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Journal of Power Sources 123 (2003) 241–246
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

A capacity and power fade study of Li-ion cells during life cycle testing

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Received 12 March 2003; accepted 30 March 2003

Abstract

We tested three lithium-ion cells to evaluate capacity and power fade during cycle life testing of a hybrid electric vehicle (HEV) cell with varying state of charge (ΔSOC). Test results showed that the cells had sufficient power and energy capability to meet the Partnership for a New Generation of Vehicles (PNGV), now called FreedomCAR, goals for Power Assist at the beginning of life and after 120,000 life cycles using 48 cells. The initial static capacity tests showed that the capacity of the cells stabilized after three discharges at an average of 14.67 Ah. Capacity faded as expected over the course of 120,000 life cycles. However, capacity fade did not vary with ΔSOC. The hybrid pulse power characterization (HPPC) tests indicated that the cells were able to meet the power and energy goals at the beginning of testing and after 120,000 life cycles. The rate of power fade of the lithium-ion cells during cycle life testing increased with increasing ΔSOC. Capacity fade is believed to be due to lithium corrosion at the anode, and power fade suggested a buildup of the SEI layer or a decrepitation of the active material.

Keywords: Cycle life; Lithium-ion cell; Capacity fade; Power fade; Delta-state of charge (ΔSOC); DOD

1. Introduction

Lithium-ion batteries have gained prominence in the last few years as the US Department of Energy (DOE) and the big three automobile 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 designs. The high power, long life, and high cycle life requirements of the Partnership for a New Generation of Vehicles (PNGV) program have led to the selection of lithium-ion batteries as one of the few possible candidates.[1] 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]. However, the effect of DOD or delta-state of charge (ΔSOC) on power fade was not clearly understood for lithium-ion cells.

1.1. Performance testing

Prototype cells were supplied to Idaho National Engineering and Environmental Laboratory (INEEL) by Saft America, Inc. for performance testing. The testing included characterization and cycle life testing. Three G4 chemistry cells were received with the following designations: 12AH6-5, 12AH6-6 and 12AH6-8, referred to here as cells 1, 2 and 4, respectively. Each cell had a nominal voltage of 4 V with a capacity of 15.5 Ah. The cells were designed to meet goals according to Revision 2 of the Testing Manual [5]. The cells were tested to investigate cycle life performance and the effects of delta-state of charge (ΔSOC) on capacity and power fade during cycle life testing. Delta-state of charge (ΔSOC) is the amount of variation in state of charge that is repetitively induced during cycle life testing. The cells were subjected to the performance test procedures defined for the program. The testing and analyses were performed in accordance with the procedures outlined in the Battery Test Manual, Revision 2 and the Battery Test Manual, Revision 3 as detailed in the cell-specific test plan [5–7]. In addition, Fast Response Engine and Slow

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[1] In 2002, the program name was changed to FeedomCAR. Some of the HEV battery goals have changed, but this work was started and completed using the PNGV goals. Results are still indicative of state-of-the-art HEV battery performance.

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doi:10.1016/S0378-7753(03)00537-8

Table 1
HEV Battery Testing Goals from [5]

Tests (units)	Power Assist	Dual Mode
Pulse discharge power (kW)	25 (18 s)	40 (18 s)
Peak regenerative pulse power (trapezoidal pulse) (kW)	30 (10 s)	40 (10 s)
Total available energy (kWh)	0.3	1.5
Round-trip energy efficiency (%)	90	95
Cycle life (cycles)	50,000 for 100 Wh	120,000 for 100 Wh
Maximum weight (kg)	40	65
Maximum volume (l)	32	40
Operating voltage limits[a] (V$_{dc}$)	Max $\leq$ 400; min $\geq$ ($0.75 \times V_{max}$)	Max $\leq$ 400; min $\geq$ ($0.75 \times V_{max}$)
Maximum allowable self-discharge rate (Wh per day)	50	50
Temperature range (°C)		
Equipment operation	From −40 to +52	From −40 to +52
Equipment survival	From −46 to +66	From −46 to +66

[a] *Note*: maximum current is limited to 217 A at any power level.

Response Engine modes as defined in Revision 2 of the manual are referred to here as Power Assist and Dual Mode in accordance with Revision 3 of the manual.

Characterization testing began 30 July 1999 and was followed by cycle life testing which was completed 23 June 2000. Testing goals in effect at the time are listed in Table 1. The purpose of the testing was to establish the baseline performance of the cells through a set of standard characterization tests and to determine cycle life performance as affected by ΔSOC.

1.2. Special considerations

The three cells were subjected to a variation of the standard cycle life procedure known as the ramp-down life cycle, and generally defined in the cell specific test plan [7]. Instead of maintaining the same nominal state of charge throughout the cycle life test, the cell's state of charge was systematically varied between two specified state of charge limits by the modified cycle life procedure. The cycle life test profile was altered from a charge-balanced profile to a charge-negative profile by decreasing the total time of the last step of the trapezoidal regen pulse. Fig. 1 shows the voltage profile for the ramp-down procedure on Saft America Cell 4.

2. Testing

The INEEL performed a receiving inspection 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 programmable testers, using a temperature chamber to minimize test temperature fluctuations (see Fig. 2). Following the receiving inspection, characterization testing was initiated with a series of three static capacity tests, each consisted of a $C_1/1$ discharge from 100% state of charge (SOC) to the minimum discharge voltage limit of 2.5 V, which was followed by a full recharge. Following the static capacity tests, the hybrid pulse power characterization (HPPC) test was performed at two current levels: low and medium. The low (L-HPPC) test was performed using a current of 46.5 A, a $3C_1/1$ rate. The medium (M-HPPC) test was

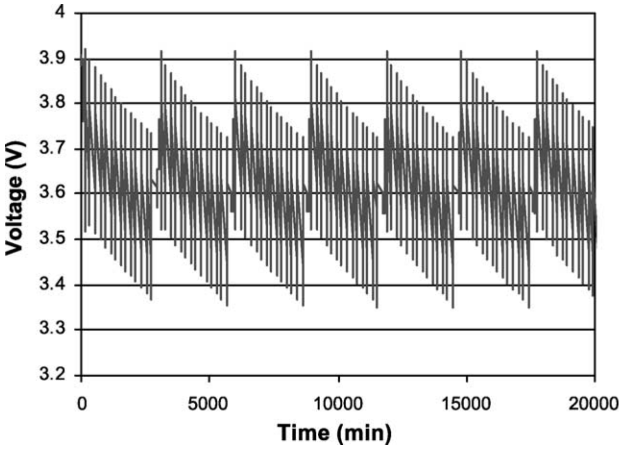

Fig. 1. Cycling data for Saft America Cell 4.

Fig. 2. Saft America cells in a temperature chamber.

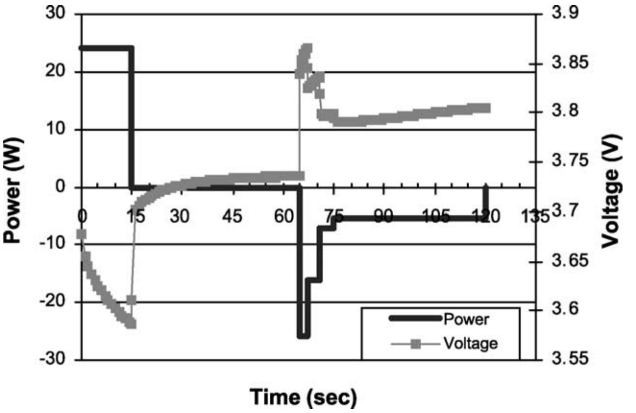

Fig. 3. 100 Wh Normal Heat Generation Cycle Life Test Profile.

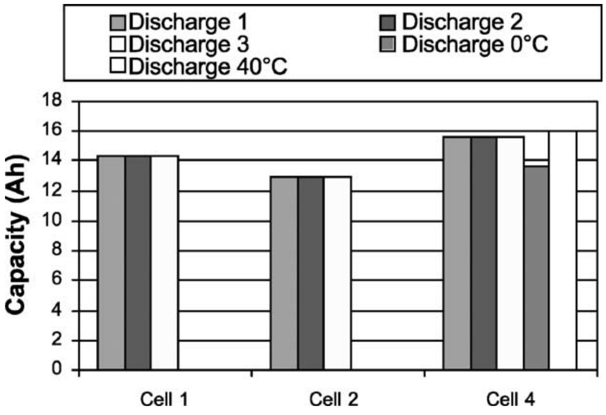

Fig. 4. Static capacity tests for the Saft America cells.

performed with a current of 245 A. The high (H-HPPC) was not performed because the high current required exceeded the available testers' current capabilities.

A self-discharge test was performed at 50% SOC and 25 °C on Cells 1 and 2. Thermal performance tests, which consist of a $C_1/1$ discharge and a L-HPPC test, were performed at 0 and 40 °C on Cell 4. The operating set point stability (OSPS) test was performed at 75% SOC and 25 °C using the scaled 100 Wh Normal Heat Generation Cycle Life Test Profile, shown in Fig. 3. The figure shows the power profile and the voltage response for the test. After the OSPS test was charge-balanced, cycle life testing was initiated using this same 100 Wh Normal Heat Generation Cycle Life Test Profile.

The cycle life test profiles were performed in blocks of 10,000 profiles rather than the 5,000 profiles recommended by the manual, to reduce the time required for non-cycling activities. The cycle life test profile was performed starting at 75% SOC, with ΔSOC values of 0, 20 and 40% SOC for Cells 1, 2 and 4, respectively (i.e. ramp-downs to 75, 55, and 35% SOC) at 25 °C. Reference performance tests (RPTs) were performed immediately prior to the start of life testing and then periodically thereafter, at every 10,000 profiles. Each set of reference performance tests consisted of a single $C_1/1$ constant-current discharge and a M-HPPC test. All reference performance tests were performed at 25 °C, using the full manufacturer's specified voltage range.

3. Results

Table 2 lists the results of the initial impedance measurements at 0 and 100% SOC. This information, combined with visual inspection, indicates that the cells suffered no significant damage during shipment to the INEEL.

Table 2
Initial impedance measurements (mΩ)

Cell no.	0% SOC	100% SOC
1	0.9055	0.8973
2	0.9731	0.9615
4	0.9765	0.9735

The results of the static capacity tests and thermal performance capacity tests performed on the cells during characterization testing are summarized in Fig. 4. The summary shows substantial variability in the capacity from cell to cell, indicative of a potential process control issue during manufacturing. However, the individual cell capacities were stable, within 2% of their original capacities after three complete discharges (Discharges 1–3 in Fig. 4). The thermal performance tests were performed at 0 and 40 °C on Cell 4. A lower capacity is expected for the low temperature thermal performance test (Discharge 0 °C), and a higher capacity is expected for the high temperature (Discharge 40 °C) due to the temperature related kinetic and thermodynamic effects.

Fig. 5 summarizes the cell capacities for the RPT results from the beginning of cycle life testing at RPT 0 (zero cycles) to RPT 12 (120,000 cycles). The capacity fade over the course of 120,000 life cycle profiles for all three cells averaged to 7.5%, with a standard deviation of 0.3%, which indicates little or no effect of ΔSOC on capacity fade. Capacity fade is generally associated with a loss of lithium available for intercalation, otherwise known as lithium

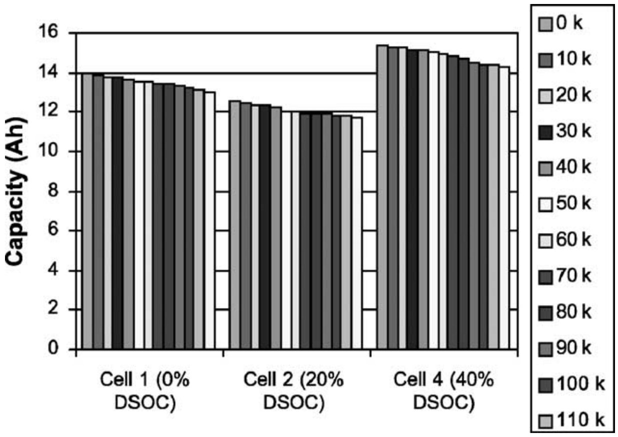

Fig. 5. Capacity summary for the Saft America cells.

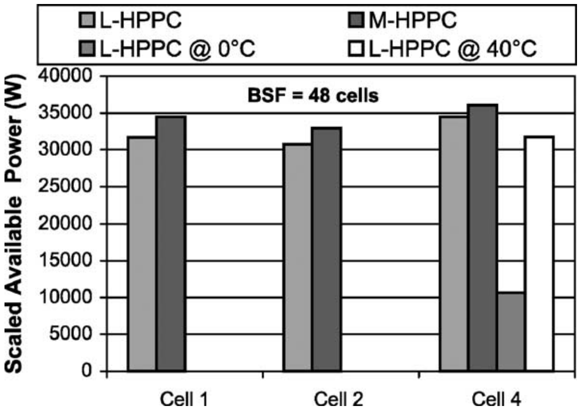

Fig. 6. Low and medium hybrid pulse power characterization test summary for the Saft America cells.

corrosion. Lithium corrosion is a parasitic loss from the negative electrode to the electrolyte. The lithium corrosion reaction produces several soluble and insoluble products. The soluble products lead to self-discharge and the insoluble products are responsible for the irreversible capacity loss. A solid electrolyte interface (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. 6 summarizes the calculated Available Power capabilities from the initial low (L-HPPC) and medium hybrid pulse power characterization (M-HPPC) tests as well as the thermal performance L-HPPC tests at 0 and 40 °C. Available Power is defined as the power that can be achieved while simultaneously producing 300 Wh of energy. The M-HPPC test is performed at a higher current than the L-HPPC and the cells experience a larger temperature increase from the Joule heating, which reduces the resistance and thus increases the Available Power. Therefore, the M-HPPC Available Power is normally higher than the L-HPPC Available Power as shown here. The Available Powers for Cell 4 at 0 and 40 °C were both lower than the Available Power for the same cell at 25 °C. Normally the Available Power at 40 °C would be higher than at 25 °C. The reasons behind this anomaly have not been determined. The variability in the Available Power from cell to cell indicates that quality control needs to be improved during manufacturing. Based on a recommendation from Saft America, a battery size factor (BSF) of 48 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.

Fig. 7 illustrates the discharge and regen resistances and the open-circuit voltage, all versus depth of discharge for Cell 1 (the cell tested with 0% ΔSOC) at the beginning of life. Plotting open-circuit voltage on a linear secondary *y*-axis shows the relationship between cell voltage and DOD.

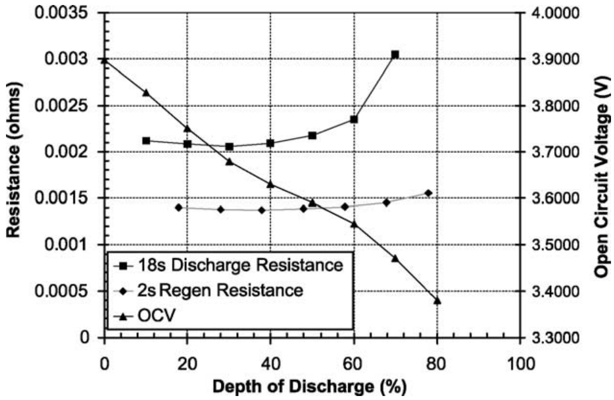

Fig. 7. Discharge and regen resistance, and the open-circuit voltage vs. depth of discharge for Saft America Cell 1.

Fig. 8 shows the discharge and regen pulse power capabilities calculated for this same cell at the beginning of life. Pulse power is calculated from the HPPC results using the discharge and regen resistances combined with the HPPC voltage limits [5]. The horizontal distance between the discharge and regen power curves at a specific power value is the discharge energy available over the DOD range where this power goal can be met.

The useable energy as a function of pulse discharge power for Cell 1 at the beginning of life is shown in Fig. 9. The curve with symbols represents the Power Assist useable energy as a function of discharge power. The horizontal and vertical lines represent, respectively, the Energy Goal and the Power Goal. The intersection of the Power Assist useable energy and the Energy Goal represents the Available Power. In order to meet the power goals, this power value must be >25,000 W.

The scaled Available Power results for all three Saft America cells from the beginning of life (BOL) to RPT 12 (120,000 cycles) is summarized in Fig. 10. All these M-HPPC tests were performed at 25 °C. The figure shows that the Saft America cells were able to simultaneously meet the power and energy goals up to 120,000 cycles. It can be seen from Fig. 10 that power fade increases with

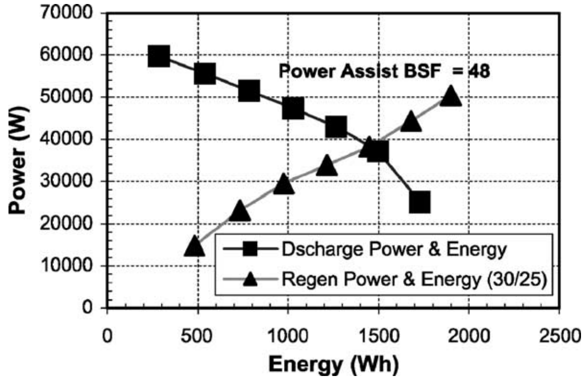

Fig. 8. Discharge and regen pulse power vs. energy for Saft America Cell 1.

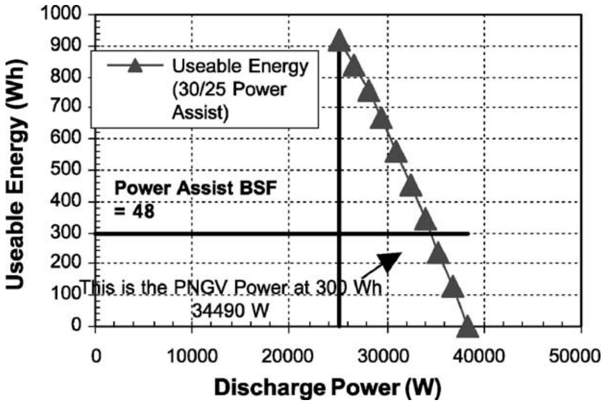

Fig. 9. Useable energy as a function of pulse discharge power for Saft America Cell 1.

Table 3
Gap analysis for Saft America Cell 1

Power Assist	EOL target	INEEL Cell 1	
		BOL[a]	EOT
18 s Discharge pulse power (kW)	25	34.5	29.9
2 s Regenerative pulse power (kW)	30	41.4	35.9
Available energy (kWh)	0.3	0.93	0.72
Efficiency (%)	>90	94.9	94.4
Cycle life (100 Wh profile)	50000	0	120000
Maximum system weight (kg)	40	32.6	32.6
Maximum system volume (l)	32	14.5	14.5
Maximum operating voltage (V_{dc})	400	187	187
Minimum operating voltage (V_{dc})	300	141	141
Maximum dc-link current (A)	217	177	177
Self discharge (Wh per day)	50	2.4	–

[a] BOL values are based on characterization data.

increasing ΔSOC. The 0% ΔSOC (Cell 1), 20% ΔSOC (Cell 2) and 40% ΔSOC (Cell 4) test conditions resulted in power fade values of 15, 27, and 43%, respectively. The results strongly suggest that increasing delta-state of charge leads to accelerated power fade. Cell 4 displayed a larger-than-expected power decrease at the start of cycle life testing compared to the BOL characterization test results. This drop was not accompanied by any notable change in capacity. On the second RPT after 20,000 cycles, the power inexplicably returned to normal. The cause of this anomalous behavior has not been established. Power fade over life is defined as the percent difference from the BOL M-HPPC test to the end of testing. A portion of the power fade at 0% ΔSOC can be attributed to the buildup of the SEI layer through lithium corrosion, which was related to capacity fade. However, the acceleration in power fade with an increase in ΔSOC seems to involve an increase in cell resistance beyond the SEI layer buildup; there appears to be some secondary mechanism involved that compounds the power fade. Saft America has proposed that this secondary power fade mechanism is caused from decrepitation of the cathode material, which is accelerated with ΔSOC.

The Gap Analysis in Table 3 summarizes performance for Cell 1, based on the Power Assist goals at both the (BOL) characterization testing and the end of testing (EOT) after 120,000 cycles. All the values in Table 3 are based on the cell tested at 0% ΔSOC. The discharge pulse power is the BSF-scaled power capability as calculated from the M-HPPC test at 300 Wh. The peak regenerative pulse power is scaled to 1.2 times the discharge pulse power. The available energy is the BSF-scaled energy at 25 kW discharge power as calculated from the M-HPPC test. Discharge pulse power, peak regenerative pulse power and the available energy all exceed the respective goals. The efficiency values also meet the goals; these are direct calculations (no scaling) of the cell's energy efficiency during a cycle life profile. The cycle data shows the number of 100 Wh profiles performed during cycle life testing. The Power Assist life goal is only 50,000 cycles; however, cycle life testing was prolonged to the dual mode goal of 120,000 cycles to determine the cell's longer-term performance capabilities. The weight and volume are scaled up from the bare cell weights to a pack value based on the battery size factor; these also meet the respective goals. 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 3 targets because the high cell power capability requires only 48 cells to meet the power and energy goals shown in the 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 goal. The values in the EOL Target column are the goals in effect at the time of the testing.

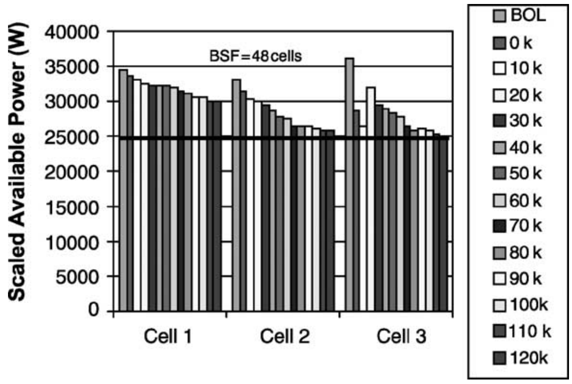

Fig. 10. Available Power summary for the Saft America cells based on M-HPPC test.

4. Conclusions

A 7.5 ± 0.3% capacity loss occurred over the course of the test, independent of cycle life testing conditions. This capacity fade is understood to be a result of lithium corrosion. The scaled Available Power summary shows that a pack of these cells would have been capable of meeting the power and energy goals after completing 120,000 cycles based on a BSF of 48. The cells subjected to greater ΔSOC values during cycle life testing experienced proportionately greater power fade. The acceleration in power fade with an increase in ΔSOC is directly related to an increase in resistance in the cell over and above the increase in resistance of the SEI layer. This increase has been linked to the decrepitation of the cathode material, which is accelerated with ΔSOC. The gap analysis and Available Power summary show that the Saft America cells were able to meet all of the technical goals. One concern with these particular cells is their non-uniformity in initial power and capacity.

Acknowledgements

This work was performed under the auspices of FreedomCAR and the US Department of Energy under DOE-ID Contract no. DE-AC07-99ID13727. The authors would like to thank Saft America Inc. for their assistance.

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