DOE Advanced Technology Development Program for Lithium-Ion Batteries:

INEEL Gen 1 Final Report

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September 2001

Idaho National Engineering and Environmental Laboratory Bechtel BWXT Idaho, LLC



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ABSTRACT

The Advanced Technology Development (ATD) Program was initiated in 1998 by the U.S. DOE Office of Advanced Automotive Technologies to find solutions to the barriers that limit the commercialization of high-power lithium ion batteries. This report marks the completion of the testing and data analysis of the first generation of cells (Gen 1 cells). These cells will form the baseline from which subsequent performance improvements in the second and third generations will be measured.

Concurrent testing was performed at the Idaho National Engineering and Environmental Laboratory (INEEL), Argonne National Laboratory, and Sandia National Laboratories. The INEEL tested 74 lithium ion ATD Gen 1 cells (with a rated capacity of 0.9 A·h). The cells were allotted to a test matrix with three states-of-charge, four state-of-charge variations, and four temperatures at which life testing was performed. Testing included standard characterization tests that have been defined in the *PNGV Battery Test Manual* and special calendar- and cycle-life tests that were useful in modeling cell behavior. Reference performance testing was performed at regular intervals during life testing.

The characterization static capacity tests showed that the capacity of the cells was stable for three successive discharges at about 0.920 A·h. The average 4-week capacity fade for 55 cells was $8.5\% \pm 3.3\%$. The average 8-week capacity fade for 18 cells was $9.5\% \pm 6.0\%$. The medium current level Hybrid Pulse Power Characterization (M-HPPC) tests showed an average power fade of $28.1\% \pm 7.6\%$ at 4 weeks for 55 cells, and $30.7\% \pm 7.2\%$ at 8 weeks for 18 cells. All cells failed the M-HPPC test before or during the 8-week reference performance test. The special calendar- and cycle-life tests were used to model the pulse resistance behavior. The model showed good predictions for cells in the lower temperature groups, but it was unsatisfactory for the high-temperature cell groups. It is believed that this is a result of a different cell degradation mechanism dominating the results at the higher temperatures.

At the completion of testing, cells were sent to the diagnostic labs (Argonne, Lawrence Berkeley, and Brookhaven National Laboratories) for further analysis. Those results are beyond the scope of this report, but are documented in the ATD Program Annual Progress Reports.

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ACRONYMS AND ABBREVIATIONS

available energy
Argonne National Laboratory
Advanced Technology Development
Brookhaven National Laboratory
1-hour charge/discharge rate for 1 hour
depth of discharge
Department of Energy
electrochemical impedance spectroscopy
end of test
Generation
hybrid electric vehicle
Idaho National Engineering and Environmental Laboratory
Lawrence Berkeley National Laboratory
low-current hybrid pulse power characterization
medium-current hybrid pulse power characterization
Office of Advanced Automotive Technologies
open-circuit voltage
Partnership for a New Generation of Vehicles
pulse-power limit
reference performance test
Sandia National Laboratories
state-of-charge

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1. INTRODUCTION

The U.S. Department of Energy (DOE) initiated the Advanced Technology Development (ATD) Program in 1998, specifically with the Partnership for a New Generation of Vehicles (PNGV) ElectroChemical Energy Storage Team. The ATD testing laboratories include the Idaho National Engineering and Environmental Laboratory (INEEL), Argonne National Laboratory, and Sandia National Laboratories. The diagnostic laboratories include Lawrence Berkeley National Laboratory (LBNL), Brookhaven National Laboratory, and Sandia National Laboratory the lead responsibility for the entire ATD program and for providing support in many of the technical areas. The INEEL is the lead test laboratory; LBNL is the lead diagnostics laboratory. These five national laboratories are working in close coordination to find solutions to technical barriers limiting the development of high-power lithium-ion batteries, specifically for hybrid electric vehicle (HEV) applications. A full description of the program and results are provided in Reference 1.

The primary ATD objective is to address three outstanding barriers to the commercialization of high-power batteries for HEV applications. These barriers include insufficient calendar life, high production costs, and poor response to abuse scenarios. To accomplish this objective, the ATD program is organized into five program areas: baseline cell development (labeled Gen 1), diagnostic evaluations, electrochemistry improvement (labeled Gen 2), advanced materials (labeled Gen 3), and low-cost packaging. The intent is to measure the baseline performance of the Gen 1 cells, then measure subsequent improvements in Gen 2 and Gen 3.

1.1 Performance Testing

This report marks the end of the baseline cell development, along with completion of the Gen 1 cell testing and data analysis. It focuses on the ATD Gen 1 cell testing, analyses, and modeling performed at the INEEL and includes some data and results from the testing performed at Argonne National Laboratory (ANL) and Sandia National Laboratories (SNL). Cell testing included standard PNGV characterization tests defined in the *PNGV Battery Test Manual*,² reference performance testing (RPT), and special life tests that helped identify factors limiting calendar life. Of the 300 ATD Gen 1 cells manufactured by PolyStor to ATD specifications, 148 cells (manufactured between March 19 and April 10, 1999) were designated for life testing. The INEEL received 69 cells on April 29, 1999. Since some cells reached end of life earlier than expected, the INEEL also received five replacement cells from ANL and SNL by October 21, 1999. ANL received 31 cells; SNL received 43 cells. The cells had lot numbers ranging from Lot C973 to Lot C1011.

Table 1 summarizes the overall cell distribution matrix. The cells were separated into cycle- and calendar-life groups. These groups were distributed over three states of charge (SOC) at which life testing was to be performed (80, 60, and 40% SOC), four SOC variations (0, 3, 6, and 9% Δ SOC, where 0% Δ SOC is the special calendar-life test), and four temperatures (40, 50, 60, and 70°C).

INEEL Gen 1 cell testing began May 28, 1999 and ended May 25, 2000. The testing and analysis was performed in accordance with the procedures outlined in the *PNGV Battery Test Manual*² and as detailed in the cell-specific test plan, TP-103, Rev 4, December 8, 1999 (see Appendices A through I). The INEEL cells were numbered 1 through 74 and randomly distributed into the matrix shown in Table 1. The group of cells at a particular condition were identified by an SOC/ Δ SOC/temperature label [e.g., 80C60 = 80% SOC, calendar-life (0% Δ SOC) and 60°C; 60340 = 60% SOC, cycle-life (3% Δ SOC), and 40°C].

		40°	C		50°C			60°C				70°C					
SOC \triangle SOC	Total	А	Ι	S	Total	А	Ι	S	Total	А	Ι	S	Total	А	Ι	S	
80% SOC																	
0 ΔSOC	8		4	4	6		3	3	7		4	3	6		3	3	27
$3 \Delta SOC$	3			3	3			3	3		3		3			3	12
6 ΔSOC	3			3	3			3	3		3		3			3	12
9 ∆SOC	5			5	3			3	3		3		4			4	<u>15</u>
		1												1			66
60% SOC																	
$0 \Delta SOC$	8		3		7	4	3		6	3	3		6	3	3		27
$3 \Delta SOC$	3	5	3		3		3		6	3	3		3		3		15
6 ΔSOC	4		4		3		3		4		4		3		3		14
9 ∆SOC	3		3		4		4		3		3		3		3		<u>13</u>
																	69
40% SOC		1												1			
0 ASOC	3	3			4	4			3	3			3	3			13
3 ∆SOC		, ,												, ,			0
6 ΔSOC		 												 			0
9 ΔSOC																	<u>0</u>
		1 1												1 1			13
Total Cells	40	8	17	15	36	8	16	12	38	9	26	3	34	6	15	13	148

Table 1. INEEL Advanced Technology Development ATD Gen 1 test matrix. (A = ANL, I = INEEL, S = SNL)

2. BATTERY RATINGS AND LIMITATIONS

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

Cell rated capacity:	0.9 A·h				
Cell operating temperature range:	-20 to +70°C discharge				
	-20 to +40°C charge				
Cell nominal weight:	41.4 g				
Minimum discharge voltage:	3.0 V				
Maximum discharge current:	2.0 A continuous				
	13 A for up to a 2-s pulse				
	7.2 A for up to a 18-s pulse				
Maximum discharge temperature:	70°C, nominal				
Maximum regen voltage:	4.1 V continuous				
	4.3 V for up to a 2-s pulse				
Maximum regen/charge current:	0.9 A continuous				
	12 A for up to a 2-s pulse				
Recharge procedure:	Charge at 0.9 A constant current rate to a voltage of 4.1 V; continue to apply a constant voltage of 4.1 V for 2.5-h total recharge time. All recharging was begun at $25 \pm 3^{\circ}$ C, unless specifically stated otherwise.				
Calendar-life test limits:	The nominal maximum pulse profile current limit was 3.6 A (a $4C_1$ rate) for the special calendar-life test.				

3. TESTING

3.1 Characterization Testing

The receiving inspection conducted before testing confirmed that no test article was damaged. This included a visual inspection and measuring the cell weights, open-circuit voltages, and the 1-kHz AC impedance. Characterization testing was then initiated with at least three, but no more than ten, static capacity tests, each consisting of a $C_1/1$ discharge to the minimum discharge voltage, followed by a full recharge. This was repeated until the measured capacity was stable within 2% for three successive discharges.

The hybrid pulse power characterization (HPPC) test was then performed at two current levels. The low-current HPPC test (L-HPPC) was performed at a $3C_1$ rate, and the medium-current HPPC test (M-HPPC) at an $8C_1$ rate. The current level for the M-HPPC test was calculated based on the guidelines in the PNGV manual and using results from the L-HPPC test.² Both of these tests were performed over the manufacturer's full voltage range of 4.3 to 3.0 V. The M-HPPC data were used to calculate the discharge and regen resistance and pulse power capability, pulse power limit, and available energy. The pulse power capability was calculated using the HPPC maximum and minimum voltages of 4.1 and 3.075 V, in accordance with Reference 2.

Following the HPPC tests, self-discharge tests were performed, consisting of a 7-day stand interval at an open-circuit condition. Last, a select number of cells were chosen to undergo thermal performance testing, which consisted of a $C_1/1$ test and a L-HPPC test at two different temperatures (+5 and +40°C). Other than the thermal performance testing, all characterization tests were performed at 25°C.

3.2 Reference Performance Testing

The reference performance test (RPT) was then conducted on the cells immediately prior to start of life testing (identified as the 0-week RPT). This included a 1-kHz impedance measurement at 0 and 100% SOC, a single C₁/1 static capacity test, and an M-HPPC test. RPTs were then repeated every 4 weeks during life testing for the 40, 50, and 60°C temperature groups (labeled 4-weeks, 8-weeks, etc.). RPTs were repeated every 2 weeks for the 70°C temperature group due to a higher rate of degradation (labeled 2-weeks, etc.). All RPTs were performed at 25°C, using the full manufacturer's specified voltage range.

Reference performance tests were used in tracking the capacity and power fade of the cells through life testing. *Capacity fade* is the percent loss in the discharge capacity during the $C_1/1$ test; *power fade* is the percent loss in the pulse power limit (calculated from the M-HPPC test). The fades are normalized to the 0-week RPT (i.e., the 0-week capacity and power fades are both 0%).

3.3 Life Testing

All INEEL cells were life tested using the new approaches developed specifically for these ATD Gen 1 cells for both calendar life and cycle life, as outlined in the test plan (Appendix A). The pulse profile for the special calendar-life test, shown in Appendix C, included a 9-second (-s) $4C_1$ -discharge and a 2-s $4C_1$ -regen portion, followed by a 47-s $0.6C_1$ charge step to return the cell to near target SOC. During the 24-hour (-h) interval between pulses, the cell voltages were clamped to the voltage corresponding to the target SOC (see Appendices H and I). The intent of the new pulse-per-day calendar-life test was to enable calculation of resistances daily at the

calendar-life test condition. Due to equipment limitations, ANL performed the standard PNGV calendar-life test (as defined in Reference 2) with the cells clamped at a target control voltage for the duration of the stand period while measuring the leakage current required to maintain that voltage.

Three different cycle-life profiles were used on the Gen 1 cells, as shown in Appendix B. The 3% Δ SOC profile included a 14-s 8C₁-discharge and a 2-s 7.2C₁-regen portion, followed by a 32-s 3.05C₁ charge step to return the cell to near target SOC and a 20-s taper current to adjust the control voltage as necessary. The 6% Δ SOC profile included two 14-s discharges and two 2-s charges, followed by a 64-s charge step and a 40-s taper current. The 9% Δ SOC profile included three 14-s discharges and three 2-s charges, followed by a 96-s charge step and a 60-s taper current. These profiles were designed to ensure that each cell was at the target SOC at the completion of each cycle-life profile. The discharge and regen resistances were calculated from every hundredth pulse.

4. RESULTS

Of the 74 INEEL ATD Gen 1 cells, nine met the end-of-test (EOT) criteria before any cycling was performed. The remaining 65 cells were able to start the 4-week RPT (2-week RPT for the 70°C cells), but pulse power limit data could only be calculated for 55 cells, nine of which were life tested at 70°C. Only 20 cells underwent the 8-week RPT, 18 for which PPL data were calculated. All 70°C cells failed before or during the 2-week RPT. All other cells reached the EOT criteria before or during the 8-week RPT.

The discharge capacities during the first three characterization $C_1/1$ static capacity tests agreed within 2% of each other, averaging about 0.920 A·h. Figures 1 through 4 summarize the results of all the static capacity tests performed on the 74 ATD Gen 1 cells, where the value reported as "Characterization" is the capacity after the third $C_1/1$ discharge. These figures show the rapid decline in discharge capacity during life testing. The average capacity fade for the 55 cells that completed the 4-week RPT (2-week RPT for the 70°C cells) was $8.5 \pm 3.3\%$. The average capacity fade for the 18 cells that completed the 8-week RPT was $9.5 \pm 6.0\%$. Due to higher stress applied to the cells during life cycling, the average capacity fade for the cycle-life cells ($10.3 \pm 2.4\%$ for the 55 cells at 2- and 4-weeks, and $12.3 \pm 5.9\%$ for the 18 cells at 8-weeks) was greater than the calendar-life cells ($5.9 \pm 2.6\%$ for the 55 cells at 2- and 4-weeks, and $4.9 \pm 1.0\%$ for the 18 cells at 8-weeks).

Standard ATD reporting for the M-HPPC data includes four plots. Figures 5 through 8 show these standard HPPC plots for a representative Gen 1 cell at characterization. These plots were generated using version 1.4a of the HPPCALC[©] calculation program. Figure 5 is the areaspecific impedance (ASI) for both the 18-s discharge and the 2-s regen (in ohm-cm²) as a function of cell voltage at the beginning of the discharge or regen pulse. The specified electrode area for the Gen 1 cells is 678 cm^2 . Figure 6 is the power density (in mW/cm²) as a function of the opencircuit voltage (OCV). The power density is calculated using the discharge and regen pulse power capability (W), defined in Reference 2, divided by the electrode area, then multiplied by 1000 to convert to units of mW/cm². For both of these plots, the discharge OCV is the voltage just before the pulse, and the regen OCV is the interpolated voltage that accounts for charge lost during the 18-s discharge pulse. Figure 7 shows the power (W) versus cumulative energy removed (Wh). This plot is used to find the pulse power limit, the point where the discharge and regen curves cross. The pulse power limit is used to gauge the overall pulse power performance for a cell. Figure 8 is the available energy (Wh) as a function of discharge power (W). The available energy (AE) is zero at the pulse power limit. The available energy is then calculated as the energy between the discharge and regen power curves as power decreases.

Figures 9 through 12 summarize the results of the pulse power limit on the 74 ATD Gen 1 cells. These figures show the rapid decline in pulse power during life testing. The average power fade for the 55 cells that completed the 2- and 4-week RPT was $28.1 \pm 7.6\%$. The average power fade for the 18 cells that completed the 8-week RPT was $30.7 \pm 7.2\%$. Due to higher stress applied to the cells during life cycling, the average power fade for the cycle-life cells ($30.9 \pm 5.9\%$ for the 55 cells at 2- and 4-weeks, and $33.9 \pm 6.1\%$ for the 18 cells at 8-weeks) was greater than the calendar-life cells ($24.1 \pm 8.0\%$ for the 55 cells at 2- and 4-weeks, and $26.6 \pm 6.4\%$ for the 18 cells at 8 weeks).



INEEL ATD Gen 1 C₁/1 Static Capacity at 40°C

Figure 1. Static capacity test for ATD Gen 1 cells life tested at 40°C.



INEEL ATD Gen 1 C₁/1 Static Capacity at 50°C

Figure 2. Static capacity test for ATD Gen 1 cells life tested at 50°C.



INEEL ATD Gen 1 C₁/1 Static Capacity at 60°C

Figure 3. Static capacity test for ATD Gen 1 cells life tested at 60°C.



INEEL ATD Gen 1 C₁/1 Static Capacity at 70°C

Figure 4. Static capacity test for ATD Gen 1 cells life tested at 70°C.



Figure 5. Area-specific impedance versus cell voltage for a representative Gen 1 cell.



Figure 6. Power density versus open-circuit voltage for a representative Gen 1 cell.

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Figure 7. Power versus cumulative energy removed for a representative Gen 1 cell.



Figure 8. Available energy versus discharge power for a representative Gen 1 cell.



INEEL ATD Gen 1 Pulse Power Limit at 40°C

Figure 9. Pulse power limit for ATD Gen 1 cells life tested at 40°C.



INEEL ATD Gen 1 Pulse Power Limit at 50°C

Figure 10. Pulse power limit for ATD Gen 1 cells life tested at 50°C.



INEEL ATD Gen 1 Pulse Power Limit at 60°C

Figure 11. Pulse power limit for ATD Gen 1 cells life tested at 60°C.



INEEL ATD Gen 1 Pulse Power Limit at 70°C

Figure 12. Pulse power limit for ATD Gen 1 cells life tested at 70°C.

Table 2 summarizes the INEEL composite averages (plus or minus one standard deviation) for capacity, 1 kHz AC impedance at 0 and 100% SOC, discharge and regen resistance, delta resistance, discharge and regen open-circuit voltage (OCV), and pulse power limit at the RPT intervals. Delta Resistance (Δ Resistance) is the difference between the discharge and regen resistance. Since this value should be similar for all cells, it was useful in identifying outlier cells (i.e., cells significantly greater or smaller than the average). The 4-week average also includes the 70°C data from the 2-week RPT.

		INEEL Averages						
	DOD	Characterization	4-Week	8-Week				
Capacity (Ah)	-	0.920 ± 0.022	0.855 ± 0.029	0.776 ± 0.048	0.788 ± 0.044			
Impodance (mQ)	100%	24.49 ± 0.79	25.05 ± 0.80	26.74 ± 1.38	26.98 ± 1.76			
	0%	23.89 ± 0.77	24.40 ± 0.84	27.74 ± 1.56	27.75 ± 1.79			
	20%	70.20 ± 3.17	76.85 ± 4.67	105.62 ± 10.18	109.00 ± 11.35			
18s Discharge Resistance (m Ω)	40%	67.43 ± 2.70	73.77 ± 3.88	97.34 ± 7.32	96.81 ± 6.27			
	60%	66.22 ± 2.83	72.36 ± 3.89	82.27 ± 2.74	83.44 ± 0.00			
	20%	47.16 ± 2.61	52.70 ± 3.92	72.63 ± 7.77	79.51 ± 13.14			
2s Regen Resistance (m Ω)	40%	44.06 ± 1.88	48.46 ± 2.63	65.07 ± 5.68	75.30 ± 11.61			
	60%	43.46 ± 1.67	47.40 ± 2.36	58.77 ± 6.53	72.08 ± 10.24			
	20%	23.04 ± 1.77	24.15 ± 1.52	32.99 ± 4.59	31.67 ± 7.16			
Δ Resistance (m Ω)	40%	23.36 ± 1.51	25.32 ± 1.67	32.15 ± 3.77	30.60 ± 3.16			
	60%	22.76 ± 1.79	24.96 ± 1.93	27.10 ± 2.48	26.37 ± 0.00			
	20%	3.94 ± 0.01	3.93 ± 0.01	3.92 ± 0.01	3.91 ± 0.01			
Discharge OCV (V)	40%	3.79 ± 0.01	3.78 ± 0.01	3.76 ± 0.01	3.76 ± 0.02			
	60%	3.63 ± 0.01	3.62 ± 0.01	3.61 ± 0.01	3.59 ± 0.02			
	20%	3.91 ± 0.01	3.90 ± 0.01	3.89 ± 0.01	3.88 ± 0.01			
Regen OCV (V)	40%	3.75 ± 0.01	3.75 ± 0.01	3.73 ± 0.01	3.73 ± 0.01			
	60%	3.61 ± 0.01	3.60 ± 0.01	3.59 ± 0.01	3.58 ± 0.02			
Pulse Power Limit (W)	-	31.53 ± 1.25	28.78 ± 1.49	20.89 ± 2.04	20.07 ± 2.14			

Table 2. INEEL Composite Averages.

Figures 13 and 14 show typical pulse resistance results from the cycle- and calendar-life tests. Both figures show the increase in pulse resistance over the course of life testing. Figure 13 is the discharge and regen resistance as a function of time during pulsing for a representative cycle-life cell. The resistances were calculated using data from every hundredth pulse. The significant drop in pulse resistance at about 650 h is a result of stopping the cycle-life test after 4 weeks for an RPT. This brief reduction in resistance was quickly regained once cycling resumed. The small drops in pulse resistance at about 227 and 886 h are due to power supply interruptions. Figure 14 shows the discharge and regen resistance for a representative calendar-life cell calculated using data from the daily pulse profile. The drop in resistance at approximately 670 h is also due to the 4-week RPT



Cycle-Life Pulse Resistance for a Representative Gen 1 Cell

Figure 13. Cycle-life pulse resistance for a representative Gen 1 cell.



Calendar-Life Pulse Resistance for a Representative Gen 1 Cell

Figure 14. Calendar-life pulse-per-day resistance for a representative Gen 1 cell.

The ATD Gen 1 data from all three testing laboratories were used to model cell resistance as a function of SOC, temperature, and time during pulsing. This was accomplished by plotting the discharge and regen pulse resistances during calendar or cycle life as a function of the squareroot of time at test for a given test temperature, i.e., Resistance (t,T,SOC) = A(T,SOC) sqrt(t) + B(T,SOC). The results of this analysis for the ATD cells indicate that the plot is a straight line. The slope, A(T,SOC), and intercept, B(T,SOC), can be further fit into an Arrhenius-like relationship that can be expressed as follows: A(T,SOC) = a(SOC)exp[b(SOC)/T] and B(T,SOC)= c(SOC)exp[d(SOC)/T]. The values of a, b, c, and d, along with the square root of time dependence, can be used to predict the resistance values at different temperatures and at latter times in the test. Insufficient data were acquired from the ATD program to determine the SOC dependence of a, b, c, and d, so this aspect of the modeling is still an open question. Caution should also be used when applying this model for test temperatures above approximately 60° C and much below 25°C, where other battery mechanisms may dominate results. Figure 15 shows the model predictions for calendar-life discharge resistance for INEEL and SNL cells tested at 80% SOC and four temperatures. The figure shows that the model works very well for the 40, 50, and 60°C temperature groups, but an anomalous cell mechanism occurs at 70°C. A comprehensive discussion of the modeling of ATD Gen 1 calendar-life and cycle-life cells is found in References 4 and 5, respectively.



Figure 15. Model predictions for calendar-life discharge resistance.

5. LESSONS LEARNED

Analysis of the ATD Gen 1 data led to several lessons learned, which were incorporated into the Advanced Technology Development program and the *PNGV Battery Test Manual*, Rev. 3 (Feb. 2001).³

5.1 Testing Procedures

A rest step of nominally 60 minutes should be observed after each charge and each discharge before proceeding with testing, to allow the cells to reach stable voltage and temperature conditions. However, for electrochemical impedance spectroscopy measurements, and when changing from one test temperature to another, even longer soak periods may be necessary.

5.2 Temperature Control

Since temperature control is one of the key parameters affecting cell performance, both cell and ambient air temperatures need to be carefully tracked during testing. Also, because of self-heating during pulsing, the cell temperature may be several degrees higher than the ambient air temperature. If desired, these temperature differences may be minimized by placing the cells in a thermal (aluminum) block and controlling the test temperature by a thermocouple mounted in the block. When the cell is not under test, the storage temperature also needs to be controlled uniformly, e.g., 10°C.

5.3 Impedance Measurements

Impedance measurements at a single frequency (e.g., 1 kHz) are useful for quickly identifying the condition of a cell (e.g., if the cell is shorted). However, this measurement only reflects a small portion of the available impedance data. The electrochemical impedance spectroscopy (EIS) measurements give a more complete picture, since the impedance is measured over a range of frequencies. These data may be useful for modeling cell behavior. Issues that need to be considered when performing EIS include the following:

- How measurements should be made (i.e., in situ or not in situ)
- The SOC and temperature of the cells
- The amount of recovery time to reach SOC and temperature equilibrium before running the EIS
- The EIS voltage
- The EIS frequency range
- The impedance of the test leads
- How the test leads are connected to the cell.

5.4 HPPC Testing

The HPPC test should continue unabated as long as a voltage limit is not reached during a $C_1/1$ discharge step. In contrast, if a voltage limit is reached during a discharge (or regen) pulse, the test should continue with certain additional considerations. Once the pulse current becomes voltage limited, the ohmic contribution to the resistance during that pulse using the relationship R = $\Delta V/\Delta I$ may be overshadowed by other polarization resistances. Therefore, voltage-limited

pulse resistance should not be compared to ohmic data from nonvoltage-limited pulses. However, useful ohmic resistance data may be obtained from one of the HPPC pulses, even if the other pulse is voltage limited.

6. CONCLUSIONS

The testing and data analysis of the first generation of Advanced Technology Development cells has been completed. Analysis of the Gen 1 data lead to several lessons learned, which have been incorporated into the Advanced Technology Development Program and the third revision of the *PNGV Battery Test Manual*.³ Performance improvements in the second and third generation of cells will be measured using the Gen 1 cells as a baseline.

The INEEL tested 74 Gen 1 cells with a rated capacity of 0.9 A·h, using Revision 1 of the *PNGV Battery Test Manual* (Reference 2) and the cell specific test plan (Appendices A through I). This test plan defines the cell test matrix and special cycle- and calendar-life tests. The cells showed a rapid decline in performance. Only 18 cells completed the 8-week reference performance test (consisting of a C₁/1, 1kHz AC impedance measurement at 0 and 100% SOC, and a M-HPPC test). These cells showed a 9.5 \pm 6.0% capacity fade and a 30.7 \pm 7.2% power fade. No cells were able to be tested beyond 8 weeks. The pulse resistance data during life testing were used for modeling cell behavior. The model shows good correlation against data at 40, 50, and 60°C, but caution should be used when applying the model to test temperatures above 60°C and much below 25°C, where other battery mechanisms may result in anomalous behavior.

7. **REFERENCES**

- 1. Advanced Technology Development, 1999 Annual Progress Report, U.S. DOE, OAAT, March 2000.
- 2. PNGV Battery Test Manual, Revision 1, DOE/ID-10597, May 1998.
- 3. PNGV Battery Test Manual, Revision 3, DOE/ID-10597, February 2001.
- 4. R. B. Wright and C. G. Motloch, *Calendar-Life Studies of Advanced Technology Development Program Gen 1 Lithium Ion Batteries*, DOE/ID-10844, March 2001.
- 5. R. B. Wright and C. G. Motloch, *Cycle-Life Studies of Advanced Technology Development Program Gen 1 Lithium Ion Batteries*, DOE/ID-10845, April 2001.

Appendix A

PNGV Test Plan for Advanced Technology Development 18650 Gen 1 Lithium Ion Cells
Appendix A

PNGV Test Plan for Advanced Technology Development 18650 Gen 1 Lithium Ion Cells

1. Purpose and Applicability

The intent of this testing is to characterize performance and to determine the cycle- and calendarlife behavior of lithium ion cells (nominal 0.9 A·h capacity). The testing will be performed at the Idaho National Engineering and Environmental Laboratory (INEEL), Argonne National Laboratory (ANL), and Sandia National Laboratories (SNL). The work is being done as part of an Advanced Technology Development (ATD) Program project for the improvement of highpower lithium-ion batteries. The testing is sponsored by the DOE Office of Advanced Automotive Technologies (OAAT). Oversight is by OAAT and the designated ATD Program Manager. In general, these cells will be subjected to the performance and life-test procedures defined for the PNGV Program. The cells covered by this test plan are size 18650, manufactured by PolyStor specifically for the PNGV ATD Program and built to ANL specifications.

Revision 1 of this test plan incorporates changes relating to calendar- and cycle-life testing. It also includes clarification regarding the Hybrid Pulse Power Characterization (HPPC) test and specification of the value of the discharge current to be used for the M-HPPC test.

Revisions 2 and 3 incorporate changes relating to the end of test in Section 5.8, self-discharge in Section 7.1, RPTs in Section 7.2, SOC versus open-circuit voltage (OCV) in Appendix I, and numerous editorial corrections.

Revision 4 incorporates changes relating to prerequisites in Section 4.5; ratings, test limitations, and other test information in Sections 5.1, 5.2, 5.3, 5.5, 5.7, and 5.8; safety in Sections 6.0 and 6.2; Reference Performance Tests in Section 7.2; end of test in Section 7.4(d); data in Section 8.1; deliverables in Section 9.2; calendar-life testing in Appendix H; and a few miscellaneous clarifications and minor editorial corrections.

2. References

2.1 PNGV Battery Test Manual, Revision 1, DOE/ID-10597, May 1998

3. Equipment

- 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 (5 V preferred, not to exceed 20 V) to ensure best voltage resolution and accuracy.
- 3.2 Except where noted, testing will be performed with the cells at $25 \pm 3^{\circ}$ C at the beginning of a test sequence. The preferred means is to use a controlled temperature chamber having both heating and cooling capabilities. Higher temperature tests (i.e., above 25°C) can be performed either in an environmental test chamber or in an oven having heating capability only. Subambient temperature tests (i.e., below 25°C) can be performed either in a refrigeration unit having cooling capability only. Note that the 3°C tolerance allows for measurement drift and for some necessary difference between the

temperature measured by a chamber controller and that measured on multiple cells within that chamber. Attempt should be made to hold the ambient temperature for any given cell stable within $\pm 1^{\circ}$ C.

3.4 The temperature of cells under test should be measured using moderately fast response sensors (e.g., $\leq 3/16$ -in. thermistors or pad-type thermocouples such as Omega Model SA-1) adhered to the side of the cell case at its midline and insulated from ambient air. Sensors should be fastened to the cell using a means (e.g., epoxy, tape, or clamp) that provides consistent contact.

4. **Prerequisites and Pretest Preparation – Incoming Inspections**

- 4.1 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.
- 4.2 The cells will be visually inspected for signs of shipping or other damage. Actual weights and open-circuit voltages of the cells will be recorded as delivered. Cell weights will include the current leads.
- **NOTE:** These cells may be susceptible to leakage of electrolyte at the crimp seals, especially at elevated temperatures. As part of each set of reference performance tests, the cell weights will be measured, recorded, and compared to the original weights to ascertain if any leakage has occurred.
 - 4.3 Prior to start of testing, a pretest readiness review should 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 the testing. An external readiness review involving DOE and the ATD program manager may be required (at their discretion), which may be in addition to or in lieu of an internal review.
 - 4.4 Impedance measurements (AC) at 1 kHz will be made before beginning testing, with the cells fully discharged and fully charged, using an HP 4338B impedance meter or equivalent. These measurements will be repeated prior to the start of cycle- or calendar-life testing and at each execution of the reference tests during life testing, and all measurements will be recorded in the log book.
- **NOTE 1:** *The following settings are recommended if the HP 4338B meter is used:*

Level of AC current – auto (This typically results in a value of either 1 or 10 mA, depending on battery resistance.)

Averaging – 16 measurements

Measurement time – short

- **NOTE 2:** It is recommended that the impedance tests be performed over a range of frequencies, from approximately 0.01Hz to 50 kHz, as an alternative to the single-frequency impedance measurement.
 - 4.5 Measure and record the open-circuit voltage versus state-of-charge on at least three cells from each batch at $25 \pm 3^{\circ}$ C and at a C₂₅ rate. Recharge the cells per Section 5.4 prior to

commencing the C_{25} discharge. See Appendix H for information on establishing OCV versus SOC. Record the results in Appendix I.

5. Ratings, Test Limitations, and Other Test Information

5.1 Ratings (discharge)

	Cell nominal capacity:	0.9 A·h ($C_1/1$ discharge rate)
	Cell rated capacity:	0.9 A·h ($C_1/1$ discharge rate)
	Cell operating temperature range:	-20 to +70°C, nominal
	Cell maximum storage temperature:	+70 <u>+</u> 5°C
	Cell nominal weight:	41.4 g (info only)
5.2	Limits (discharge)	
	Minimum discharge voltage:	3.0 V
	Maximum discharge current:	2.0 A continuous; 13 A for up to a 2-s pulse; and 7.2 A (8C) for up to a 18-s pulse
	Maximum discharge temperature:	70°C, nominal
5.3	Limits (charge and regen)	
	Maximum regen/charge voltage:	4.1 V continuous, 4.3 V for up to a 2-second pulse
	Maximum regen/charge current:	0.9 A continuous charge current; 12 A max regen current for up to a 2-s pulse
	Maximum charge temperature:	40°C ambient
	Maximum regen temperature:	70°C, nominal

5.4 Recharge Procedure:

Charge at 0.9 A constant current rate to 4.1 V; continue to apply a constant 4.1 V for 2.5-h total recharge time. All recharging is to begin at $25 \pm 3^{\circ}$ C, unless specifically stated otherwise.

5.5 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., it need not be subjected to a *top off* charge) if it was fully recharged no more than one week previously. (This may need adjustment if the self-discharge rate of these cells exceeds 0.5% per day, and it is not applicable to the self-discharge test, which should be started within 8 h of completing a full charge.)

If a test requires a cell to be at a given state-of-charge, this SOC value must be achieved by discharging the cell at the $C_1/1$ rate to a stable voltage condition corresponding to this SOC, based on measurements made on a representative group of cells at the beginning of the test program. (See Appendix H for additional definition, Appendix I for the OCV versus SOC curve, and special note in Section 7.3(c) regarding HPPC tests.) For the purposes of this test plan, all references to state-of-charge must be in reference to the voltages given in Appendix I.

5.6 Cycle-Life Test Conditions

Peak discharge test current for life-cycle testing:	Determined from HPPC results.
Nominal state-of-charge for life-cycle testing:	Specified in test matrix

(Note: If required, a step voltage limit should be set on the last recharge step of the trapezoidal pulse for each test profile such that the target SOC value will not be exceeded by more than 5%. This will require calculating the voltage that will be reached at the end of the charge step for each life-cycle profile starting at an assumed target SOC, and using this voltage value as a charge step limit. The length of the charge pulse may be adjusted up to +6% for this.)

5.7 Temperature Control

During life testing, cell temperatures must be controlled to within the following ranges. Cells tested at a nominal ambient temperature of 70°C must be maintained to within $+5^{\circ}$ C, -10° C. Cells tested at nominal ambient temperatures of 40, 50, and 60°C must be maintained to within $+ 10^{\circ}$ C, -10° C.

5.8 End-of-Testing Criterion:

Testing will continue until cells reach their set time frame for life testing, or reach an end-of-test criterion (EOT), or until directed otherwise by the ATD program manager. End-of-testing is reached when a cell is unable to perform the medium-HPPC at 60% DOD.

The set time frame for life testing is 8 weeks. However, if all cells within a given matrix test condition fail to pass the EOT criterion before completing 8 weeks of life testing, select the best of the cells based on the HPPC results and continue life testing for a total of 8 weeks.

Cells that have been removed from life testing should be stored at 10°C.

6. 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. Importantly, in an accelerated rate calorimetry (ARC) test, these cells exhibited the onset of thermal runaway at 80°C.

6.1 Cell Handling

- Cells should be handled whenever possible in the discharged state.
- Personnel handling or approaching the cells should wear face shields. Gloves should also be worn for handling cells unless the specific operations being performed cannot be accomplished while gloved.

- Due care should be taken to avoid shorting the cell terminals. Caution: the can is electrically tied to the negative terminal!
- After testing is completed, cells should be stored or shipped in a discharged state (<25% SOC) unless other instructions are provided.
- 6.2 Other Safety Precautions
 - For both testing and storage, cells should be located within an area shielded from nondeliberate exposure to personnel. Cells that show any sign of deterioration or unanticipated behavior should be segregated from other cells to avoid propagation of damage in the event of a failure.
 - During calendar-life testing, some cells will be nominally tested at 60 and 70°C. Extra care should be taken to ensure that all cells are at or near room ambient temperature (nominally 25°C) before handling.
 - Charged cells should not be located close to flammable or combustible materials
 - Venting of cells should be regarded as a possibility. Laboratory 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 before 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 for a period of up to 30 minutes to determine whether the release ceases without further action.)
 - In case of unexpected cell behavior (e.g., venting), the cells should not be approached for at least one hour afterward.

7. Tests to be Performed Under this Test Plan

All cells to be tested under this test plan will be subjected to the performance test sequence presented in Table A-1, after which selected cells will be subjected to additional tests as specified in Table A-2. The cells will then be separated into groups for the cycle-life testing and calendar-life testing, defined in Table A-3 in Section 7.2. All recharging between performance tests (as well as between reference tests conducted during life testing) is to be done using the recharge procedure of Section 5.4, except for the temperature constraints noted in Item 1 of Table A-2, following. In general, a rest step of nominally 5 min must be observed after each charge, and nominally 30 min after each discharge, to allow cells to reach stable voltage and temperature prior to proceeding with testing.

7.1 Performance Testing – Benchmark Characteristics

Perform the test indicated in Table A-1 on all cells.

Item	Performance Testing	No. of Iterations
1	Static Capacity Tests (see Reference 2.1, Section 3.1.1.)	*
	This test consists of a nominal constant current $C_1/1$ discharge at 25°C (i.e., initial temperature of 25 ± 3 °C), beginning with a fully charged cell. (see Sections 5.4 and 5.5.)	
	Note: A rest step of nominally 5 min must be observed after each charge, and nominally 30 min after each discharge to allow cells to reach stable voltage and temperature prior to proceeding with testing.	
	Note: This test is to be terminated at the specified cutoff of 3.0 V, <i>not</i> rated capacity	
	* Repeat discharge until measured capacity is stable within 2% for three successive discharges (maximum 10 discharges).	
2	Hybrid Pulse Power Characterization Test (see Reference 2.1, Section 3.1.2)	1
	Perform this test at the low- and medium-current levels and within the voltage limits of Section 5.0. PNGV pulse power capability will be computed using a voltage range of 4.1 to 3.075 V. However, as specified in Section 5.0, the maximum allowed voltages during the test are 4.3 V for a 2-s pulse and 4.1 V continuous, and the lower voltage limit is 3.0 V.	
	Note: A peak current of 2.7 A (nominally 3C) may be used for the low current execution of the HPPC test. The medium current execution of the test will be scaled according to Reference 2.1, Section 3.1.2 for initial performance testing. However, subsequent HPPC medium-current reference tests must be performed at a peak discharge current of 7.2 A (8C), as agreed to and used by all laboratories performing this testing (i.e., INEEL, ANL, and SNL.) Other modifications to the standard HPPC test procedure are noted in Section 7.3.	
3	Self-Discharge Test (see Reference 2.1, Section 3.1.4)	1
	Conduct this test on all cells for a 7-day stand interval at open-circuit conditions of 3.660 V, corresponding to 50% SOC and at an ambient temperature of $25 \pm 3^{\circ}$ C. The expected capacity loss during the stand interval is less than 1% per day.	
	Note: If the final measured C_1 discharge capacity is significantly less than the pretest value, contact the program engineer prior to beginning life testing.	

Table A-1. Performance test sequence (all cells).

|--|

Item	Performance Testing	No. of Iterations
1	Thermal Performance Tests (see Reference 2.1, Section 3.1.7)	1
	Repeat the static capacity test and HPPC low-current test (see Table 1 above) on up to four cells at ambient temperatures of +5 and +40°C, using cells <i>not</i> selected for life testing. (See 7.2 for selection criteria.)	
	Recharging and discharging for these tests can be done at the target test temperatures, in which case the normal soak period of nominally 8 h (5 h minimum) can be replaced by a voltage stabilization interval of nominally 5 min for recharge and nominally 30 min for discharge.	

7.2 Cycle- and Calendar-Life Testing (Reference 2.1, Sections 3.1.5 and 3.1.8)

A number of cells will be selected for calendar-life testing using one of the combinations of temperature and target state-of-charge shown in the matrices in Appendix E, F, or G. Cells selected for calendar-life testing should be those having the lowest self-discharge rates as measured in Table 1 Item 3 above. Note that for this body of testing, calendar-life testing is treated as the limiting case of cycle-life testing, where a zero fraction of the cell capacity is removed/returned during cycling. This implies that those cells that share the same temperature and target state-of-charge should be treated exactly the same, regardless of whether they are undergoing cycle- or calendar-life testing. This means, for example, that they should share the same temperature control chamber wherever possible. They should also be subjected to periodic reference testing at the same time intervals, so that they will have the same times at their target test conditions as well as at ambient temperature.

Additionally, a number of the remaining cells will be selected for life-cycle testing using one of the combinations of life-cycle test profile, temperature, and target state-of-charge defined in the test matrix in Appendix E, F, or G. Testing of these groups of cells will differ only in the choice of these three parameters. All other test conditions will be identical for all groups. Each group of cells chosen for cycling at a given temperature and state-of-charge combination should be matched as closely as possible in capacity and pulse power capability.

Appendix I presents open-circuit voltage versus state-of-charge information.

Item	Life Testing	No. of Iterations
1	Reference Performance Tests	N/A
	Conduct reference performance tests (RPTs) at 25 ± 3 °C on all cells prior to commencing the calendar- and life-cycle tests, and periodically during life testing on the schedule specified below. Each set of RPTs consist of a single C ₁ /1 constant-current discharge, one medium-current HPPC test, 1 kHz AC impedance measurements at 100 and 0% SOC.	
	Cells undergoing life testing at 40, 50, and 60°C must undergo RPTs every 4 weeks. Cells undergoing life testing at 70°C must initially undergo RPTs every 2 weeks. (Note: The interval for the 70°C cells may be subsequently changed, as discussed under Cycle-Life Testing, Item 3 below.)	
	Note: These cells may be susceptible to leakage of electrolyte at the crimp seals, especially at elevated temperatures. At the end of testing, measure and record the cell weights and compare them to the original weights to ascertain if any leakage has occurred.	
	Once cells have been determined as being unable to pass the end-of-test criterion specified in Section 5.7, perform one final L-HPPC and one C_{25} discharge, and then store the cells at 10°C.	
2	Operating Set Point Stability Test (see Reference 2.1, Section 3.1.3)	N/A
	For each cell selected for cycle-life testing, perform the selected life-testing profile (see following item) at the target temperature for 100 iterations, with a 1-h rest period before and after the 100 profiles. These data are reviewed to determine whether the target SOC and other test conditions are achieved during cycling; otherwise, modification of the test profile is needed before life-cycle testing continues. Note that this voltage/SOC verification can be performed at the target cycling temperature, and removal of the residual capacity is not necessarily required due to the use of voltage to determine SOC. (This test can be repeated at the beginning of any block of life-cycle test profiles if there is reason to believe that cell-operating conditions may have changed significantly.)	
	The intent of this test is to determine whether a charge neutral cycling condition at approximately the desired target state-of-charge/OCV is reached for life-cycle testing.	
	A new approach for maintaining a charge-neutral profile has been developed for the ATD Program. Instead of using a control voltage on the discharge pulse, a control voltage is applied to the last step during the regen portion. To facilitate this change, the 3, 6, and 9% pulse profiles have been modified in this test plan, as shown in Appendix B. The new pulse profiles also include several other changes resulting from a lower-than-originally anticipated upper current limit. These changes include reduced current levels, extended pulse lengths, and an additional rest step at the end of each pulse.	
	Monitor the OCV at the end of this test to verify that the target SOC has been attained. At completion of the test, the actual SOC should be within $+0$ to -5% of the target SOC. Appendix I presents the OCV for each target SOC.	

 Table A-3.
 Cycle- and Calendar-Life Test Sequence.

Item	Life Testing	No. of Iterations
3	Cycle-Life Testing (see Reference 2.1, Section 3.1.5)	N/A
	Each of the cells selected for cycle-life testing should be assigned a test profile, temperature, and target SOC in accordance with the test matrix in Appendix E, F, or G. Cycle these cells in accordance with the referenced procedure until an end-of-test criterion is reached.	
	Conduct the reference performance tests as described above. Cells tested at 70°C, will initially have RPTs conducted after approximately 2-week intervals at temperature; this interval may be increased later if test data indicate a longer interval will yield adequate data (e.g., capacity or power degradation not exceeding 10–15% per interval.)	
	Repeat the OSPS test at the target temperature after each set of RPTs prior to resuming cycle-life testing.	
	Modifications to the standard PNGV cycle-life test procedure are described in Section 7.4, and changes to the standard PNGV test profiles are described in Appendix B.	
	Note: A new approach for cycle-life testing has been developed for the ATD Program to ensure that each cell is at the target SOC at the completion of each cycle-life profile. The idea is to apply a control voltage during the last regen step in the trapezoidal pulse and then taper charge/discharge to bring the cell back to the target SOC. An additional rest period has been added to the end of each pulse to allow adequate time for the taper charge/discharge to occur. The test protocols for the 3, 6, and 9% SOC pulse profiles as given in Appendix B may be modified as more information becomes available.	
4	Calendar-Life Testing (see Reference 2.1, Section 3.1.8)	N/A
	Each of the cells selected for calendar-life testing should be assigned a temperature and target SOC in accordance with the test matrix in Appendix E, F, or G. Test these cells in accordance with the referenced procedure until an end-of-test criterion is reached. Conduct the same reference performance tests as required in (3) above at the same intervals.	
	Section 7.5 describes modifications to the standard PNGV calendar-life test procedure.	
	A new approach for calendar-life testing is being developed for ATD to obtain additional resistance data at regular (e.g., daily) intervals without unduly cycling the cells undergoing calendar-life testing. The idea is to apply a single-pulse profile once each day from which the discharge and regen resistances may be calculated. A new calendar-life test appendix has been added (Appendix C), and the previous appendices have been relettered accordingly.	

7.3 Changes to the Standard PNGV HPPC Test Procedure

This test plan modifies the hybrid pulse-power characterization test procedure in Reference 2.1, Section 3.1.2, in the following ways:

- The high-current execution of the procedure is omitted.
- After initial performance testing, all subsequent reference HPPC tests will be performed at a common peak current value agreed to by the three laboratories using this test plan, rather than at the value that would be determined from the test results for each individual cell. This change is made to facilitate comparisons between results from the various laboratories.
- Notwithstanding the SOC criterion of Section 5.5, HPPC tests may be performed at the standard increments of (approximately) 10% of cell rated capacity in A·h (i.e., nominally 0.09 A·h); however, results may be reported with respect to the various voltage SOC criteria as well.
- 7.4 Changes to the Standard PNGV Cycle-Life Test Procedure

This test plan modifies the cycle-life test procedure in Reference 2.1, Section 3.1.5 in the following ways:

- The number of test profile iterations between reference tests (specified in Reference 2.1, Table 3.1.5) is changed to a value that permits all groups of cells at a common temperature (except the cells at 70°C) to be subjected to reference tests at the same time at 4-week intervals. (The RPTs for the cells tested at 70°C should be performed at 2-week intervals.) This number of iterations depends on the selected cycle-life test profile. For a profile 80 s in length, this will require about 30,000 profiles between reference tests. This change is made in order to minimize the fraction of the cell life that is not at life test conditions and to improve consistency between groups of cells at different test conditions. Note that this will have the undesirable side effect of reducing the number of reference data points acquired over each cell's life.
- Both the nominal C₁/1 and HPPC reference tests will be performed at the completion of each block of continuous cycle-life test profiles. This change is due to the longer duration of the cycling blocks as required above.
- Appendix B defines the cycle-life test profiles to be used for this testing. These test profiles, which differ from the standard PNGV test profiles, are used because of the research nature of the ATD program. They are designed to provide a family of test profiles that cycle known fractions of the cell capacity while using the same time-weighted (root-mean-square) rms current. This change is made in order to minimize the effects of different test profiles on the life results.
- End-of-test (EOT) occurs when a cell reaches its set time frame of cycling, or otherwise meets the EOT criteria specified in Section 5.8.
- The target SOC for each cell subjected to cycle-life testing will be established using the voltage criterion of Section 5.5, rather than the standard method based on the fraction of the rated capacity removed. The target voltage condition will be constant

over the life of the cell. This change is made to provide a more nearly constant electrochemical state for cycling as the available cell capacity declines.

7.5 Changes to Standard PNGV Calendar-Life Testing Procedure

This test plan modifies the calendar-life test procedure in Reference 2.1, Section 3.1.8, in the following ways:

- The target temperatures and SOC conditions specified in the test matrix in Appendices E, F, and G are specific to this body of testing and take precedence over the values suggested in the referenced procedure
- Because of equipment and personnel limitations, at their discretion, INEEL, ANL, and SNL may perform the calendar-life test in either of two ways. The first is the standard PNGV approach with the cells clamped at a target control voltage for the duration of each stand period. The second involves performing a special calendarlife pulse profile, once per day. The purpose of the latter is to gain additional test data without unduly stressing the cell and from which calendar-life predictions may be formulated. Cells should be clamped at a voltage corresponding to the target SOC, rather than using the secondary alternative means allowed by the procedure. Follow the steps in Appendix C to perform the special calendar-life test with the once-per-day pulse. Follow the steps below to perform the standard PNGV calendarlife test (1) with the cell fully charged at 25°C, discharge the cell at a $C_1/1$ constant current rate to the target voltage/SOC; (2) maintain this voltage for 2.5 h; (3) raise the temperature to the target stand temperature; and (4) after 5 h, clamp the cell voltage to the *actual* value that results (or a voltage very slightly above this actual value). Note that accurate monitoring of cell current during the voltage clamp condition may require use of different test hardware than that used for reference testing because of current range limitations.
- The 6-month execution of a cycle-life test profile (Part 5 of 3.1.8) will not be performed. The reference tests will include only a single C₁/1 discharge rather than the two required by 3.1.8. This change is made for consistency with those cells that are being life cycled under similar conditions.
- The target SOC for each cell subjected to calendar-life testing will be established using the voltage criterion of Section 5.5, rather than the standard method based on the fraction of the rated capacity removed. The target voltage condition will be constant over the life of the cell. This change is made to provide a more nearly constant electrochemical state for testing as the available cell capacity declines.

8. Measurement and Data Acquisition Requirements

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

Data acquisition and reporting requirements for the characterization and cycle-life 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 ms. The response of Maccor cell test channels is known to be adequate to meet this requirement; the response of other data acquisition systems (if used) may need to be reviewed further.

During HPPC and cycle-life testing, data should be acquired at a periodic rate of approximately once per second during discharge pulses, regen pulses, and the rest intervals between them. Pulses of 2 seconds in duration or less require at least a 2 per second rate. 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 of each HPPC discharge and initial regen pulse (i.e., immediately after the start of these pulses.) During the HPPC rest intervals and $C_1/1$ discharge periods, data may be acquired based on a voltage change criterion (e.g., ΔV since last data point) or other heuristic approach as long as an adequate number of data points (typically 10 or more) is acquired during a particular test segment. This same goal should be applied to other rest intervals, such as the soak periods during temperature testing, the rest period at the end of a life cycling interval, and the stand period during a self-discharge test. In general, specified rest periods should be treated as part of the associated test with respect to data acquisition and archiving. Stand periods during self-discharge tests may be exempted from this requirement if the expected stand loss is so low that measurement channel loading could affect the results.

During life cycling, data are required for the first 100 and last 100 profiles in each continuous block of test profiles. Data should also be acquired for approximately one of every 100 profiles during the remainder of these cycling intervals; however, these data will only be used if anomalous cell behavior is noted during this period.

During standard PNGV calendar-life testing, data requirements for periodic reference tests are the same as for initial performance tests. During the storage periods at target temperature and SOC, cell voltage, current, and temperature (cell and ambient) data should be acquired at intervals that are roughly similar to those used for cycle-life testing, e.g., (a) 1 s for both the first h while stable storage conditions are being established and the last hour as cooldown for reference testing begins, and (b) 1-h intervals during the remainder of the storage period. (At these 1-h intervals, it is desirable to acquire a group of 10 or more data points at 1-s intervals to check consistency and noise levels. If desired, only the average and standard deviation of this group of values can be retained.) Note that acquiring meaningful current data during storage periods will require exceptional attention to measurement calibration and stability due to the low current values encountered. (Leakage currents during stand periods are expected to be less than 10 mA, possibly even <<1 mm stability due to current range limitations.

For the special calendar-life test with the once-per-day pulse, the data acquisition requirements are the same as for HPPC cycle-life testing, but only during the pulsing period.

8.1 Data Retention and Data Access

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

Data files should be separated into individual discharge and charge files for constant current tests (though this is not mandatory.) Individual HPPC tests can be archived as a single data file, which may or may not include the charge prior to the start of the test but

must include the end of the rest interval before discharge begins. Cycle-life test data can be separated if necessary, but into no more than 3 or 4 data files for each block of continuous test profiles: the first 100 profiles, the last 100 profiles, and the residual capacity discharge after them, and all other data acquired between the first and last 100 profiles. Data from each self-discharge test sequence (partial discharge, stand, completion of discharge) can be archived as a single data file, preferably not including the preceding and following $C_1/1$ constant current discharges. Data acquired during calendar-life storage periods can be treated as a single discharge data file, including heatup and cooldown periods.

At completion of testing, transcribe the reference performance test results (and special calendar-life test results, as applicable) to a compact disk and send the CD to the ATD, PNGV, and DOE program and technical contacts, and to the other two testing laboratories (i.e., INEEL, SNL, or ANL), and put the final form of the data on the laboratory Web site.

9. Anticipated Results

9.1 Performance and Life Testing

This testing will produce data that characterizes the performance and determines the cycle- and calendar-life behavior of lithium ion cells (nominal 0.9 A·h capacity) developed for the ATD Program for improvement of high-power lithium-ion batteries.

9.2 Testing Deliverables

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

Reported information should include, but is not limited to, cell capacity, resistance, and power versus SOC and time, all at temperature, as well as such other data as impedance or other requested test results. Also, the following four graphs should be prepared for each cell for each set of HPPC tests: (1) ASI (ohm-cm²) versus cell voltage measured at the start of discharge or regen pulse (V); (2) power density (mW/cm²) versus equilibrium open-circuit voltage corresponding to the start of discharge or regen pulse (V); (3) power (W) versus cumulative energy removed (Wh); and (4) available energy (Wh) versus power (W).

All charts, curves, tables, graphs, etc., should be clearly labeled. This information should include, as appropriate, cell number, serial number, test name, test date, test file number, SOC, temperature, and units. Also, we highly recommend the use of annotation to identify any special or unusual conditions.

10. Posttest Examination and Analysis

Cells from the test matrix will be provided to other ATD participants (e.g., LBNL and/or BNL) for posttest analysis on an as-requested basis. Any cell disassembly should be coordinated with the diagnostics labs. Cells to be shipped to other laboratories should be fully discharged to 3.0 V, or they may be shipped as disassembled components. Shipments of cells or components should

be closely coordinated between the shipping and receiving laboratory, including providing complete cell/component identification per Section 4.1.

11. Contact Persons

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Appendix B

Advanced Technology Development Program Cycle-Life and HPPC Test Profiles for Gen 1 Cell Testing

Appendix B

Advanced Technology Development Program Cycle-Life and HPPC Test Profiles for Gen 1 Cell Testing

Notes

Positive values represent discharge currents in all test profiles shown in this appendix.

A new approach is being developed for Advanced Technology Development (ATD) to ensure that each cell is at the target state-of-charge (SOC) at the completion of each profile. The test protocols for the 3, 6, and 9% SOC pulse profiles may be modified as more information becomes available. The charge balance for the 3, 6, and 9% Δ SOC test profiles is regulated by applying a control voltage at the completion of the last regen step and taper charging/discharging to the target open-circuit voltage. This control voltage is determined from the associated operating set point stability test.

Step Time (s)	Cumulative Time (s)	Current	Charge (A·s)	Cumulative Charge (A·s)
14	14	7.20	100.80	100.80
10	24	0.00	0.00	100.80
2	26	-6.48	-12.96	87.84
2	28	0.00	0.00	87.84
32	60	-2.745	-87.84	0.00
20	80	Adjust CV, as r	necessary, starting	with OCV - SOC

Table B-1. Advanced Technology Development cycle-life 3% SOC pulse profile.



Step Time (s)	Cumulative Time (s)	Current	Charge (A·s)	Cumulative Charge (A·s)
14	14	7.20	100.80	100.80
10	24	0.00	0.00	100.80
2	26	-6.48	-12.96	87.84
2	28	0.00	0.00	87.84
14	42	7.20	100.80	188.64
10	52	0.00	0.0	188.64
2	54	-6.48	-12.96	175.68
2	56	0.00	0.0	175.68
64	120	-2.745	-175.68	0
40	160	Adjust CV, as 1	necessary, starting	with OCV - SOC

 Table B-2.
 Advanced Technology Development cycle-life 6% SOC pulse profile.

Advanced Technology Development Cycle-Life Testing Pulse Profile State-of-Charge Swing 6% Nominal



Step Time (s)	Cumulative Time (s)	Current	Charge (A·s)	Cumulative Charge (A·s)
14	14	7.20	100.80	100.80
10	24	0.00	0.00	100.80
2	26	-6.48	-12.96	87.84
2	28	0.00	0.00	87.84
14	42	7.20	100.80	188.64
10	52	0.00	0.00	188.64
2	54	-6.48	-12.96	175.68
2	56	0.00	0.00	175.68
14	70	7.20	100.80	276.48
10	80	0.00	0.00	276.48
2	82	-6.48	-12.96	263.52
2	84	0.00	0.00	263.52
96	180	-2.745	-263.52	0.00
60	240	Adjust CV, as r	necessary, starting	with OCV - SOC

 Table B-3.
 Advanced Technology Development cycle-life 9% SOC pulse profile.





Time Increment (s)	Cumulative Time (s)	Power (kW)	Energy Increment (Wh)	Cumulative Energy (Wh)	Equiv. Current (A)	Capacity Removed (A-s)
18	18	65	325	325	216	3888
32	50	0	0	325	0	3888
2	52	-70	-38.8	286.2	-175	3538
4	56	-55	-61.1	225.1	-137.5	2988
4	60	-47.5	-52.8	172.3	-118.8	2513

Table B-4. PNGV Pulse Power Characterization Profile (Reference 2.1, Sec. 2.1.1).



Table B-5. Test Current Ratios for PNGV HPPC Test Pulse Profile (Reference 2.1 Table 3.1.2).

Step Number	Step Length (s)	Cumul.Time (s)	Relative Current Ratio
1	18	18	1.0
2	32	50	0
3	2	52	-0.81
4	4	56	-0.63
5	4	60	-0.55

Appendix C Special Calendar-Life Test

Appendix C

Special Calendar-Life Test

Background

A new version of the calendar-life test has been developed for the Advanced Technology Development Program. This special test will be conducted similarly to the existing calendar-life testing described in this test plan, with the addition of a once-per-day execution of a special pulse profile at the target calendar-life stand temperature and state-of-charge. We anticipate that these data will provide additional details regarding the rate and extent of cell degradation during the intervals between periodic reference tests. Cell discharge and regen resistances will be calculated from the pulse profile data and compared to results obtained from the normal reference tests. Because of equipment and personnel limitations at INEEL, SNL, and ANL, the use of this test is at the discretion of the individual laboratories.

General Description

The special test will differ from the standard calendar-life test only to the extent that a special pulse profile will be executed once during each 24-h period while the cell under test is being maintained at a given temperature and state-of-charge. The pulse profile, shown in Table C-1 and the accompanying figure, is designed to have the following characteristics:

- It is theoretically charge-neutral, so that it will not perturb the SOC of the cell under test any more than absolutely necessary.
- The magnitude and duration of its discharge and regen pulses are relatively modest (compared to the corresponding HPPC test profile), so that it will have minimal effect on the thermal condition of the cell under test. (The magnitude and duration of the discharge pulse for this test (i.e., 3.6 A for 9 s) has been set to half of the corresponding values use for the M-HPPC test.
- It incorporates a somewhat longer-than-normal rest period after the discharge pulse to allow additional time for voltage recovery before the regen pulse.

Note: That this pulse profile is intended only for use in calculating relative values of discharge and regen resistance. It is not intended for the direct calculation of pulse power capabilities, as is the HPPC pulse test profile. Additionally, it will be performed at the target calendar-life test temperature, so its results will not be directly comparable to reference tests done at 25°C.

Units to Be Tested

At the discretion of the individual testing laboratory, this test will be performed on all or part of the ATD cells designated for calendar-life testing. These cells should be subjected to the same test regime at the same time.

Test Equipment Requirements

Test equipment requirements for this special test are the same as those for the planned regular calendar-life testing, except that the use of special low-current test channels for leakage-current

monitoring during temperature stand periods is not required or recommended. This is due to the fact that higher-current test channels will be required for the execution of the pulse profile every 24 h, and the resulting manual disconnections and reconnections would unnecessarily complicate both the testing process and the resulting data files. It is permissible, but not required, to perform spectral impedance measurements or AC impedance measurements at 1 kHz before or after each pulse profile is performed (while the test channel is in an open circuit condition.)

Test Procedure

Procedure Assumptions, Constraints, and Initial Condition

- Cells to be used with this test procedure should have recent reference performance test data available. This includes a medium-current HPPC test and a C/1 constant current discharge test, both of which should have been performed within 10 days or less of the start of testing (and subsequent to any testing at temperatures above 25°C.)
- The ATD cells to be used with this procedure will be tested at the target state-of-charge and temperature as specified in the test matrices in Appendices D, E, and F
- Cell behavior should be manually observed during the initial heatup to the target temperature, and during the first execution of the pulse profile in a given stand period.

Procedure Outline

- 1. Bring the cell(s) to the target SOC at 25°C and hold for 2.5 h, as described in Appendix G.
- 2. Raise the temperature to the target stand temperature. After 1 h of stable temperature operation at the target stand temperature, execute the pulse profile of Table C-1 one time.
- 3. Clamp the voltage to the value reached after the initial hour at the target temperature (i.e., just before the pulse profile), and maintain this voltage.
- 4. Repeat the pulse profile once every 24 h for a total of approximately 28 days of testing for the cells at 40, 50, and 60°C, and for a total for approximately 14 days of testing for the cells at 70°C. (Note: These periods should be synchronized with the corresponding temperature life-cycle cells so that the RPTs may be performed in unison. These periods may be further adjusted, as necessary, based on evaluation of the test data.)
- 5. After completion of approximately the 28th pulse profile (or, 14th pulse profile for the 70°C cells) at the target temperature, reduce the cell temperature to 25°C. After 1 h at stable temperature, repeat the pulse profile.
- 6. Clamp the voltage to the value corresponding to the target SOC and hold for 1 h (to determine the variance between final and desired SOC.) Remove the cell(s) residual capacity at a $C_1/1$ rate.
- 7. Recharge the cell(s) and perform the medium-current HPPC test and a $C_1/1$ constant current capacity discharge as reference performance tests.
- 8. Repeat Steps 1 through 7 for another 28-day (or, 14-day for the 70°C cells) test interval.

Step Time (s)	Cumulative Time (s)	Current (A)	Cumulative Charge (A-s)
9	9	3.6	32.40
60	69	0.0	32.40
2	71	-3.6	25.20
2	73	0	25.20
47	120	-0.54	0.18

Table C-1. Special calendar-life test pulse profile.



C-3

Appendix D

Tabulation of Advanced Technology Development Cell Identification Numbers and Test Conditions

Appendix D

Tabulation of Advanced Technology Development Cell Identification Numbers and Test Conditions

To ensure that the correspondence between specific cells and their test conditions is identified and maintained throughout the testing program, the following form (or a facsimile thereof) can be used to assign and track this information. A copy should be placed in the battery notebook, and copies of this information should be provided with any batteries furnished to other laboratories for additional testing or post-test analysis.

Table D-1. Tabulation of Advanced Technology Development cell identification numbers and test conditions.

INEEL/ANL/SNL Cell No.	ATD Cell Number	Date of Receipt	Life-Test Temperature	Life-Test SOC	Life-Test Profile

Appendix E

INEEL Advanced Technology Development 18650 Gen 1 Cell Test Matrix

Appendix E

INEEL Advanced Technology Development 18650 Gen 1 Cell Test Matrix

The following baseline matrix of test conditions is planned for the Advanced Technology Development 18650 GEN 1 cells to be tested at the INEEL. For each set of conditions evaluated, three replicate cells will be studied.

SOC ASOC	Test Temperature			
	40°C	50°C	60°C	70°C
80%				
zero (calendar life)	3	3	3	3
3%			3	
6%			3	
9%			3	
60%				
zero (calendar life)	3	3	3	3
3%	3	3	3	3
6%	3	3	3	3
9%	3	3	3	3
40%				
zero (calendar life)				
3%				
6%				
9%				
TOTALS	15	15	24	15

Table E-1. Matrix for ATD GEN 1 baseline cells at the INEEL.
Appendix F

SNL Advanced Technology Development 18650 Gen 1 Cell Test Matrix

Appendix F

SNL Advanced Technology Development 18650 Gen 1 Cell Test Matrix

The following baseline matrix of test conditions is planned for the ATD 18650 GEN 1 cells to be tested at SNL. For each set of conditions evaluated, three replicate cells will be studied.

SOC	ΔSOC	Temperature				
		40°C	50°C	60°C	70°C	
80%						
	zero (calendar life)	3	3	3	3	
	3%	3	3		3	
	6%	3	3		3	
	9%	3	3		3	
60%						
	zero (calendar life)					
	3%					
	6%					
	9%					
40%						
	zero (calendar life)					
	3%					
	6%					
	9%					
Totals		12	12	3	12	

Table F-1. Matrix for ATD GEN 1 Baseline Cells at Sandia National Laboratories.

Appendix G

ANL Advanced Technology Development 18650 Gen 1 Cell Test Matrix

Appendix G

ANL Advanced Technology Development 18650 Gen 1 Cell Test Matrix

The following baseline matrix of test conditions is planned for the ATD 18650 GEN 1 cells to be tested at ANL. For each set of conditions evaluated, three replicate cells will be studied.

-

Table G-1.	Matrix for ATD	GEN 1	Baseline	Cells at	t Argonne	National	Laboratorie	es.

SOC	ΔSOC	Temperature				
		40°C	50°C	60°C	70°C	
80%						
	zero (calendar life)					
	3%					
	6%					
	9%					
60%						
	zero (calendar life)	3	3	3	3	
	3%					
	6%			3		
	9%					
40%						
	zero (calendar life)	3	3	3	3	
	3%					
	6%					
	9%					
Totals		6	6	9	6	

Appendix H

Establishing State-of-Charge for Life Testing

Appendix H

Establishing State-of-Charge for Life Testing

For this testing program, a decision has been made to use open-circuit voltage as the measure of state-of-charge, rather than the normal PNGV criterion based on the fraction of rated capacity (in $A \cdot h$) removed from a fully charged cell. This requires alteration of the method for establishing the target SOC value for cycle- and calendar-life testing. The procedures for accomplishing this are defined as follows.

Reference State-of-Charge and Voltage Data

The correspondence between SOC and voltage will be established by discharging a representative group of cells at 25°C, using a nominal $C_{25}/25$ constant-current rate from the fully charged condition to the minimum discharge voltage. These discharge data will be averaged over the group of cells, and the resulting voltage versus the fraction of rated capacity remaining will constitute the reference for SOC values for the entire group of cells to be tested. For example, for these 0.9 A·h (rated) cells, the (average) voltage when 0.09 A·h are removed will be defined as 90% SOC. These cells will subsequently be recharged at a $C_{25}/25$ rate (to 4.1 V without any top off charge) to verify symmetric voltage behavior, and the data will also be compared to the opencircuit voltage (OCV) curves obtained during hybrid pulse power characterization (HPPC) testing for consistency. (Differences of more than 50 mV between the $C_{25}/25$ and HPPC values will be grounds for additional testing.) This voltage versus SOC correspondence will be established at beginning of life and will be considered constant over the life of the cells, i.e., the same voltage value will represent a given SOC value as the cell capability degrades over life.

Calendar-Life Testing

The target voltage/SOC for each calendar-life test condition will be determined and maintained according to the following sequence:

- 1. Using the reference SOC/voltage curve, 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 h 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. If life testing is being done at other than 25°C, raise the temperature to the target value. Soak the cell at the target temperature for 5 h and observe the cell voltage.
- 5. Clamp the cell voltage at the actual value achieved at the end of step 4, and maintain this voltage during the calendar-life test period.

Cycle-Life Testing

The target voltage/SOC for each cycle-life test condition will be determined and maintained according to the following sequence:

- 1. (Same as Steps 1, 2, 3, and 4 for calendar-life testing)
- 2. Perform the operating set point stability test (100 repetitions of the selected cycle-life test profile), followed by a 1-h rest.
- 3. Compare the cell voltage to the voltage prior to cycling. If they differ by an amount corresponding to more than 5% SOC, adjust the cycling conditions (control voltage and/or duration of the discharge pulse) and repeat Step 2 until the target conditions are reached.
- 4. Proceed with life cycling. At the end of each block of life cycling, return the cell to a temperature of 25°C (as required for reference performance tests) and compare the cell voltage after a 1-h rest period to the target SOC/voltage. A significant change in this voltage compared to the value prior to cycling (>50 mV) should be reviewed to determine whether the change is due to a change in the cell itself or failure to maintain the target cycling conditions.

Remove the residual capacity from the cell at a $C_1/1$ constant-current rate prior to performing reference performance tests.

Appendix I

Open-Circuit Voltage versus State-of-Charge

Appendix I

Open-Circuit Voltage versus State-of-Charge

Table I-1. Calibration	Table.
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SOC	Voltage	SOC	Voltage	SOC	Voltage	SOC	Voltage
100	4.098	75	3.881	50	3.660	25	3.503
99	4.090	74	3.873	49	3.653	24	3.495
98	4.083	73	3.865	48	3.646	23	3.487
97	4.077	72	3.858	47	3.640	22	3.479
96	4.070	71	3.850	46	3.634	21	3.472
95	4.063	70	3.842	45	3.628	20	3.463
94	4.055	69	3.833	44	3.622	19	3.455
93	4.045	68	3.824	43	3.617	18	3.445
92	4.034	67	3.815	42	3.611	17	3.437
91	4.024	66	3.805	41	3.605	16	3.427
90	4.014	65	3.796	40	3.600	15	3.417
89	4.003	64	3.786	39	3.594	14	3.407
88	3.993	63	3.776	38	3.589	13	3.397
87	3.982	62	3.766	37	3.583	12	3.385
86	3.972	61	3.756	36	3.578	11	3.373
85	3.962	60	3.747	35	3.572	10	3.360
84	3.952	59	3.737	34	3.566	9	3.346
83	3.943	58	3.727	33	3.560	8	3.332
82	3.935	57	3.718	32	3.553	7	3.315
81	3.926	56	3.709	31	3.546	6	3.293
80	3.918	55	3.700	30	3.539	5	3.263
79	3.910	54	3.691	29	3.532	4	3.224
78	3.902	53	3.682	28	3.524	3	3.183
77	3.896	52	3.675	27	3.517	2	3.133
76	3.888	51	3.667	26	3.510	1	3.075
						0	3.000

Note: Voltages are averaged from C/25 rate curve from ANL Cells:

 $90315\text{-}210,\,90318\text{-}119,\,90318\text{-}120,\,90318\text{-}121,\,90319\text{-}122,\,90324\text{-}112$

ATD GEN 1 OCV vs. SOC



Figure I-1. ANL ATD GEN 1 open-circuit voltage versus state-of-charge.