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Cycling and Low Temperature Performance of Li Ion Cells

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ABSTRACT
Lithium-ions cells, of DD and D size, are being developed under a contract with the USAF for NASA's Mars Rover missions. The cells contain spirally wound electrodes of $LiNiO_2$ positive electrode material and graphite anode in cylindrical stainless steel hardware. The electrolytes were selected based on the mission needs of good low temperature (-20°C) performance, combined with adequate stability at ambient temperature. The cells are being subjected to 100% DOD cycling at –20° C as well as at ambient temperature. In addition, the cells are being tested in 30% depth of discharge (DOD) Low Earth Orbit (LEO) regime and 60% DOD Geosynchronous Earth Orbit (GEO) regime. The cells have so far completed 5000 accelerated LEO cycles and about 500 accelerated GEO cycles. In this paper, the results of these on-going tests will be presented.

INTRODUCTION
SAFT's Li ion D cells were delivered to JPL as baseline cells. The cylindrical cell diameter is 1.32 inches, height is 2.26 inches and the average cell weight is 118 grams. The capacity of the D cells is 4 Ah using a 4.0 V charge limit. The D cells contain an electrolyte consisting of 1.0M $LiPF_6$ in 1EC:1DMC:1EMC (developed by the Army Research Lab). Rate capability and cycling were performed at different temperatures.
SAFT's Li ion DD cells (stainless steel hardware), developed under the contract with USAF for NASA's Mars Rover Missions, are 4.8 inch long and have a diameter of 1.32 inches. The case negative cells utilized a stainless steel cell case and glass to metal seals. The cell chemistry was based on a $LiNiO_2$ positive electrode, coated onto Al foil with a PVDF binder, and graphite negative coated onto copper foil with non-PVDF binder. The cells have multiple tabs on the electrodes to lower the overall ohmic component of impedance. The electrolytes in the DD cells are 1.0 M Li $LiPF_6$ in 1EC:1DEC:1DMC:2EMC (developed at JPL) and 1.0 M Li $LiPF_6$ in 15EC:25DMC:60EA + VC additive. The average cell capacity is 9.2 Ah and display an energy density of 135 Wh/Kg.

CELL TESTING RESULTS

DISCHARGE AND CYCLE LIFE PERFORMANCE AT DIFFERENT TEMPERATURES OF D-SIZE CELLS

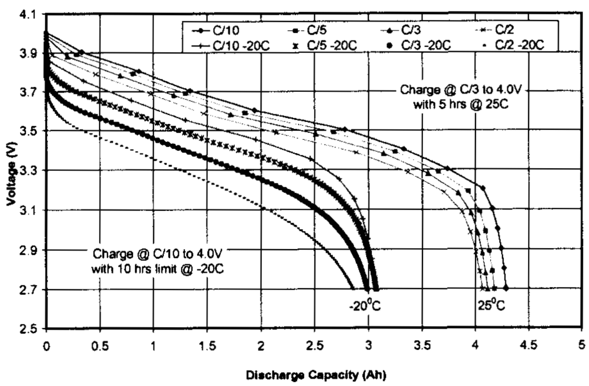

Fig. 1 Discharge curves at 25°C and –20 °C

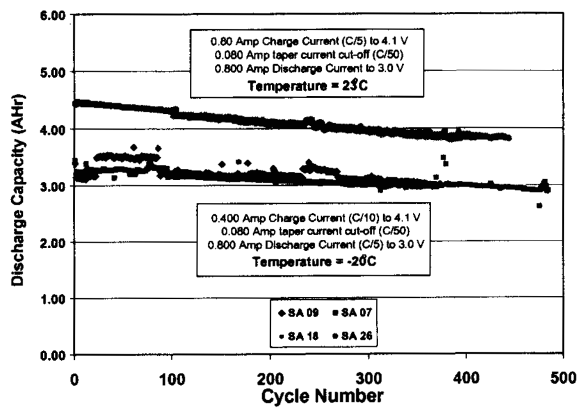

Fig. 2 Discharge capacities at 100% DOD at 25°C and –20 °C

Discharge capacities at different rates (C/10, C/5, C/3 and C/2, C and 2C) were characterized at different temperatures (-20°C, 0°C, 25°C, and 40°C). At 25°C, 2C discharge capacity is 89% compared to the capacity delivered at a C/10 rate. At C/3, the capacity at -20°C is 74% of the capacity at 25°C. Figure 1 shows the discharge curves at different rates and at different temperatures.

Fig. 2 shows the cycle life performance of D cells at 23°C and –20°C. Less than 8% capacity loss has occured in 500 cycles at -20 °C and there is about 13% loss while cycling at ambient temperature.

DD CELL CHARACTERIZATION

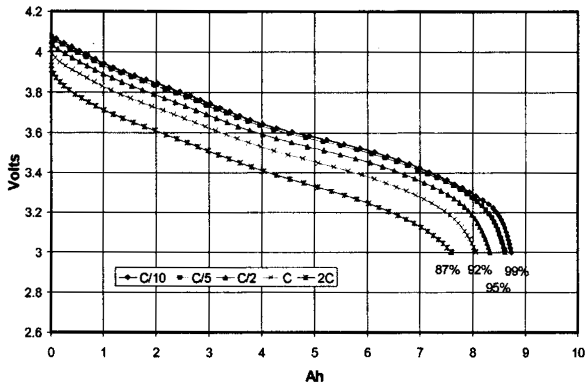

Fig. 3 DD Cell discharge Curves at 25°C

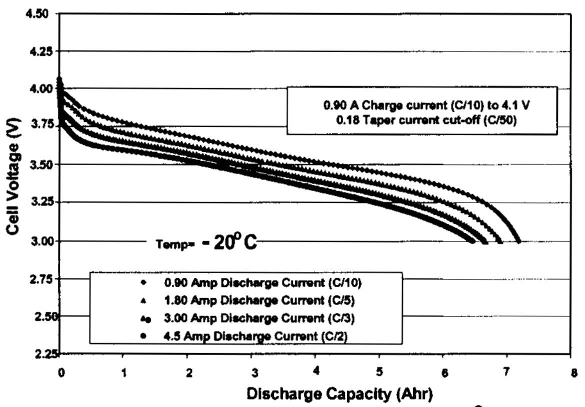

Fig. 4 DD Cell dscharge Curves at -20°C

The DD cells SAFT delivered to JPL were tested for different rates (C/10, C/5, C/3 and C/2, C and 2C) at different temperatures (-20°C, 0°C, 25°C, and 40°C). At 25°C, the discharge capacity at a 2C rate is 87% of the C/10 capacity. At C/3, the capacity at -20°C is 74% of the capacity at 25°C. Figure 3 shows the discharge curves at different rates at 25°C, whereas, Fig. 4 shows the discharge curves at different discharge rates at -20°C.

DD CELL CYCLING AT VARIOUS TEMPERATURES

Cycling at various temperatures were performed on the DD cells. Fig. 5 shows the 100% depth of discharge (DOD) cycling at 25°C. One cell has a charge limit of 4.0V, whereas, the other cell has a charge limit of 4.1V. In 600 cycles, both display about 5.4% loss of the initial capacities.

Fig. 6 shows the 100% DOD cycling tests at 23°C, -20°C and –40°C. At –40°C, 6 Ah was obtained.

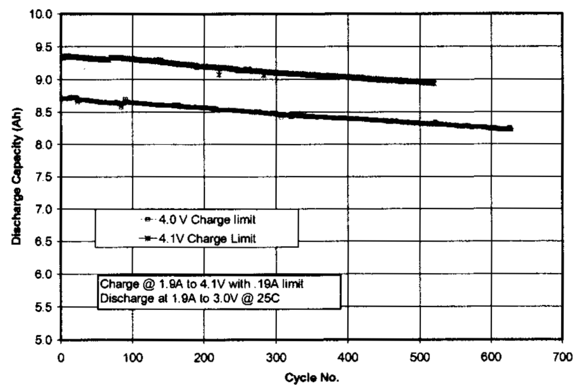

Fig. 5. DD Cells 100% DOD Cycling at 25°C

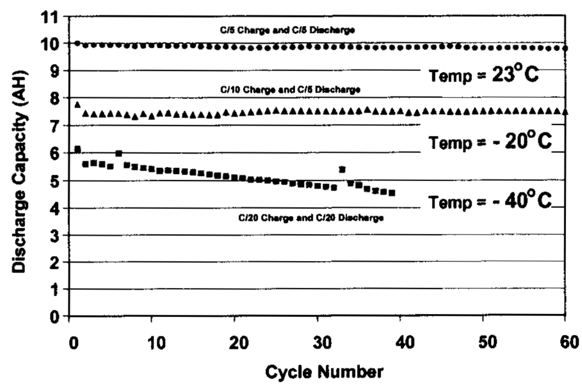

Fig. 6 Cycle Life Performance at Different Temperatures

DD cells were developed for cold temperature applications for Mars Rover mission. We tested accelerated 30% DOD Low Earth Orbit (LEO) regime and 60% DOD Geosynchronous Earth Orbit (GEO) regime cycling to demonstrate performances for planary and interplanary applications.

Accelerated 60% DOD GEO CYCLING AT 25^{0}C

In a real time GEO test, there are forty-five eclipse cycles per season and there are two seasons per year. Thus, each year there are ninety cycles. GEO applications typically require 15 years cycle life which equates to 1,350 cycles. Accelerated 60% DOD GEO tests were started in July of 1999 at 25^{0}C. The cycling is continuous in the same manner as SAFT's 40Ah space cells.[1, 2] During the accelerated tests, the maximum charge potential is 3.85V at 3.85A for 4.8 hours and the discharge is 60% of full state of charge capacity or 5.4Ah for 1.2 hours. Diagnostics are performed every fifty cycles for residual capacity and energy at the operating voltage 3.85V and at the full state of charge 4.0V. Instantaneous and polarization impedance are also measured in the diagnostics.

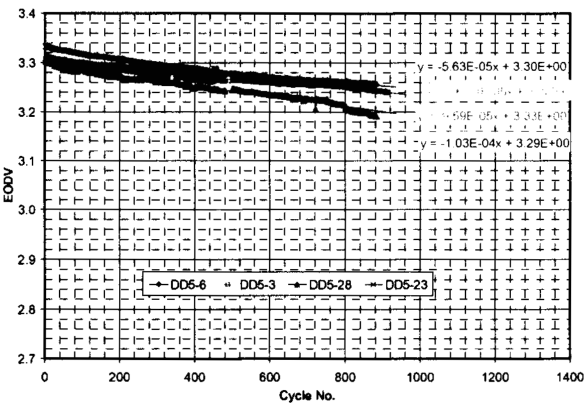

Fig. 7. DD Cells – 60% DOD GEO Test @ 25^{0}C End of Discharge Voltage

Fig. 7 shows the end of discharge voltage run-down. Fig. 8 shows the discharge energy at 4.0V and residual energy at 3.85V, as determined by the diagnostic cycles. Fig. 9 shows the impedance growth which causes the end of discharge voltage run-down and there is material consumption which results in capacity fade. The average energy fade rate at 4.0V is .00430% per cycle. After 1,350 cycles, there would be 5.80% energy loss from cycling, which implies that End of Life (EOL) 4.0V energy would be 28.3 Wh.

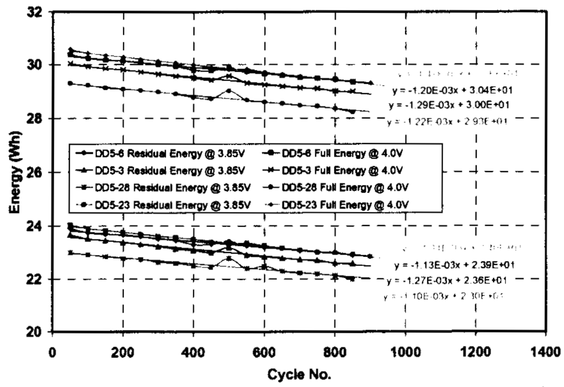

Fig. 8. DD Cells – 60% DOD GEO Test @ 25^{0}C Energy

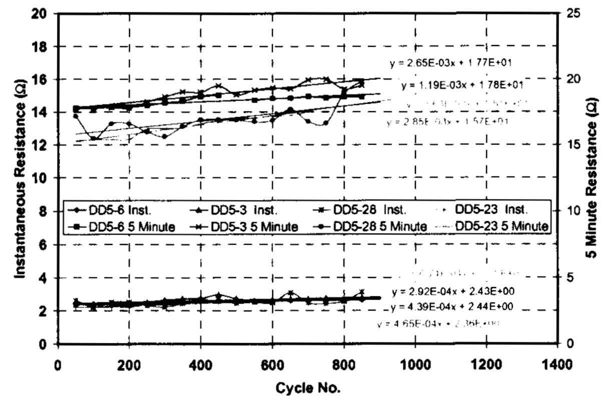

Fig. 9. DD Cells – GEO Test - Internal Resistance

Accelerated 30% DOD LEO CYCLING AT 25^{0}C

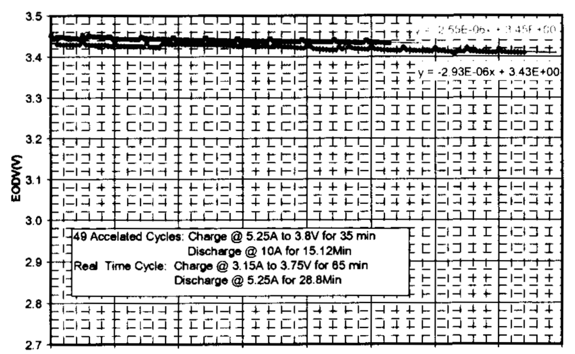

Fig. 10. DD Cells LEO Test – 30% DOD @ 25^{0}C End of Discharge Voltage

An accelerated LEO cycle consists of a 35 minute charge at 5.25 A to 3.8 V and a 15.12 minute discharge at 10 A, which is 30% of the 4.0V full state of charge capacity. There are 48 accelerated cycles, and then an accelerated 35 minute charge at 5.25A to 3.8V and a normal LEO rate of 28.8 minute discharge at 5.25A and the 50^{th} cycle is a normal LEO rate cycle which is a 65 minute charge to 3.75V and a 28.8 minute discharge.

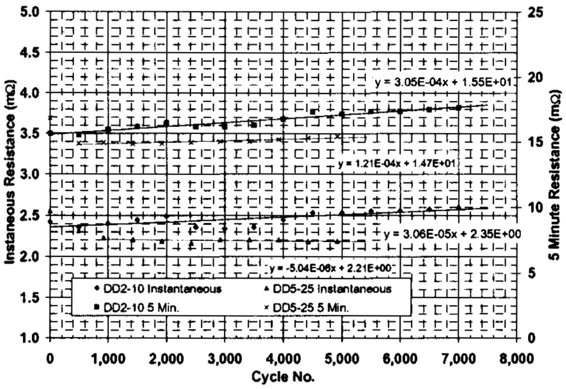

Fig. 11. Internal resistance measurements of DD-size cells undergoing LEO testing.

Fig. 10 shows the end of discharge voltage run-down of the real time cycles of two cells. Diagnostics are performed every five hundred cycles. The diagnostics include capacity measurements at both 3.8V and 4.0V, followed by dc impedance measurements. Instantaneous and polarization impedances are measured at 60% SOC, which are shown in Fig. 11. Fig. 12 shows the discharge energy at 4.0V and residual energy of the diagnostic cycles. The average energy fade rate at 4.0V is .000704% per cycle. After a typical LEO requirement of 40,000 cycles, there would be 28% energy loss from cycling, implying that EOL 4.0V energy (uncorrected for calendar life) would be 21.6 Wh (Versus a BOL of 30 Wh). The average energy fade at 3.8V is .00058% per cycle, similar to the 4.0V rate, which suggests that the energy loss is reasonably uniform over the entire energy spectrum of the cells.

Calendar life loss has been presented at the Space Power Workshop[2]. For LEO, there would be 9.65% loss in 8 years and 15.87% loss in 15 years for GEO. The results of GEO and LEO testing due to both cycling and calendar life are summarized in Table 1

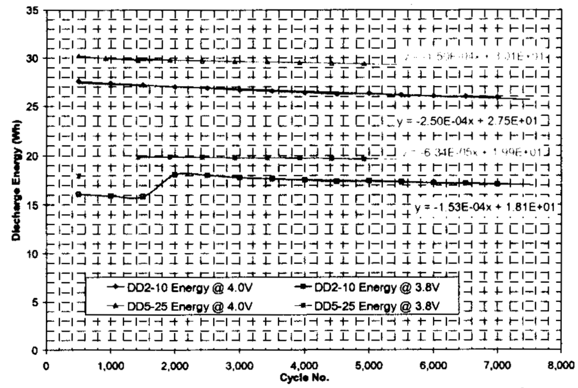

Fig. 12 DD Cells LEO 30% DOD @ 25^0C - Energy

Table 1 Cycle Life Extrapolation

Depth of Discharge %	Cycles Achieved	Wh Fade Rate @4V %/cycle	Typical Req. For Cycles	EOL Energy* @4V Wh 25^0C
30	7,500	.000704	40,000	21.6-2.9 = 18.7
60	900	.00430	1,350	28.3-4.8 = 23.3

*Corrected for calendar Life (8 years for LEO; 15 years for GEO) assuming at 25^0C.

CONCLUSIONS

DD cells developed for the Mars Rover Mission offer good low temperature performance and very stable performance at room temperature. The cycle life projections for either GEO or LEO profiles are excellent which suggests with high confidence that the cell chemistry is robust to losses sustained during both storage and cycling.

ACKNOWLEDGEMENT

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