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The effect of temperature on capacity and power in cycled lithium ion batteries

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Abstract

The Idaho National Laboratory (INL) tested six Saft America HP-12 (Generation 2000), 12-Ah lithium ion cells to evaluate cycle life performance as a power assist vehicle battery. The cells were tested to investigate the effects of temperature on capacity and power fade. Test results showed that five of the six cells were able to meet the power assist power and energy goals at the beginning of test and after 300,000 cycles using a battery size factor (BSF) of 44.3 cells. The initial static capacity tests showed that the capacities of the cells were stable for three discharges and had an average of 16.4 Ah. All the cells met the self-discharge goal, but failed to meet the cold cranking goal. As is typical for lithium ion cells, both power and capacity decreased during the low-temperature thermal performance test and increased during the high-temperature thermal performance test. Capacity faded as expected over the course of 300,000 life cycles and showed a weak inverse relationship to increasing temperature. Power fade was mostly a result of cycling while temperature had a minor effect compared to cycle life testing. Consequently, temperature had very little effect on capacity and power fade for the proprietary G4 chemistry.
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Keywords: Lithium ion; Capacity fade; Power fade; Cycle life

1. Introduction

Lithium ion batteries have gained prominence in the last few years as the U.S. Department of Energy (DOE) and the automotive companies, Ford, GM and Daimler-Chrysler have focused on high-energy storage devices that will contribute to the viability of their individual hybrid electric vehicle (HEV) designs. Although nickel metal hydride batteries are currently being used in HEVs, lithium ion technology offers high power, long life, and high cycle life to meet the requirements of the FreedomCAR partnership. (This work was started under the partnership for a new generation of vehicles (PNGV), which preceded FreedomCAR. Some of the HEV battery goals have subsequently changed, but this work was started and hence completed using the PNGV goals. Results are still indicative of state-of-the-art HEV battery performance.) Much of the research in lithium ion battery life in the past has focused on capacity fade rather than power fade [1–4]. Previous studies have shown that capacity fade is accelerated with temperature, charge rate, and maximum charge voltage, but capacity fade is independent of depth of discharge (DOD [2,4]). It has also been shown that delta state of charge affects power fade, but not capacity fade [5]. However, heretofore the effect of temperature on power fade on the SAFT America proprietary G4 lithium ion chemistry had not been thoroughly investigated.

Prototype FreedomCAR cells were supplied to the INL by Saft America, Inc. for performance testing, see Fig. 1. The testing included characterization and cycle life testing. Six

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Fig. 1. Saft America cell.

G4 chemistry cells were received with the following designations: 47178-5, 47178-15, 47178-22, 47178-32, 47178-33, and 47178-39, referred to herein as Cells 1, 2, 3, 4, 5, and 6, respectively. Each cell had a nominal voltage of 4 V with a capacity of 16 Ah.

Characterization testing began December 5, 2000 and was followed by cycle life testing, which was completed June 2002. The cells were tested to investigate cycle life performance and the effects of temperature on capacity and power fade in accordance with the performance test procedures defined for the program. Testing and analyses were performed in accordance with the procedures outlined in the *PNGV Battery Test Manual*, Revision 3, as detailed in the cell-specific test plan [6–7]. Cell performance was measured against the goals summarized in Table 1.

2. Testing

The INL performed a receiving inspection in accordance with our standard procedures before performance testing to confirm that the test articles were not damaged. This included visual inspection and measurement of cell weights and open-circuit voltages. The cells were tested with Maccor Series 4000 programmable testers and placed in an environmental chamber to minimize test temperature fluctuations and maintain the target temperatures during testing. Following the receiving inspection, characterization testing was initiated with a series of three static capacity tests, each consisting of a $C_1/1$ discharge from 100% state of charge (SOC) to the minimum discharge voltage limit of 2.5 V, followed by a full recharge. Following the static capacity tests, the low hybrid pulse power characterization (L-HPPC) test was performed using a current of 80 amps, a $5C_1/1$ rate. The HPPC test is "intended to determine the dynamic power capability over the device's useable charge and voltage range ..." The high current test, while originally planned, was not performed in order to quickly advance to cycle life testing.

Table 1
HEV battery testing goals from reference [6]

Goals (units)	Power assist
Pulse discharge power (kW)	25 (18 s)
Peak regenerative pulse power (trapezoidal pulse) (kW)	30 (2 s)
Total available energy (kWh)	0.3
Round-trip energy efficiency (%)	90
Cycle-life (cycles)	300,000 for 25 Wh
Cold cranking power (kW)	5
Calendar life (years)	15
Maximum weight (kg)	40
Maximum volume (l)	32
Operating voltage limits (V_{dc})	max $\leq$ 400 min $\geq$ (0.55 × V_{max})
Maximum allowable self-discharge rate (Wh/day)	50
Temperature range (°C)	
Equipment operation	−30 to +52
Equipment survival	−46 to +66

Thermal performance tests, which consist of a $C_1/1$ discharge capacity test and a L-HPPC test at temperatures other than 30 °C, were performed at 10 and 45 °C on all the cells. The thermal performance test determines the effect of temperature on capacity and power capability. A self-discharge test, intended to determine the temporary capacity loss for a specified stand time, was performed at 25% DOD and 30 °C on all cells. The cold cranking test was performed on all the cells at −30 °C at 76% DOD. The cold cranking capability is the capability at the end of three consecutive battery size factor (BSF)-scaled, 5 kW, 2 s pulses at −30 °C, which simulates an automobile cold start. The efficiency test was performed at 25% DOD and 30 °C, using the BSF scaled 25 Wh power-assist life cycle test profile. The BSF for these cells was calculated to be 44.3, which is the number of cells required to meet the power and energy goals at BOT with a 30% power margin. The operating set point stability (OSPS) test was performed at 25% DOD, with Cells 1 and 2 at 30 °C, Cells 3 and 4 at 40 °C, and Cells 5 and 6 at 50 °C, which corresponds to their designated cycle-life DOD and temperatures. After the OSPS test was charge-balanced, cycle life testing was initiated using the 25 Wh power-assist life cycle test profile. During cycle life testing a reference performance test (RPT) is periodically performed to measure and track the capacity and power degradation throughout cycle life testing.

The cycle life test profiles were initially performed in blocks of 20,000 profiles. After the second RPT, however, cycling was performed in blocks of 30,000 to reduce the time required for non-cycling activities. Each set of RPTs consisted of a single $C_1/1$ constant-current discharge and a L-HPPC test. All RPTs were performed at 30 °C, using the full manufacturer's specified voltage range. After RPT 10, another 20,000 profiles were performed to bring the total cycle count to 300,000.

3. Results

Table 2 lists the results of the initial impedance measurements at 0 and 100% DOD using a 1 kHz impedance meter. This information, combined with visual inspection, indicated

Table 2
Initial impedance measurements

INL ID	Cell ID	Impedance (mΩ)	
		100% DOD	0% DOD
1	47178-5	1.274	1.229
2	47178-15	1.217	1.264
3	47178-22	1.170	1.157
4	47178-32	1.135	1.175
5	47178-33	1.146	1.159
6	47178-39	1.202	1.186

that the cells suffered no significant damage during shipment to the INL.

The results of the static capacity tests and thermal performance capacity tests performed on the cells during characterization testing are summarized in Fig. 2. The individual cell capacities were stable, within 2% of their original capacities after three complete discharges (Dis 1, Dis 2, and Dis 3 in Fig. 2). The Thermal Performance tests were performed at 10 °C and 45 °C (10 and 45 °C in Fig. 2.) A lower capacity is expected for the low temperature thermal performance test (10 °C), and a higher capacity is expected for the high temperature (45 °C) due to the temperature-related kinetic and thermodynamic effects.

Fig. 3 illustrates the cell capacities for the RPT results from the beginning of cycle life testing at RPT 0 (zero cycles) to RPT 11 (300,000 cycles). The capacity fade over the course of 300,000 cycle life profiles was 15.3% for Cells 1 and 2 at 30 °C, 13.7% for Cells 3 and 4 at 40 °C, and 11.7% for Cells 5 and 6 at 50 °C, which indicates a weak inverse temperature relationship to capacity fade over this temperature range. Capacity fade is generally associated with a loss of lithium available for intercalation, otherwise known as lithium corrosion. Lithium corrosion is a parasitic loss that occurs between the lithium in the negative electrode and the electrolyte. The lithium corrosion reaction produces several soluble and insoluble products. This mechanism may be responsible for the bulk of the capacity fade, but it does not explain the inverse temperature relationship. The soluble products lead to self-discharge and the insoluble products are responsible for the irreversible capacity loss. A solid–electrolyte-interphase (SEI) or passivation layer results from the reduction of the electrolyte at the negative electrode. This SEI layer is a good ionic (Li^+) conductor and a poor electronic conductor. The stability of this layer and its ability to reduce lithium oxidation has an effect on the overall capacity fade of the cell during long-term cycling [1].

Fig. 4 summarizes the self-discharge at the beginning and end of test for all of the Saft America HP-12 cells. The self-discharge is calculated as an average single-day loss in energy (Wh/day) from the 7-day energy loss test. The cell level self-discharge is scaled by the BSF in Fig. 4. All of the cells are well below the maximum allowable self-discharge rate of 50 Wh/day. The negative self-discharge for Cell 1 is a measurement artifact.

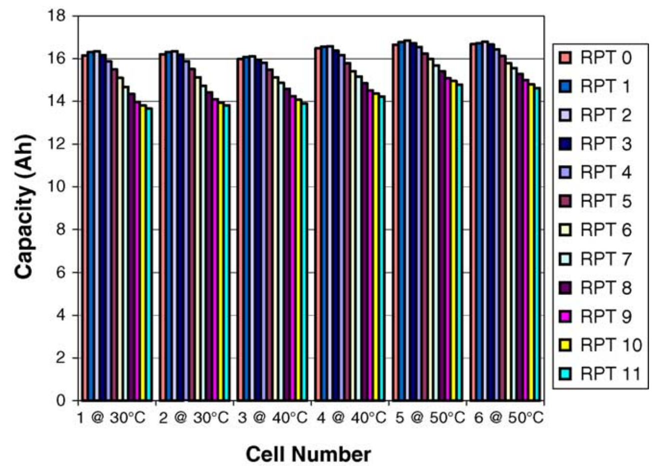

Fig. 3. Cycle life capacity summary for Saft America HP-12 cells.

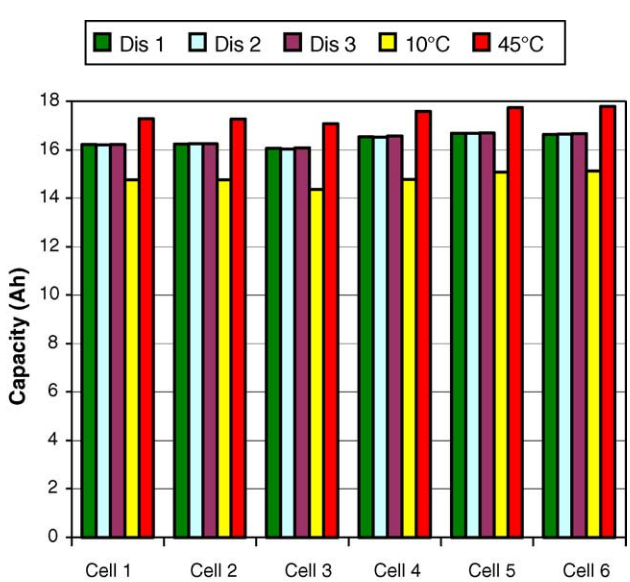

Fig. 2. Characterization capacity summary for Saft America HP-12 cells.

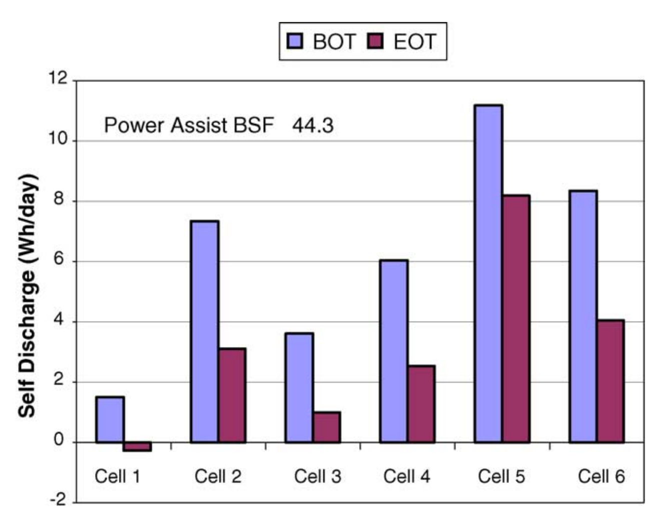

Fig. 4. Self-Discharge summary for Saft America HP-12 cells.

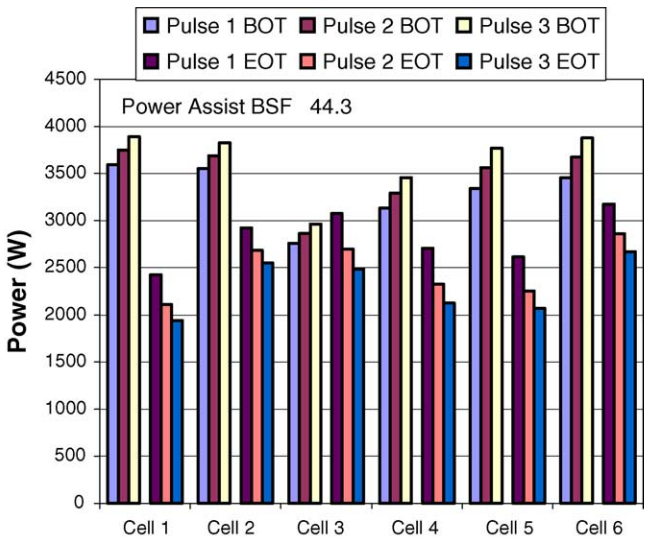

Fig. 5. Cold Cranking summary for Saft America HP-12 cells.

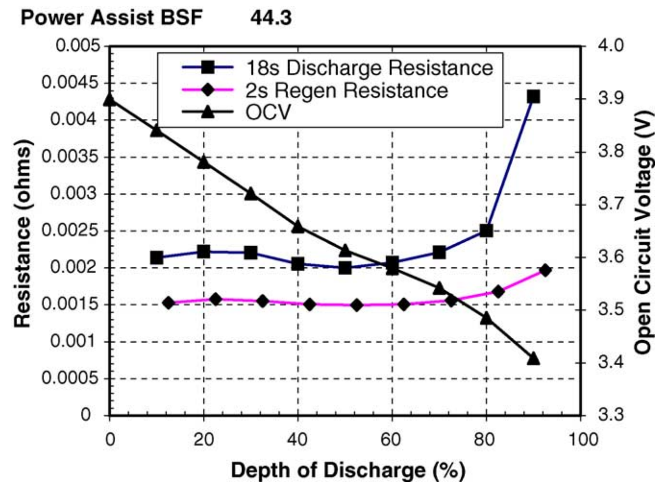

Fig. 7. Discharge and regen resistance, and the open circuit voltage vs. DOD for Saft America Cell 1.

Fig. 5 demonstrates the cold cranking capability of the Saft America HP-12 cells at the beginning and end of test. Interestingly, the BOT power capability increased with each pulse, whereas the EOT power capability decreased with each pulse. None of these cells meet the cold cranking power goal of 5 kW, but later cells from Saft have met the cold cranking goal.

Fig. 6 shows the efficiency summary as measured during the beginning and end of test. The efficiency is a measure of the energy efficiency divided by the coulombic efficiency for a scaled 25 Wh power assist life cycle test profile. All the cells exceeded the goal of 90% efficiency both at BOT and EOT.

Fig. 7 illustrates the discharge and regen resistances and the open-circuit voltage, all versus DOD for Cell 1 (tested at 30 °C) at the beginning of test. Plotting open-circuit voltage on a linear secondary *y*-axis shows the correlation between cell voltage and DOD. In testing of other lithium ion cells, it has been determined that the major cause of the difference in the regen and discharge resistances is due to the increased polarization resistance of the 18 s discharge pulse compared to the only 2 s regen pulse.

Fig. 8 shows the discharge and regen pulse power capabilities calculated for Cell 1 at the beginning of test. Pulse power is calculated from the HPPC results using the discharge and regen resistances combined with the HPPC voltage limits. For a given power the area between the discharge and regen power when plotted as a function of discharge energy is the energy available over the associated DOD range, otherwise known as useable energy.

The useable energy as a function of pulse discharge power for Cell 1 at the beginning of test is graphed in Fig. 9. The

Fig. 6. Efficiency summary for Saft America HP-12 cells at beginning (BOT) and end of test (EOT).

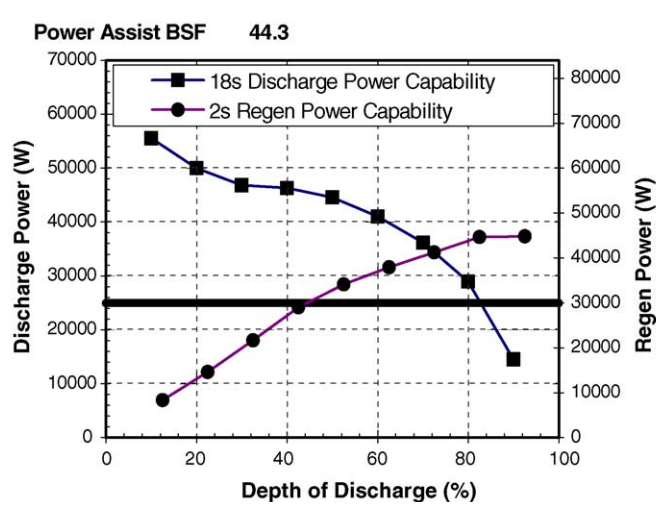

Fig. 8. Discharge and regen pulse power vs. DOD for Saft America Cell 1.

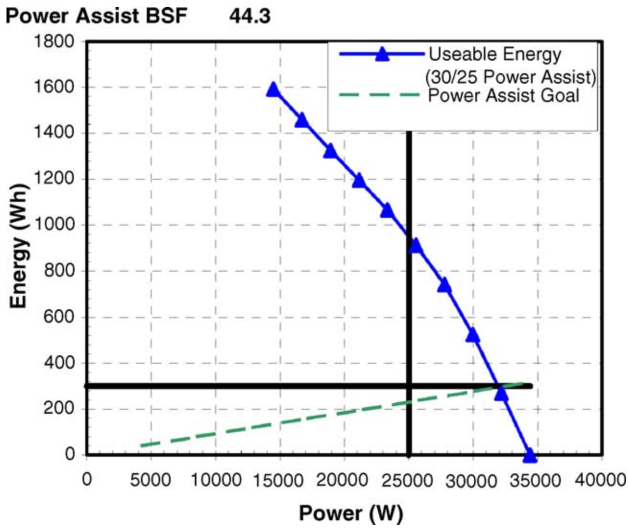

Fig. 9. Useable energy as a function of peak discharge power demand for Saft America Cell 1.

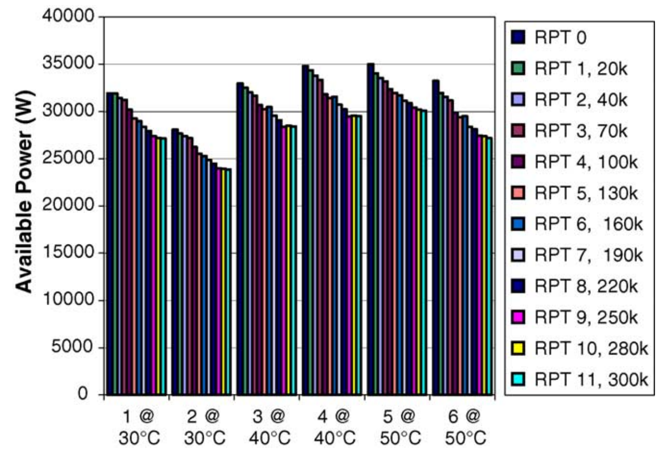

Fig. 11. Cycle life available power summary for Saft America HP-12 cells.

horizontal and vertical lines represent, respectively, the power assist energy goal and the power assist power goal. The intersection of the power assist useable energy line and the energy goal line is the available power. To meet power assist power goals, this power value must be greater than or equal to 25,000 W throughout life. Available power is defined as the power that can be achieved while simultaneously producing 300 Wh of energy.

Fig. 10 summarizes the calculated available power capabilities from the initial L-HPPC tests at 30 °C as well as the thermal performance L-HPPC tests at 10 and 45 °C. Typical of lithium ion cells, the available powers at 10 °C were lower than the available powers at 30 °C, which were lower than the available powers at 45 °C. This is a result of a drop in ohmic resistance with increasing temperature. Based on

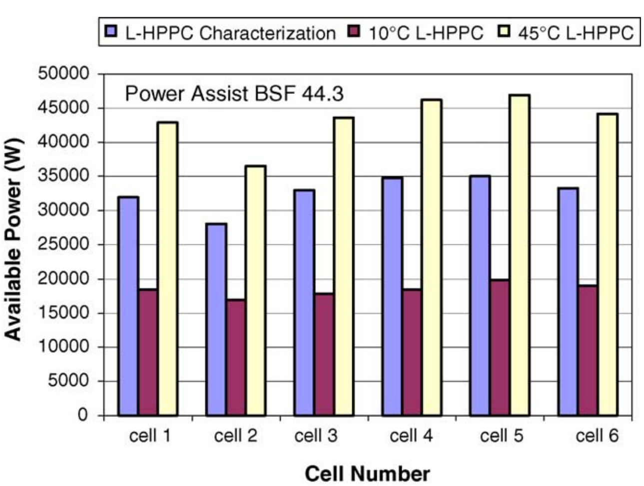

Fig. 10. Available power summary during characterization for Saft America HP-12 cells.

a recommendation from Saft America, a battery size factor of 44.3 was used to scale the cell power and energy in order to estimate the performance of a full-size HEV battery system from single-cell data. This approach represents the present method of comparing the cell power capability to the goals.

The scaled available power results for all six Saft America cells from the RPT 0 (0 cycles) to RPT 11 (300,000 cycles) are shown in Fig. 11. All of these RPTs were performed at 30 °C. The figure shows that the Saft America cells were able to simultaneously meet the power and energy goals initially. However, Cell 2 failed to meet the goals after 190,000 cycles because of its lower than average initial power. Power fade over testing is defined as the percentage difference in Available Power from RPT 0 to the end of testing, RPT 11. The average power fade was $15.2 \pm 1.6\%$. The average power fades for the cells at 30, 40, and 50 °C were 15.0, 14.5, and 16.1%, respectively. The standard deviations for the two cells at each of the three temperatures were 0.03, 1.04, and 2.90. The data shows that power fade does not appreciably increase with increasing temperature, which was unexpected. Testing of other lithium ion cells from SAFT America with G5 chemistry has shown a temperature dependence on power fade, the subject of future papers. However, the standard deviation reveals greater variation as a result of temperature. The G4 chemistry shows about the same power stability for the three temperatures, 30, 40, and 50 °C. Consequently, power fade is most affected by the total number of cycles, and, only secondarily, the temperature at which the cycles are performed. The cause of the power fade is believed to be a result of the increased resistance due to the build-up of the solid-electrolyte-interface layer with aging.

The Gap analysis in Table 3 summarizes performance for Cell 1, based on the power assist goals at both RPT 0, beginning of cycle life testing, and RPT 11, the end of testing (EOT) after 300,000 cycles. The discharge pulse power is the BSF-scaled power capability calculated from the L-HPPC test at 300 Wh. The peak regenerative pulse power is scaled

Table 3
Gap analysis for Saft America Cell 1

Power assist	EOL target	INEEL (1)	
		BOT	EOT
18 s discharge pulse power (kW)	25	32	27.1
2 s regenerative pulse power (kW)	30	38.4	32.52
Available energy (kWh)	0.3	0.95	0.51
Efficiency (%)	>90	95.5	94.7
Cycle life (25 Wh profile)	300 k	0	300 k
Cold cranking power @ −30 °C (kW)	5	3.9	1.9
Calendar life (years)	15		
Maximum system weight (kg)	40	0.680/30.1	0.680/30.1
Maximum system volume (liters)	32	0.303/13.4	0.303/13.4
Selling price ($/system @ 100 k/year)	300		
Maximum operating voltage (V_{dc})	440	173	173
Minimum operating voltage (V_{dc})	$0.55 \times V_{max}$	130	130
Maximum dc-link current (A)	217	193	193
Self discharge (Wh/day)	50	1.5	0
Operating temperature range (°C)	−30 to +52	22–52	
Survival temperature range (°C)	−46 to +66	−46 to +66	
Build date/progress date		Dec-00	Jun-02
INEEL ID number		P68-1	
Hardware level		Cell	
Ampere hour capacity		16	
Battery size factor (BSF)		44.3	
Design basis		Pack Series	

to 1.2 times the discharge pulse power. The available energy is the BSF-scaled energy at 25 kW calculated from the L-HPPC test. Discharge pulse power, peak regenerative pulse power, and the available energy all exceed their respective goals. The efficiency values meet the goals; these are direct calculations (no scaling) of the cell's energy efficiency during a cycle life profile. The value for cycle life reflects the number of 25 Wh profiles performed during cycle life testing, 300,000 cycles. None of the cells meet the cold cranking power goal. The weight and volume are scaled up to a pack value based on the multiplication of the cell values by the manufacturer-specified BSF; these also meet the respective goals. The weight and volume values shown do not include burden for packaging. The maximum and minimum voltages shown are the cell maximum and minimum voltages of 3.9 and 2.93 V, respectively, scaled by the BSF. The maximum and minimum voltages are much smaller than the Table 2 targets because the high cell power capability requires only 44.3 cells to meet the power and energy goals shown in the end of life (EOL) target column. The maximum allowable self-discharge rate is the cell-specific daily self-discharge rate scaled by the BSF, which also meets the goals. Build date/progress date indicates the date the cells were built and the latest date for the data reported in the EOT column. INL ID number indicates the pack number that was used for identification during testing. Hardware level indicates that the cells were tested with a rated capacity of 16 Ah. These cells were scaled up to a pack level (design basis) using the BSF 44.3. Configuration indicates the cells were connected in series for the scale up exercise.

4. Conclusions

A 13.6 ± 1.7% average capacity loss occurred over the course of the test, which showed a weak inverse temperature relationship. The scaled available power summary shows that a pack made of Cell 1 would have been capable of meeting the power and energy goals after completing 300,000 cycles based on a BSF of 44.3. The cells subjected to higher temperature during cycle life testing did not experience significantly greater power fade (which was unexpected) but they did show increased variability when looking at the standard deviation for the cells at the same temperature. The power fade is probably partially related to an increase in resistance of the SEI layer. Power fade has also been linked to the decrepitation of the cathode material, which is brought about through cycling. The gap analysis and available power summary show that the Saft America cells were able to meet almost all of the technical goals. One concern with these particular cells is their non-uniformity in initial power and capacity. Consequently, temperature had very little effect on capacity and power fade for the proprietary G4 chemistry.

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