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DOE Advanced Technology Development Program for Lithium-Ion Batteries:

INEEL Interim Report for Gen 2 Cycle-Life Testing

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Idaho National Engineering and Environmental Laboratory
Bechtel BWXT Idaho, LLC

FreedomCAR

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ABSTRACT

In conjunction with the Partnership for a New Generation of Vehicles (PNGV), the Advanced Technology Development (ATD) Program was initiated in 1998 by the U.S. Department of Energy Office of Advanced Automotive Technologies to find solutions to the barriers that limit the commercialization of high-power lithium-ion batteries. In 2002, PNGV was superceded by FreedomCAR (Freedom Cooperative Automotive Research) and this work is now under the auspices of the FreedomCAR and Vehicle Technologies Program. This report documents the performance evaluation of the second generation of ATD cells (i.e., Gen 2 cells) that were cycle-life tested at the Idaho National Engineering and Environmental Laboratory (INEEL). The Gen 2 cells consist of a baseline chemistry and one variant chemistry (i.e., Variant C).

Testing began with standard characterization tests as defined in the *PNGV Battery Test Manual*, Revision 3, and the cell-specific test plan. These tests include the $C_1/1$ static capacity test, the $C_1/25$ static capacity test, the low-current hybrid pulse power characterization (L-HPPC) test, and the electrochemical impedance spectroscopy (EIS) test. These four tests also make up the reference performance tests (RPTs) that are performed every four weeks (33,600 cycles) during cycle-life testing. INEEL received 30 Baseline cells and divided them into two groups of 15, one group being cycle-life tested at 25°C, the other at 45°C. INEEL also received 15 Variant C cells and is cycle-life testing them at 45°C. All cycle-life testing is performed at 60% state-of-charge (SOC) using the PNGV 25-W·h power assist cycle-life profile.

The Baseline cells have completed 48 weeks of aging; the Variant C cells have completed 28 weeks. At 45°C, the Variant C cells consistently show a lower capacity fade than do the Baseline cells. Further, the Variant C $C_1/25$ capacity fade and differential capacity at 45°C is similar to the 25°C Baseline cells. For all cells, the majority of the capacity fade occurs within the peaks of the differential capacity curves, which decrease as a function of cycle-time and temperature. Although the chemistry change in the Variant C cells improves capacity fade, it has a deleterious effect on power fade, as measured from the L-HPPC test. The Variant C cells were no longer capable of simultaneously meeting the FreedomCAR power and energy goals after 20 weeks of aging. In contrast, the 45°C Baseline cells fell below the goals after 36 weeks, and the 25°C Baseline cells are still capable of meeting the goals. The Variant C cells also show a very high impedance growth at the semicircle trough, as measured from the EIS test. At characterization, the Variant C cell impedance is larger than the Baseline cell impedance, and, after 28 weeks, the impedance growth at the trough is larger than the 48-week impedance growth for the Baseline cells.

Eight 25°C Baseline, two 45°C Baseline, and four 45°C Variant C cells remain on test. For diagnostic purposes, the 25°C Baseline cells will reach end of test at 36% power fade, whereas the 45°C Baseline and Variant C cells will continue testing until they reach 50% power fade.

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ACRONYMS

ANL	Argonne National Laboratory
ASI	area-specific impedance
ATD	Advanced Technology Development
BNL	Brookhaven National Laboratory
BOL	beginning-of-life
BSF	battery size factor
DOD	depth-of-discharge
DOE	Department of Energy
EIS	electrochemical impedance spectroscopy
EOT	end of test
FreedomCAR	Freedom Cooperative Automotive Research
Gen	Generation
INEEL	Idaho National Engineering and Environmental Laboratory
LBNL	Lawrence Berkeley National Laboratory
L-HPPC	low-current hybrid pulse power characterization
LPM	lumped parameter model
OCV	open-circuit voltage
OSPS	operating set point stability
PNGV	Partnership for a New Generation of Vehicles
RPT	reference performance test
RTD	resistance temperature detector
SOC	state-of-charge
SNL	Sandia National Laboratories

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1. INTRODUCTION

In conjunction with the Partnership for a New Generation of Vehicles (PNGV), the U.S. Department of Energy (DOE) initiated the Advanced Technology Development (ATD) Program in 1998 to address the technical barriers impeding the commercialization of high-power Lithium-ion batteries for hybrid electric vehicle applications. These barriers include insufficient calendar life, high production costs, and poor response to abuse scenarios. The ATD Program is organized into four program areas, including long life, low cost, abuse tolerance, and technology transfer. A full description of the program is provided in Reference 1. [Note: In 2002, PNGV was superceded by the formation of a new program between the U.S. Government and the U.S. Council for Automotive Research, dubbed FreedomCAR (Freedom Cooperative Automotive Research). Also in 2002, the U.S. DOE Office of Energy Efficiency was reorganized and this work is now sponsored under the auspices of the FreedomCAR and Vehicle Technologies Program.]

The ATD Program is using five DOE laboratories to address these critical barriers. Argonne National Laboratory (ANL) has overall programmatic and technical lead responsibilities, including cell chemistry. The Idaho National Engineering and Environmental Laboratory (INEEL) has lead responsibility for cell testing and aging in collaboration with ANL and Sandia National Laboratories (SNL). SNL also has lead responsibility for the investigation of abuse tolerance. Lawrence Berkeley National Laboratory (LBNL) is the lead diagnostic laboratory in concert with Brookhaven National Laboratory (BNL), ANL, SNL, and INEEL. These five national laboratories are working in close coordination to:

- Identify and quantify the factors responsible for power fade through data analysis of aged cells
- Provide aged cells and analyzed performance data to enable correlation against diagnostic results and facilitate selection of the most useful analytical tools
- Develop aging protocols and explore new tests, analyses, and modeling methodologies relating to calendar life and provide results to battery developers and other laboratories.

1.1 ATD Testing Summary

Testing and analyses of the first generation of ATD cells (i.e., Gen 1 cells) have been completed and are summarized in Reference 2. Detailed results from the Gen 1 calendar and cycle-life testing performed at INEEL are provided in References 3 through 5. Testing of the second generation of cells (i.e., Gen 2 cells) is now underway. The 18650-size Gen 2 cells were manufactured by Quallion LLC, and consist of a baseline cell chemistry and one variant chemistry (referred to as Variant C). The difference between the Gen 1 and Gen 2 Baseline cells chemistries is defined in Reference 6 and summarized in Table 1.

The Variant C cell chemistry differs from the Gen 2 Baseline chemistry by an increase to the aluminum dopant from 5% to 10% and a decrease to the cobalt from 15% to 10% in the cathode (i.e., $LiNi_{0.8}Co_{0.1}Al_{0.1}O_2$). This change resulted in a 20% drop in rated capacity (0.8 A·h) at beginning of life

(BOL) compared to the Baseline cell rated capacity of 1.0 A·h. Otherwise, the Gen 2 Baseline and Variant C chemistries are identical.

Table 1. Gen 1 and Gen 2 baseline cell chemistries.

	Gen 1 Baseline Cells	Gen 2 Baseline Cells
Positive Electrode	8 wt% PVDF binder 4 wt% SFG-6 graphite 4 wt% carbon black 84 wt% $LiNi_{0.8}Co_{0.2}O_2$	8 wt% PVDF binder 4 wt% SFG-6 graphite 4 wt% carbon black 84 wt% $LiNi_{0.8}Co_{0.15}Al_{0.5}O_2$
Negative Electrode	9 wt% PVDF binder 16 wt% SFG-6 graphite 75 wt% MCMB-6 graphite	8 wt% PVDF binder 92 wt% MAG-10 graphite
Electrolyte	1 M $LiPF_6$ in EC:DEC(1:1)	1.2 M $LiPF_6$ in EC:EMC (3:7)
Separator	37 µm thick PE	25 µm thick PE

The ATD Program purchased 195 Gen 2 cells (165 Baseline cells and 30 Variant C cells) for testing. INEEL received 45 cells (30 Baseline cells and 15 Variant C cells) for cycle-life testing. ANL received 30 cells (15 Baseline and Variant C cells each) for calendar-life testing. ANL also received 7 Baseline cells for archiving. SNL received 62 Baseline cells for accelerated-life testing and 48 Baseline cells for thermal abuse. Each diagnostic laboratory (LBNL, ANL, and BNL) received 1 Baseline cell without aging. This report documents the testing and analyses of the cycle-life testing performed at the INEEL.

1.2 Cycle-Life Testing Overview

Gen 2 cycle-life testing at the INEEL is performed with oversight by the DOE FreedomCAR and Vehicle Technologies Program. Testing and analyses are performed in accordance with the procedures outlined in the *PNGV Battery Test Manual,* Revision 3 (Reference 7) and as detailed in the cell-specific test plan (Attachment 1). The Gen 2 cells are testing against the FreedomCAR power-assist goals.

INEEL received 30 Baseline cells on January 8, 2001 and initiated testing between January 23 and February 2, 2001. INEEL received 15 Variant C cells on July 30, 2001, and began testing on August 16, 2001. This report marks the completion of 403,200 cycles on the Baseline cells and 235,200 cycles on the Variant C cells. Ten baseline cells and four Variant C cells remain on test, and testing will continue until the specified end-of-test (EOT) criteria are met (Section 3.4). Once all cells have met the EOT criteria, a final report will also be issued.

2. BATTERY INFORMATION

2.1 Battery Rating and Limitations

The following battery ratings and limitations were used for the testing:

	Baseline Cells	Variant C Cells
$C_1/1$ rated capacity	1.0 A·h	0.8 A·h
$C_1/1$ nominal capacity (average)	0.979 A·h	0.826 A·h
Cell nominal weight (average)	38.8 g	38.3 g
Battery Size Factor	553	651

Temperature	
Operating Range	-20 to +60ºC (discharge)
Storage	10°C ± 3°C
Maximum (discharge)	60°C
Maximum (charge)	40°C
Voltage Limits	
Minimum discharge voltage	3.0 V (18-s pulse)
	3.0 V (continuous)
Maximum charge voltage	4.3 V (10-s pulse)
	4.1 V (continuous)
HPPC Calculation voltages	
Maximum	4.1 V
Minimum	3.0 V
Current Limits	
Maximum discharge current	8.0 A (18-s pulse)
	2.0 A (continuous)
Maximum charge current	8.0 A (10-s pulse)
	1.0 A (continuous)

Special Considerations

Special considerations, including the ATD labeling scheme, temperature control, tab issue, and a tab and vent failure at the INEEL, are provided in Appendix 1.

3. TESTING

Characterization and life testing were performed in accordance with the *PNGV Battery Test Manual*, Revision 3 (Reference 7) and the ATD Gen 2 test plan (Attachment 1). FreedomCAR performance goals, procedures, analytical methodologies, and ATD specific testing requirements are detailed in these two documents and are summarized below.

3.1 Characterization Testing

All characterization testing was performed at 25°C. Following the receipt inspection (Section 4.1), testing was initiated with five consecutive C_1 discharges at the $C_1/1$ rate, beginning with a fully charged cell and terminating at the specified cutoff voltage of 3.0 V. Next, a $C_1/25$ discharge and charge test was performed, with a 1-h rest between the full discharge to 3.0 V and the full charge to 4.1 V.

Following the static capacity tests, the cells underwent electrochemical impedance spectroscopy (EIS) tests. The EIS test begins by discharging the cells from a fully charged state to the specified OCV, corresponding to 60% SOC (Appendix D of Attachment 1). Following an 8-h rest at OCV, which allows the cells to reach electrochemical equilibrium, the impedance is measured over a frequency range of 10 kHz to 0.01 Hz, with 10 points per decade of frequency. The INEEL conducts EIS testing with a Model 273A EG&G Potentiostat/Galvanostat, a Model 1260 Solartron Frequency Analyzer, and the ZPlot control software (Appendix E of Attachment 1). The INEEL measures impedance using a four-terminal connection, eliminating the need to subtract cable impedance.

The low-current hybrid pulse power characterization (L-HPPC) test was performed next. It consists of a constant-current discharge and regen pulse with a rest period in between, for a total duration of 60 s. The 18-s constant-current discharge pulse is performed at a $5C_1$ rate for the ATD Gen 2 cells (i.e., 5 A for the Baseline cells and 4 A for the Variant C cells). This profile is repeated at every 10% depth-of-discharge (DOD) increment, with a 1-h rest at OCV at each DOD increment to ensure that the cells have electrochemically and thermally equilibrated.

The BOL L-HPPC test is used to calculate a scaling factor known as the battery size factor (BSF). The BSF is the minimum number of cells required to meet the FreedomCAR power and energy goals (25 kW and 300 W·h, respectively) based on a 30% BOL power margin (i.e., 25 kW * 1.3, or 32.5 kW), as specified in Reference 7. The 30% BOL power margin provides an allowance for cell degradation over time. The BSF is used to scale all subsequent FreedomCAR power and energy-based tests, including the 25-W·h Power Assist cycle-life profile (see Reference 7). The ATD Gen 2 Baseline and Variant C cells require an average BSF of 553 and 651, respectively.

3.2 Cycle-Life Testing

All INEEL Gen 2 cells are cycle-life testing using the standard 25-W·h power assist cycle-life profile, as defined in Reference 7. It consists of a constant power discharge and regen pulse with interspersed rest periods centered around 60% SOC. The cumulative length of a single profile is 72 s and constitutes one cycle. This cycle is repeated continuously during life testing. Due to the length of the test, only the first and last one hundred consecutive cycles and every hundredth cycle in between are recorded (see Attachment 1). The INEEL Gen 2 Baseline cells were split into two groups of 15 with one group cycle-life testing at 25°C, and the other at 45°C (one cell from each group was removed from test and sent for diagnostic analysis after characterization testing, see Section 3.4). The 15 INEEL Gen 2 Variant C cells are cycle-life testing at 45°C (again, with one cell sent for diagnostic analysis after characterization testing, Section 3.4).

Prior to cycle-life testing, the operating set point stability (OSPS) test was performed to verify cycling stability. The OSPS test consists of 100 consecutive cycle-life profiles. The requirement is that at its completion, the actual SOC should be within ±2% of the target SOC (60% SOC), based on the OCV following a 1-h rest at the beginning and end of the 100 pulses. If the SOC is charge positive or charge negative (i.e., unstable), then a control voltage is established, and the OSPS test is repeated until stable cycling occurs.

3.3 Reference Performance Tests

Every 4 weeks (i.e., 33,600 cycles), cycle-life testing is interrupted for reference performance tests (RPTs), which are used to quantify changes in capacity, resistance, and power. *Capacity fade* is the percentage loss in the discharge capacity during the $C_1/1$ test. *Power fade* is the percentage loss in the power at 300 W·h (Reference 7). The fades are normalized to the characterization RPT (i.e., at characterization, the capacity and power fades are both 0%). RPTs consist of a $C_1/1$ static capacity test, a L-HPPC test, a $C_1/25$ static capacity test, and an EIS test (Attachment 1). All RPTs are performed at 25°C.

Initially, the EOT criteria (Section 3.4) specified that only two cells would receive full RPTs every four weeks. The other cells would undergo full RPTs at characterization and EOT, and only partial RPTs (a $C_1/1$ and L-HPPC test) every four weeks in between. After assessing the first 12 weeks of aging data, the RPT criteria was changed to a full RPT every four weeks for each cell on test.

3.4 End-of-Test Criteria

The Gen 2 EOT criteria are specified in Appendix C of Attachment 1. The cells are organized in groups of 15 (15 Baseline cells each at 25 and 45°C, and 15 Variant C cells at 45°C). One cell from each group is sent to a diagnostic laboratory for evaluation after characterization testing is complete. Following four weeks of aging, another two cells are removed from test and sent to diagnostic laboratories. The EOT criteria for the remaining 12 cells are based on equal power fade increments such that the penultimate pair of cells are sent for diagnostic evaluation when the power fade reaches 30%. The remaining two 25°C Baseline cells will continue testing one power fade increment beyond 30%. The remaining four 45°C cells (two cells each for the Baseline and Variant C chemistries) will continue testing until they reach 50% power fade.

3.5 Testing Status

The Gen 2 cell aging is on track, and the cells are performing well. Eight 25°C Baseline cells and two 45°C Baseline cells remain on test and have completed 48 weeks of aging (403,200 cycles). The 25°C Baseline cells have an average power fade of 17.4%, with the next target power fade (see Appendix C of Attachment 1) at 19.5%. The remaining two 45°C Baseline cells have an average power fade of 34.7% and will continue testing until they reach 50.0% power fade. Four 45°C Variant C cells remain on test and have completed 28 weeks of aging (235,200 cycles) with an average power fade of 26.5%. Two of these cell will be taken off test at 30.0% power fade; the remaining two will continue until they reach 50.0% power fade.

4. RESULTS

Due to a large number of Gen 2 data, only cell averages or results from a representative cell from each cell group (i.e., 25°C Baseline cells, 45°C Baseline cells, and 45°C Variant C cells) are presented in this report. Detailed test results for all Gen 2 cycle-life cells are available on the INEEL ATD web page (http://atd.inel.gov). Individual usernames and passwords are required and can be requested online.

4.1 Receipt Inspection

The receiving inspection conducted before testing confirmed that no cells were damaged other than G2C.60L45.I173.00.NA.NA.L.Q (see Section A1.1 in Appendix 1 for details on the ATD labeling scheme and Section A1.5 for information on this cell). This included visual inspection and measuring cell weights, OCVs, and impedance at 1 kHz. Figure 1 shows the 15 Variant C cells that arrived on July 30, 2001. Table 2 summarizes the average receipt inspection measurements for the 25°C Baseline cell, the 45°C Baseline cell, and the 45°C Variant C cell groups, respectively. All three cell groups show similar weights and OCVs, but the Variant C cells show a lower impedance at 1 kHz. (The Variant C cell group average does not include Cell 173, which was returned to Quallion, LLC, due to poor performance.)

Figure 1. Fifteen Variant C cells, as received.

Table 2. Receipt inspection measurements for the three INEEL cell groups.

INEEL Cell Group	Receipt Inspection Date	Weight ($g \pm \sigma$)	OCV ($V \pm \sigma$)	Real Impedance at 1 kHz ($m\Omega \pm \sigma$)
Baseline Cells at 25°C	01/09/01	38.85 ± 0.28	3.56 ± 0.04	12.67 ± 0.97
Baseline Cells at 45°C	01/09/01	38.76 ± 0.14	3.58 ± 0.03	12.26 ± 0.21
Variant C Cells at 45°C	07/30/01	38.33 ± 0.21	3.53 ± 0.25	10.61 ± 0.42

4.2 Capacity

4.2.1 C_1/1 Capacity Fade and Model

The last three characterization discharge capacities agreed within 2% of each other, with the fifth C_1/1 discharge averaging to 0.979 ± 0.010 A·h for all 30 Baseline cells and 0.826 ± 0.016 A·h for the 15

Variant C cells. Figures 2 and 3 show the average $C_1/1$ capacity and the average capacity fade, respectively, as a function of test time for all three INEEL cell groups. Both the Baseline and Variant C cells show a uniform and monotonic decline in discharge capacity during life testing. The Baseline cell capacities are larger than the Variant C capacities, but they are also fading much more rapidly.

Figure 4 shows that the average $C_1/1$ capacity fades increase as a function of the square root of time for all cycle-life cells. The 25°C Baseline cells show a steady increase with cycle time, but the 45°C Baseline cells show a mechanistic change between 28 weeks and 32 weeks of cycling; after 28 weeks, the average capacity begins to fade more rapidly. The Variant C cells show a mechanistic change after 8 weeks of cycle-life testing, with the capacity fade slowing down after 8 weeks.

4.2.2 $C_1/25$ Capacity Fade and Model

Figure 5 shows the average $C_1/25$ static capacity for the INEEL Baseline and Variant C cells. Like the $C_1/1$ capacity, the 45°C Variant C cell $C_1/25$ capacity is lower than the Baseline cells. Figure 6 shows the average capacity fade as a function of cycle time. The average 45°C Baseline cell capacity is showing the most fade. The average 45°C Variant C cell $C_1/25$ capacity fade is similar to the average 25°C Baseline cell $C_1/25$ capacity fade through 28 weeks of cycle-life testing.

Figure 7 shows that the average $C_1/25$ capacity fades also increase as a function of the square root of time for all cycle-life cells. The 25°C Baseline and 45°C Variant C cells show a steady growth, while the 45°C Baseline cells show a mechanistic change between 36 and 40 weeks. After 36 weeks, the average capacity fade rate increases slightly.

4.2.3 $C_1/25$ Differential Capacity

The $C_1/25$ static capacity data are used to calculate the relative change in capacity as a function of the voltage, normalized to the average BOL $C_1/25$ capacity. The data are first smoothed by taking the capacity every ninth minute and averaging the voltage during that 9-min period. The differential capacity [i.e., 1/Q * d(A·h)/dV] is calculated with a three-point numerical differentiation of the smoothed data.

The Baseline cell $C_1/25$ differential capacity for G2.60L25.I114.20.48.18.G.T through 48 weeks of cycling at 25° is shown in Figure 8. Its performance is similar to the average and is therefore representative of all 25°C Baseline cells. This figure shows that the differential capacity for this cell decreases as a function of cycle time. The capacity loss predominately occurs at the three different SOC peaks (i.e., 9, 40, and 77% SOC from the characterization discharge curve). The locations of the peaks also increase slightly in SOC as a function of aging, as shown by small shifts to the right. The point at which cycle-life testing is performed (60% SOC) shows no significant capacity loss as a function of time.

Figure 9 shows the differential capacity for G2.60L45.I130.50.48.36.G.T, a representative 45°C Baseline cell. As expected, the differential capacity through 48 weeks at 45°C decreases more rapidly than the 25°C Baseline cells. The location of the peaks occurs at near the same SOCs as the 25°C Baseline cells, and the capacity loss also occurs predominately at the location of the peaks. The shift in the peak locations is more pronounced at 45°C.

Figure 10 shows the differential capacity for G2C.60L45.I162.30.28.26.G.T, a representative 45°C Variant C cell through 28 weeks of aging. The differential capacity for the Variant C cells is missing the initial discharge peak, and the charge peak at 5% SOC has a lower amplitude than the Baseline cells. The rate of decrease and shift in the differential capacity for the 45°C Variant C cells is similar to that of the 25°C Baseline cells. This is consistent with the results seen in the $C_1/25$ capacity fade (Figure 6).

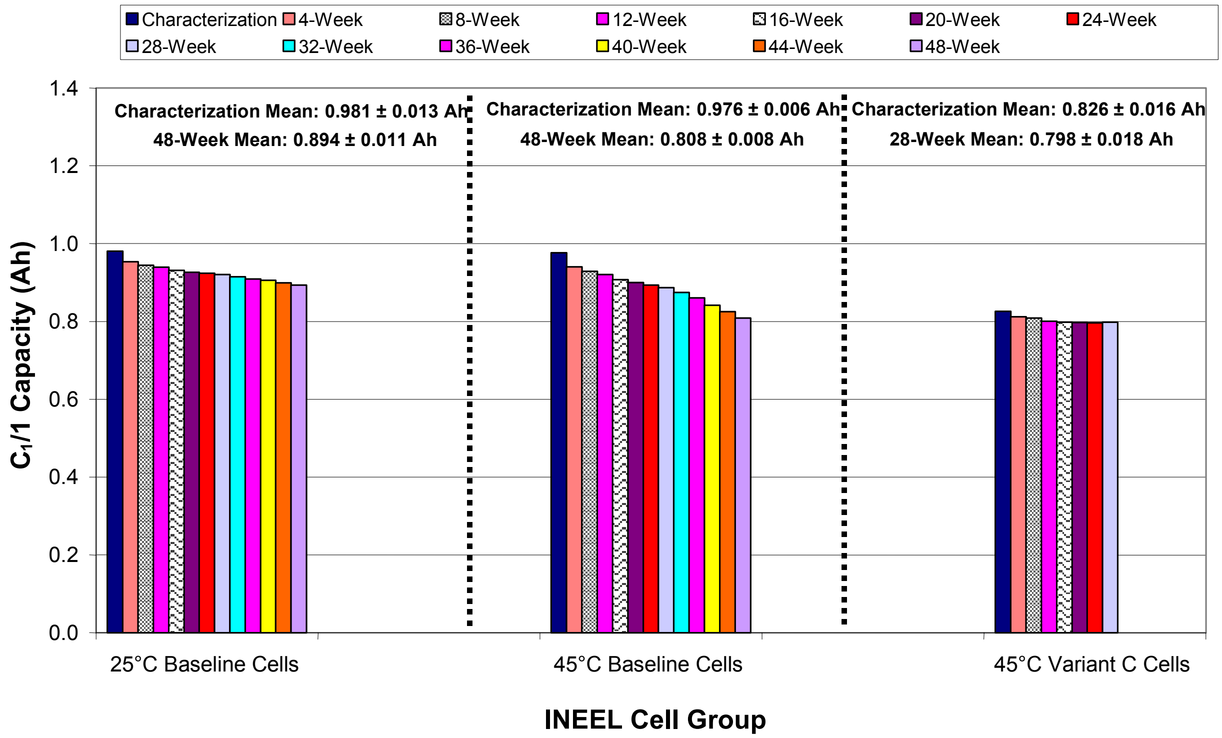

Figure 2. Average $C_1/1$ static capacity.

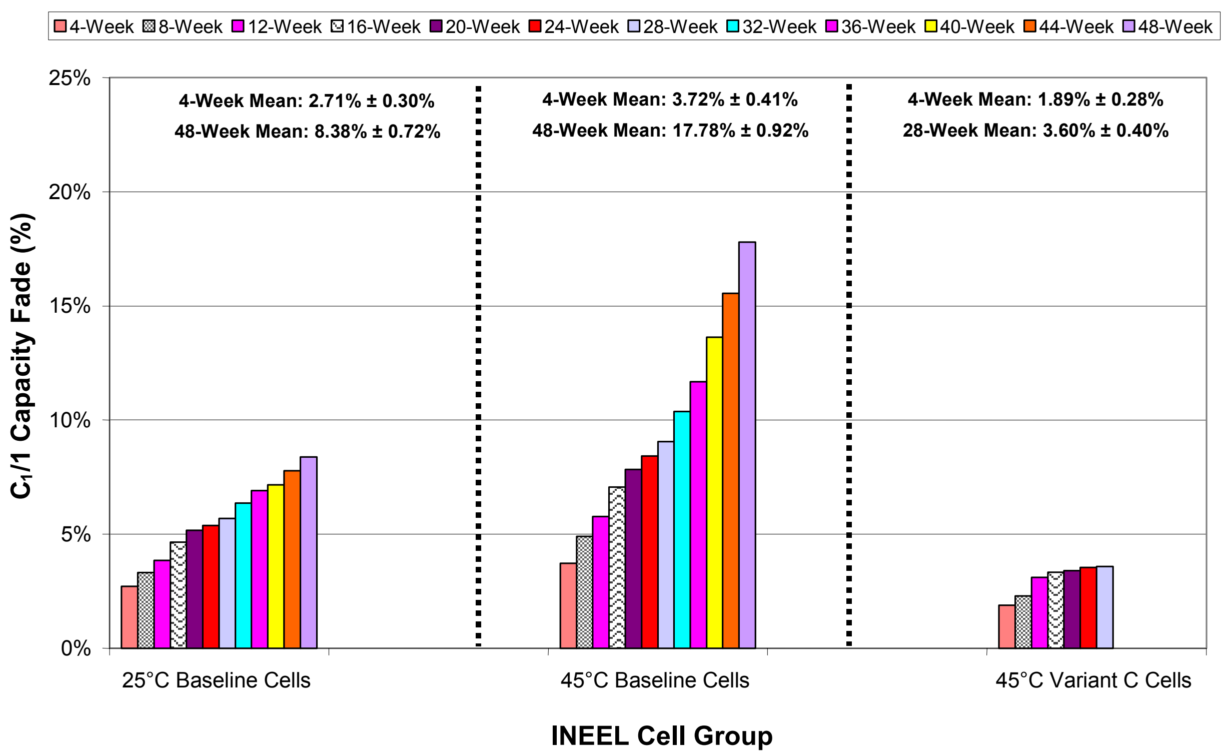

Figure 3. Average $C_1/1$ static capacity fade.

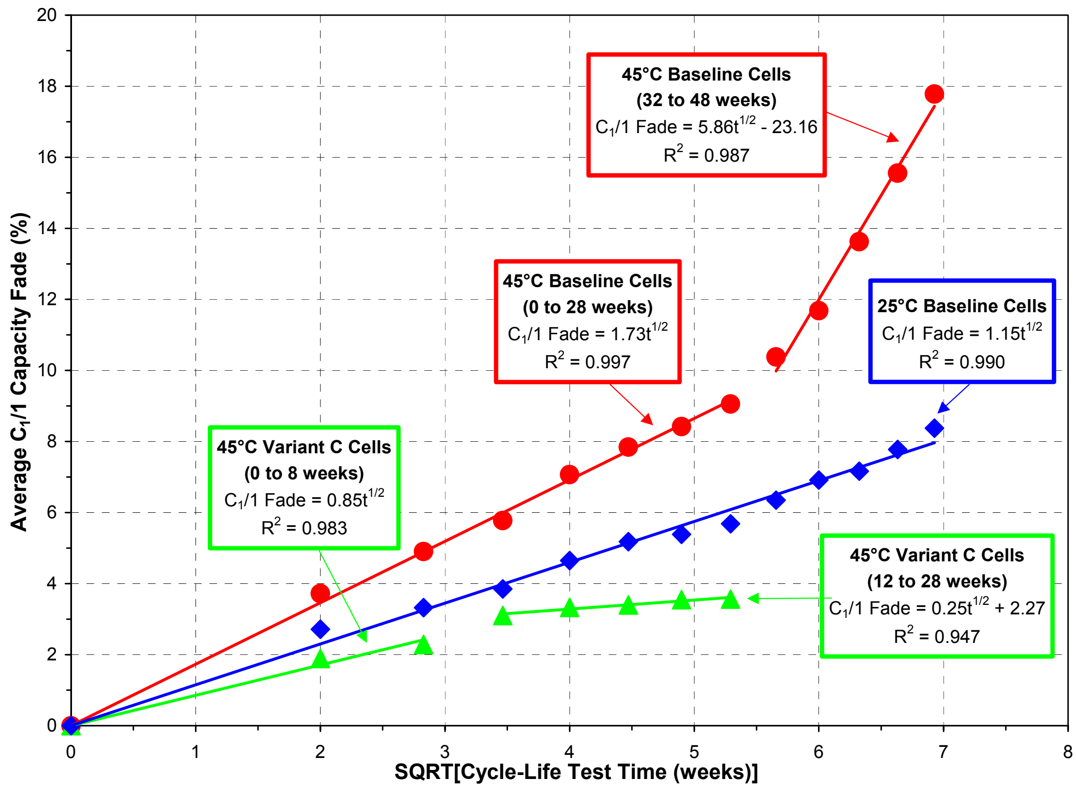

Figure 4. Average $C_1/1$ static capacity fade as a function of cycle time.

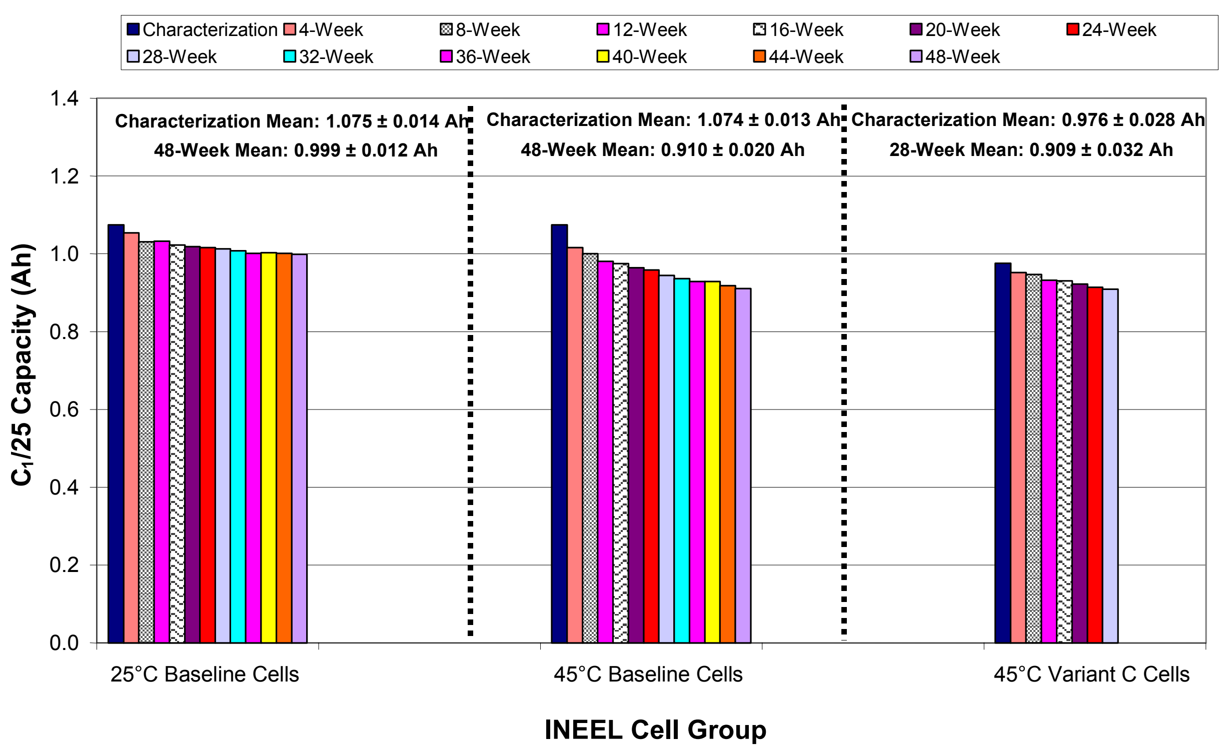

Figure 5. Average $C_1/25$ static capacity.

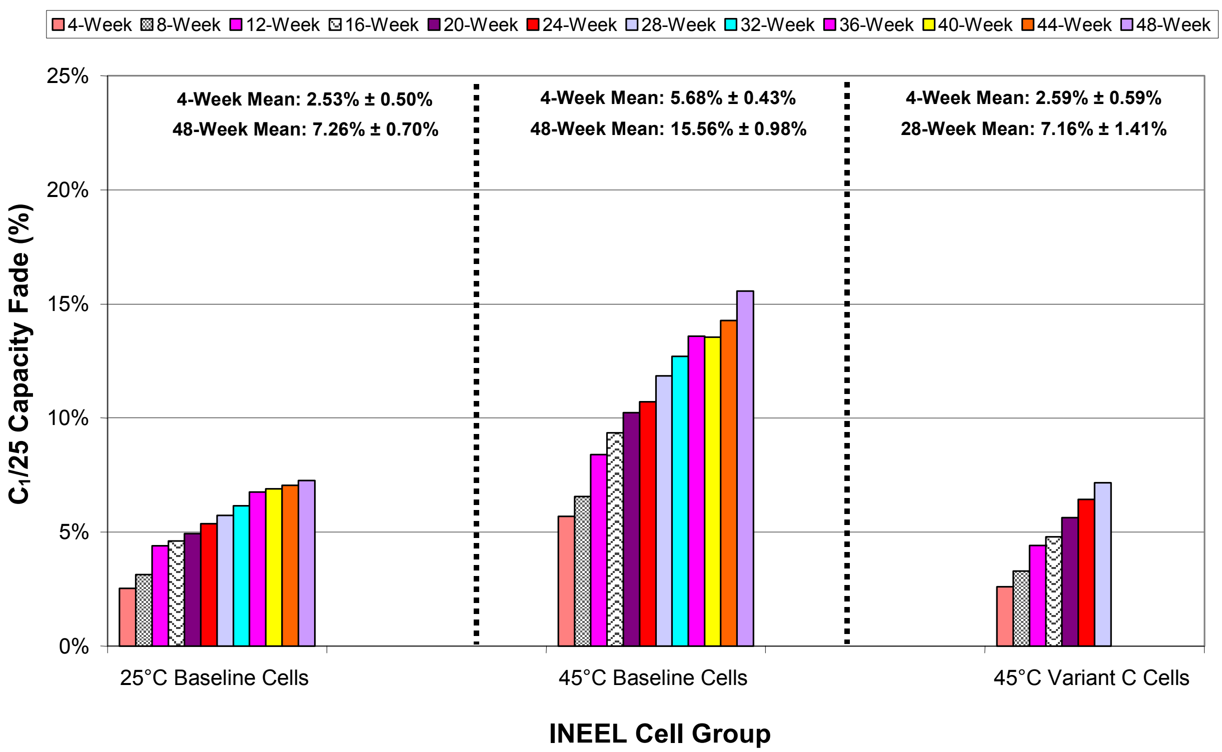

Figure 6. Average $C_1/25$ static capacity fade.

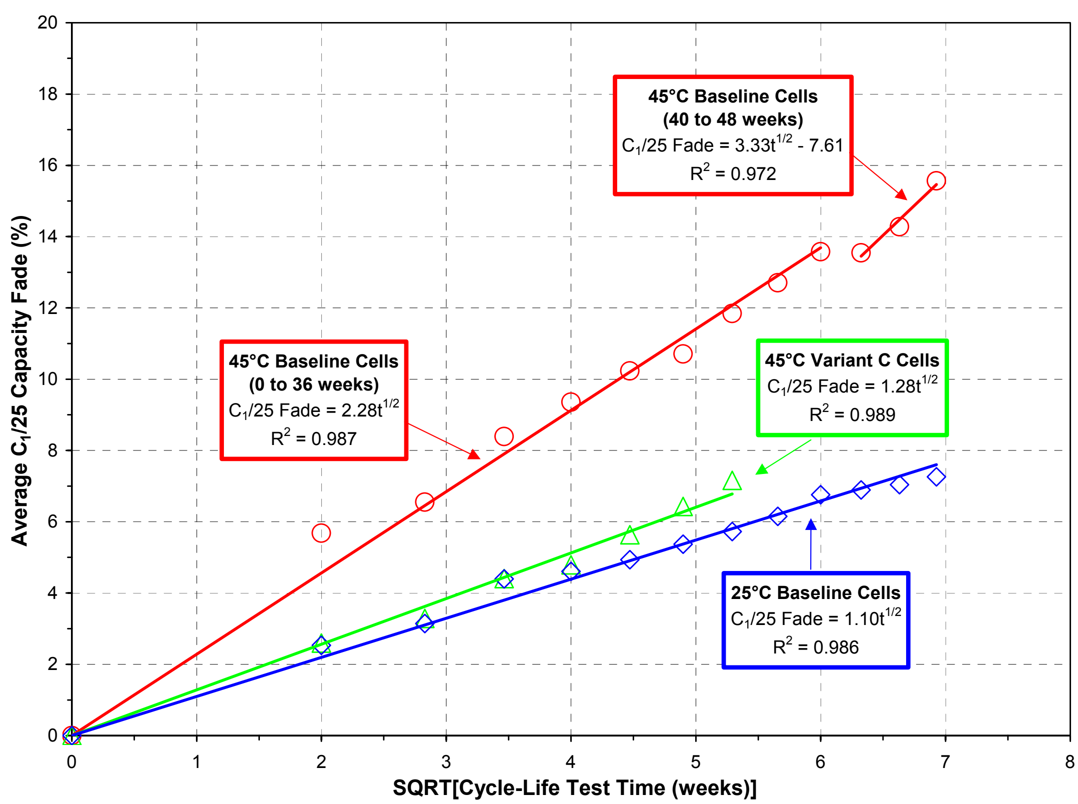

Figure 7. Average $C_1/25$ static capacity fade as a function of cycle time.

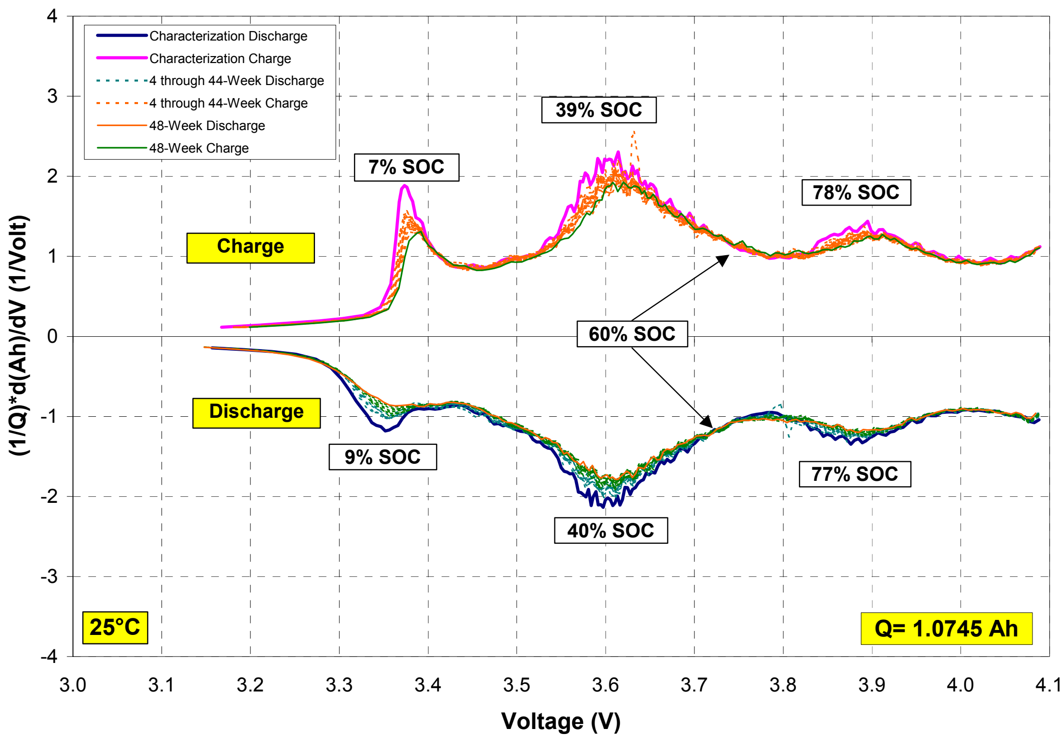

Figure 8. Differential capacity curves for G2.60L25.I114.20.48.18.G.T (25°C Baseline cell).

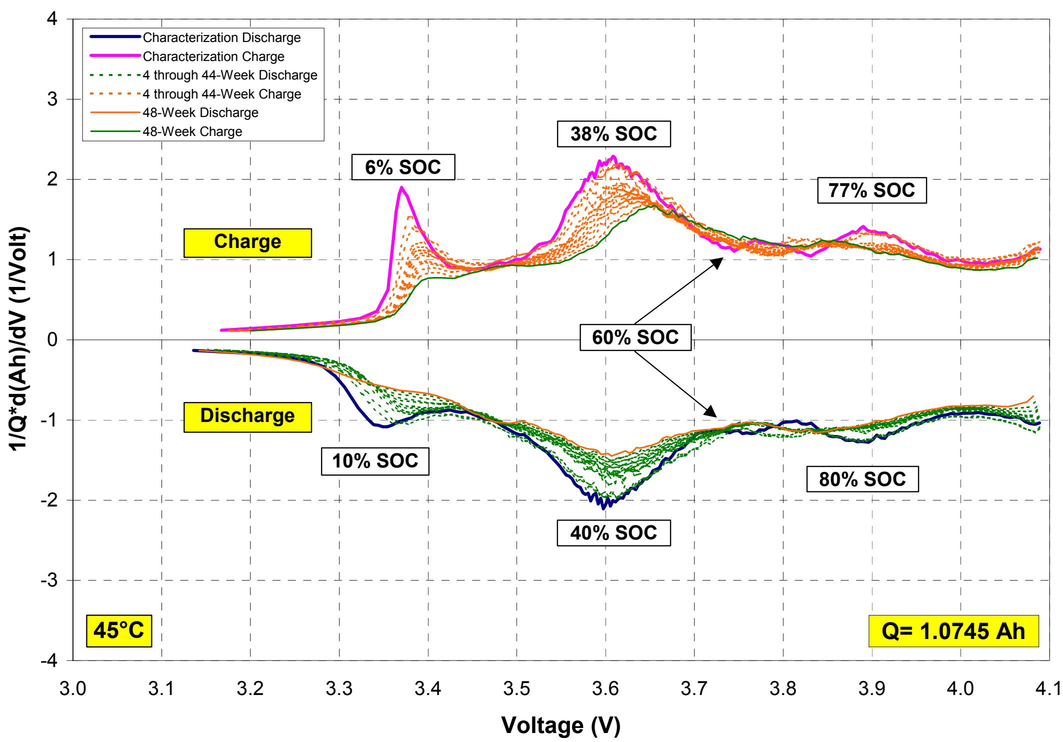

Figure 9. Differential capacity curves for G2.60L45.I130.50.48.36.G.T (45°C Baseline cell).

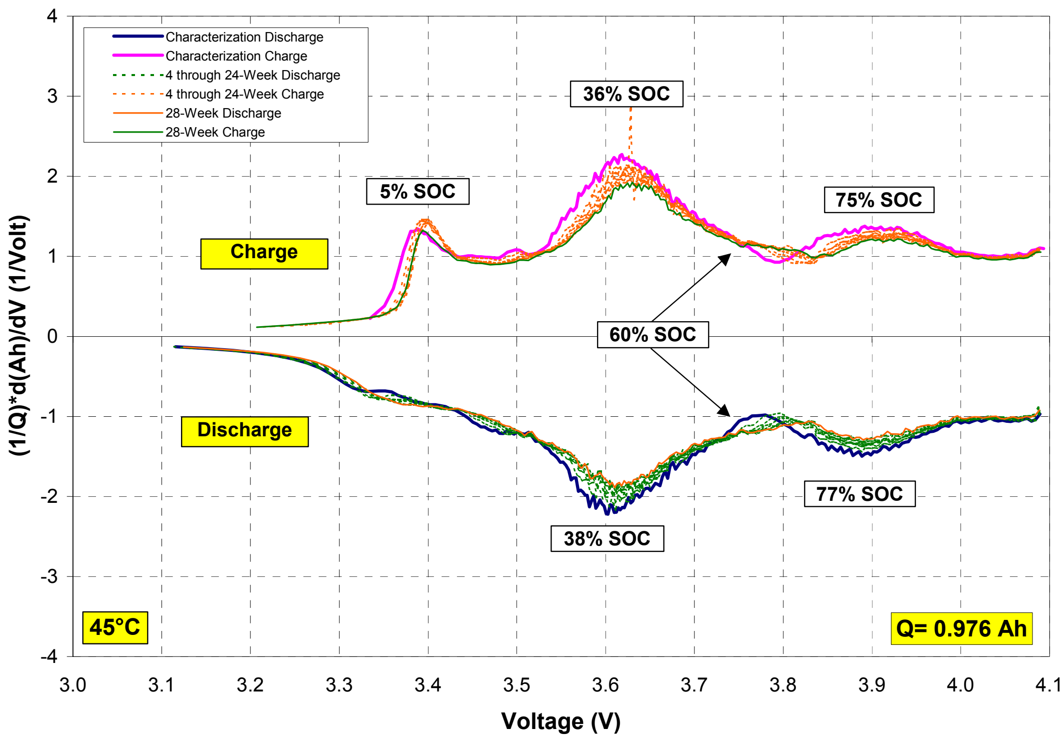

Figure 10. Differential capacity curves for G2C.60L45.I162.30.28.26.G.T (45°C Variant C cell).

4.3 Power

4.3.1 Area Specific Impedance

Area-specific impedance (ASI) is found by multiplying the pulse resistance (ΔV/ΔI) from the L-HPPC test by the electrode area (846.3 cm^2 for the Gen 2 cells). Figure 11 (page 16) shows the ASI as a function of OCV for G2.60L25.I114.20.48.18.G.T (a 25°C Baseline cell) at characterization and 48 weeks. As expected, both the discharge and regen ASIs increase with aging. Figure 12 shows the ASI at characterization and 48 weeks for G2.60L45.I130.50.48.36.G.T (a 45°C Baseline cell). This also shows that the ASIs increase with aging, but more rapidly than the 25°C Baseline cells. Figure 13 shows the ASI for G2C.60L45.I162.30.28.26.G.T (a 45°C Variant C cell) through 28 weeks of cycle-life testing. The Variant C cell ASIs are higher at characterization, and grow more rapidly than the 45°C Baseline cells.

Figure 14 compares an INEEL Baseline cycle-life cell (G2.60L45.I130.50.44.33.G.T) and a representative Baseline calendar-life cell (G2.60C45.A217.50.44.27.G.T) from ANL through 44 weeks of aging at 45°C. At BOL, the ASIs are similar, but at 44 weeks, the cycle-life cells show a greater growth in resistance. Figure 15 compares INEEL Variant C cell G2C.60L45.I162.30.28.26.G.T and a representative ANL Variant C calendar-life cell (G2C.60C45.A224.25.28.20.G.T) through 28 weeks of aging at 45°C. The Variant C characterization ASIs are also similar, and the calendar-life cells also show a lower ASI after 28 weeks.

4.3.2 Available Energy

Available energy is the difference between the discharge and regen energy at a given power (Reference 7). Figure 16 shows the BSF-scaled available energy as a function of the BSF-scaled discharge power for G2.60L25.I114.20.48.18.G.T (a 25°C Baseline cell). After 48 weeks of cycling at 60% SOC, the 25°C Baseline cells are still capable of simultaneously meeting the FreedomCAR power and energy goals of 25 kW and 300 W·h, respectively. The available energy decreases steadily as a function of time, and shows a 17.6% power fade for INEEL Cell 114 (compared to an average 25°C Baseline cell power fade of 17.4%). Figure 17 shows the available energy curves through 48 weeks of cycle-life testing on G2.60L45.I130.50.48.36.G.T (a 45°C Baseline cell). The 45°C Baseline cell available energy decreases more rapidly and the cells are no longer capable of simultaneously meeting the FreedomCAR power and energy goals. INEEL Cell 130 dropped below the FreedomCAR goals at 36 weeks (i.e., 302,400 cycles, narrowly passing the FreedomCAR cycle-life goal of 300,000 cycles, see Reference 7) and now shows a power fade of 36.1% (compared to an average 45°C Baseline cell power fade of 34.7%). Figure 18 shows the available energy for G2C.60L45.I162.30.28.26.G.T (a 45°C Variant C cell) through 28 weeks. The available energy for the Variant C cells decreases more rapidly than the Baseline cells. INEEL Cell 162 dropped below the FreedomCAR goals at 20 weeks (i.e., 168,000 cycles), and shows a power fade of 25.7% after 28 weeks (compared to an average 45°C Variant C cell power fade of 26.5%).

4.3.3 Power Fade

Figure 19 shows the average power at 300 W·h for the INEEL Baseline and Variant C cells. All three cell groups have similar initial powers due to the BSF scaling. The Variant C chemistry requires 98 more cells to meet the same power and energy goals as the Baseline cells. The average power decreases monotonically as a function of test time, with the Variant C cells losing power more quickly. Figure 20 shows that the average power fade rate is significantly greater for the 45°C Variant C cells. At 28 weeks, the average 45°C Variant C power fade is 26.5%, whereas the 45°C Baseline cell average power fade is 21.5%.

4.3.4 Power Fade Models

Figure 21 shows the average power fade for the 25°C Baseline cells as a function of cycle time. At 25°C, the average power fade increases linearly with time and shows a mechanistic change between 28 and 32 weeks. Figure 22 shows the average 45°C Baseline and Variant C cell average power fades. At 45°C, the average power fade is square-root of time dependent. The Baseline and Variant C cells show mechanistic changes at 28 and 8 weeks, respectively. These are identical to the breakpoints seen in the 45°C $C_1/1$ capacity fade model (Figure 4).

4.3.5 Power Fade vs. Capacity Fade Models

The driving motivation for comparing power fade to capacity fade is to algebraically quantify the graphical information shown in the available energy versus discharge power curves (Figures 16–18). However, a simple direct correlation is not easily identified. Figure 23 shows the power fade versus capacity fade model for the 25°C Baseline cells. Since the $C_1/1$ and $C_1/25$ capacity fades are square-root of time dependent (Figures 4 and 7), and the power fades linearly with time (Figure 21), the correlation between power fade and capacity fade is a second order polynomial. Mechanistic changes occur between 28 and 32 weeks for both the $C_1/1$ and $C_1/25$ capacity fades, which is the same breakpoint seen in the power fade model (Figure 21). Figure 23 also shows that the relationship between power fade and capacity fade is not discharge-rate dependent through 28 weeks. However, when the second mechanism dominates, the relationship does depend on the discharge rate, with the $C_1/1$ capacity fade showing a higher rate of degradation.

Figure 24 shows the correlation between power fade and capacity fade for the 45°C Baseline cells. Since both the capacity fades (Figures 4 and 7) and power fade (Figure 22) are square-root of time dependent, the correlation between power fade and capacity fade is linear with time. When the first mechanism dominates, the 45°C Baseline cells show a higher $C_1/25$ capacity fade. Once the second mechanism takes effect, the $C_1/25$ capacity fade slows down, while the $C_1/1$ capacity fade grows more rapidly. The changes in mechanism occur at the same points as the capacity fade versus time models (Figures 4 and 7). Figure 25 shows the correlation between power fade and capacity fade for the 45°C Variant C cells. This is also linear, since the capacity fades and power fade are square-root of time dependent. The $C_1/25$ capacity fade is initially higher and grows at a much faster rate when the second mechanism takes effect at 12 weeks. The Variant C cells do not show a mechanistic change for the $C_1/1$ capacity fade versus power fade. Unlike the 25°C Baseline cells, the 45°C Baseline and Variant C cells are discharge-rate dependent when either mechanism dominates.

The functional relationships shown in Figures 23 through 25 are summarized in Tables 3 and 4. Table 3 summarizes the effects from the first mechanism; Table 4 shows the effects from the second mechanism.

Table 3. Power and capacity fade dependence relationships (first mechanism).

Cell Designation	Temperature	Static Capacity Test	Time Dependence (t)		Power Fade Dependence on Capacity Fade (c)
			Capacity Fade	Power Fade	
Baseline	25°C	$C_1/1$	$\mathbf{t}^{1/2}_{(0-48\text{ wks})}$	$\mathbf{t}_{(0-28\text{ wks})}$	$\mathbf{c}^2_{(0-28\text{ wks})}$
		$C_1/25$	$\mathbf{t}^{1/2}_{(0-48\text{ wks})}$		$\mathbf{c}^2_{(0-28\text{ wks})}$
	45°C	$C_1/1$	$\mathbf{t}^{1/2}_{(0-28\text{ wks})}$	$\mathbf{t}^{1/2}_{(0-28\text{ wks})}$	$\mathbf{c}_{(0-28\text{ wks})}$
		$C_1/25$	$\mathbf{t}^{1/2}_{(0-36\text{ wks})}$		$\mathbf{c}_{(0-36\text{ wks})}$
Variant C	45°C	$C_1/1$	$\mathbf{t}^{1/2}_{(0-8\text{ wks})}$	$\mathbf{t}^{1/2}_{(0-8\text{ wks})}$	$\mathbf{c}_{(0-28\text{ wks})}$
		$C_1/25$	$\mathbf{t}^{1/2}_{(0-28\text{ wks})}$		$\mathbf{c}_{(0-8\text{ wks})}$

Table 4. Power and capacity fade dependence relationships (second mechanism).

Cell Designation	Temperature	Static Capacity Test	Time Dependence (t)		Power Fade Dependence on Capacity Fade (c)
			Capacity Fade	Power Fade	
Baseline	25°C	$C_1/1$	**N/A**	$\mathbf{t}_{(32-48\text{ wks})}$	$\mathbf{c}^2_{(32-48\text{ wks})}$
		$C_1/25$	**N/A**		$\mathbf{c}^2_{(32-48\text{ wks})}$
	45°C	$C_1/1$	$\mathbf{t}^{1/2}_{(32-48\text{ wks})}$	$\mathbf{t}^{1/2}_{(32-48\text{ wks})}$	$\mathbf{c}_{(32-48\text{ wks})}$
		$C_1/25$	$\mathbf{t}^{1/2}_{(40-48\text{ wks})}$		$\mathbf{c}_{(40-48\text{ wks})}$
Variant C	45°C	$C_1/1$	$\mathbf{t}^{1/2}_{(12-28\text{ wks})}$	$\mathbf{t}^{1/2}_{(12-28\text{ wks})}$	**N/A**
		$C_1/25$	**N/A**		$\mathbf{c}_{(12-28\text{ wks})}$

Since the power fade is measured at 300 W·h, an alternative correlation would be with the capacity fade at 300 W·h (instead of the total capacity fade, as shown in Figures 23 through 25). The capacity at 300 W·h was found by calculating the amp-hours removed during a $C_1/1$ test at the DOD value of the power at 300 W·h (the $C_1/25$ capacity at 300 W·h has not yet been completed). Figure 26 shows the average power fade as a function of the $C_1/1$ static capacity fade at 300 W·h. The correlation is also a second order polynomial with a mechanistic change between 28 and 32 weeks. The slopes of the two curves in Figure 26 are lower than the ones shown in Figure 23 since the power at 300 W·h is generally between 54 and 57% DOD, which is within the region of the middle peak of the differential capacity curve (Figure 8).

Figures 27 and 28 show the correlation between power fade and $C_1/1$ capacity fade at 300 W·h for the 45°C Baseline and Variant C cells, respectively. These models show linear fits with mechanistic changes at 28 and 8 weeks, respectively. Like the 25°C Baseline cells, the 45°C Baseline cells also show a lower slope with the capacity fade at 300 W·h when compared to the total capacity fade (Figure 24). The Variant C cells do not show a $C_1/1$ mechanistic change when correlating power fade to total capacity fade (Figure 25) but shows a breakpoint with the capacity fade at 300 W·h. The capacity fade at 300 W·h slows down significantly after 8 weeks, but its initial capacity fade is significantly greater than the total capacity fade. This is because the Variant C cell power at 300 W·h is generally between 64 and 67% DOD, which is around the center of the middle peak in the differential capacity curves (Figure 10).

4.3.6 Lumped Parameter Model

The lumped parameter model (LPM) is a simplified linear battery model that can be used to predict the voltage response of a battery under pulse conditions (see Reference 7). The parameters estimated by the model can help to analyze the increase in polarization (R_p) or ohmic (R_o) resistance, which is related to power fade. Figure 29 shows the LPM circuit diagram.

This model was applied to the L-HPPC pulse testing at 40% DOD. Figures 30 and 31 show the ohmic resistance (R_o) as a function of cycle time for the Baseline and Variant C cells. The 25°C Baseline cells are linearly dependent (Figure 30), whereas the 45°C Baseline and Variant C cells are square root of time dependent (Figure 31), which is the same time dependence seen in the power fade versus time models (Figures 21 and 22). The Baseline cells still show mechanistic changes at 28 weeks, but the Variant C cells do not show any breakpoints.

Figure 32 and 33 show the L-HPPC 40% DOD polarization resistance (R_p) as a function of cycle-time for the Baseline and Variant C cells, respectively. The polarization resistance grows linearly with time for the Baseline cells, but is square-root of time dependent for the Variant C cells. Although the Baseline cell polarization resistance growth has no apparent mechanistic change, the Variant C cells show a breakpoint at 8 weeks.

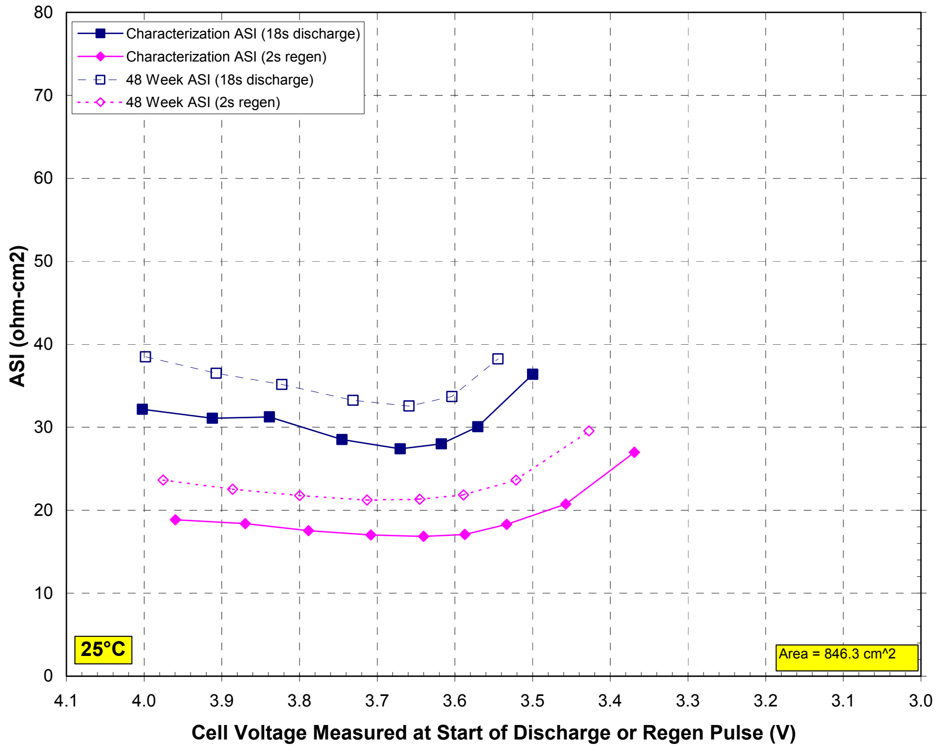

Figure 11. ASI for G2.60L25.I114.20.48.18.G.T (25°C Baseline cell).

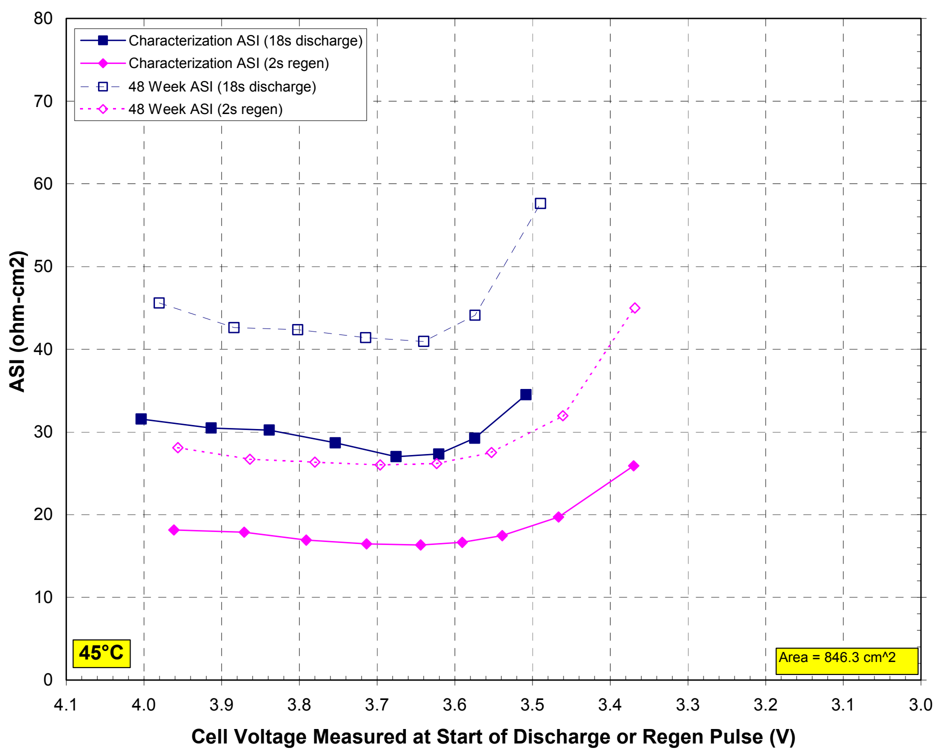

Figure 12. ASI for G2.60L45.I130.50.48.36.G.T (45°C Baseline cell).

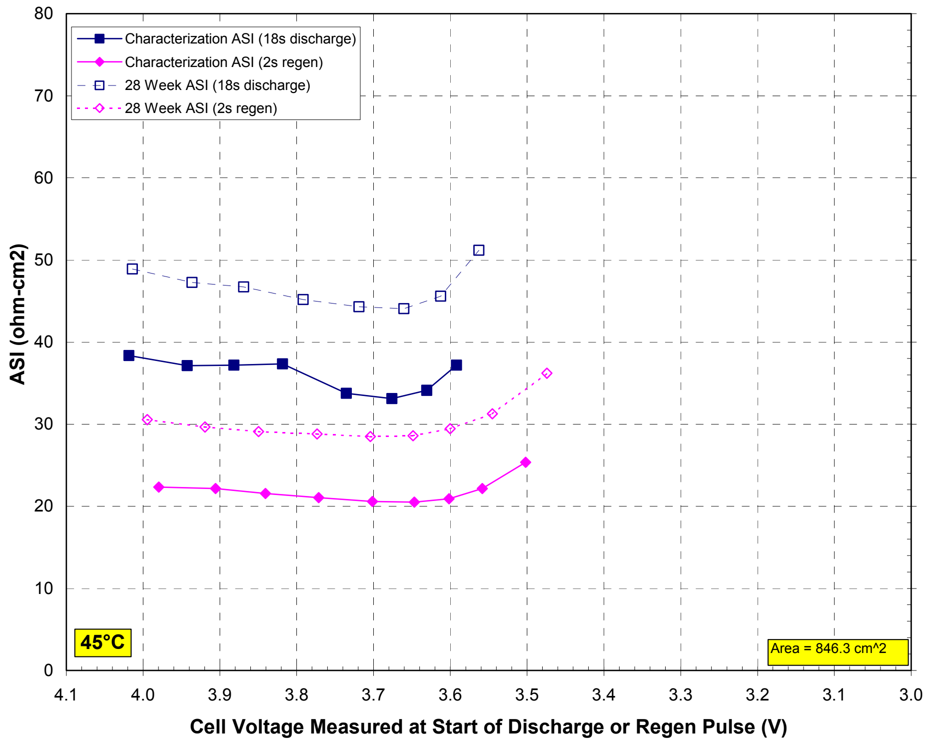

Figure 13. ASI for G2C.60L45.I162.30.28.26.G.T (45°C Variant C cell).

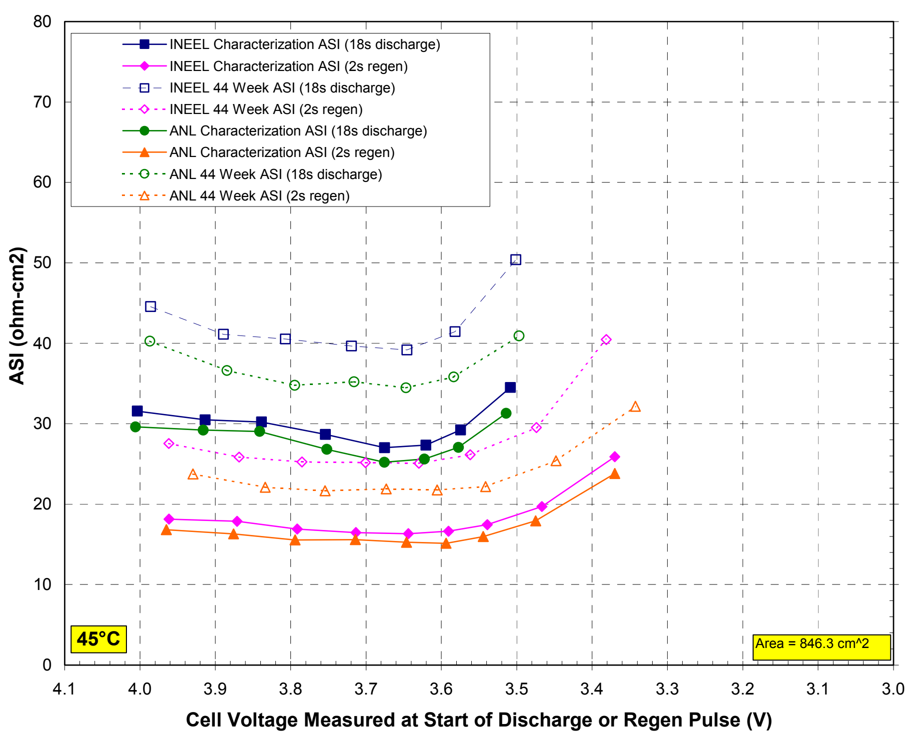

Figure 14. ASI for G2.60L45.I130.50.44.33.G.T (INEEL 45°C Baseline cell) and G2.60C45.A217.50.44.27.G.T (ANL 45°C Baseline cell).

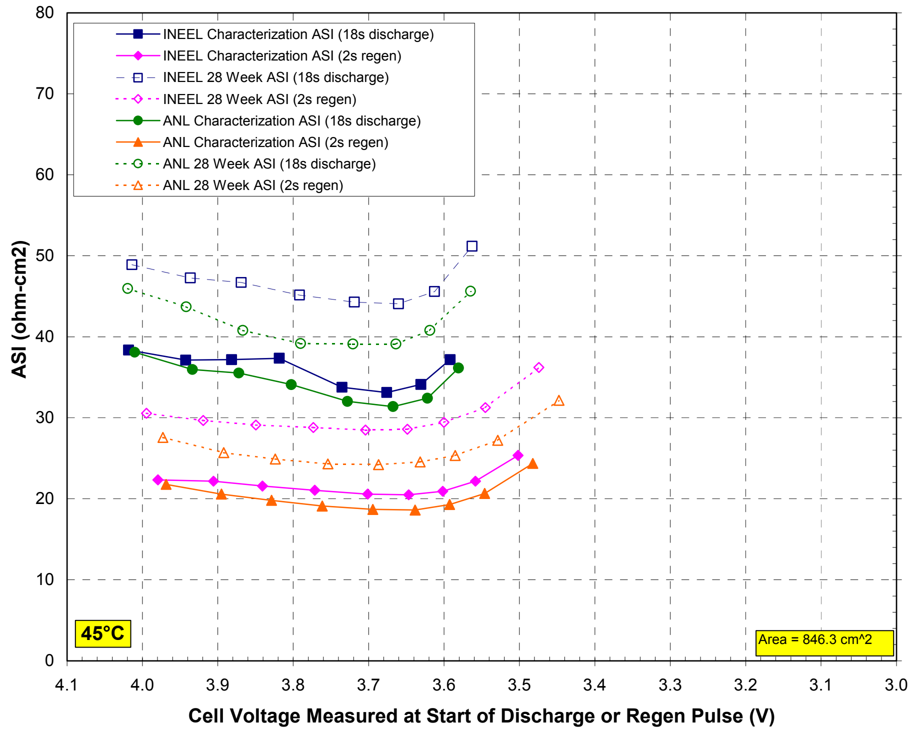

Figure 15. ASI for G2C.60L45.I162.30.28.26.G.T (INEEL 45°C Variant C cell) and G2C.60C45.A224.25.28.20.G.T (ANL 45°C Variant C cell).

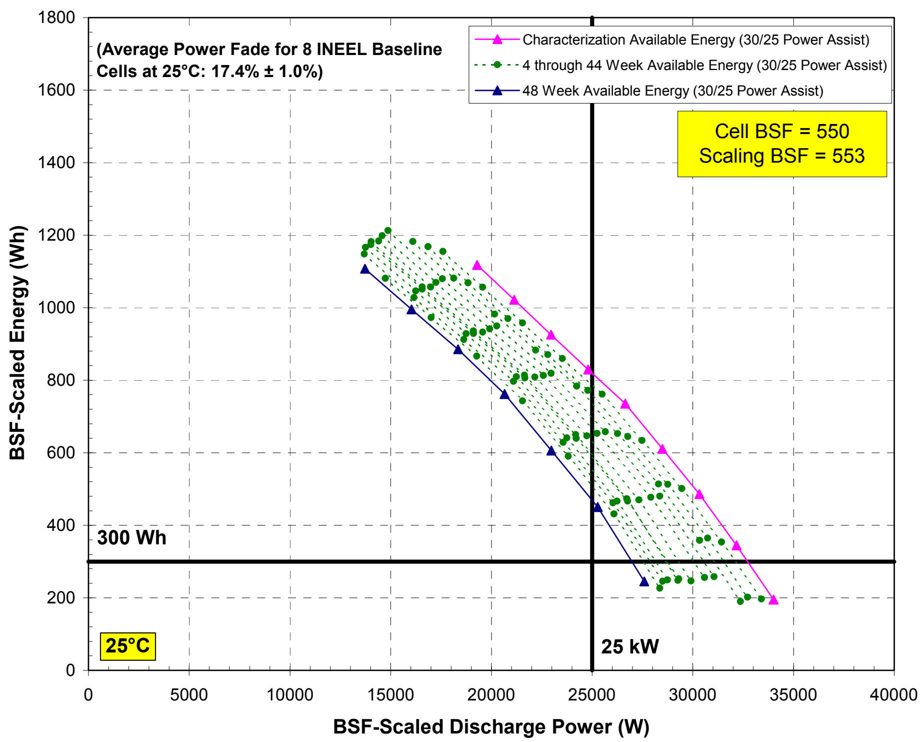

Figure 16. BSF-scaled available energy for G2.60L25.I114.20.48.18.G.T (25°C Baseline cell).

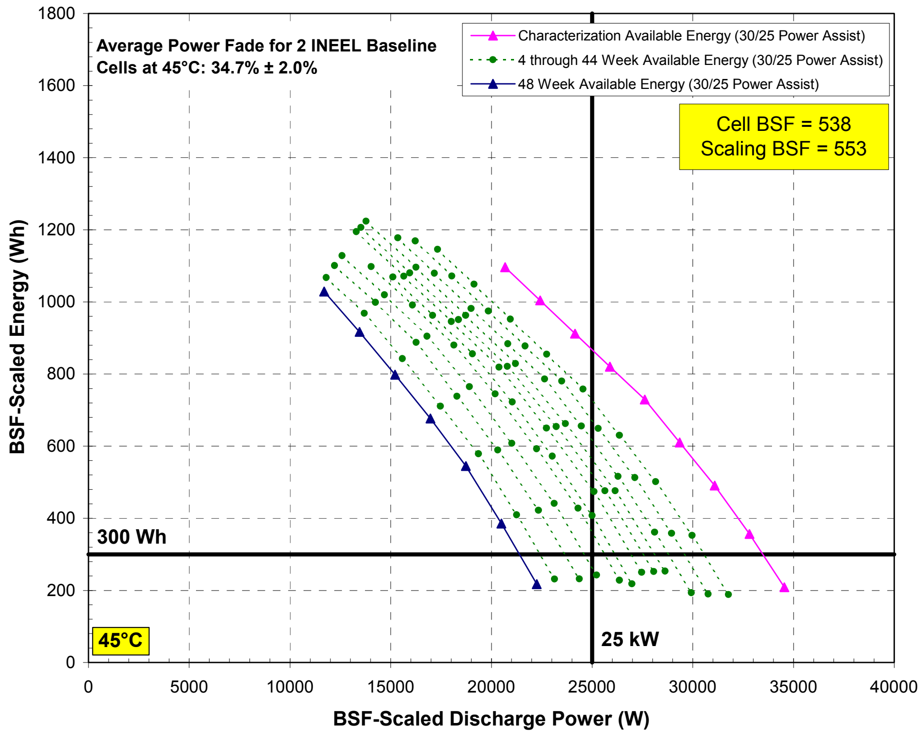

Figure 17. BSF-scaled available energy for G2.60L45.I130.50.48.36.G.T (45°C Baseline cell).

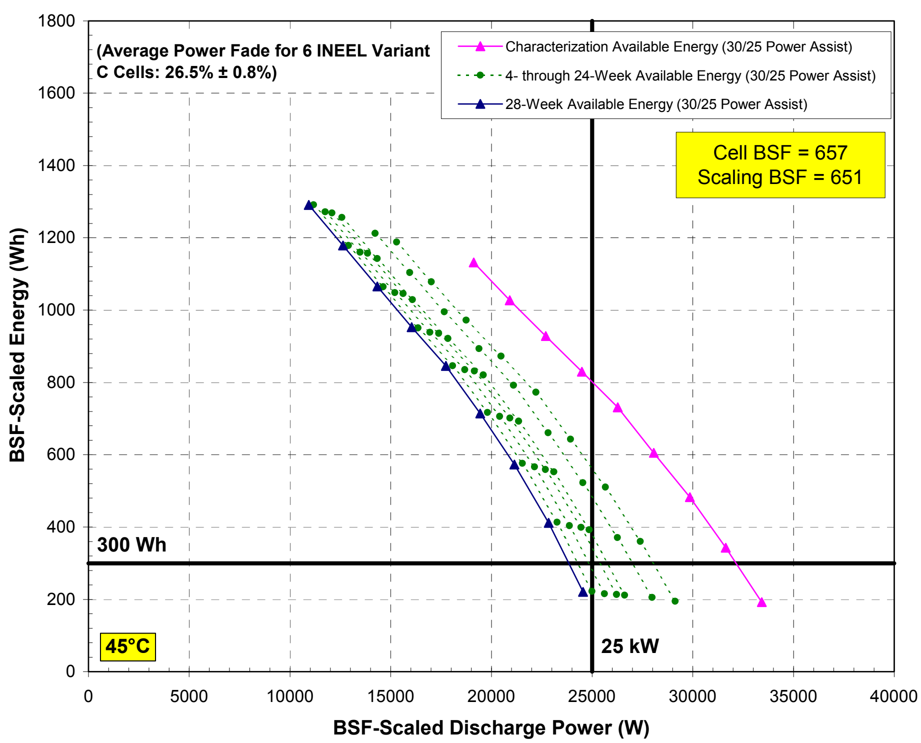

Figure 18. BSF-scaled available energy for G2C.60L45.I162.30.28.26.G.T (45°C Variant C cell).

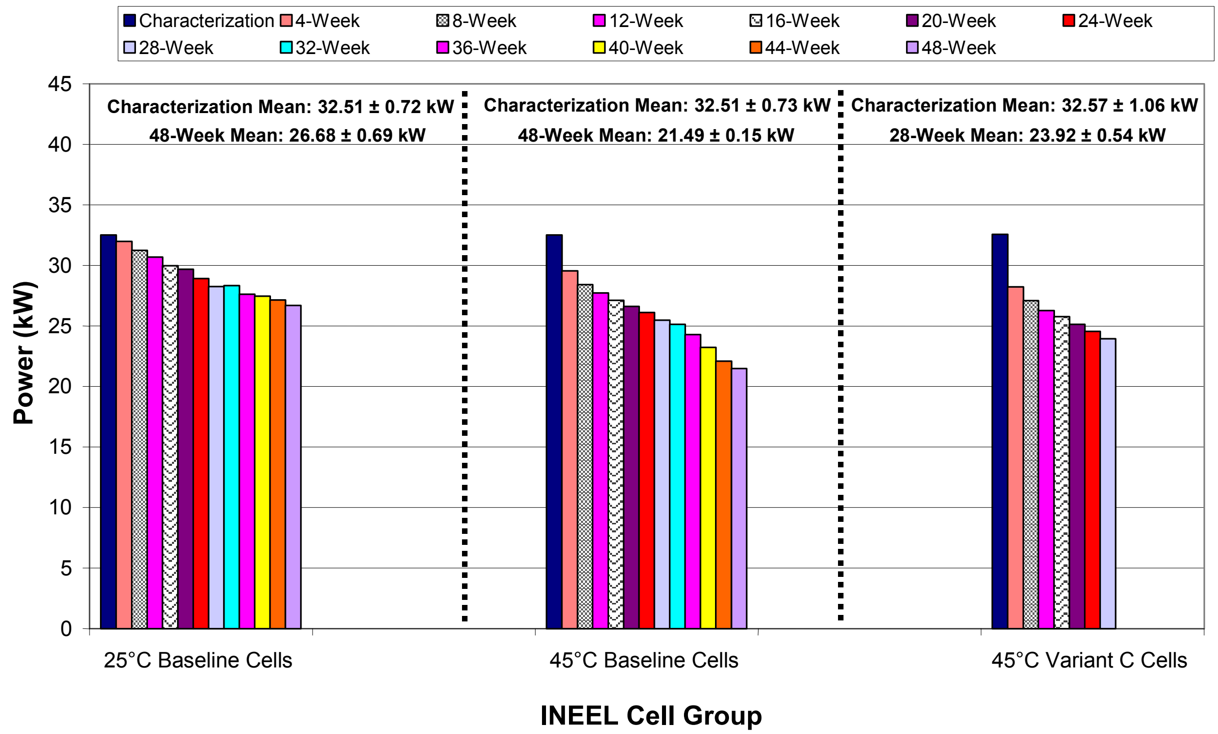

Figure 19. Average power at 300 W·h.

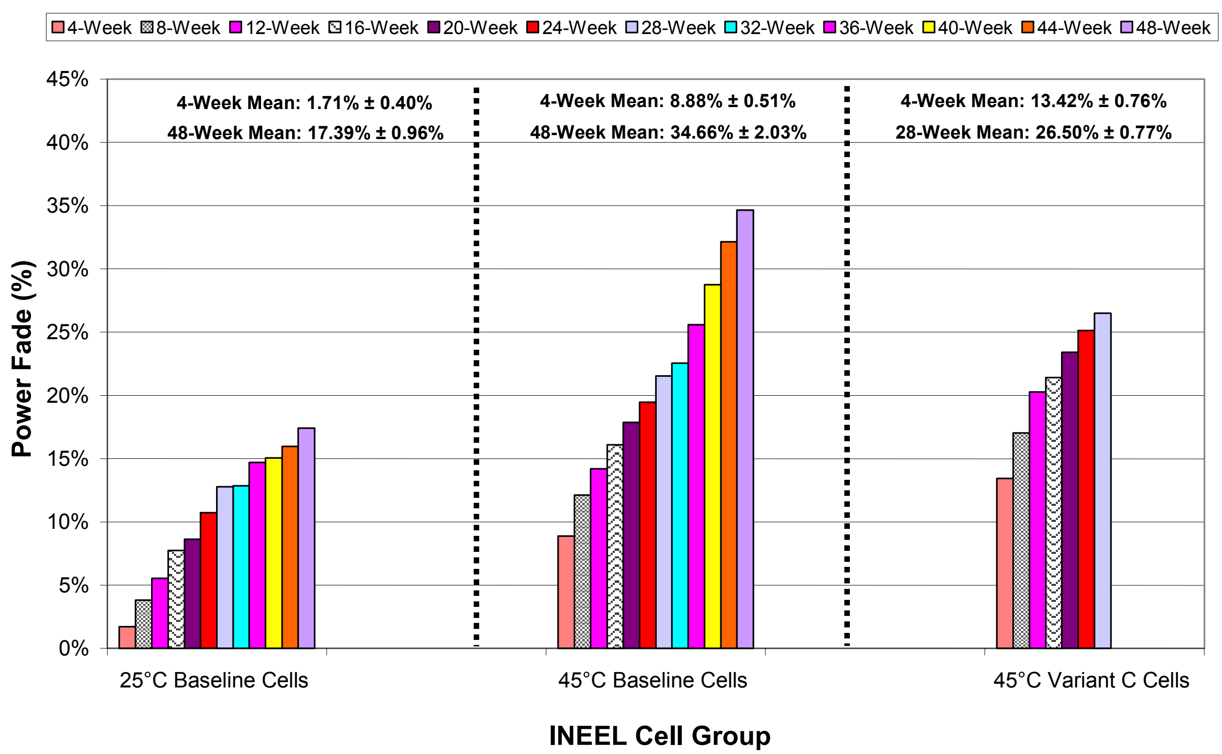

Figure 20. Average power fade at 300 W·h.

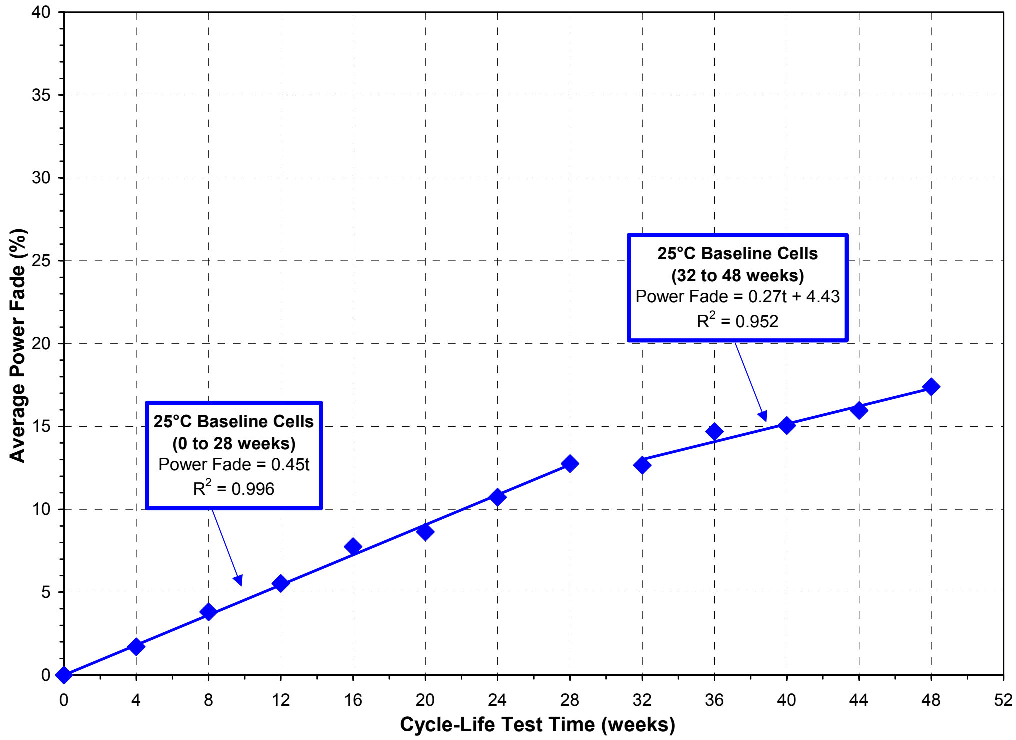

Figure 21. Average power fade as a function of cycle time for the 25°C Baseline cells.

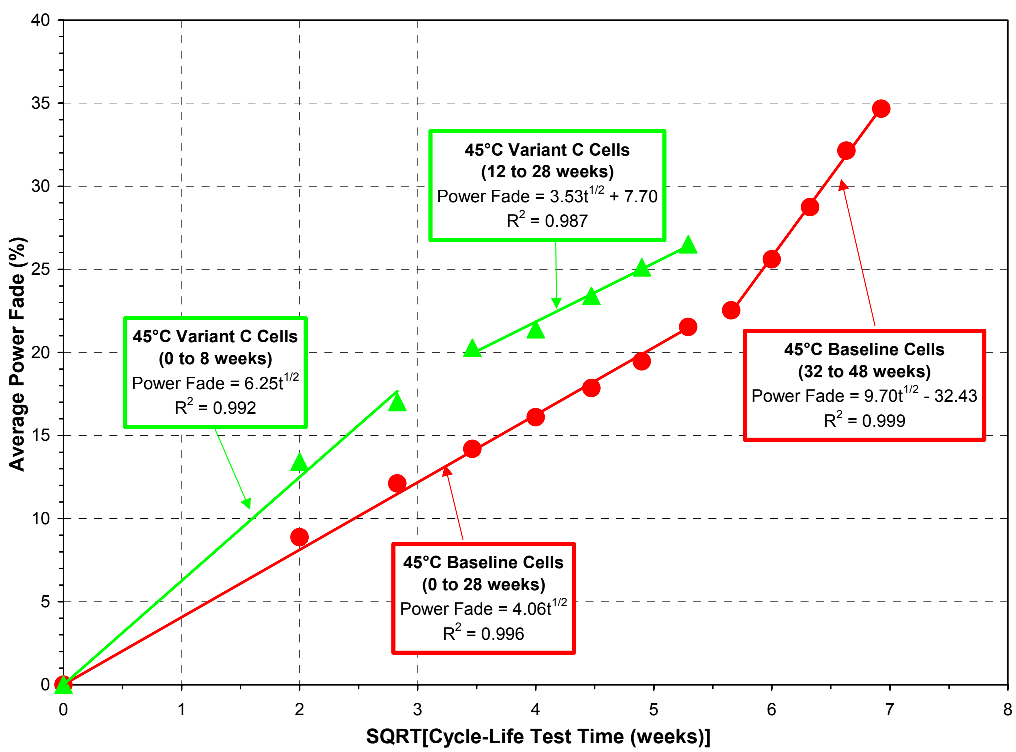

Figure 22. Average power fade as a function of cycle time for the 45°C Baseline and Variant C cells.

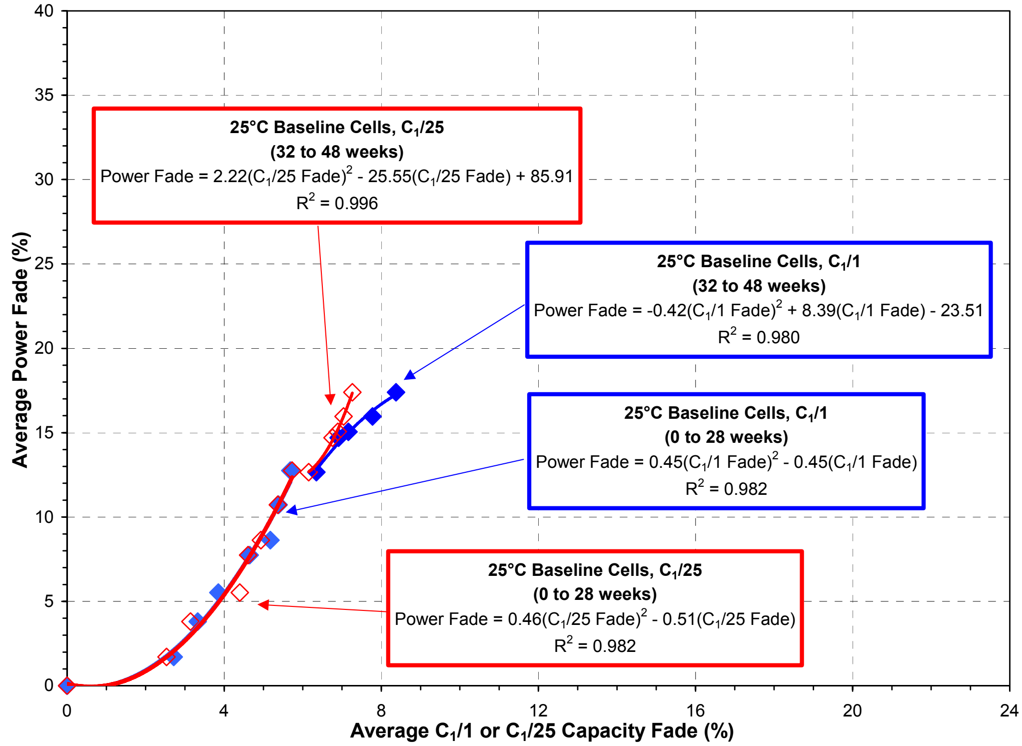

Figure 23. Correlation between power fade and capacity fade for the 25°C Baseline cells.

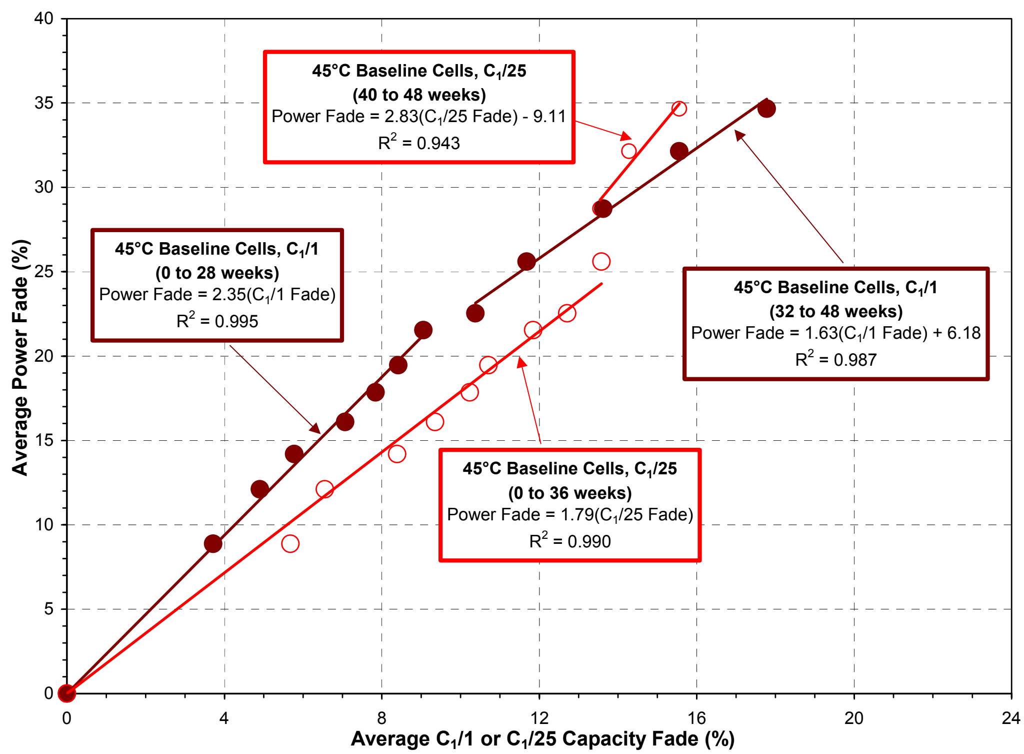

Figure 24. Correlation between power fade and capacity fade for the 45°C Baseline cells.

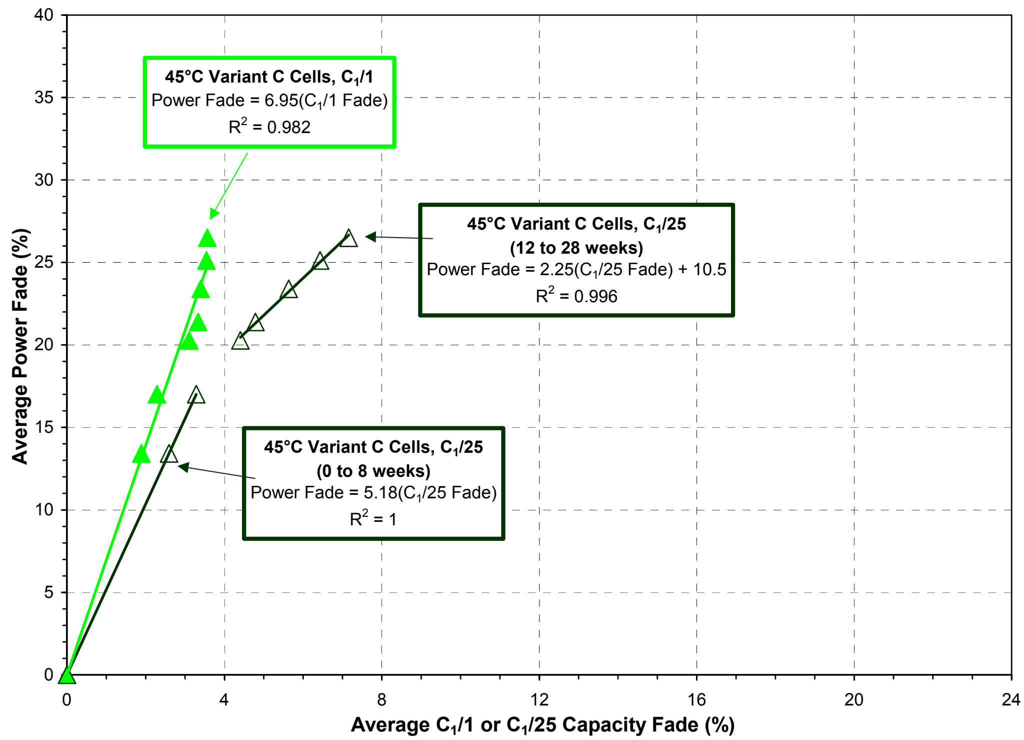

Figure 25. Correlation between power fade and capacity fade for the 45°C Variant C cells.

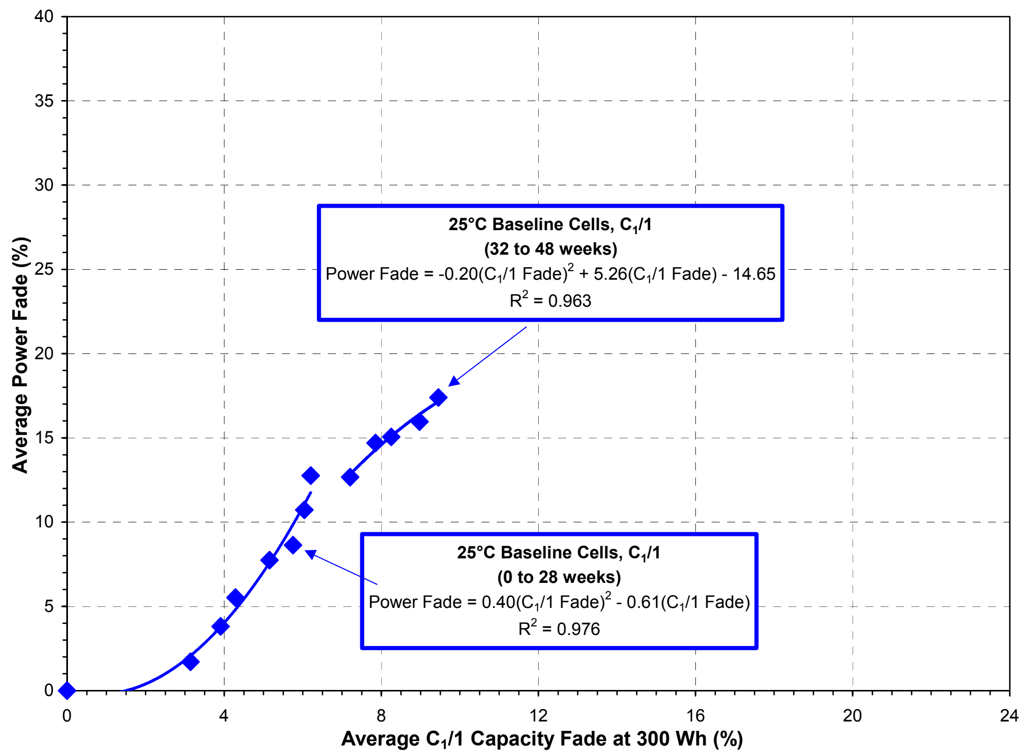

Figure 26. Correlation between power fade and capacity fade at 300 W·h for the 25°C Baseline cells.

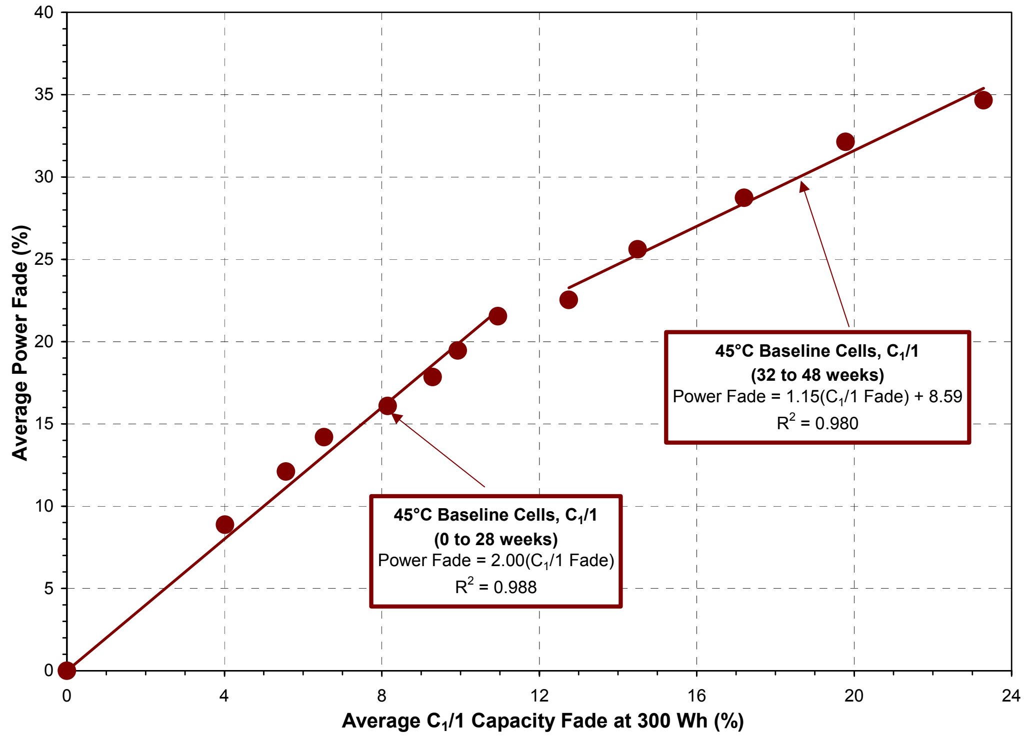

Figure 27. Correlation between power fade and capacity fade at 300 W·h for the 45°C Baseline cells.

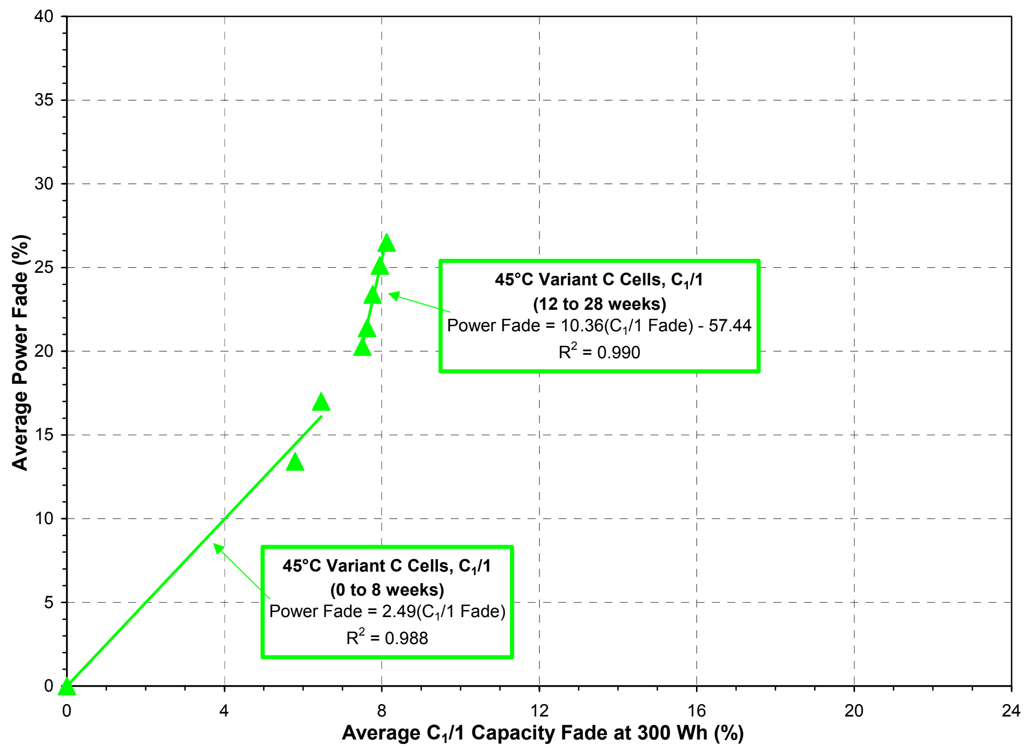

Figure 28. Correlation between power fade and capacity fade at 300 W·h for the 45°C Variant C cells.

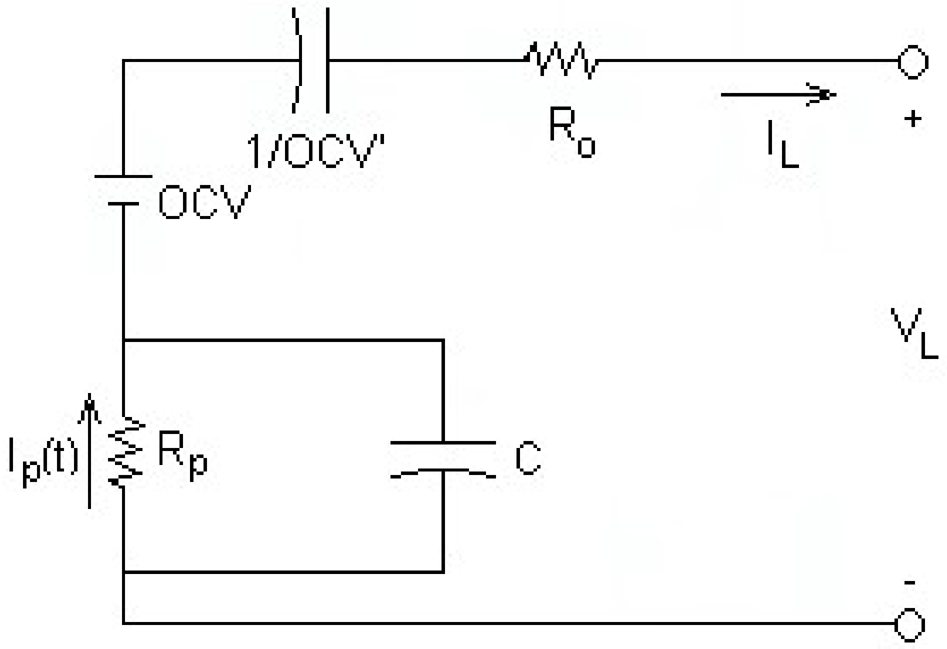

Figure 29. Lumped parameter model circuit diagram.

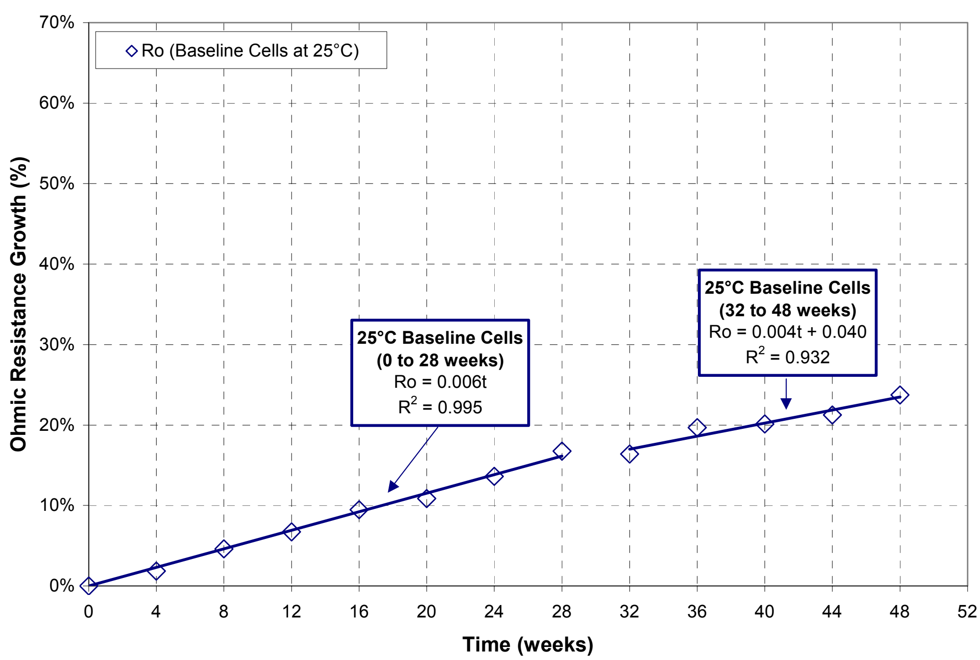

Figure 30. Average ohmic resistance growth from the LPM for the 25°C Baseline cells.

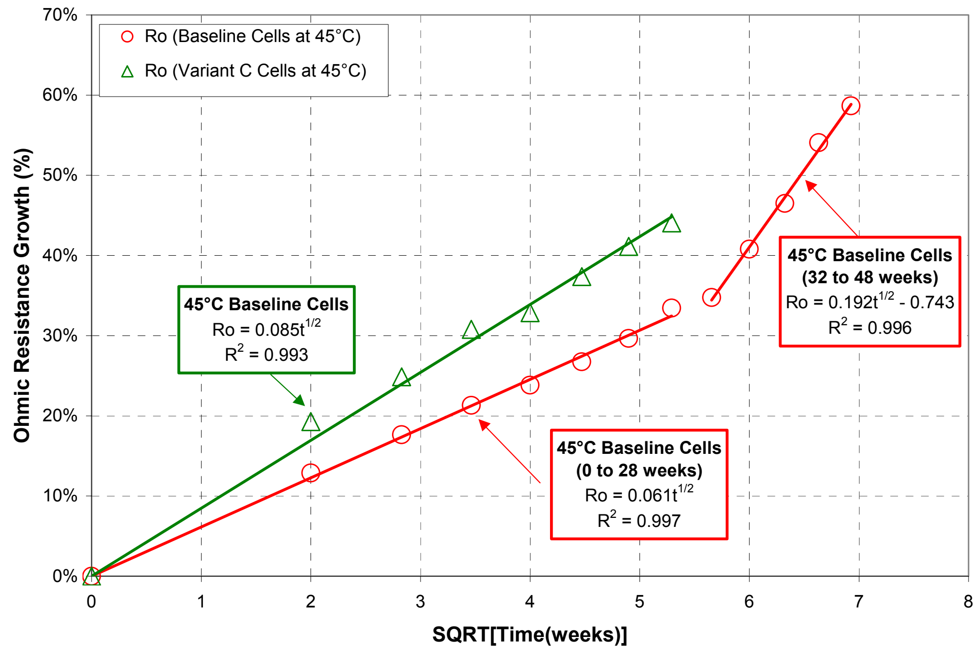

Figure 31. Average ohmic resistance growth from the LPM for the 45°C Baseline and Variant C cells.

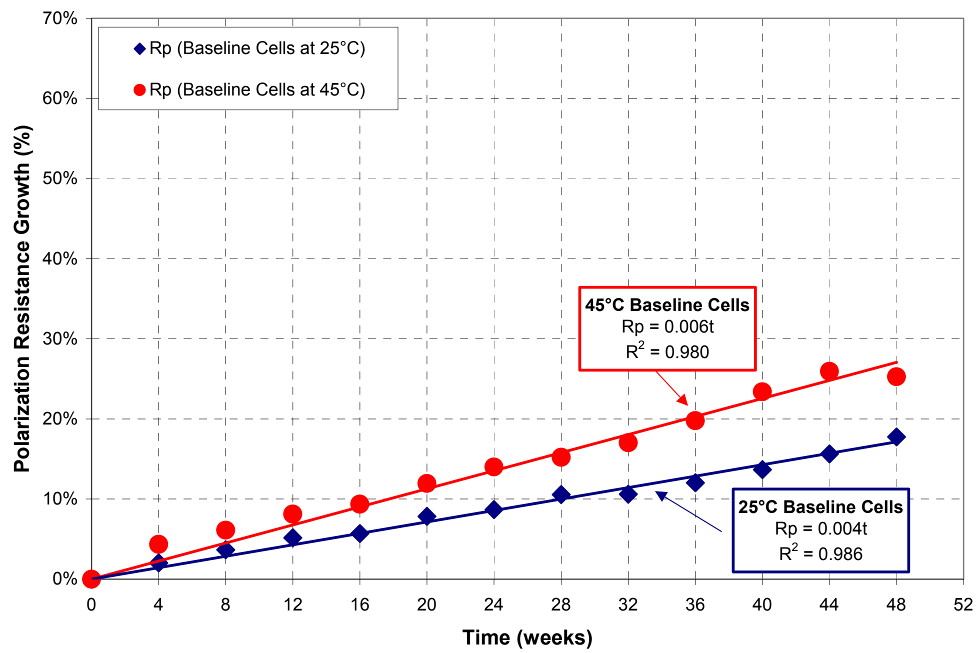

Figure 32. Average polarization resistance growth from the LPM for the Baseline cells.

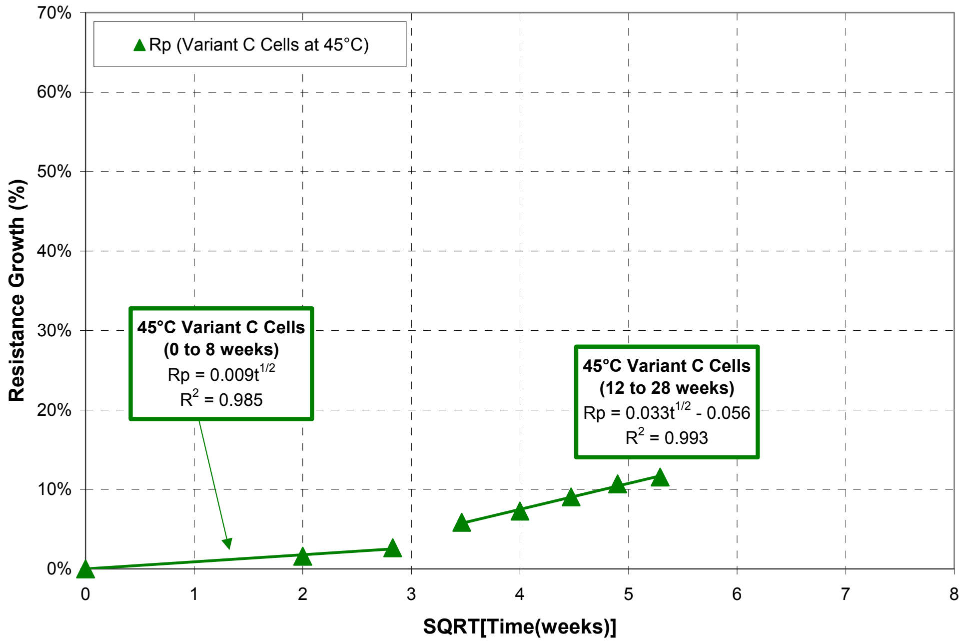

Figure 33. Average polarization resistance growth from the LPM for the Variant C cells.

4.4 Electrochemical Impedance Spectroscopy

4.4.1 Nyquist Plots

Figures 34 and 35 show the EIS Nyquist plots at each RPT increment from BOL to 48 weeks for G2.60L25.I114.20.48.18.G.T (a 25°C Baseline cell) and G2.60L45.I130.50.48.36.G.T (a 45°C Baseline cell), respectively. Figure 36 shows the EIS Nyquist plot for G2C.60L45.I162.30.28.26.G.T (a 45°C Variant C cell) through 28 weeks of aging. Data are only plotted over a frequency range of 2.5 kHz to 0.01 Hz to better show the changes in the semicircle trough frequency (the lowest point on the Nyquist curve) as a function of test time. The impedance for the 45°C Baseline cells increases more rapidly than the 25°C Baseline cells. The Variant C cell average characterization real impedance at the semicircle trough (20.03 ± 1.13 mΩ) is higher than the average real impedance for the Baseline cells (16.97 ± 0.45 mΩ). The Variant C real impedance is also growing much more rapidly than the Baseline cells. The average real impedance for the Variant C cells after 28 weeks is 30.03 ± 0.96 mΩ, compared to 28.77 ± 0.18 mΩ for the 45°C Baseline cells after 48 weeks of aging. The average growth of the EIS magnitude at the semicircle trough for the Baseline and Variant C cells is summarized in Figure 37. The magnitude grows monotonically for all three cell groups, with the 25°C Baseline cells showing the slowest growth and the 45°C Variant C cells showing the fastest growth.

4.4.2 EIS Modeling

Figure 38 shows the EIS Nyquist plot for G2.60L45.I130.50.48.36.G.T (a 45°C Baseline cell) after 48 weeks of cycle-life testing. These data can be modeled using four parallel RC networks connected in series. Figure 38 also shows the outputs of each individual RC network, resulting in four distinct curves. Progressing from left to right, the first curve represents the high-frequency capacitive tail, which is an artifact arising from apparatus contributions resulting from the four-terminal connection. The anode and cathode primarily influence the first and second semicircles, respectively (Reference 8). The leftmost curve may be a Warburg impedance, which represents a diffusional impedance. The ideal method of measuring cell degradation from the EIS test is to track the growth of these two semicircles as a function of time. However, as shown, the two semicircles are poorly resolved due to the influence of the high-frequency capacitive tail and the low-frequency Warburg impedance. Although the semicircles become progressively more distinct as the cells age (Figures 34-36), an alternative method of measuring cell degradation from the EIS test needs to be identified.

Figure 39 shows that the average EIS magnitude growth at the semicircle trough highly correlates with the average power fade for both the INEEL cycle-life and ANL calendar-life Baseline and Variant C cells. Except for the ANL 45°C Variant C cells, the correlation appears to be temperature dependent. The EIS magnitude growth at the semicircle trough increases with increasing test temperature. The correlation also appears to be test independent, with the INEEL cycle-life cells and ANL calendar-life cells having virtually identical slopes. These observations indicate that the mechanisms responsible for the power fade rate are also responsible for the EIS growth rate.

An alternative approach to measuring cell degradation from the EIS test is to divide the Nyquist plot into three different frequency bands (high, mid, and low, respectively). The transition from the mid- to low-frequency band is at the trough frequency. To find the transition between the high- and mid-frequency bands, the INEEL calculated the point at which the rate of change of the slope of the Nyquist curve was a maximum (i.e., where the third derivative equals zero). This was done by curve-fitting the data using a fourth order polynomial over a frequency range of 1 kHz to 100 Hz, and taking its third derivative. Figures 40 through 42 show the resulting average delta impedance magnitudes at each frequency band at each RPT for the three INEEL cell groups. The delta impedance magnitude at the mid-frequency band was found by subtracting the magnitude at the trough by the magnitude at $f'''(x) = 0$. The low-frequency delta magnitude was found by subtracting the magnitude at 50 mHz by the initial average trough frequency (2.5 Hz for the Baseline cells and 2.0 Hz for the Variant C cells). The high- and low-frequency bands show some minor growth, but the majority of the impedance growth from BOL occurs at the mid-frequency band (146.9%, 323.9%, and 159.0% growth for Figures 40 through 42, respectively).

Since the mid-frequency band shows the most significant growth, it can be used as an alternate measure of power fade. Figure 43 shows that the EIS delta magnitude growth at the mid-frequency band also highly correlates with the power fade for the INEEL cycle-life Baseline and Variant C cells (ANL results have not yet been analyzed). However, the model does not show the same temperature dependency seen in Figure 39. The 45°C Variant C cells show a slower EIS delta magnitude growth rate than the 45°C Baseline cells.

4.5 Cycle-Life Pulse Resistance

Figure 44 shows the discharge and regen cycle-life pulse resistances through 48 weeks of aging for G2.60L25.I114.20.48.18.G.T (a 25°C Baseline cell). The pulse resistances increase steadily, but show sudden drops every 672 h (four weeks) due to the RPTs. Evidently, the RPTs cause a short-lived decrease in the resistances that may be a result of "reconditioning" from the static capacity tests. This phenomenon has been observed for other Lithium-ion technologies as well. Figure 45 shows the cycle-life pulse resistance for G2.60L45.I130.50.48.36.G.T (a 45°C Baseline cell). As expected, the 45°C Baseline cell pulse resistance data are lower than the 25°C Baseline cells because of the decreased resistance at the higher temperatures. Figure 46 shows the cycle-life pulse resistance for G2C.60L45.I162.30.28.26.G.T (a 45°C Variant C cell) through 28 weeks of cycle-life testing. The 45°C Variant C cell pulse resistances fall between the 25 and 45°C Baseline cells and are showing higher growth rates than the 45°C Baseline cells. The Variant C pulse resistances at 28 weeks are higher than the 45°C Baseline cells pulse resistances at 48 weeks.

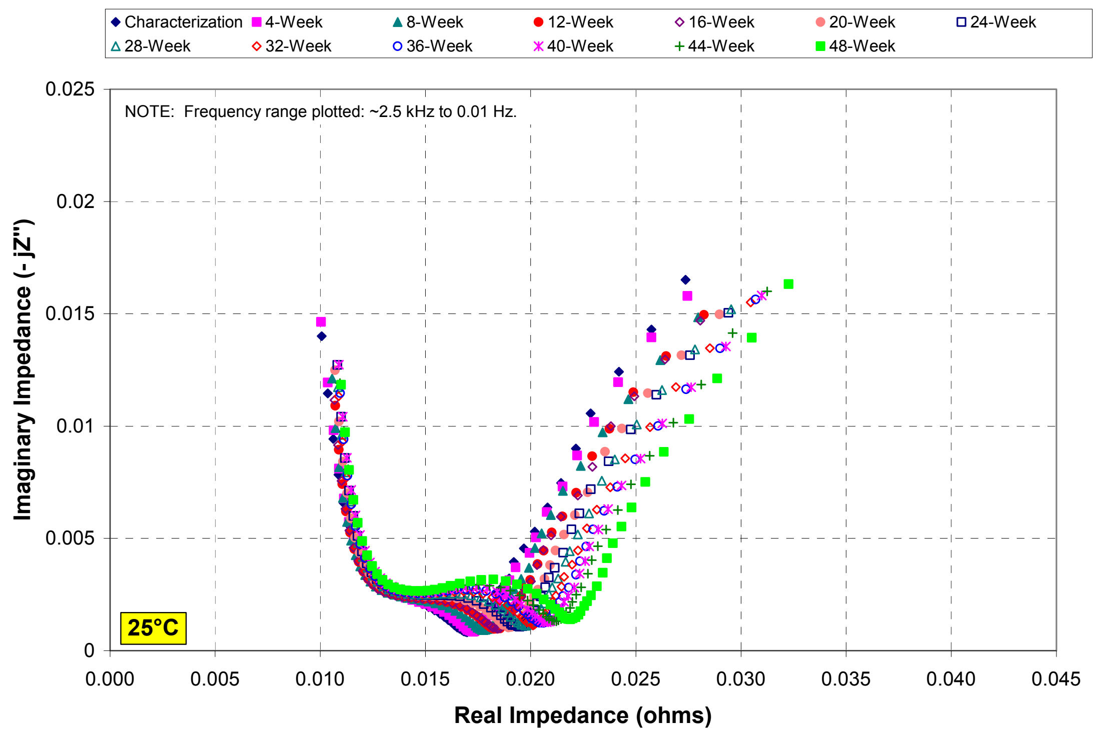

Figure 34. EIS Nyquist plot for G2.60L25.I114.20.48.18.G.T (25°C Baseline cell).

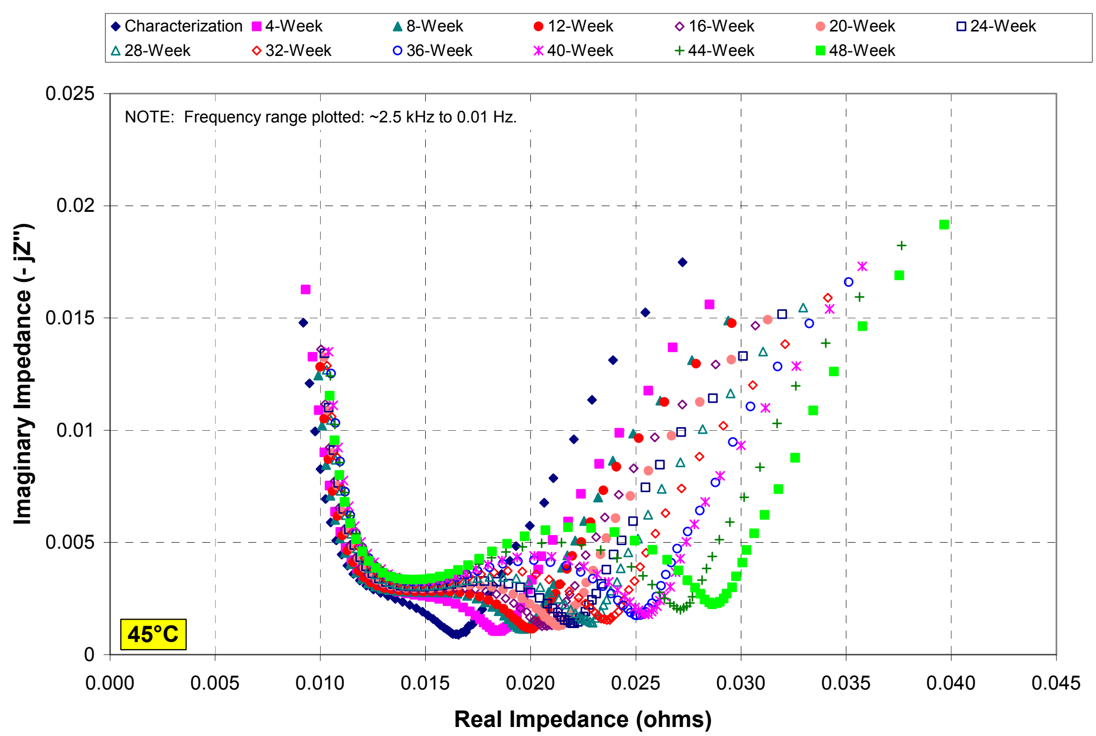

Figure 35. EIS Nyquist plot for G2.60L45.I130.50.48.36.G.T (45°C Baseline cell).

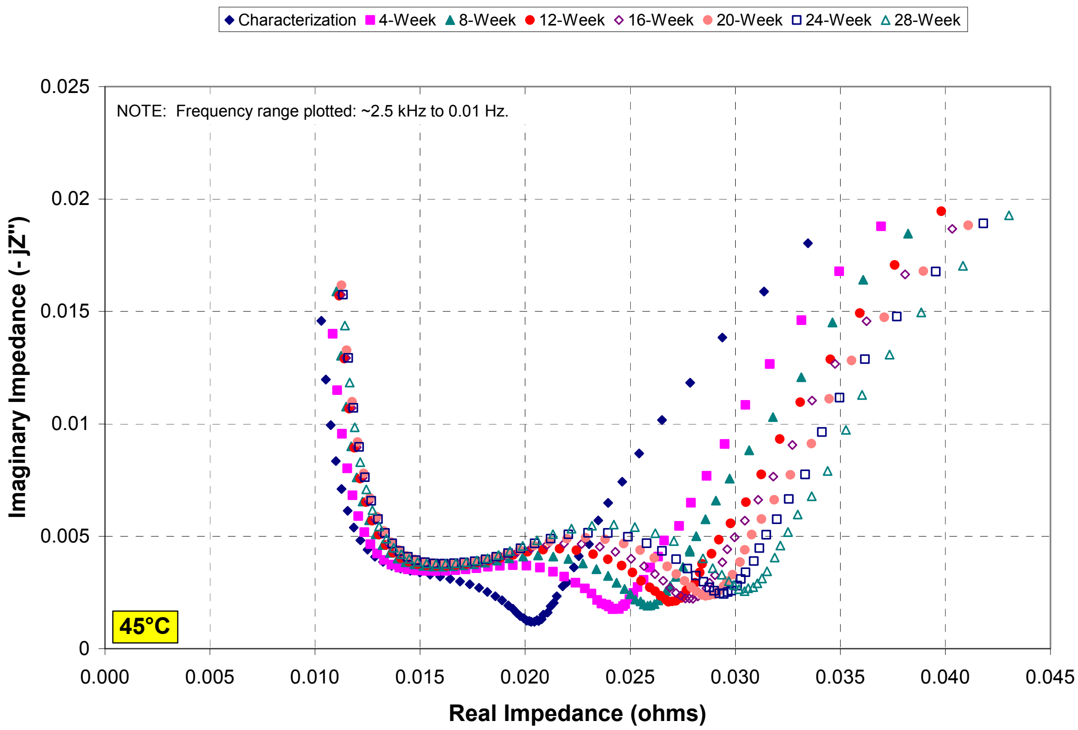

Figure 36. EIS Nyquist plot for G2C.60L45.I162.30.28.26.G.T (45°C Variant C cell).

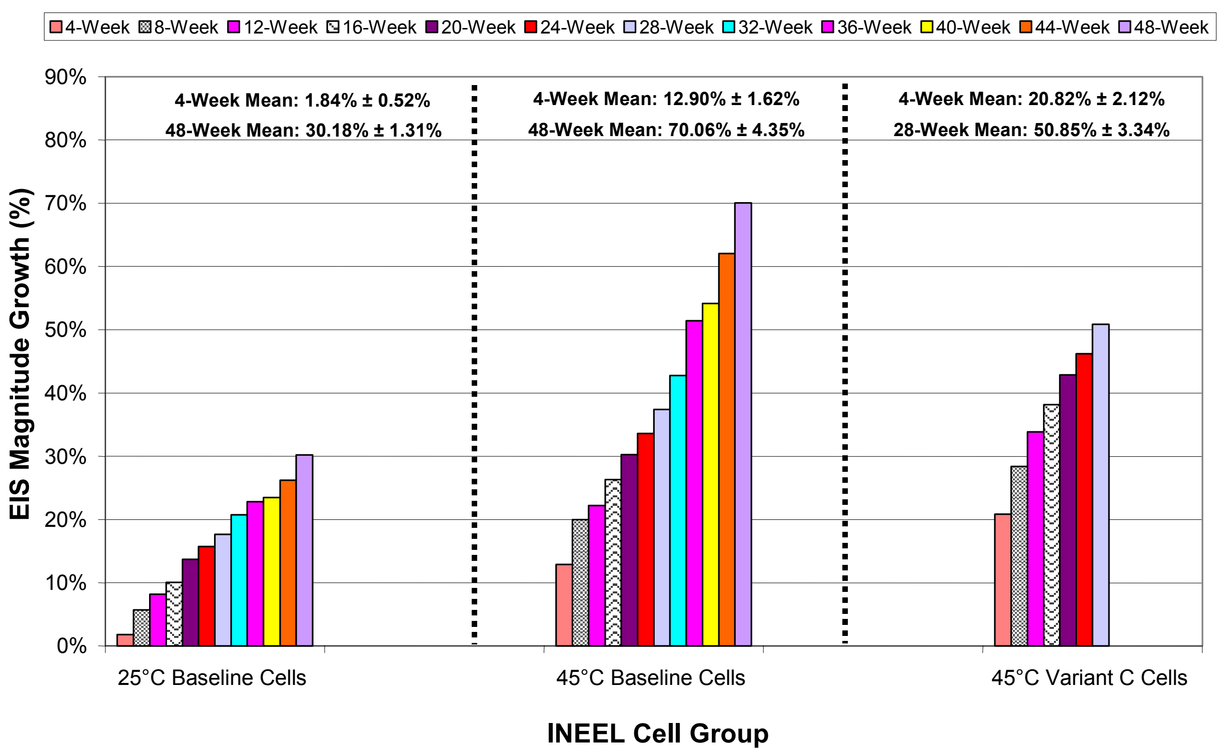

Figure 37. Average EIS magnitude growth at the semicircle trough.

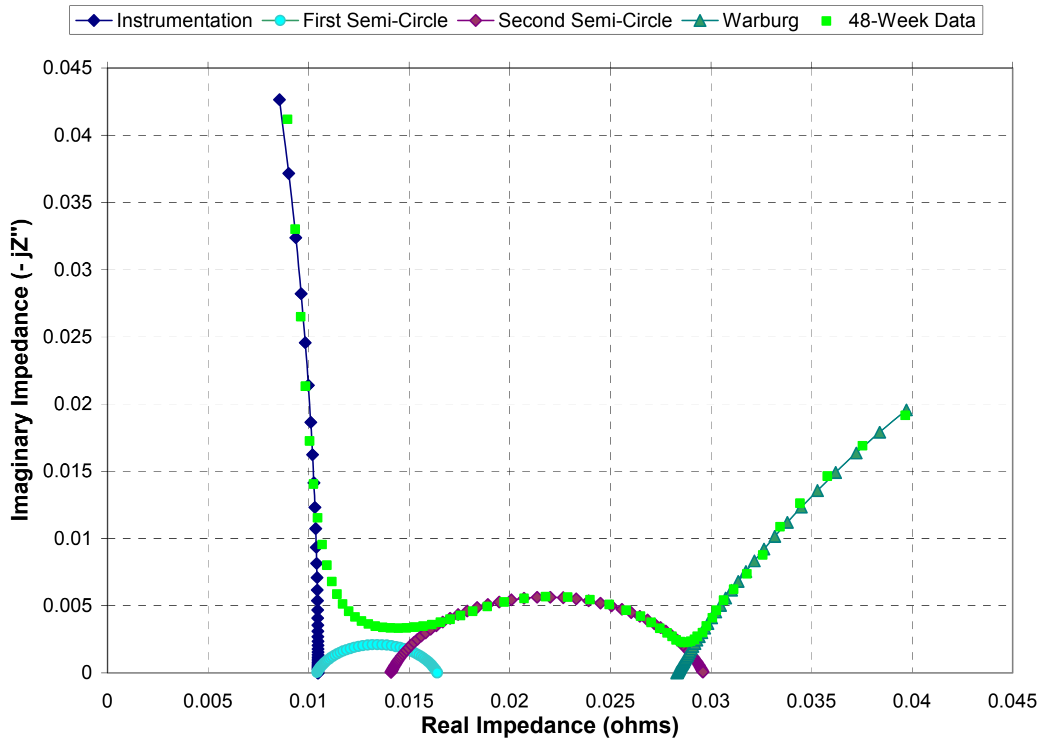

Figure 38. EIS Nyquist plot at 48 weeks for G2.60L45.I130.50.48.36.G.T (45°C Baseline cell) with RC network model.

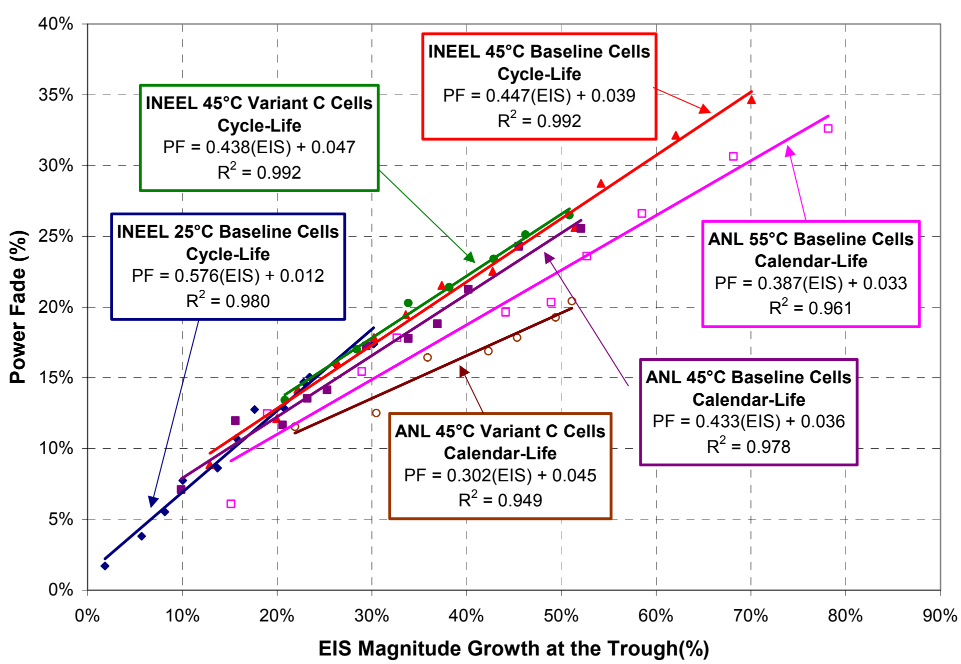

Figure 39. Power fade versus EIS growth.

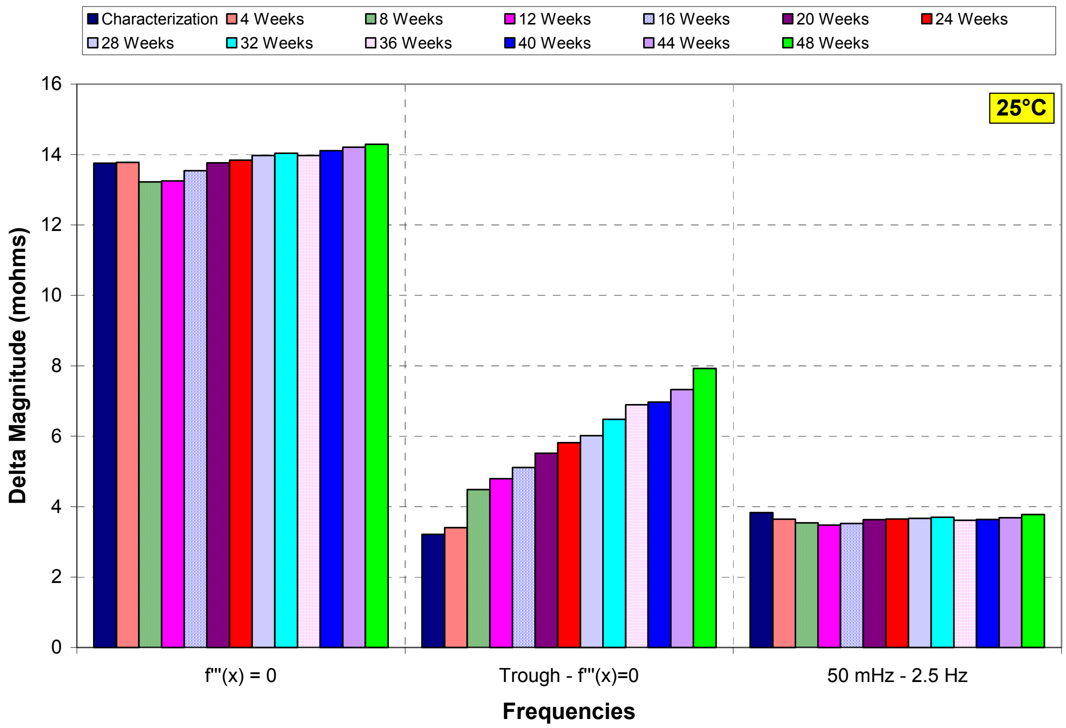

Figure 40. EIS frequency bands for the 25°C Baseline cells.

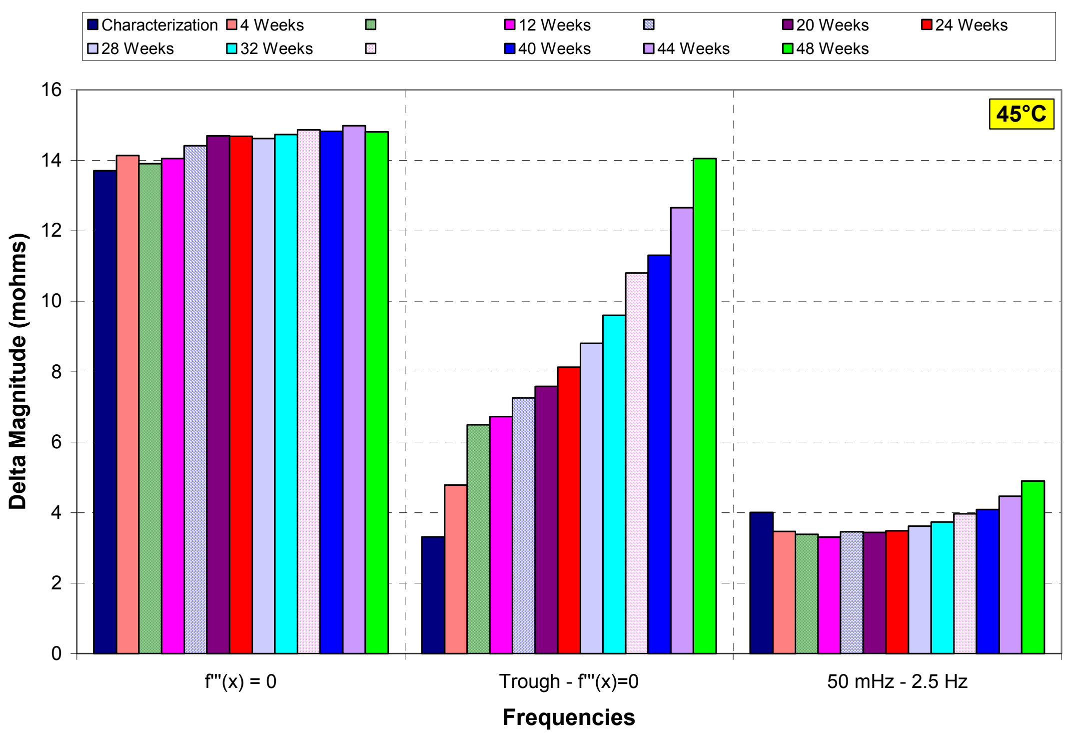

Figure 41. EIS frequency bands for the 45°C Baseline cells.

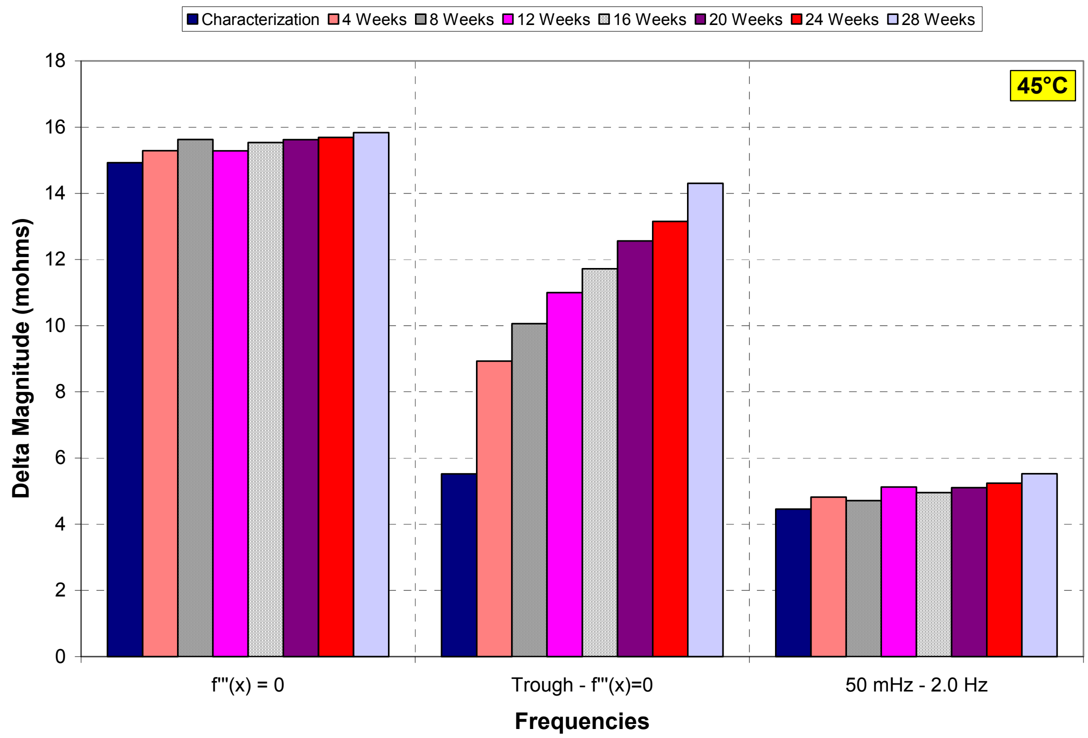

Figure 42. EIS frequency bands for the 45°C Variant C cells.

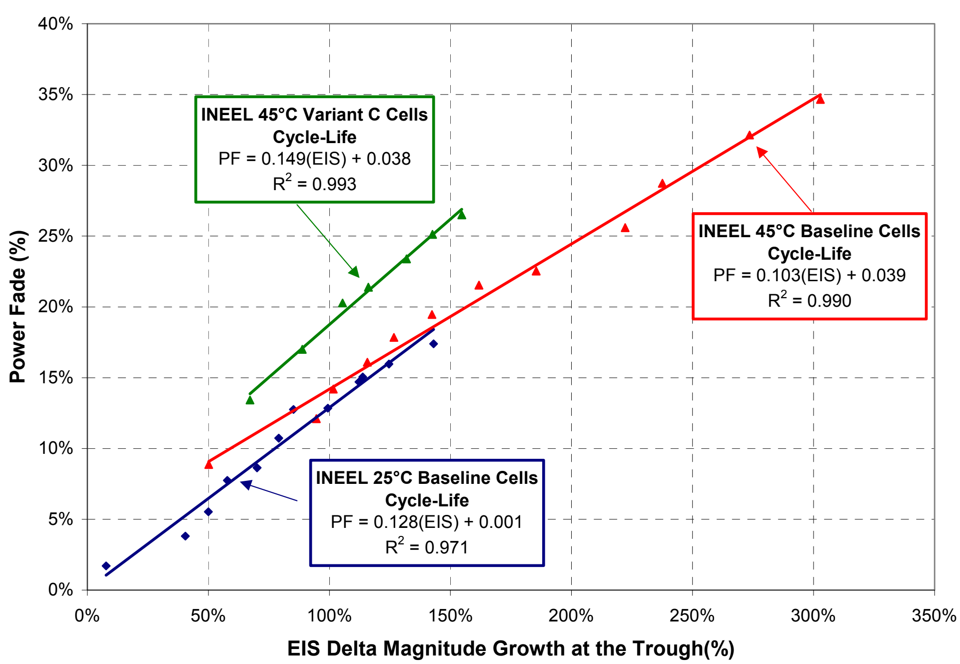

Figure 43. Power fade versus EIS delta magnitude growth.

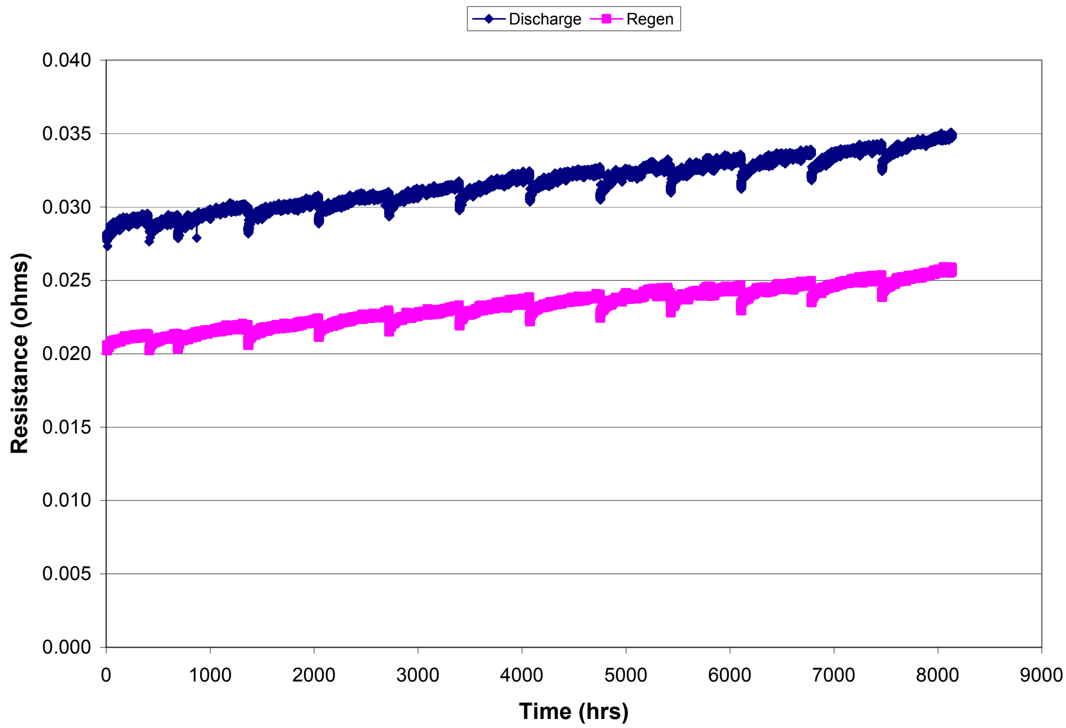

Figure 44. Cycle-life pulse resistance for G2.60L25.I114.20.48.18.G.T (25°C Baseline cell).

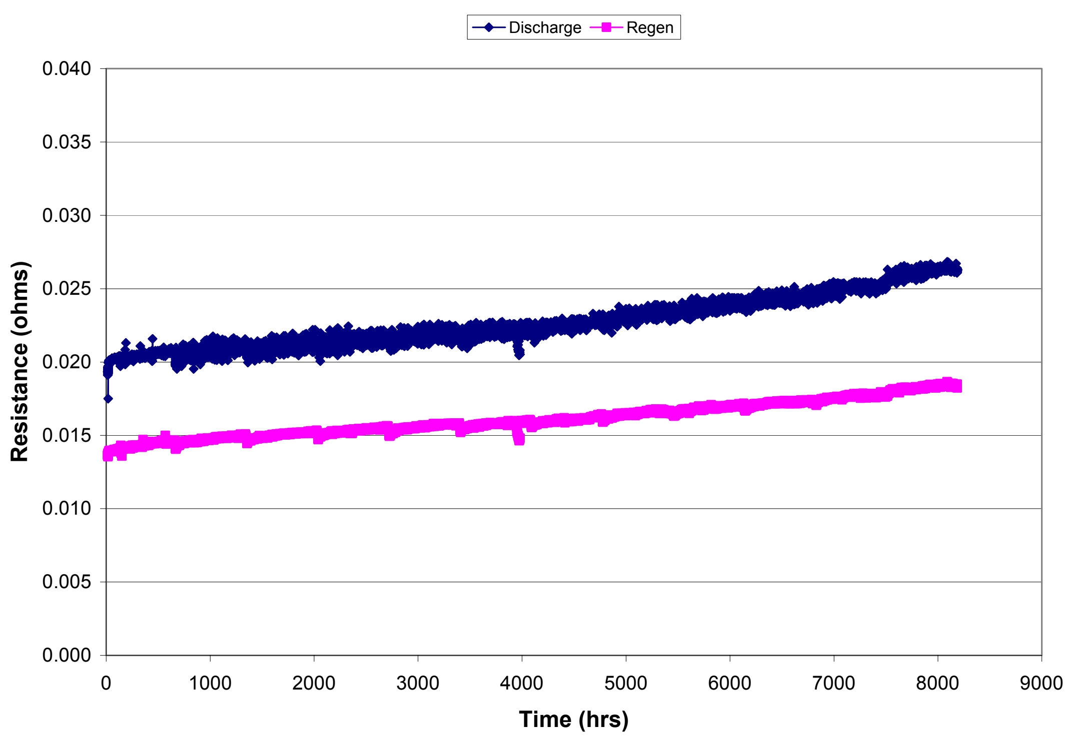

Figure 45. Cycle-life pulse resistance for G2.60L45.I130.50.48.36.G.T (45°C Baseline cell).

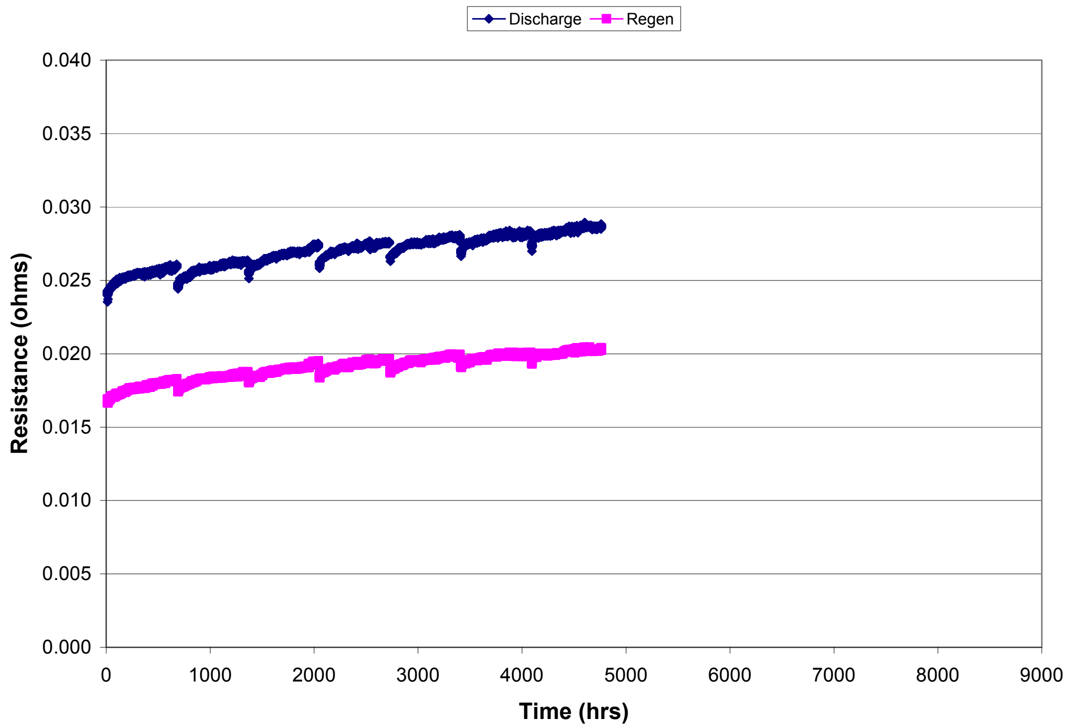

Figure 46. Cycle-life pulse resistance for G2C.60L45.I162.30.28.26.G.T (45°C Variant C cell).

4.6 Summary

4.6.1 Performance Summary

The capacity fade, power fade, and EIS growth at the semicircle trough for the Baseline and Variant C cells are summarized in Table 5. The 45°C Baseline cells show a higher capacity and power fade and EIS growth than at 25°C. The Variant C cells consistently show a very low capacity fade and a very high power fade and EIS growth. Table 6 compares that capacity fade, power fade, and EIS growth at 28 weeks for the 45°C Baseline and Variant C cells. The Baseline cells have a higher capacity fade, but the Variant C cells have a higher power fade and EIS growth.

Table 5. Overall performance summary for the Baseline and Variant C cells.

Cell Designation	Temperature	Capacity Fade	Power Fade	EIS Growth	Weeks Completed
Baseline	25°C	8.4%	17.4%	30.2%	48
	45°C	17.8%	34.7%	70.1%	48
Variant C	45°C	3.6%	26.5%	50.8%	28

Table 6. Performance summary at 28 weeks for the 45°C Baseline and Variant C cells.

Cell Designation	Temperature	Capacity Fade	Power Fade	EIS Growth	Weeks Completed
Baseline	45°C	9.1%	21.5%	37.4%	28
Variant C	45°C	3.6%	26.5%	50.8%	28

4.6.2 Gap Analysis

Table 7 compares the FreedomCAR power-assist goals to the measured performance of Baseline cells G2.60L25.I114.20.48.18.G.T (at 25°C) and G2.60L45.I130.50.48.36.G.T (at 45°C) at characterization and at 48 weeks, and Variant C cell G2C.60L45.I162.30.28.26.G.T (at 45°C) at characterization and 28 weeks. The green background indicates that the FreedomCAR goal was met, whereas the red background indicates a failure to meet the goal. The 18-s discharge pulse power is equivalent to the power at 300 W·h (Figure 19). The corresponding 2-s regen pulse power is the discharge power scaled by 1.2, as described in Reference 7. The available energy is calculated at a power of 25 kW (Figures 16 through 18). The standard FreedomCAR efficiency, cold cranking, and self-discharge tests are not a part of the ATD cell conditioning for diagnostics. The efficiency shown in Table 7 was calculated based on the cycle-life test. The maximum system weight is found by multiplying the cell weights (38.7, 39.0, and 38.5 g for INEEL Cells 114, 130, and 162, respectively) by the BSF (553 for the Baseline cells and 651 for the Variant C cells). The system volume is found by measuring the cell height (h) and maximum cell radius (r) and calculating $\pi r^2 h$ multiplied by the BSF. To stay within the maximum operating voltage goal, the 553 Baseline cells would need to be divided into seven parallel strings. The maximum operating voltage is then found by multiplying the HPPC pulse power maximum voltage (4.1 V) by 79 (i.e., 553 / 7). Likewise, the Variant C cells require seven parallel strings (i.e., 93 cells per string) to meet the maximum operating voltage goal. The minimum operating voltage is found by multiplying the HPPC pulse power minimum voltage (3.0 V) by the BSF divided by seven parallel strings. The maximum DC-link current is the discharge pulse power goal (25 kW) divided by the minimum operating voltage.

4.7 Continuing Work

The INEEL ATD Gen 2 Baseline and Variant C cells will continue cycling until the EOT criteria are met (Appendix C of Attachment 1). No Baseline cells were removed from test after 48 weeks of aging. Eight 25°C Baseline cells and two 45°C Baseline cells are continuing with cycle-life testing. The next target power fades to remove cells from test for the 25 and 45°C Baseline cells are 19.5 and 50.0%, respectively. The 25°C Baseline cells are projected to complete aging in September 2003 (i.e., 100 weeks with 840,000 cycles and approximately 36% power fade). The 45°C Baseline cells are projected to complete aging in March 2003 (i.e., 80 weeks with 672,000 cycles and about 50% power fade).

Two Variant C cells were removed from test after 28 weeks of aging because they exceeded the target power fade of 26.9%. Two of the remaining four Variant C cells will test until they meet or exceed 30.0% power fade; the other two cells will test to 50% power fade. The 45°C Variant C cells are projected to complete aging in July 2003 (i.e., 72 weeks with 604,800 cycles and approximately 50% power fade).

Table 7. ATD Gen 2 gap analysis chart.

Power Assist	EOT Target	Baseline Cells G2.60L25.I114.20.48.18.G.T Char.	Baseline Cells G2.60L25.I114.20.48.18.G.T 48-Weeks	Baseline Cells G2.60L45.I130.50.48.36.G.T Char.	Baseline Cells G2.60L45.I130.50.48.36.G.T 48-Weeks	Variant C Cell G2C.60L45.I162.30.28.26.G.T Char.	Variant C Cell G2C.60L45.I162.30.28.26.G.T 28-Weeks
18s Discharge Pulse Power (kW)	25	32.7	27.0	33.5	21.4	32.1	23.8
2s Regenerative Pulse Power (kW)	30	39.3	32.4	40.2	25.7	38.6	28.6
Available Energy (kWh)	0.3	0.820	0.469	0.867	0	0.802	0.170
Efficiency[1] (%)	>90	94.2%	93.5%	96.0%	95.2%	95.9%	95.5%
Cycle Life (25Wh profile)	300k	0	403.2 k	0	403.2 k	0	235.2 k
Cold Cranking Power @ -30C (kW)	5	NA	NA	NA	NA	NA	NA
Calendar Life (Yrs)	15	NA	NA	NA	NA	NA	NA
Maximum System Weight (kg)	40	0.04/21.4		0.04/21.6		0.04/25.1	
Maximum System Volume (Liters)	32	9.67		9.70		11.21	
Selling Price ($/system @ 100k/yr)	300	NA	NA	NA	NA	NA	NA
Maximum Operating Voltage (Vdc)	440	323.9		323.9		381.3	
Minimum Operating Voltage (Vdc)	0.55 x V_{max}	237		237		279.0	
Maximum DC-Link Current (A)	217	105.5		105.5		89.6	
Self Discharge (Wh/day)	50	NA	NA	NA	NA	NA	NA
Thermal Management (Avg. Wh/Day)		NA	NA	NA	NA	NA	NA
Operating Temperature Range (Degrees C)	-30 to +52	NA	NA	NA	NA	NA	NA
Survival Temperature Range (Degrees C)	-46 to +66	NA	NA	NA	NA	NA	NA
			P72		P72		P72
Hardware Level		Cell	Cell	Cell	Cell	Cell	Cell
Design Basis		Pack	Pack	Pack	Pack	Pack	Pack
BSF / Parallel Strings		553	7	553	7	651	7

5. CONCLUSIONS

The INEEL has completed 48 weeks (403,200 cycles) of cycle-life testing on the ATD Gen 2 Baseline cells and 28 weeks (235,200 cycles) on the Variant C cells. Eight 25°C Baseline cells, two 45°C Baseline cells, and four 45°C Variant C cells remain on test. Although the 25°C Baseline cells have exceeded the FreedomCAR goal of 300,000 cycles, they are still able to simultaneously meet the FreedomCAR power and energy goals. The 45°C Baseline and Variant C cells are no longer capable of meeting the goals, but testing will continue until the specified EOT criteria are met.

The Variant C cells consistently show a lower capacity fade than the Baseline cells. The increase in aluminum-dopant for the Variant C cells decreases the $C_1/1$ capacity fade by a factor of 2.5, and the $C_1/25$ capacity fade by 1.7 after 28 weeks of aging when compared to the 45°C Baseline cells. For all three cell groups, the average capacity fade for both the $C_1/1$ and $C_1/25$ increases as a function of the square-root of time. The 25°C Baseline cells show steady and monotonic growth, while the 45°C Baseline cells show mechanistic changes resulting in increases to the capacity fade rate. The 45°C Variant C cells only show a mechanistic change for the $C_1/1$ capacity fade. Unlike the 45°C Baseline cells, the Variant C $C_1/1$ capacity fade rate decreases once the change in mechanism takes place. The Variant C $C_1/25$ capacity fade is similar to the 25°C Baseline cells. This is also true for the Variant C $C_1/25$ differential capacity. For all cells, the capacity fade predominately occurs within the peaks of the differential capacity curves. The amplitudes of these peaks decrease with cycle-time and temperature. All differential capacity results are consistent with the cell capacity fade.

From the L-HPPC test, the cell ASIs increase as a function of cycle-time and temperature. The ASIs also grow as a function of test, with the cycle-life cells growing more rapidly than the calendar-life cells from ANL. The Variant C ASIs are initially higher and grow more rapidly than the Baseline cells. Since power is directly related to resistance, the increase in aluminum-dopant (although it improves capacity fade) has a deleterious effect on power fade. The Variant C cell power fade after 28 weeks of aging is 1.2 time higher than the 45°C Baseline cells. The 25°C Baseline cell power fade increases linearly with time, whereas the 45°C Baseline and Variant C cells are square-root of time dependent. All three cell groups show mechanistic changes, but only the 45°C Baseline cells show an increase in the power fade rate as a result of the change; the 25°C Baseline cells and 45°C Variant C cells show slower power fade rates. From these data, along with the capacity fade data, attempts were made to correlate power fade to capacity fade. However, a simple direct correlation is not easily identified. The L-HPPC test was also used to find ohmic and polarization resistances at 40% DOD from the LPM. The ohmic resistance growth for the Baseline cells show the same time dependence and mechanistic changes as the power fade, but the Variant C cells show the same relationships as power fade with the polarization resistance growth.

The 45°C Variant C cells also show a consistently higher EIS impedance growth at the semicircle trough. They show an initially higher impedance and are growing at a significantly faster rate than the Baseline cells. The Nyquist plots show that the EIS impedance grows as a function of test time and temperature. The growth in the EIS magnitude at the semicircle trough highly correlates with the power fade and shows temperature dependency. However, the temperature dependency goes away when correlating the delta magnitude growth at the mid-frequency band to power fade.

The 25°C Baseline cells are expected to continue testing for a total of 100 weeks before reaching their EOT criteria of 36% power fade. The 45°C Baseline cells should reach 50% power fade after a total of 80 weeks of cycle-life testing. Due to the high power fade, the Variant C cells are projected to reach EOT first, reaching 50% power fade after approximately 72 weeks. These projections may vary as other mechanistic changes as a function of cell aging become obvious.

6. REFERENCES

1. Raymond A. Sutula et al., *FY 2001 Progress Report for the Advanced Technology Development Program*, U.S. Department of Energy, Office of Advanced Automotive Technologies, February 2001.

2. Raymond A. Sutula et al., *FY 1999 Progress Report for the Advanced Technology Development Program*, U.S. Department of Energy, Office of Advanced Automotive Technologies, March 2000.

3. Jon P. Christophersen et al., *DOE Advanced Technology Development Program for Lithium-Ion Batteries: INEEL Gen 1 Final Report*, INEEL/EXT-2001-00417, September 2001.

4. Randy B. Wright and Chester G. Motloch, *Calendar-Life Studies of Advanced Technology Development Program Gen 1 Lithium-Ion Batteries*, DOE/ID-10844, March 2001.

5. Randy B. Wright and Chester G. Motloch, *Cycle-Life Studies of Advanced Technology Development Program Gen 1 Lithium-Ion Batteries*, DOE/ID-10845, April 2001.

6. Gary Henriksen, "Gen 1 & Gen 2 Cells," ATD Merit Review presentation, Argonne, IL, July 2002.

7. *PNGV Battery Test Manual*, Revision 3, Idaho National Engineering and Environmental Laboratory, DOE/ID-10597, February 2001.

8. D. Zhang at al., "Studies on capacity fade of lithium-ion batteries," *Journal of Power Sources,* vol. 91, pp. 122-129, 2000.

Appendix 1

Special Considerations

A1. SPECIAL CONSIDERATIONS

A1.1 ATD Labeling Scheme

An ATD labeling scheme was established to provide the diagnostic laboratories with succinct information regarding the EOT status of the test cells. The label is updated periodically as testing progresses and is finalized at EOT. It is in the form of GX[X].AABCC.DEEE.FF.TT.PP.Z.S, where:

- GX[X] = G2[C]
- AA = Test matrix state-of-charge (%)
- B = Test matrix profile (A, L, or C)
- CC = Test matrix temperature (°C)
- D = Original DOE laboratory (A, B, I, L, or S)
- EEE = Lab-specific cell number
- FF = Target power fade (%)
- TT = Time at life testing (weeks)
- PP = Power fade (%)
- Z = Abnormal condition flag
- S = Status

The label begins with either G2 for the Baseline cells or G2C for the Variant C cells. The test matrix state-of-charge (SOC), profile, and temperature (i.e., AABCC) identify the type of test, where accelerated-life (A), cycle-life (L), or calendar-life (C) testing is performed at a designated SOC and temperature. Next, the original DOE laboratory is identified (A = ANL, B = BNL, I = INEEL, L = LBNL, and S = SNL), along with the laboratory-specific cell number. The testing laboratories established a sequential numbering scheme such that all INEEL cells are numbered from 101 to 1XX, all ANL cells are numbered from 201 to 2XX and all SNL cells are numbered from 301 to 3XX and 401 through 4XX.

The target power fade (i.e., FF) is the desired power fade at EOT (Appendix C of Attachment 1). Once the actual power fade (i.e., PP) meets or exceeds the target power fade, the cell is removed from test and shipped to a diagnostic laboratory. The time at life testing (i.e., TT) shows the number of weeks the cell has been aging in four-week increments. Two unique situations occur for these three slots (i.e., FF.TT.PP). If the cell has only been characterized, a target power fade cannot be established (Appendix C in Attachment 1), and power fade is 0% (Section 3.3). Therefore, these slots will be identified as 00.CC.00 to indicate characterization testing only. If, however, a cell fails before characterization testing, the three slots are labeled 00.NA.NA.

The abnormal condition flag identifies any problems, such as shorting (S), venting (V), leaking (L), puncturing (P), or damaged tab(s) (T). Otherwise, the cell is marked good (G). The status flag either shows that the cell is still on test (T), has finished testing (F), or has been sent to a diagnostic laboratory (e.g., A, L, B, or Q for Quallion, LLC.).

For example, G2.60L25.I110.14.36.16.G.L is INEEL Cell 110, a Gen 2 Baseline cell. It was cycle-life tested at 60% SOC and 25°C for 36 weeks before being taken off test with 16% power fade, having exceeded the target power fade of 14%. The cell was in good condition when it was shipped to LBNL for diagnostic analysis.

A1.2 Temperature Control

All testing was performed with the cells placed in environmental chambers to control the ambient temperature. The chambers were able to control the temperature to within ±3°C, as specified in the test plan (see Attachment 1). Also, incorporating lessons learned from Gen 1 (Reference 3), all testing laboratories utilized thermal blocks for the Gen 2 cells in order to more uniformly control the cell and ambient temperatures. Before testing Gen 2 cells, the INEEL conducted two thermal block temperature control experiments. Ten 1.5-W heaters were placed in a block to simulate the Gen 2 cells under representative testing loads. Thermocouples were placed on each heater, and seven additional thermocouples were placed in various positions on the block itself. The ambient temperature was brought to 25°C, and after 5 minutes, the heat sources were activated. After 30 minutes, the heat sources were deactivated. This procedure was then repeated at 35, 45, and 55°C. The first control experiment involved controlling the ambient temperature using the resistance temperature detector (RTD) in the environmental chamber. Figure A1.1 shows the results from a block that was controlled using the RTD. The heater (simulated cell) temperatures rise monotonically and become steady at about 5°C hotter than the control (ambient) temperature. The second test involved controlling the ambient temperature using the thermocouples embedded in the block. The results are presented in Figure A1.2. At lower temperatures (i.e., 25 and 35°C), this yielded nonsteady heater temperatures that varied by ±2°C around the target temperature. At higher temperatures (i.e., 45 and 55°C), the heater temperature was steady. For both Figures A1.1 and A1.2, the block temperatures are slightly higher than the heater temperatures, since the thermocouples on the heaters were insulated. These figures demonstrate that controlling the ambient temperature using the RTD is more stable.

Figure A1.3 shows seven Gen 2 cells in a thermal block. The sense lead wires were secured to a stress relief fastener above and to the right of each cell, and another fastener on the top of the block. Figure A1.3 also shows the thermocouple attached to each cell using adhesive tape. The adhesive tape is secured to the cell with cable tie. All thermocouple wires are cable-tied together with the voltage and current sense leads, and held in place with a stress relief fastener (as shown on the far left fastener on the top of the thermal block). These restraints allow for some movement of the sense lead wires (e.g., plugging and unplugging the leads from the tester) without stressing the cell tabs.

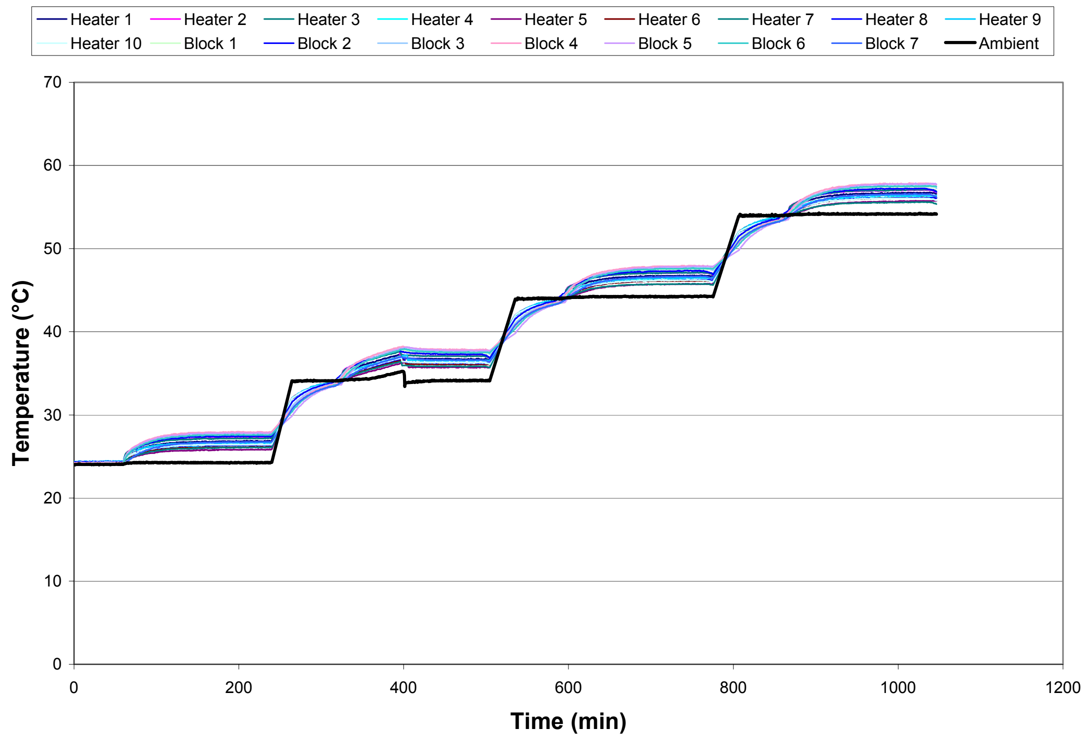

Figure A1.1. Thermal block temperature control experiment with ten heat sources (RTD control).

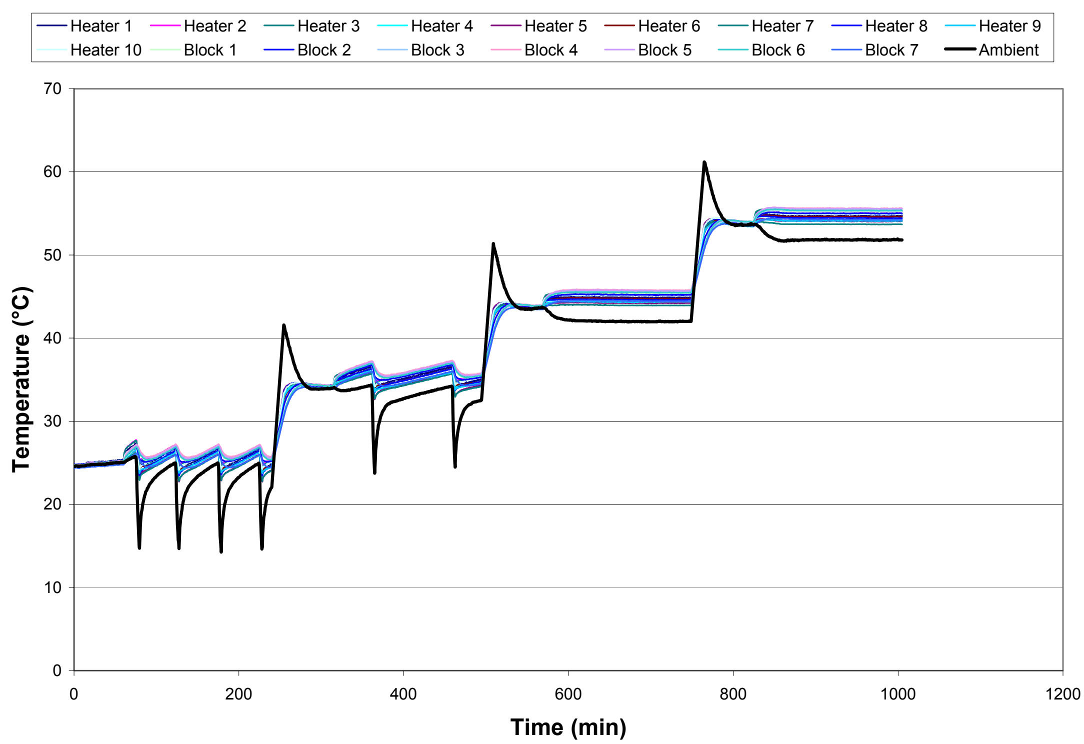

Figure A1.2. Thermal block temperature control experiment with ten heat sources (block control).

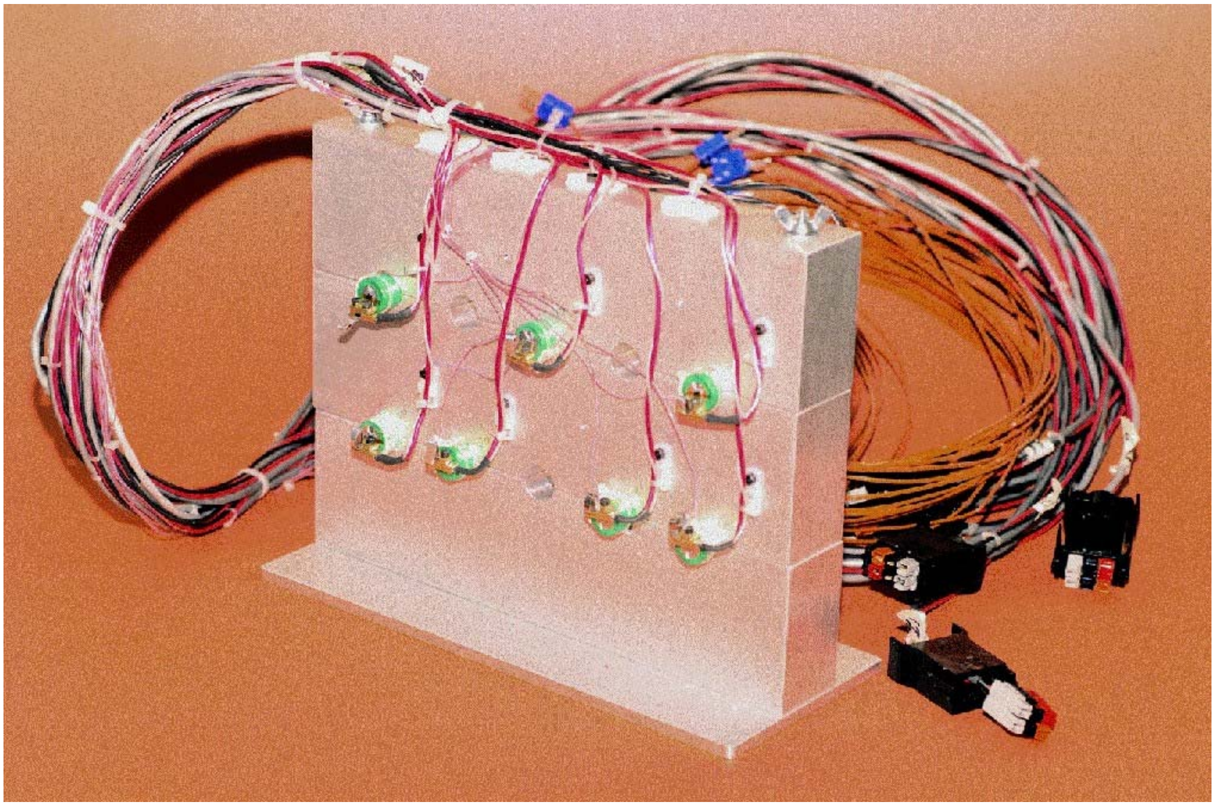

Figure A1.3. Thermal block with seven Gen 2 cells.

A1.3 Tab Issue

The Gen 2 cells arrived with aluminum positive tabs and high impedance nickel negative tabs. Since the tab welds were very weak and it was difficult to attach test leads, INEEL built ⅛- by ¼-in brass connectors for the cells. The tester voltage and current sense leads were soldered into the brass connectors. In addition, to minimize the tab impedance, the INEEL installed thin round vellum insulators (with a small slit in the middle for the tab) on the negative end of each cell. Their purpose is to provide electrical isolation and allow the connectors to be attached as close to the cell as possible, thereby minimizing the impedance of the tab to the tester connector. Figure A1.4 shows a close-up of a cell on a thermal block. The vellum insulator and brass connectors on the negative tab are shown, along with the voltage and current sense lead wires (black wires) attached to the cell tab through the brass connector.

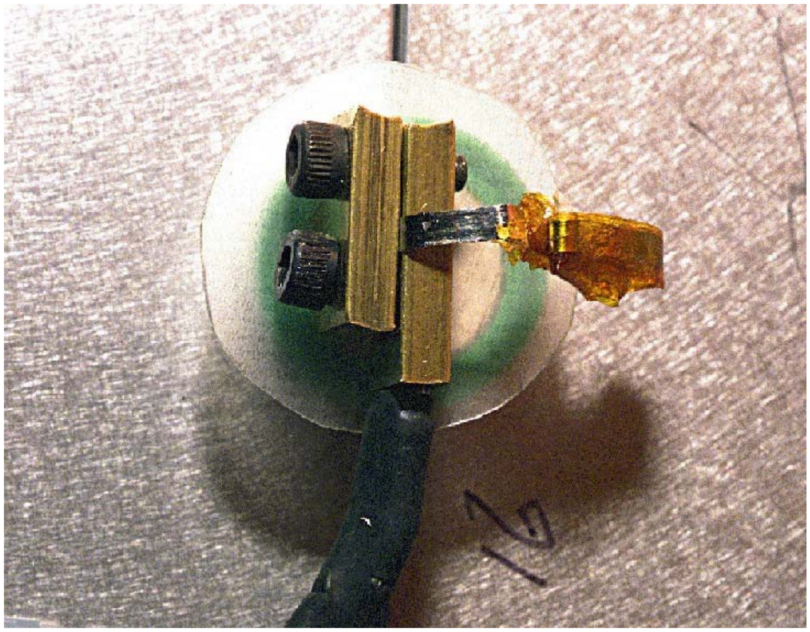

Figure A1.4. ATD Gen 2 cell with brass connectors and vellum insulator on the negative tab.

A1.4 Tab Failure

On January 23, 2001, the INEEL hooked up one cell (G2.60L25.I101.00.NA.NA.T.A) to the tester and began characterization testing in accordance with the cell-specific test plan (Attachment 1). Shortly after completing five $C_1/1$ static capacity tests and three electrochemical impedance spectroscopy tests at 60% SOC (test descriptions are provided in Section 3), it was discovered that the negative tab had failed. The INEEL measured the open-circuit voltage (OCV) and found it still at the target corresponding to 60% SOC (Appendix D of Attachment 1). The cell may have been inadvertently shorted, resulting in a melted tab. The cell did not appear to have any internal damage, and there was no evidence of venting. As directed by the ATD Program Manager, the cell was shipped to ANL for diagnostic work, and the INEEL received a replacement cell (G2.60L25.I176.00.CC.00.G.B) on February 5, 2001. Figure A1.5 shows the failed negative tab on G2.60L25.I101.00.NA.NA.T.A.

A1.5 Vent Failure

INEEL's receipt inspection (Section 4.1) revealed that one of the 15 Variant C cells that arrived on July 30, 2001 (G2C.60L45.I173.00.NA.NA.L.Q), had self-discharged below the 3.0 V minimum. This cell also showed high impedance at 1 kHz (15.0 – j2.5 mΩ compared to an average of 10.6 – j0.2 mΩ). Two days later, when all Variant C cells were connected to the tester for $C_1/1$ testing, the open-circuit voltage (OCV) of G2C.60L45.I173.00.NA.NA.L.Q had drifted down to 0.92 V. The $C_1/1$ capacity test showed only 0.67 A·h. Therefore, as directed by the ATD Program Manager, the cell was returned to Quallion, LLC. Quallion, LLC, discovered that the vent on this cell was broken, and some electrolyte had leaked out. Figure A1.6 shows the hole in the vent along with the electrolyte leakage.

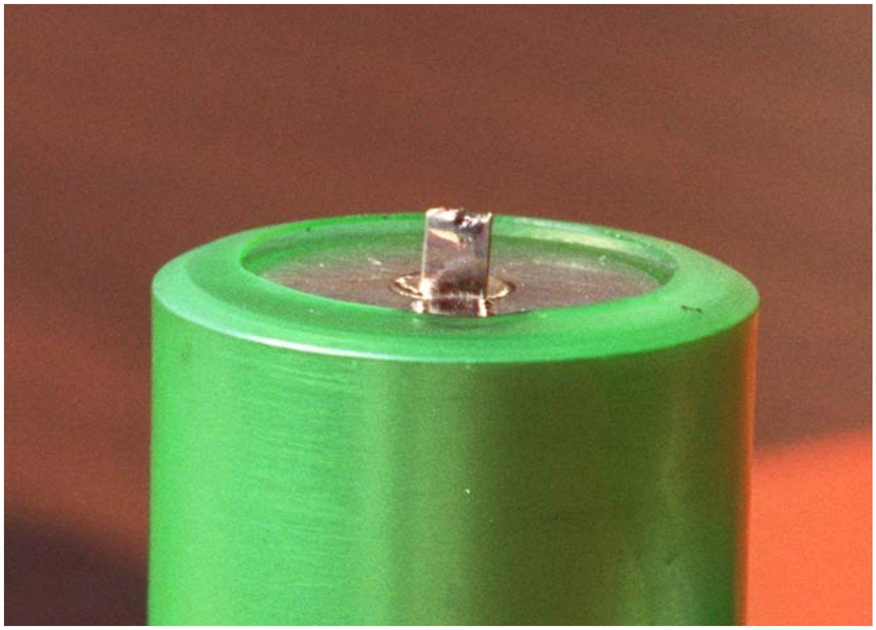

Figure A1.5. G2.60L25.I101.00.NA.NA.T.A with failed tab.

Figure A1.6. G2C.60L45.I173.00.NA.NA.L.Q with broken vent and electrolyte leakage.

Attachment 1*

PNGV Test Plan for Advanced Technology Development Gen 2 Lithium-Ion Cells

* Attachment 1 is Revision 6a of the ATD Gen 2 test plan. This incorporates some minor editorial changes from the previously released version (Revision 6 on October 5, 2001) and does not impact testing procedures. If significant changes to the test plan are required in the future, INEEL will issue Revision 7 and include the changes from Revision 6a.

PNGV TEST PLAN FOR ADVANCED TECHNOLOGY DEVELOPMENT GEN 2 LITHIUM-ION CELLS

Reviewed: ______________________________ ________________
INEEL/ANL/SNL Program/Project Engineer — Date

Reviewed: ______________________________ ________________
INEEL/ANL/SNL Laboratory Manager — Date

Approved: ______________________________ ________________
INEEL/ANL/SNL Department Manager — Date

PNGV TEST PLAN
FOR
ADVANCED TECHNOLOGY DEVELOPMENT
GEN 2 LITHIUM-ION CELLS

Concurred: ________________________________ ________________
DOE Program Manager Date

Concurred: ________________________________ ________________
DOE Test Manager Date

Concurred: ________________________________ ________________
DOE Technical Contact Date

PNGV Test Plan for ATD GEN 2 Lithium-Ion Cells

1.0 Purpose and Applicability

The intent of this testing is to characterize the performance and to determine the cycle life and calendar life behavior of lithium-ion cells (nominal 1.0 Ah capacity). The cycle life testing will be performed at the Idaho National Engineering and Environmental Laboratory (INEEL) and the calendar life testing will be performed at the Argonne National Laboratory (ANL). This work is being done as part of an Advanced Technology Development (ATD) Program project for the improvement of high-power lithium-ion batteries. The testing is sponsored by the DOE Office of Advanced Automotive Technologies (OAAT) and is under the oversight of OAAT and the designated DOE Program Manager. In general, these cells will be subjected to the characterization, reference performance, and life test procedures that have been defined for the PNGV Program as specified in Reference 2.1. The cells covered by this test plan are 18650-size baseline and variant cells manufactured by Quallion specifically for Gen 2 of the PNGV ATD Program, which have been built to ATD specifications. The baseline cell chemistry is defined in Reference 2.4. The Variant C chemistry uses the baseline chemistry except for the a change to the Cathode.

2.0 References

2.1 PNGV Battery Test Manual, Revision 3, DOE/ID-10597, February 2001
2.2 EST Laboratory Standard Practices
2.3 IHRG# BAT-99-622 Battery and Capacitor Testing in the Energy Storage Technologies Laboratory (Expires on 9/9/2002).
2.4 "Gen 2 Baseline & Variant Cells," ATD Quarterly, Presentation by Gary Henriksen, Albuquerque, N.M., November 2000.

3.0 Equipment and Hardware

3.1 All testing will be performed on laboratory cell test channels with current and voltage capabilities adequate for the specific test procedures to be performed. In general, lower voltage ranges should be used where available (5V preferred, not to exceed 20V) to assure the best voltage resolution and accuracy.

3.2 Except where noted otherwise, testing will be performed with the cells at a temperature of 25 ± 3°C at the beginning of a test sequence, although maintaining a tighter tolerance should be attempted. The preferred means to accomplish this is by the use of a thermal block and a controlled temperature chamber having both heating and cooling capabilities. Unless otherwise specified, all temperature measurement and control should be based upon the cell skin temperature, or equivalent. Test temperature will be controlled by the RTD (Resistance Temperature Detector) in the environmental chamber.

3.3 The temperature of cells under test should be measured using moderately fast response sensors (e.g. ≤3/16" thermistors or pad-type thermocouples such as Omega Model SA-1) adhered to the positive end of each cell. Sensors should be fastened to the cell using a means (e.g. epoxy, tape or clamp) which provides consistent contact.

3.4 AC impedance measurements at 1 kHz will only be made as part of the receipt inspection. Spectral impedance measurements will be made throughout testing. The associated equipment is described in Appendix E.

4.0 Prerequisites and Pre-Test Preparation

4.1 Before testing starts, the cells will be assigned lab-specific identification numbers. A battery notebook for the cells will be started, and both the ATD and test laboratory identification numbers (if different) will be recorded for each cell. The table described in Appendix A should be completed and maintained throughout the ATD test program. Once testing begins, additional information should be added to the table, including the periodic recording of capacity, pulse power, temperature, dates, and other pertinent information. An End-Of-Testing (EOT) labeling convention has been created for Gen 2. The principal purpose is to provide the diagnostics labs succinct information regarding the EOT status of these cells. At a minimum, the label for each cell will be established at the beginning of testing and updated at the end of testing. Optionally, the label may be updated periodically as testing progresses. The ATD labeling convention is as follows:

GX.AABCC.DEEE.FF.TT.PP.Z.S, where

GX[X] G1, G2, or G3 for Gen 1, Gen 2, or Gen 3, respectively, and [X] = A, B, or C as appropriate for each variant.
AA Test Matrix State of Charge, e.g., 60%
B Test Matrix profile, e.g., S, L, C and A, where S = in storage, L = cycle life cell, C = calendar life cell, and A = accelerated life test
CC Test Matrix Temperature, (°C)
D Original DOE Laboratory, A = ANL; B = BNL; I = INEEL; L = LBNL; S = SNL
EEE Sequential cell number as assigned by Original DOE Laboratory:
INEEL: 101 through 1XX
ANL: 201 through 2XX
SNL: 301 through 3XX, and
401 through 4XX
FF Target power fade (%) based on equal power fade increments (see Appendix C).
TT Time at life testing, CC = Characterization or 00, 04, etc (wks)

PP PNGV Power fade relative to the 0 week L-HPPC Reference Performance Test (%). By definition the PNGV power fade at 0 weeks is 00%. (Enter NA for Characterization Power Fade, and ND for No Data.) If the characterization tests are performed within 2 weeks prior to commencing life testing, they are defined as the 0 week L-HPPC Reference Performance Test.

Z Abnormal condition flag: S = shorted; V = vented; P = punctured; L = leaked; T = tab problem; G = Good.

S[S] Status: T = test continuing; F = finished testing and in storage. Or if shipped to another laboratory then, A = shipped to ANL; B = shipped to BNL; I = shipped to INEEL; L = shipped to LBNL; Q = shipped to Quallion; S = shipped SNL. [S] = additional status flags as appropriate to track the history of the cell.

Note: Diagnostic lab cells may utilize this convention by placing an X in any field that is not applicable to that cell.

4.2 The cells will be visually inspected for signs of shipping or other damage. Any signs of damage should be documented. The maximum outside diameter of the cells, the cell lengths, actual weights and open circuit voltages as delivered will be recorded. The cell weights will include the cell current tabs. Also, to further confirm that the cells are not damaged, perform an AC impedance measurement at 1 kHz and record the value for each cell.

4.3 Prior to start of testing, a pre-test readiness review shall be conducted using the released version of this test plan and the associated test procedures. This review should be attended by (as a minimum) the project engineer (or designee), the laboratory manager, and the test engineer assigned to perform this testing. An external readiness review involving DOE and the ATD Program Manager may be required at their discretion, and it may be in addition to, or in lieu of, an internal review. This review may be conducted by conference call.

5.0 Cell Ratings, Test Limitations and Other Test Information

5.1 Ratings

Baseline Cell Rated Capacity:	1.0 Ah (C_1/1 rate)
Variant C Cell Rated Capacity	0.8 Ah (C_1/1 rate)
PNGV Application:	*Power Assist*
Battery Size Factor:	*553 (Baseline)* *651 (Variant C)*

HPPC Pulse Power Voltage Calculation Range:

Vmin	*3.0 V*
Vmax	*4.1 V*

Operating Temperature Range:	-20°C to +60°C
Maximum Discharge Temperature:	60°C, cell temperature
Maximum Charge Temperature:	40°C, cell temperature
Storage Temperature:	10°C ± 3°C

5.2 Nominal Values

Baseline Cell Nominal Capacity:	0.979 Ah
Variant C Cell Nominal Capacity	0.826 Ah
Nominal Weight:	TBD kg
Nominal Volume:	TBD L

5.3 Discharge Limits

Minimum Discharge Voltage:	3.0 V	*18 sec pulse*
	3.0 V	*Continuous*
Maximum Discharge Current:	8.0 A	*18 sec pulse (I_{max})*
	2.0 A	*Continuous*

5.4 Charge and Regen Limits

Maximum Regen Voltage:	4.3 V	*10 sec pulse*
	4.1 V	*Continuous*
Maximum Regen Current:	8.0 A	*10 sec pulse*
	1.0 A	*Continuous*

5.5 Charge Procedure: For the baseline cells, charge at 1.0 A constant current rate to a voltage of 4.1 V (charge at 0.8 A for the Variant C cells); continue to maintain a constant voltage of 4.1 V for 2.5 hours total recharge time. All recharging is to begin at 25 ± 3ºC, unless specifically stated otherwise.

5.6 Recharge Constraints

If a procedure requires a cell to be fully charged at the start of the test sequence, the cell will be considered fully charged (i.e. need not be subjected to a 'top off' charge) if it was fully recharged no more than 72 hours previously, and the SOC is within 2% (see Appendix D).

5.7 Life Cycle Test Conditions:

Nominal State of Charge For Life Cycle and Calendar Life Testing:	60% SOC (see Appendix D for corresponding voltage)

5.8 End-of-Testing Criterion:	1. Completion of the specified life interval (see Appendix C); or 2. When directed by the DOE Program Manager or DOE Technical Contact.

Note: Notify the DOE Program Manager or DOE Technical Contact if the cell is unable to successfully perform the HPPC test through the 60% DOD pulse.

6.0 Safety Concerns and Precautions

In general, the safety issues with these cells are similar to those encountered previously with lithium-ion cells tested for the PNGV program. Thus, the same precautions will be exercised as are normally used for lithium-ion cells.

6.1 Cell Handling

- Cells should be handled whenever possible in the discharged state.
- Safety gloves suitable for handling high-energy batteries should also be worn for cell handling unless the specific operations being performed cannot be accomplished while gloved.
- Due care should be taken to avoid shorting the cell terminals. Caution: the cell case is electrically tied to the positive terminal! Electrically isolate the thermal blocks from the environmental chamber.
- Cells should be shipped in a discharged state (between 10% to 25% SOC).

6.2 Other Safety Precautions

- For both testing and storage, cells should be located within an area shielded from non-deliberate exposure to personnel. Cells that show any signs of deterioration or unanticipated behavior should be segregated from other cells to avoid propagation of damage in the event of a failure.

- Charged cells should not be located close to flammable and/or combustible materials

- Venting of cells should be regarded as a possibility. Lab personnel response to any unanticipated release of fumes or smoke at the test location should be to evacuate the immediate area (e.g., test room). The laboratory manager (or equivalent) and safety personnel should be notified. Approval from the laboratory manager should be obtained prior to reentering the testing area. (Note: if it is very clear that only minor venting is occurring, the situation may be observed at a safe distance to determine whether the release ceases without further action.)

- It has been shown during abuse testing (thermal abuse and intentional overcharging) that the cells experienced catastrophic failure and the vents did not function.

In case of unexpected cell behavior (e.g. venting), the cells should not be approached for at least one hour afterward.

7.0 Tests to be Performed Under this Test Plan

All cells will be subjected to the characterization performance test sequence in Table 1. The cells will be tested according to the Power Assist goals and requirements. Battery Size Factors (BSF) for the four types of Gen 2 cells (e.g. baseline and the three variants) will be calculated using an average of the cells of that type.

All recharging between tests is to be done using the recharge procedure of Section 5.5. In general, a rest step of nominally 60 minutes shall be observed after each charge, and nominally 60 minutes after each discharge, to allow cells to reach stable voltage and temperature conditions prior to proceeding with testing.

Note 1. Except for the HPPC tests, use the corresponding open circuit voltage as a measure of State-of-Charge. (For HPPC tests, removed-capacity will be used as the measure of Depth of Discharge). The following sequence describes a suitable means to reach the target voltage/SOC. Other approaches that accomplish the same end conditions are also acceptable.

1. Using the reference SOC/voltage curve (Appendix D), determine the voltage corresponding to the target SOC (at 25 °C).

2. Discharge the cell at a $C_1/1$ constant current rate from a fully charged condition to the target voltage value at 25 °C.

3. Maintain the target voltage for 2.5 hours or until the current is less than 10 mA, whichever comes first, to ensure that the cell state of charge is stable at this voltage.

4. Place the cell in an open circuit condition.

Note 2. When not under active testing for prolonged periods, the cells shall be stored at 10°C at a low state of charge, e.g., between 10% to 25% SOC.

7.1 Characterization Testing

Perform the tests specified in Table 1 on all cells.

Table 1. Characterization Performance Test Sequence (All Cells)

Item	Performance Test	Frequency
1	**C_1 Static Capacity Tests** *(Reference 2.1, Section 3.2)* This test consists of a constant C_1 discharge at a $C_1/1$ rate at 25ºC (i.e., initial temperature of 25 $\pm$ 3ºC) beginning with a fully charged cell and terminating at the specified cutoff voltage of 3.0 V, NOT rated capacity. Note: Use the value of the last discharge from each cell for reporting the actual C_1 individual cell capacities. Repeat the C_1 test five (5) times and confirm that the measured capacity of the last three tests are within 2%.	5 iterations at beginning of testing
2	**C_1/25 Static Capacity Test** *(Reference 2.1, Section 3.2)* Perform one $C_1/25$ discharge and charge at 25 $\pm$ 3°C on all cells. The procedure is as follows: 1. Fully charge the cell, as defined in Section 5.5. 2. Rest for 1 hour at OCV. 3. Discharge at a $C_1/25$ rate until 3.0 V is reached. 4. Rest for 1 hour at OCV. 5. Charge at a $C_1/25$ rate until 4.1 V is reached.	1

	Resting for 1 hour between the discharge and charge will result in some cell relaxation, so the initial charge voltage will be greater than 3.0 V. Calculate the relative change in capacity as a function of voltage using the following equation: $\frac{1}{Q} \cdot \frac{d(Ah)}{dV} = \frac{(Ah_2 - Ah_1)/(Cell\ \ Capacity)}{(V_2 - V_1)}$, where Q is the $C_1/25$ discharge capacity. Smooth the data by taking the capacity every ninth minute and average the voltage during that nine-minute period, or use another approach that accomplishes the same goal. Calculate the differential capacitance [1/Q * d(Ah)/dV] using a three-point numerical differentiation to take the derivative of the smoothed data.	
3	**AC Impedance Test** *(Appendix E, and Reference 2.1, Section 3.13)* Spectral impedance measurements will be performed over a range of frequencies from 0.01 Hz to 10 kHz at an appropriate voltage level, 60% SOC and 25°C with 10 points per decade of frequency. Rest between 8 and 12 hours at 60% SOC before commencing the measurements. The AC Impedance Test will be repeated at the end of life testing.	1
4	**Hybrid Pulse Power Characterization Test** *(Reference 2.1, Section 3.3)* The Low Current Test is to be performed at a 5C rate and at 25°C. PNGV Pulse Power Capability will be computed using a voltage range 3.0 V, to 4.1 V. However, as specified in Section 5.0, the maximum allowed voltages during the test are 4.3 V for a 10-second pulse and 4.1 V continuous, and the lower voltage limit is 3.0 V. See Section 8.4 for HPPC analysis requirements.	1

7.2 Life Cycle and Calendar Life Testing *(Reference 2.1, Sections 3.10 and 3.11)*

Appendix C describes the cycle life and calendar life testing schedule and when cells are to be taken off test. Note that a leaking cell is not an end of test criterion.

Table 2. Cycle Life and Calendar Life Test Sequence

Item	Life Cycle Test	Frequency
1	**Reference Performance Tests** Conduct Reference Performance Tests (RPT's) on all cells at 25 ± 3°C within 2 weeks prior to commencing the Calendar Life Tests and the Life Cycle Tests, and every four weeks, thereafter. The RPT consists of one nominal C_1 constant current discharge from 100% SOC to 3.0 V and one L-HPPC (in the same data file), one $C_1/25$ discharge and charge, and one AC spectral impedance measurement, including a measurement at the 1 kHz point (see Section 7.1 (3), AC Impedance Test, and Appendix E). Note: The sequence of tests that constitute the RPT may be done in any order that best meets the capabilities and limitations of each laboratory. However, once a sequence has been established, it should not be changed without a compelling reason and concurrence from the DOE Technical Contact. At the end of testing, also measure and record the weights.	Once at beginning of life testing, and then every four weeks, thereafter
2	**Operating Set Point Stability Test** *(Reference 2.1, Section 3.9)* This test is conducted on all cycle life cells at the beginning of life cycle testing using the same test profile and conditions required for life cycle testing. At the completion of this test, the actual SOC should be within ±2 % of the target SOC. The OCV versus SOC tables for the baseline and variant cells are given in Appendix D. * As needed	*

3	**Cycle Life Testing** *(Reference 2.1, Section 3.10)* Subject the cells to the 25 Wh Power Assist Life Cycle Test Profile *(Reference 2.1, Table 6)* @ 60% SOC at the appropriate temperature. The discharge and regen voltages and currents should be estimated such that the cells do not fail during cycle life testing. Once a BSF has been determined based on the L-HPPC test, Section 7.1 (4), use the pulse power equations in Section 4.3.3 of Reference 2.1 to find V_{min} and V_{max} based on the OCV corresponding to 60% SOC (see Appendix D). Also estimate the associated current values based on these voltage drops. Quantity — Temp 15 (15 Baseline) — 25°C 30 (15 Baseline, 15 Variant C) — 45°C Every four weeks conduct the Reference Performance Tests as described above. Also, if the OCV at the end of the one-hour rest following completion of each four-week block of life cycle testing is not within ± 2% of the target SOC, adjust the control voltage and repeat the OSPS test at the target temperature and SOC prior to resuming life cycle testing.	Continue until an end of testing criterion is met
4	**Calendar Life Testing** *(Reference 2.1, Section 3.11)* Subject the cells to the calendar life test profile *(Reference 2.1, Table 8)* @ 60% SOC and 55 °C. The profile will be scaled based upon a 3C current. An additional pulse at 25 °C will be performed at the start and end of each 4-week interval. Also subject two archived baseline cells to the calendar life test at 60% SOC and 45°C. Quantity — Temp 15 (15 Baseline) — 55°C 15 (15 Variant C) — 45°C 2 Archived Baseline Cells — 45°C	Continue until an end of testing criterion is met

8.0 Measurement and Reporting Requirements

Note: These measurement requirements are for INEEL testing. Other labs may record data at different frequencies based upon their data needs and equipment capabilities.

8.1 Measurements

For each group of cells subjected to a common test regime at a given temperature, the ambient temperature for this cell group should also be measured and included in the data for the first (lowest numbered) cell in that group. For data consistency, this should normally be the last recorded variable for that particular cell.

Detailed data acquisition and reporting requirements for the characterization and life cycle tests are as required for the applicable test procedures in Reference 2.1. For measurements made near the start of discharge or regen pulses, current and voltage measurements must be made near-simultaneously. Measurements at other times during pulse steps should have channel-to-channel latency between current and voltage measurements of less than 100 milliseconds. The response of Maccor test channels is considered adequate to meet this requirement provided that a data point is acquired near the beginning of each pulse-type step; the response of other data acquisition systems may need to be reviewed further.

8.2 Data Recording Intervals

During the once-per-day Calendar Life pulse profiles, data should be acquired at a periodic rate of once per second during discharge pulses, regen pulses and the rest intervals between them. This rate may be decreased to once per 2 seconds for pulses or rest intervals that are longer than 30 seconds. Voltage and current data should also be acquired at the beginning and end of each discharge and initial regen pulse.

During the 1-hour HPPC rest intervals and charge periods, data may be acquired once per minute; a data point is also required at the termination of all these periods. Data should be acquired every 10 seconds for $C_1/1$ discharge periods, and every 30 seconds for $C_1/25$ discharge periods. For HPPC discharge pulses, data should be acquired at 2 points per second for the first 12 seconds, and 1 point per second for the last 6 seconds. For HPPC regen pulse, data should be acquired at 5 points per second for the first 2 seconds, and every 0.4 seconds during the last 8 seconds. Data should be acquired every 2 seconds during the 32-second HPPC rest. For rest intervals greater than 1 hour (e.g. calendar life periods), the data may be acquired once per half an hour. In general, specified rest periods should be treated as part of the associated test with respect to data acquisition and archiving; voltage and temperature data should be acquired during these periods.

Data should be acquired at one-second intervals for Operating Set Point Stability (OSPS) tests. Data should also be acquired at one-second intervals during Life

Cycle testing for those test profiles that are recorded; however, not all profiles need to be recorded. For Power Assist Life Cycle testing, the first and last 100 profiles of each test interval are required to be recorded, along with at least one complete profile out of every 100.

8.3 Data Access

All data acquired will be archived. The customer designation for this data is DOE, and data should not be marked as "CRADA Protected" or "Protected Battery Information."

8.4 Data Files

Individual HPPC tests should be archived as a single data file. It is recommended that this HPPC file should also include (where available) the associated $C_1/1$ discharge for Power Assist devices.[a] This file may or may not include the charge prior to the start of the test. Life Cycle Test data should be separated into no more than 3 data files for each testing interval: the initial profiles required to be recorded, the final profiles required to be recorded, and all other data acquired between these two groups of profiles. At the completion of testing, the characterization and RPT results should normally be transcribed to a compact disk and sent to the PNGV Technical Contact.

The following four graphs should be prepared for each cell for each set of HPPC tests: (1) ASI (ohm-cm^2) vs. Cell Voltage Measured at the Start of Discharge or Regen Pulse (V); (2) Power Density (mW/cm^2) vs. Equilibrium Open Circuit Voltage Corresponding to the Start of Discharge or Regen Pulse (V); (3) BSF-scaled Power (W) vs. BSF-scaled Cumulative C_1 Energy Removed (Wh); and (4) BSF-scaled Available C_1 Energy (Wh) vs. BSF-scaled Power (W). The power, the point at which the scaled available energy curve crosses the 300 Wh energy goal, will also be reported for each cell for each set of HPPC tests.

Within two weeks of completion of each set of RPT's, transcribe the RPT and pulse-per-day calendar life test results to a compact disk and send the CD to the other testing labs. Also within the two week interval, put the final analyzed form of the data on the lab's web site in PDF format.

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[a] *Combining these files is done to facilitate automated analysis of the results. The revised PNGV goals require that Available Energy is calculated using the HPPC power results and the $C_1/1$ energy (for Power Assist) results simultaneously.*

9.0 Anticipated Results

9.1 Performance and Life Testing

This testing will produce data that characterizes the performance and determines the cycle life and calendar life behavior of lithium-ion cells (1 Ah rated capacity) developed for the ATD Program for the improvement of high-power lithium-ion batteries.

9.2 Testing Deliverables

Summary testing status and results to date will be provided to the DOE Program Manager, DOE Technical Contact, and other ATD program participants on a monthly basis. Detailed test data files for specific tests will be provided to the DOE Program Manager and DOE Technical Contact or to other laboratories for comparison of results, as requested.

10.0 Post-Test Examination and Analysis

At the completion of testing, cells will be provided for post-test analysis to other ATD participants (e.g., LBNL and/or BNL) as shown in Appendix B or as directed by the DOE Technical Contact. Any cell disassembly should be coordinated with the diagnostics labs. Cells to be shipped to other labs should be discharged to between 10% and 25% SOC, or they may be shipped as disassembled components. Shipments of cells or components should be closely coordinated between the shipping and receiving lab including providing complete cell/component identification per Section 4.1 and the table referenced in Appendix A.

11.0 Contact Persons

ATD Program Designated Technical Contact List

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Appendix A

Tabulation of ATD Cell Identification Numbers, Test Conditions, and Results

To help ensure that the correspondence between specific cells, their test conditions, test results, and other pertinent information is identified and maintained throughout the testing program, an Excel table should be used to assign and track information such as weights, impedance, dates, temperature, capacity, and pulse power. Update the table within two weeks of the completion of characterization testing and at the completion of each set of RPT's. Copies of this information should be provided with any batteries furnished to other laboratories for additional testing or post-test analysis.

Appendix B

ATD GEN 2 Cell Distribution Matrix

There are a total of 195 Gen 2 cells (165 Baseline cells and 30 Variant C cells). INEEL will receive 45 cells (30 Baseline and 15 Variant C cells) and ANL will receive 37 (22 Baseline and 15 Variant C). Seven of the ANL baseline cells will be archived. The INEEL baseline cells will be divided into two groups of 15. The complete cell distribution is shown in Table B.1.

Table B.1. Cell Distribution

First 20 cells sent to ANL will be transferred to SNL							
	Baseline			Variant C			**Total**
	Testing	Therm. Ab.	Diag.	Testing	Therm. Ab.	Diag.	
ANL	22		1	15			**38**
BNL			1				**1**
INEEL	30			15			**45**
LBNL			1				**1**
SNL 1	15						**15**
ANL to SNL 2	20						**20**
3	27	48					**75**
4							**0**
Total	**114**	**48**	**3**	**30**	**0**	**0**	**195**
			165			**30**	**195**

The cell being sent for diagnostics after characterization will be shipped to ANL, BNL or LBNL, as directed by the DOE Program Manager. After characterization, the cells will come off test in pairs (see Appendix C). One of these cells will be shipped to ANL and the other to LBNL for diagnostic analysis. ANL and LBNL are responsible for distributing some cells to BNL.

Appendix C

End-of-Test Criterion

After characterization, send one randomly selected cell from each group of 15 to the designated diagnostic lab. After 4 weeks of cycling, remove two more cells from each group of 15 as follows:

- **Baseline Cells:** remove two randomly selected cells
- **Variant Cells:** remove the two cells with the highest power fades

The End-of-Test (EOT) criteria for the remaining 12 cells will be based on equal power fade increments. The objective is to have 2 cells life tested until the power fade reaches 30% and another 2 cells life tested beyond 30% power fade, and the remaining cells removed from test in pairs at approximately equal power fade increments.

***Baseline Cell Initialization**:*
- Calculate the individual cell power fades at 8-weeks using Equation 1
- Calculate the average power fade at 8-weeks using Equation 2 (w = 8 and i = 12 cells)
- Calculate the incremental power fade using Equation 3
- Calculate the target power fade (P_{Target}) using Equation 4

***Variant Cell Initialization**:*
- Calculate the average power fade of the two cells designated to come off test at 4-weeks, i.e., the cells with the highest fades (Equation 2 with w = 4 and i = 2 cells)
  - Calculate the incremental power fade using Equation 3 ($\overline{F}_w$ is from the previous calculation and i = 12)
  - Calculate the target power fade (P_{Target}) using Equation 4

***Baseline and Variant Cells**:*
- Follow the flowchart sequence shown in Figure C.1
- **NOTE:** If a cell fails prematurely, send it to the designated diagnostic lab (as specified by the DOE Program Manager). This means that only one cell should be taken off test once it meets the target power fade. After that cell has been removed, calculate the new target, and start following the sequence shown in Figure C.1 again.

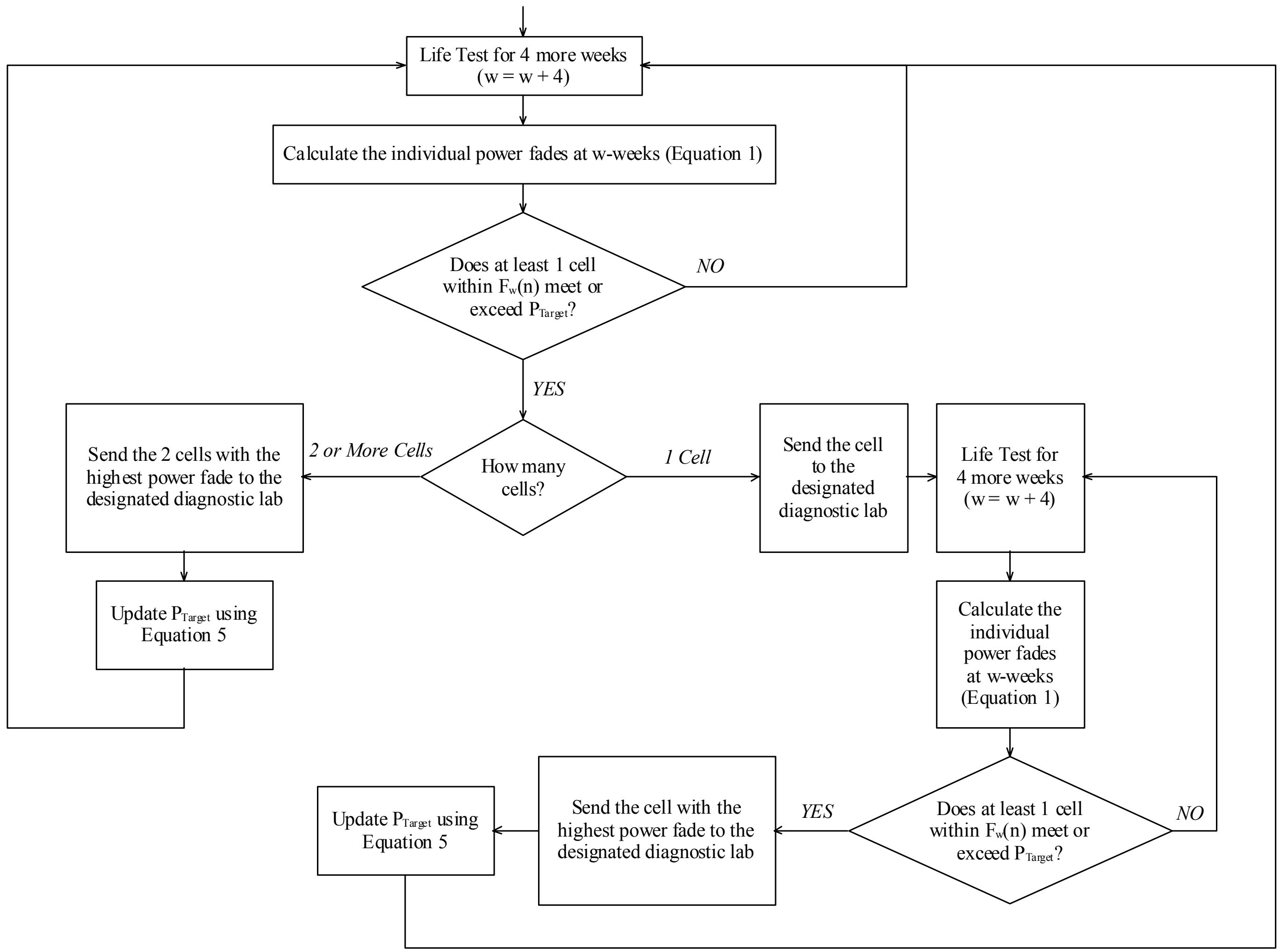

Figure C.1. EOT Criteria Flowchart

Equations:

- w = weeks
- n = cell number
- i = number of cells remaining
- P_0 = Power at 0-weeks (a.k.a. characterization)
- P_w = Power at w-weeks
- $F_w(n)$ = Individual cell power fade for cell n at w-weeks (an array of size i)
- $\overline{F}_w$ = Average power fade at w-weeks
- ΔF = Incremental Power Fade
- P_{Target} = Target power fade for removal of the next pair of cells

$$F_w(n) = \left.\frac{P_0 - P_w}{P_0}\right|_n * 100\% \qquad (1)$$

$$\overline{F}_w = \frac{\sum_i \left.\frac{P_0 - P_w}{P_0}\right|_i}{i} * 100\% \qquad (2)$$

$$\Delta F = \frac{30\% - \overline{F}_w}{\frac{i}{2} - 1} \qquad (3)$$

$$P_{Target} = \overline{F}_w + \Delta F \qquad (4)$$

$$P_{Target} = P_{Target} + \Delta F \qquad (5)$$

Appendix D

ATD GEN 2 Open Circuit Voltage vs. State of Charge Tables and Curves

Table D.1. Calibration Table for ATD Gen 2 Baseline Cells

SOC	Voltage	SOC	Voltage	SOC	Voltage	SOC	Voltage
100%	4.096						
99%	4.084	74%	3.851	49%	3.644	24%	3.499
98%	4.075	73%	3.843	48%	3.639	23%	3.490
97%	4.065	72%	3.833	47%	3.633	22%	3.481
96%	4.055	71%	3.824	46%	3.628	21%	3.472
95%	4.045	70%	3.815	45%	3.623	20%	3.462
94%	4.034	69%	3.805	44%	3.618	19%	3.451
93%	4.023	68%	3.795	43%	3.613	18%	3.440
92%	4.012	67%	3.786	42%	3.608	17%	3.429
91%	4.001	66%	3.776	41%	3.603	16%	3.418
90%	3.990	65%	3.767	40%	3.598	15%	3.406
89%	3.980	64%	3.758	39%	3.594	14%	3.395
88%	3.970	63%	3.749	38%	3.589	13%	3.384
87%	3.960	62%	3.740	37%	3.584	12%	3.374
86%	3.950	61%	3.731	36%	3.578	11%	3.365
85%	3.941	60%	3.723	35%	3.573	10%	3.357
84%	3.932	59%	3.714	34%	3.568	9%	3.349
83%	3.923	58%	3.705	33%	3.562	8%	3.340
82%	3.915	57%	3.698	32%	3.556	7%	3.331
81%	3.906	56%	3.690	31%	3.551	6%	3.320
80%	3.898	55%	3.683	30%	3.544	5%	3.304
79%	3.891	54%	3.675	29%	3.537	4%	3.278
78%	3.883	53%	3.669	28%	3.530	3%	3.235
77%	3.875	52%	3.662	27%	3.523	2%	3.177
76%	3.868	51%	3.656	26%	3.515	1%	3.106
75%	3.860	50%	3.650	25%	3.507	0%	3.000

Note: The voltages are averaged using the C/25 discharge curves from 3 ANL trial cells (Quallion s/n-17, s/n-20, and s/n-29).

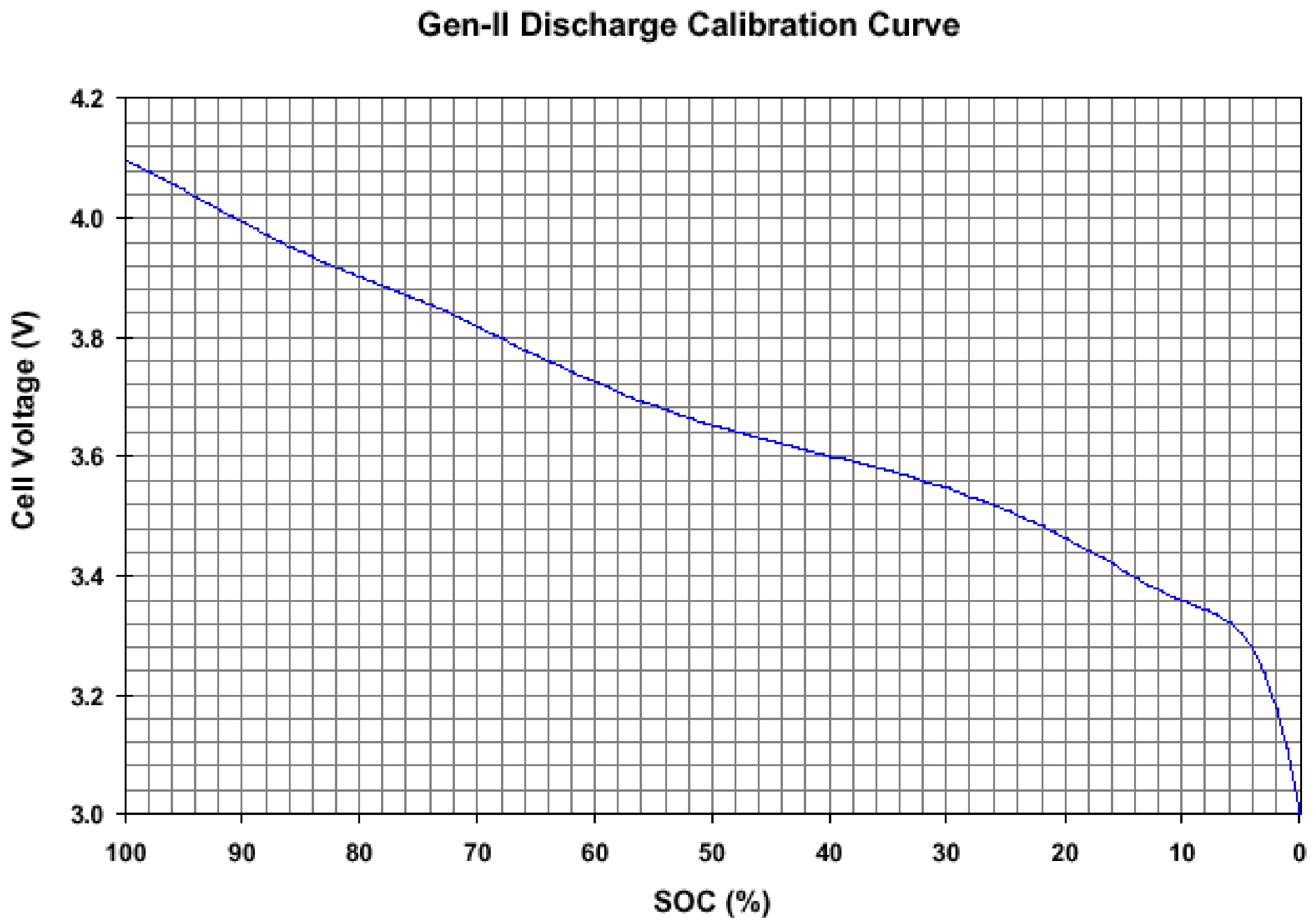

Figure D.1. ATD Gen 2 Baseline Cell OCV vs. SOC Curve

Table D.2. Calibration Table for ATD Gen 2 Variant C Cells

SOC	Voltage	SOC	Voltage	SOC	Voltage	SOC	Voltage
100%	4.099						
99%	4.086	74%	3.866	49%	3.661	24%	3.518
98%	4.076	73%	3.859	48%	3.655	23%	3.510
97%	4.066	72%	3.851	47%	3.649	22%	3.501
96%	4.055	71%	3.843	46%	3.644	21%	3.493
95%	4.045	70%	3.835	45%	3.639	20%	3.484
94%	4.035	69%	3.827	44%	3.634	19%	3.475
93%	4.025	68%	3.818	43%	3.628	18%	3.465
92%	4.015	67%	3.809	42%	3.623	17%	3.456
91%	4.004	66%	3.800	41%	3.618	16%	3.445
90%	3.995	65%	3.790	40%	3.613	15%	3.435
89%	3.985	64%	3.780	39%	3.608	14%	3.423
88%	3.976	63%	3.770	38%	3.604	13%	3.411
87%	3.967	62%	3.760	37%	3.599	12%	3.399
86%	3.958	61%	3.751	36%	3.594	11%	3.386
85%	3.949	60%	3.741	35%	3.589	10%	3.372
84%	3.941	59%	3.733	34%	3.583	9%	3.358
83%	3.933	58%	3.724	33%	3.578	8%	3.343
82%	3.925	57%	3.716	32%	3.573	7%	3.329
81%	3.918	56%	3.708	31%	3.567	6%	3.313
80%	3.910	55%	3.701	30%	3.561	5%	3.294
79%	3.903	54%	3.693	29%	3.555	4%	3.269
78%	3.896	53%	3.686	28%	3.548	3%	3.232
77%	3.888	52%	3.680	27%	3.541	2%	3.180
76%	3.881	51%	3.673	26%	3.534	1%	3.107
75%	3.874	50%	3.667	25%	3.526	0%	3.000

Note: The voltages are averaged using the C/25 discharge curves from 14 INEEL cells.

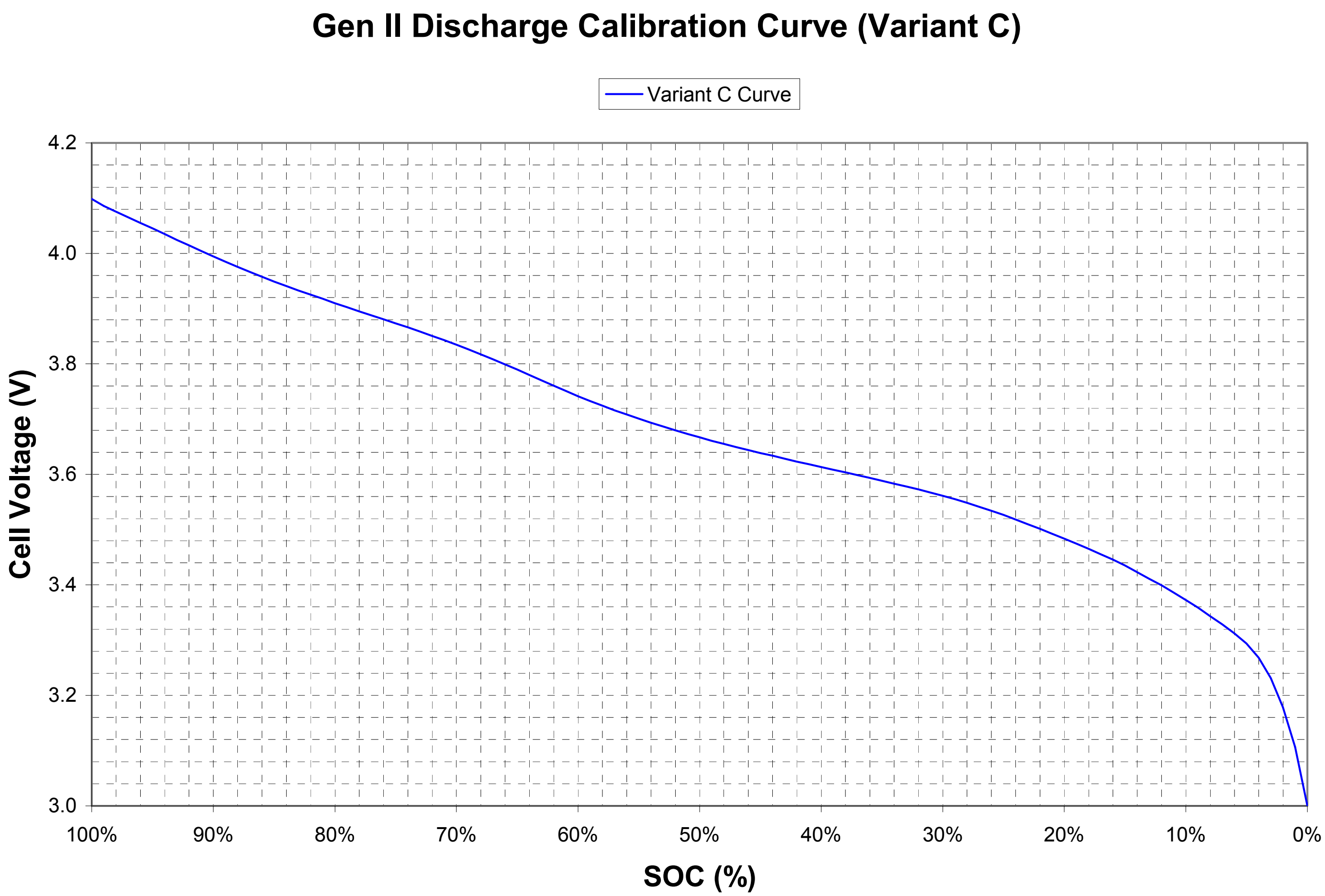

Figure D.2. ATD Gen 2 Variant C Cell OCV vs. SOC Curve

Appendix E

Spectral Impedance Measurements

A representative approach for spectral impedance measurements is described below. The general methodology should be used to the extent possible, although specific equipment may vary amongst the testing labs.

Equipment:

Equipment	INEEL	ANL	SNL
EG&G Potentiostat/Galvanostat	Model 273A	Model 273A	Model 273A
Solartron Frequency Analyzer	Model 1260	Model 1260	Model 1255
Control Software	ZPlot	Zplot	M398

Test Procedure:

Perform this test on each cell, as specified in Appendix C, at 60% SOC and 25°C. Follow the guidance in Appendix C of Reference 2.1 to establish the target SOC. Rest between 8 and 12 hours at 60% SOC before starting the measurements.

Set the initial frequency to 10 kHz and final frequency to 0.01 Hz. Set the voltage of the sine wave to an appropriate voltage level, and the number of points per decade of frequency to 10. Record the magnitude of the impedance (the real and imaginary components) vs. the frequency, temperature, and SOC.

Use a 4-terminal connection to measure impedance.