Lithium-Ion Performance and Abuse Evaluation Using Lithium Technologies 9Ah cell

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Abstract: Lithium-ion batteries in a pouch form offer high energy density and safety in their designs and more recently they are offering performance at higher rates. Lithium Technologies 9Ah high-power pouch cells were studied at different rates, thermal environments, under vacuum and several different conditions of abuse including overcharge, overdischarge and external short circuit. Results of this study will be presented

Keywords: overcharge, overdischarge, resistance, lithium-ion, short circuit, vacuum cycling.

Introduction

Lithium-ion pouch batteries are currently being designed and certified for manned space applications[1], the Extravehicular Mobility Unit (EMU) battery is an example. Lithium-ion is also being aggressively pursued for microsatellite applications[2,3]. Both these space applications are pursuing lithium-ion because of their high energy density, high voltage, low self discharge and high flexibility in configuration. Some laminated gel electrolyte designs have been shown to be stable in the vacuum environment[2]. To support the implementation of lithium-ion in space, their performance and safety has been extensively studied in the past by various methods[4,5].

Although there have been numerous advantages for the lithium-ion chemistry, actual implementations for high power applications such as electric vehicles remain with other chemistries such as nickel metal hydride. Likewise, previous design efforts for high-power space applications used nickel metal hydride and nickel cadmium[6]. In contrast, Lithium Technologies has recently produced the 9Ah HP-04170260 that can operate with a maximum charge current of 18A and a maximum discharge current of 72A. This paper describes the tests carried out to characterize its performance with rate, temperature, pressure, and abuse.

Experimental

Lithium Technologies/GAIA high power 9Ah HP-04170260 cell was tested at the Energy Systems Test Area at NASA Johnson Space Center (JSC), Houston, TX. Cells had large robust copper and aluminum tabs, dimensions of 260mm by 170mm by 4mm with a specified weight of 360 g and a capacity of 9Ah. Charging and discharging was carried out using a constant-current-constant-voltage (CC-CV) mode with a limiting voltage of 4.2V and a taper current of 0.18A. Six groups of cells were subjected to a matrix of three discharge rates to 3V—9A, 18A and 45A—and two charge rates—9A and 18A and cycled for 200 cycles for a total of 6 groups. Cells were also tested at four different temperatures -10°C, 0°C, 25°C, and 45°C for 10 cycles.

Cell performance under vacuum was tested using two cells types—one containing a laminated separator XP-04170260 and the other using the standard product HP-04170260. Cells were placed in a constraining fixture and placed in a vacuum chamber, evacuated to 0.03 torr, and run for 10 cycles at a charge current of 9A, CC-CV mode and a discharge of 9A to 3 V.

To test the cell behavior in abusive conditions one cell was fully charged to 4.2V then subjected to a 1.8A charge with a 12V limit and terminated after temperature reached steady state. Next another fully charged cell was discharged at 1.8A until a full 150% capacity reversal was obtained beyond a 3V. Lastly a cell was subjected to short circuit. This cell was fully charged and shorted using a 30-50 mohm apparatus. Testing was stopped when the current tapered to 1.0A and the time was at least 5 minutes. Current, voltage and temperature data versus time were recorded as well as physical changes accompanied with the abuse.

Table 1. Charge and discharge rates for groups.

	Method	Charge Rate	Discharge Rate
Rate Cycling	4.2V Limit on charge; discharge to 3.0V; 200 cycles	9A	9A
		9A	18A
		9A	45A
		18A	9A
		18A	18A
		18A	45A
Vacuum Cycling	0.03 torr; 10 Cycles	9A	9A
Over-charge	Charge to 12V limit or until steady state	1.8A	N/A
Over-discharge	Discharge to 13.5 Ah (150%)	1.8A	1.8A
Short Circuit	30-50 mohm shunt	9A	N/A

Results and Discussion

Capacity results for the 9Ah HP-04170260 cell are for two groups—one at a charge rate of 9A and the other at 18A.

For each of these groups the capacity of the initial and 200^{th} cycle is shown at each rate in Figure 1. Initial cycling of groups shown charged at 9A exceeded 9Ah capacity for all groups, even the one discharged at 45A. At a charge rate of 18A initial capacity averaged less than those charged at 9A with greater differences between cells discharged at 45A.

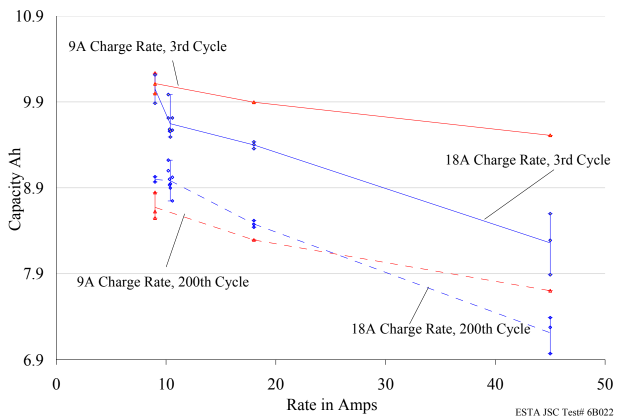

Figure 1. HP-04170260 capacity with discharge rate to 3.0 volts for select cells both initial and final 200th cycle tested at various regimes. (Δ) 9A Charge: Discharge a)9A, b) 18A, c) 45A; (◊) 18A Charge: a)9A, b) 18A, c) 45A.

Results after 200 cycles shows that cells charged at 9A degraded at a faster rate than those charged at 18A. The degradation was so significant that at the 200^{th} cycle capacities were very similar for cells charged at either rate.

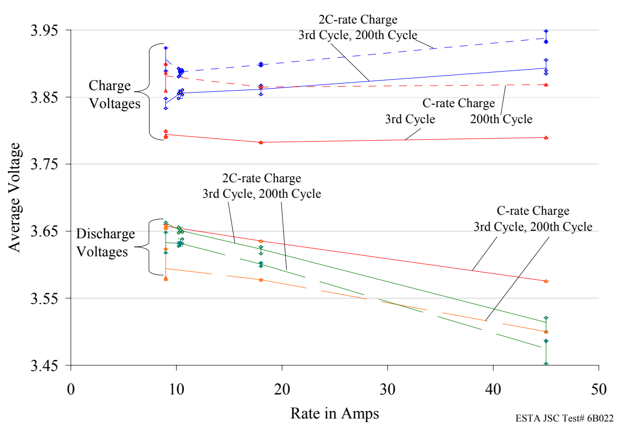

Figure 2. HP-04170260 average voltage on charge and discharge to 3.0V for select cells both initial and final 200th cycle tested at various regimes. (Δ) 9A Charge: Discharge a)9A, b) 18A, c) 45A; (◊) 18A Charge: a)9A, b) 18A, c) 45A.

Time average voltage (TAV) or watthours/amphours results of the 9Ah HP-04170260 cell are shown in Figure 2. Both charge and discharge time-average-voltages are displayed at three different discharge rates and two charge rates. Time-average-discharge voltages during the initial cycles show explicit relationship with discharge rate ranging from 3.66 V_{TAV} at 9A and 3.58V_{TAV} at 45A for cells charged at 9A with an average slope of 2.3 mV/A. Cells charged at 18A also displayed a similar relationship but with an average slope 4.0mV/A. Time-average-charge voltages displayed a stronger relationship with charging rate with slopes of 5.1 mV/A, 9.9 mV/A, 11 mV/A for each respective discharge at 9A, 18A and 45A. Results after 200 cycles show acceptable performance with similar trends.

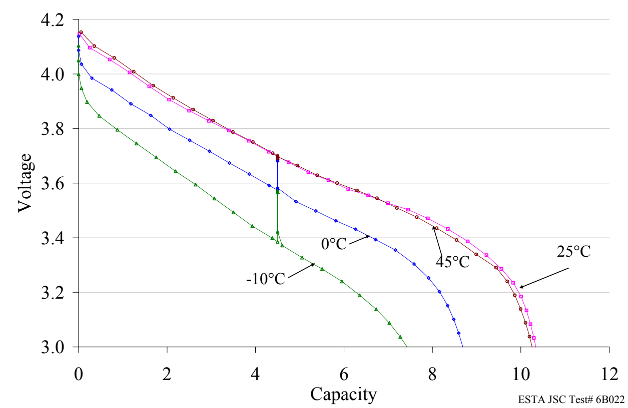

Figure 3. Voltage with capacity for HP-04170260 at different temperatures. Cells were charged at 9A using CC-CV mode, 4.2V, 0.18A taper cutoff at temperature. (□) 25°C (○) 45°C (◊) 0°C (Δ) -10°C.

Figure 3 shows the discharge curves of HP-04170260 at 9A at various temperatures. Capacity varies with temperature ranging from 10.34Ah at 25°C to 7.43Ah at -10°C. Due to the low resistance of these cells, performance did not vary significantly at 45°C versus 25°C. Resistances were calculated from discharge curves using a 100 millisecond 13.5 A (1.5 C) pulse at the midpoint of the discharge cycle.

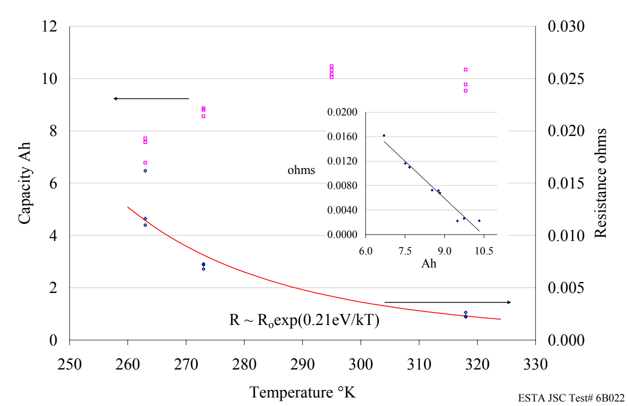

Figure 4. Resistance and capacity for HP-04170260 at different temperatures. Cells were charged at 9A with a 4.2 volt limit, and 0.18A taper cutoff at temperature. Detail graph shows capacity with resistance for cells. (□) Capacity (◊) Resistances (–) $R_o exp(Q/kT)$ trend.

Resistances progressively decreased with temperature with values ranging from 11.6mOhms at -10°C to 2.2mOhms at 45°C. Figure 4 shows the behavior of capacity and resistance with temperature. The detail graph also shows that capacity is strongly correlated with resistance for cells at various temperatures. The resistances generally follows a logarithmic relationship with 1/T as described in other lithium chemistries[7]—$R_o exp(Q/kT)$—were Q is the activation energy, k the Boltzman constant, and R_o the limiting resistance at high temperature. Arrhenius-type behavior is typical for interface charge transfer, chemical reactions and diffusion processes. Application of the Arrhenius equation $R = R_o exp(Q/kT)$ while ignoring the linear ohmic resistances yields an activation energy Q of ~0.21eV. Further improvement of this design at low temperature requires a look at the components that affect activation energy.

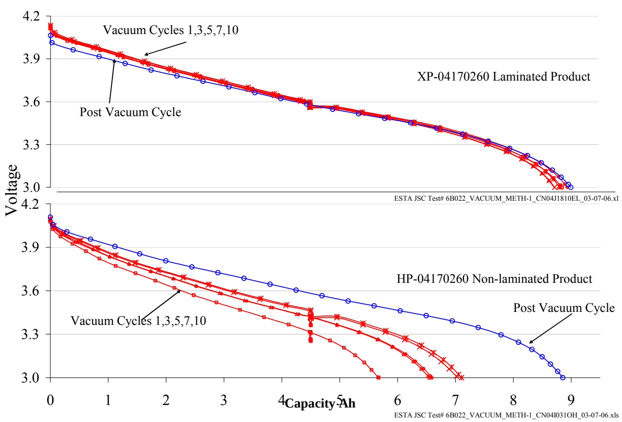

Figure 5. Voltage versus capacity for two cell designs, both tested at vacuum for 10 cycles with a final baseline at ambient pressure. a) Top: Laminated separator XP-04170260, b) Bottom: Standard product HP-04170260.

Cells were also cycled at 9A charge and 9A discharge under vacuum conditions for 10 cycles. Two cell types were tested—one containing a laminated separator XP-04170260 and the other using the standard product HP-04170260. Figure 5 shows voltage with capacity for selected cycles. A final cycle under ambient conditions was run for comparison. The standard product cell HP-04170260, shows capacities ranging from 5.67 Ah to 7.106 Ah with a final ambient capacity at 8.85 Ah. The laminated product cell however XP-04170260 ranged from 8.735 Ah to 8.908 Ah at vacuum and a final ambient cycle of 9.02 Ah. Examination of coulombic efficiencies showed that the laminated product obtained consistently better discharge efficiencies over the standard product. Final discharge at ambient pressure revealed an accumulation of charge during the vacuum testing for the standard product.

In order to characterize the abuse performance, HP-04170260 was overcharged. Figure 6 shows voltage, temperature and current of the cell during overcharge at constant current of 1.8A. Beginning at 4.2A the cell's voltage rose to a plateau at ~5.4V. After approximately 1.37Ah of additional overcharge a sharp rise in voltage was noted. Total overcharge to the voltage spike of 5.5V was 4.24Ah (47% overcharge). Examination of the cell after testing showed that it had vented. The venting was presumed to have happened here, however direct observation in the abuse chamber was not possible. After this the voltage sharply decreased to 5.11V decreasing to a steady state value of 4.78V. A peak temperature of 44.4°C was observed after 12Ah (6.7 hours). After 20 hours of overcharge (400%) the temperature reached steady state at 37°C. No fire or smoke was observed during this test.

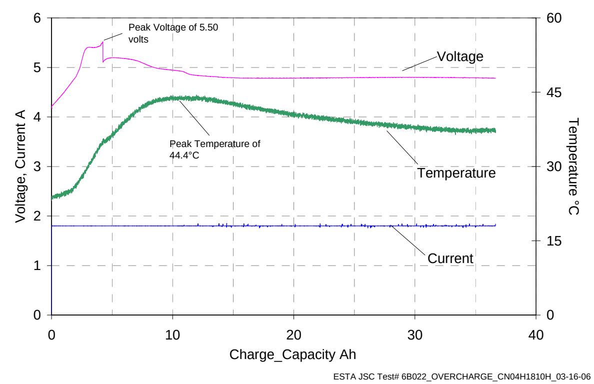

Figure 6. Voltage, current and temperature versus capacity for HP-04170260 overcharged at 0.18A (C/5).

Figure 7 shows voltage, temperature and current of the cell during overdischarge. From a fully charged state a cell was discharged to 3.0 volts, then further discharge 150% of rated capacity. A minimum voltage of -1.53 volts and a maximum temperature of 37.4°C were observed during the overdischarge. The cells were not usable after this reversal test but they failed in a safe manner.

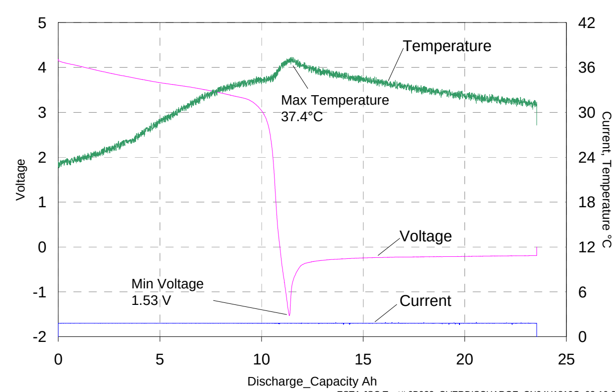

Figure 7. Voltage, current and temperature versus capacity for HP-04170260 undergoing overdischarge at 0.18A (C/5).

This displays typical results of the lithium-ion chemistry on overdischarge. At the negative voltages experienced, cells are rendered unusable due to the dissolution of the negative current collector (Cu) resulting in the creation of a short circuit path inside the cell[4].

Figure 8 shows voltage, temperature and current of HP-04170260 during short circuit with a <50mohm shunt. A peak current of 111.7A and a peak temperature of 73.7°C were observed. Voltages remained above 2V for a large part of the discharge indicating capability to discharge at higher rates given a more conductive shunt. Maximum power delivered was 348 watts at the start of the short circuit. Instantaneous power density can be estimated at greater than 967 W/kg. Final examination of the cell did show venting but also a rebound voltage above 3.0V. No explosion or fire was observed for this test.

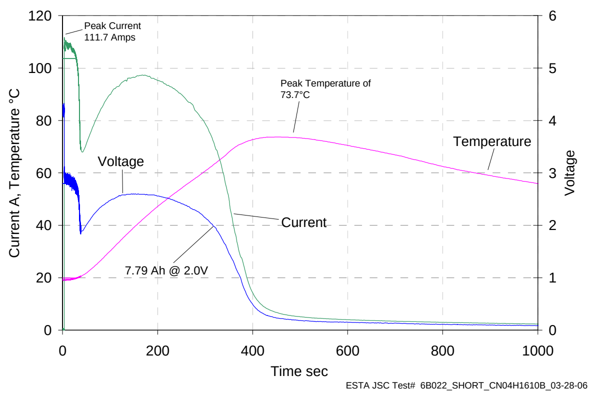

Figure 8. Voltage, current and temperature versus time for HP-04170260 undergoing short circuit at <50mohms.

Conclusion

The performance of the Lithium Technologies/GAIA high power 9Ah HP-04170260 cell was characterized with rate, temperature, pressure and abuse. The cells were observed to have stable cycling behavior for C and 2C charging rates and C, 2C and 5C discharge rates. Resistances progressively decreased with temperature rise with values ranging from 11.6mOhms at -10°C to 2.2mOhms at 45°C. Vacuum cycling was poor even with constraining fixtures for HP-04170260, however with XP-04170260 it was stable for 10 cycles. HP-04170260 was tolerant to overcharge and overdischarge at 1.8A venting without fire or smoke. The results of the short circuit test indicated a high power cell capable of delivering at least 967W/kg instantaneous power limited in this test case by the shunting resistances of the apparatus. HP-04170260 was tolerant to short circuit showing no fire or explosion for shunting resistances up to 30mohm.

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