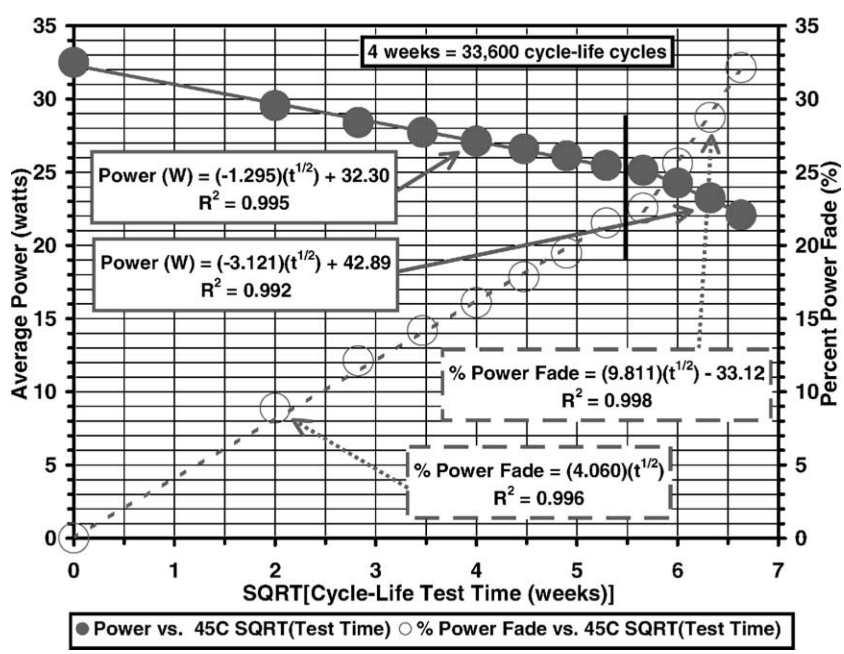

Fig. 2. The average power and the average % power fade as a function of cycle-life test time (i.e. number cycle-life test cycles) for ATD Gen 2 Baseline cells tested at 45 °C. Fits of the data to a square root function of the test time are shown. Test data is shown for a test period of 44 weeks. The rate of change in the power and the % power fade increases between the 28- and 32-week test periods.

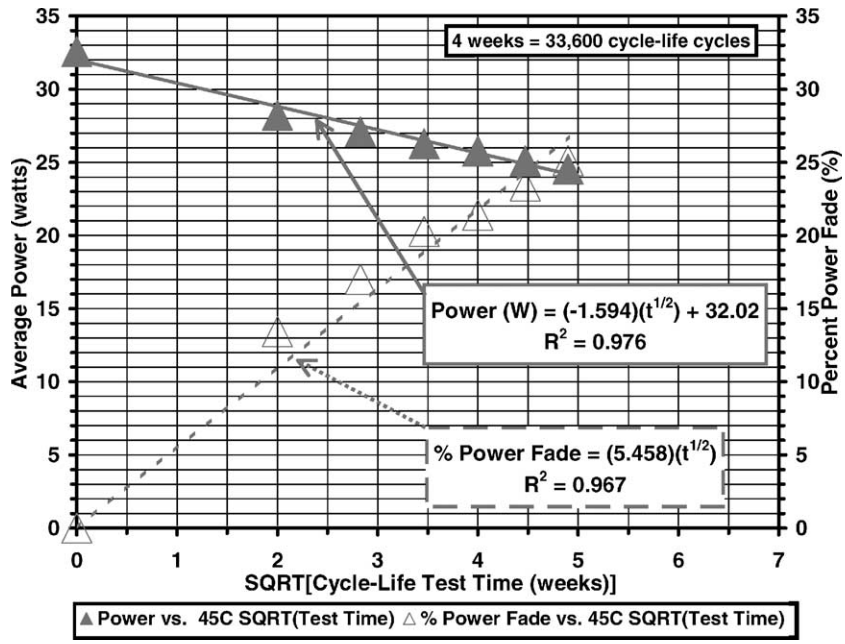

Fig. 3. The average power and the average % power fade as a function of cycle-life test time (i.e. number cycle-life test cycles) for ATD Gen 2 Variant C cells tested at 45 °C. Fits of the data to a square root function of the test time are shown. Test data for a period of 24 weeks are shown.

responsible for the power fade, whose time dependence changes with cycle-life test temperature and test time. One mechanism thought to be responsible for the power fade is the growth of a solid electrolyte interface (SEI) film that grows on the anode and/or cathode as the cell ages. The rate of growth of the SEI layer can be highly time and temperature dependent [6–8].

Fig. 3 shows the power and % power fade for the Variant C cells tested at 45 °C over a period of 24 weeks. The average power decreases as a function of the *square root* of the test time as does the % power fade. Compared to the Baseline cells tested at 45 °C, the Variant C cells' power decreases a factor of ~1.3 times faster, at least over a test period of 24 weeks.

Concurrent with the studies of the changes in the power and the power fade rate, it was found that the *C*/1 and *C*/25 discharge Ah capacities of the cells also changed as the cells aged. For the Baseline cells tested at 25 and 45 °C, as well as the Variant C cells tested at 45 °C, it was found that both the *C*/1 and *C*/25 charge capacities *decreased* as the *square root* of the test time. The rate of change of the Baseline cell *C*/1 capacity was ~1.5 times greater at 45 °C than at 25 °C. However, the *C*/1 capacity decrease for the Variant C cell tested at 45 °C was only a factor of ~0.46 times the rate of decrease of the *C*/1 capacity for those Baseline cells also tested at 45 °C. The change in the *C*/25 charge capacity for the Baseline cells tested at 45 °C was a factor of ~2 times greater than the change in the *C*/25 charge capacity for the Baseline cells tested at 25 °C. The Variant C cells *C*/25 capacity was a factor of ~0.56 *slower* that the *C*/25 capacity decrease of the Baseline cells also tested at 45 °C, and was about the same as the change in the *C*/25 capacity of the Baseline cells tested at 25 °C.

There was found to be a definite correlation between the decrease in the power and the decrease in both the *C*/1 and *C*/25 charge capacities with aging due to cycle-life testing. However, the correlation is not a simple one, and was found to require a second or higher order polynomial fits of the power decrease as a function of the change in the *C*/1 and *C*/25 charge capacity. Thus, the change in a cells charge capacity does have an impact on the power capability of the cell since the power is related to an energy change per unit time. The energy change in turn is related to a change in the voltage of the cell and the change in its capacity per unit time by the relation: $P = \text{energy/time} = (\Delta V)(\Delta Q)/\Delta t$. Further, during discharge of the battery there must be lithium in the anode that can be transported out of the carbon anode, through the SEI layer on the anode, through the electrolyte and separator, through the SEI layer on the oxide cathode, and finally be intercalated into the various available crystallographic sites in the cathode. The rate of the transport of the lithium through these various structures is related to the number of transportable lithium atoms (or ions) that in turn is highly dependent on the resistance to transport of the lithium through the various barriers present in the Li-ion battery. The physical/chemical properties of these barriers are highly dependent on the details of the cell chemistry and structure. The resistance to the transport of the lithium through these structures can be very dependent on how the properties of these barriers change with cell aging due to testing, the nature of the test, the SOC and change in the SOC during the test, the current and power of the discharge/charge test cycles, and the temperatures at which the aging test and the performance tests, such as the L-HPPC, *C*/1 and *C*/25 capacity tests are conducted.

4. Summary and conclusions

The following statements summarize the results of the cycle-life testing with regard to changes in the power and charge capacity of the ATD Gen 2 cells to date.

- Baseline cell power fade
  1. At 25 °C, the power decreases and the % power fade increases *linearly* with the test time (over a 44-week cycle-life test period, i.e. 369,600 cycles).
  2. The power fade rate is less at 25 °C than at 45 °C.
  3. At 45 °C, the power decreases and the % power fade increases as the *square root* of the test time. The *rates* of the decrease in the power and % power fade *increase* after ~28 weeks (~235,200 cycles) of testing.
- Variant C cell power fade
  1. At the 45 °C test temperature, the power decreases and the % power fade increases as the *square root* of the test time over a 24-week cycle-life test period (201,600 cycles).
  2. The rates of the decrease in the power and the increase in the % power fade have not changed over a 24-week test period.
  3. The power fade rate is greater for the Variant C cells than for the Baseline cells also tested at 45 °C.
- *C*/1 and *C*/25 discharge capacities
  1. At 25 and 45 °C, the *C*/1 and *C*/25 capacities *decrease* as a function the *square root* of the cycle-life test time, i.e. the number of test cycles (over a test period 44 weeks = 369,600 test cycles for the Baseline cells, and over a test period of 24 weeks = 201,600 test cycles for the Variant C cells). The rates-of-change with respect to test time are different for the two capacity rates and for the different cell chemistries.
  2. The rates of change for the *C*/1 and *C*/25 capacities are higher at 45 °C than at 25 °C.
  3. The change in the *C*/1 and *C*/25 capacities are *less* for the Variant C cell tested at 45 °C than for the Baseline cells tested at 45 °C.
- Correlation of power fade with *C*/1 and *C*/25 CHARGE capacities
  1. For both the Baseline and Variant C cells, the change in the decrease in the power and the decrease in the *C*/1 and *C*/25 capacities are correlated in that both decrease with aging. However, the correlation is not a simple function of the test time with the change in power being a non-linear function of the change in the *C*/1 and *C*/25 capacities.

One possible mechanism for these changes is thought to be the growth of a SEI layer on the anode and/or cathode as the battery ages, as well as changes in the properties of the separator. More detailed studies of the physical/chemical changes that occur in the test cells by examining the components of disassembled cells at various stages in their cycle-life need to be done. These studies are currently underway as part of the ATD Program.

Acknowledgements

This work was performed under the auspices of the US Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy (EE), specifically the Office of Advanced Automotive Technologies (OATT), under DOE Idaho Operations Office, Contract DE-AC07-00ID13727. Funding for this work was provided by the US DOE Office of Advanced Automotive Technologies (OAAT).

References

[1] Advanced Technology Development, 1999 Annual Progress Report, US DOE, OAAT, March 2000.

[2] PNGV Test Plan for Advanced Technology Development Gen 2 Lithium-Ion Cells, INEEL EHV-TP-121, Revision 6, October 5, 2001.

[3] PNGV Battery Test Manual, Revision 3, DOE/ID-10597, February 2001.

[4] G. Henriksen, "Gen 2 Baseline & Variant C Cells", ATD Quarterly Review Presentation in Albuquerque, NM, November 2000.

[5] J.P. Christophersen, D.F. Glenn, C.G. Motloch, R.B. Wright, C.D. Ho, V.S. Battaglia, Electrochemical impedance spectroscopy testing on the Advanced Technology Development Program lithium-ion cells, in: Proceedings of the 2002 IEEE 56th Vehicular Technology Conference, VTC Fall, 2002.

[6] R.B. Wright, C.G. Motloch, Calendar-Life Studies of Advanced Technology Development Program Gen 1 Lithium Ion Batteries, Report DOE/ID-10844, March 2001.

[7] R.B. Wright, C.G. Motloch, Cycle-Life Studies of Advanced Technology Development Program Gen 1 Lithium Ion Batteries, Report DOE/ID-10845, April 2001.

[8] R.B. Wright, C.G. Motloch, J.R. Belt, J P. Christophersen, C.D. Ho, R.A. Richardson, I. Bloom, S.A. Jones, V.S. Battaglia, G.L. Henriksen, T. Unkelhaeuser, D. Ingersoll, H.L. Case, S.A. Rogers, R.A. Sutula, J. Power Sources, in press.