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High Power Lithium Ion Battery Facilitated by an Advanced Cathode

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ABSTRACT

This paper presents the test results from cells fabricated using an advanced NMC cathode incorporated into the Electro Energy wafer cell which will increase the specific energy and specific power of the completed battery. The NMC material is processed to produce a cathode with loading and porosity which will result in an electrolyte interface capable of high ionic conduction. In addition electron conductivity is enhanced by a unique coating process which provides intimate contact between the NMC and the aluminum current collector. Many cells were fabricated to determine the optimum electrode and cell parameters to optimize the energy density, specific energy, power density and specific power of the cells. Cells were subjected to rate versus temperature discharge test regimes to determine capacity at various temperatures and rates from C/2 to 40C. Test results show a high energy lithium ion battery can be fabricated using Electro Energy wafer cells which will have a specific energy greater 200 Wh/kg and capable of greater than the C-rate. High power cells give greater than 120 Wh/kg and are capable of 2.5 KW/kg during continuous discharge at moderate temperatures. In addition, the battery is capable of much higher specific power than typical lithium ion batteries in use today. The battery design allows for increased discharge efficiency at high rates, compact packaging, and low manufacturing costs which will make available batteries capable of meeting DoD requirements of fast recharge, high temperature performance, higher energy density, cost effectiveness and safety in lithium ion batteries.

INTRODUCTION

With the increased use of rechargeable batteries in military applications, there exists a need for an, efficient, higher energy density and lower cost rechargeable battery technology with faster recharge and higher power capability. The performance requirements of advanced Department of Defense (DoD) applications can be met only with improved battery chemistries and advanced packaging technologies[2,3,4]. In this respect, lithium ion technology is of particular interest to the DoD due to its higher energy density, and potential for high power charge/discharge capabilities over a wide temperature range. It has been recognized that certain layered mixed metal oxides containing appropriate combinations of nickel and cobalt, nickel and manganese, or nickel, manganese and cobalt, are superior Li-ion battery cathode materials than the traditional lithium cobalt oxide, $LiCoO_2$, in terms of capacity and overall safety of the cell. Particularly noteworthy is $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC). This material has a reversible capacity of 170 - 180 mAh/g[1] versus ~140 mAh/g for $LiCoO_2$[1], and in the fully charged state it decomposes around 100ºC higher than $LiCoO_2$, at ~280ºC as opposed to ~180ºC for $LiCoO_2$. These properties translate into higher energy density Li-ion cells with improved safety characteristics. The NMC material has an optimum particle size, and particle size distribution, surface area and tap density in order to promote higher current as well as high capacity.

Electro Energy has focused on two designs implementing the NMC material. One design focuses on high energy the other on high power. The high energy design was implemented into a BB-x590 format for the Army (CERDEC). The high power design is in its initial stages and focuses on bringing a high power battery for aircraft applications which will function at very low temperatures, down to -40^{o}C.

HIGH ENERGY BB-X590 BATTERY

Electro Energy working with the Army (CERDEC) has constructed a BB-x590 battery that delivered greater than 9Ah of capacity and 271 Wh of energy at a C-rate discharge, with a potential for greater than 10 Ah and 300 Wh once the design is fully engineered.
The cathode material used was lithium nickel-cobalt-manganese oxide of the formula $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NMC). This cathode material was chosen for several reasons: it has a high reversible capacity of 140-150 mAh/g, it cycles for several hundred cycles, it is safer compared to other Li-Ion cathode materials, and it allows for substantial discharge rates at thick loadings.

Two different NMC materials were used in the battery builds. The NMC used for the initial batteries had an average particle size of 5-6 µm with a tap density of 1.78 g/ml. High rates were achievable using this material even at very heavy loadings, greater than 30 mg/cm2. The cathode material was changed to a more dense material for later batteries. This NMC had an average particle size of 5-6 µm with a tap density of 2.5 g/ml. This powder allowed for the same rate capability as the initial material, but electrodes had a higher density. This resulted in a battery with a higher energy density. The energy density of the cell increased from 450 Wh/l using the initial material to 480 Wh/l using the second material. The later batteries required shims to maintain compression on the cells which equated to around 5% of dead space in the battery. With a redesign, the battery would be approximately 9.7 Ah instead of 9.2 Ah obtained with the first material.

We also built one battery with lithiated nickel-cobalt-aluminum oxide, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), to compare its capacity with the NMC battery.

A standard polyolefin separator was used for the initial cells. Pursuant to safety studies with prototype cells, it was replaced a polyolefin/ceramic separator, which produced batteries with better safety characteristics. This separator has a ceramic coating which prevents shrinking of the polyolefin at elevated temperatures. The ceramic coating also raises the melt temperature of the separator hindering thermal runaway of the cells. Several studies were conducted to compare the rate capability of the polyolefin/ceramic separator to the standard polyolefin based material. It was determined the separator material does not limit the rate capability of our cells, especially at the rates required for the BB-2590.

EEI used a standard graphite anode, MCMB 6-28, in all cells. The MCMB 6-28 has a high reversible capacity of 300-330 mAh/g and allows for several hundred cycles. It has a low charge transfer over-potential, which allows for high rates at thick loadings.

A solution of 1 M $LiPF_6$ in a 1:1:1 EC:EMC:DEC solvent mixture was used as the electrolyte. It has a conductivity of greater than 10 mS/cm at room temperature, and allows for battery discharge down to –30 centigrade with good utilization.

CAPACITY

The capacity test of the nominal 28 V BB-x590 batteries was performed at room temperature. The battery consists of two sections each consisting of 4 Li-Ion wafer cells connected in series to form 14 V modules. The two sections can be connected either in series to produce a 28 V battery, or in parallel to produce a 14 V battery with twice the capacity as the 28 V battery. We tested the 28 V battery as follows. It was charged at a C/10 (0.9 Ampere) rate until the first cell reached 4.2 V when the battery was subjected to a constant voltage taper to C/20 rate. The baseline capacity was determined at a standard C/10 discharge rate. Figure 1 shows the beginning of life (BOL) discharge curve. The discharge was terminated when the first cell reached 2.8 V, which resulted in a capacity of 9.2 Ah for an energy of 271 Wh from the battery.

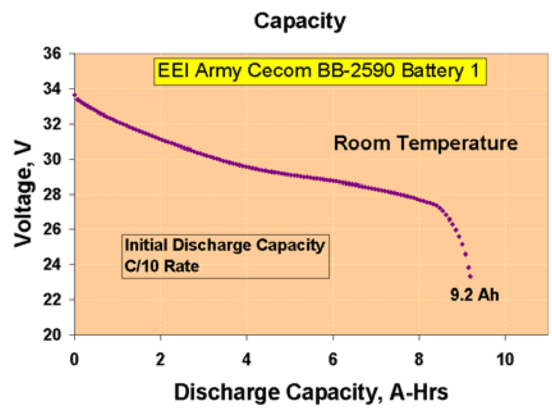

Figure 1. BOL Capacity of NCM Battery

Two additional capacity tests were performed at higher discharge rates. Figure 2 presents the standard C/10 discharge curve mentioned above along with the higher discharge rates of C/2 and C; or 4.5 A and 9 A discharges, respectively.

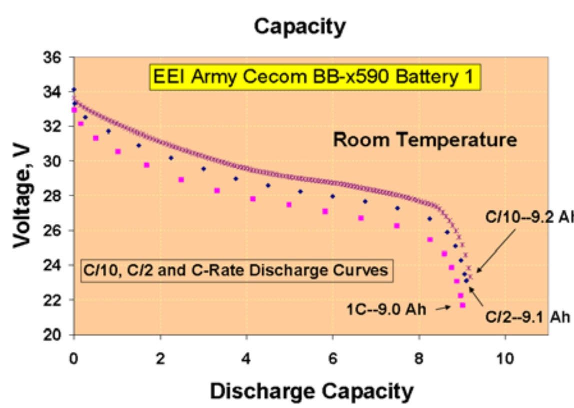

Figure 2. Capacity at Various Discharge Rates

these currents are significantly greater than the 2 A requirement, the higher rate capacities far exceed the minimum requirement of 6.0 Ah. In addition, the impact of the discharge rate within the range tested had little effect on deliverable capacity of our batttery.

The capacity of the NCA battery tested in the same way as described above is presented in Figure 3. The battery delivered a capacity of 10.1 Ah and an energy of 299 Wh. The NCA cells showed a high internal resistance and poorer rate capability than the NMC cells. There was also higher heat generation from this cell due to the high impedance of the cells.

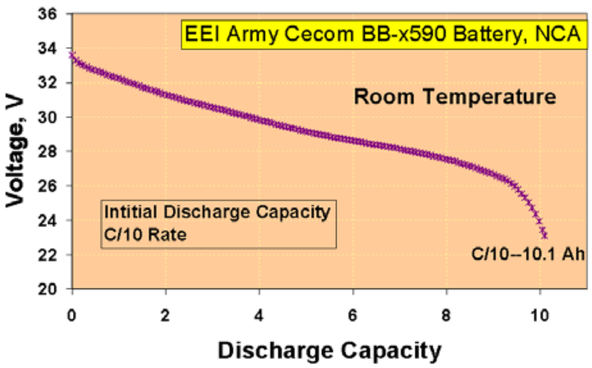

Figure 3. BOL Discharge Capacity of NCA Battery

CYCLE TEST

Continuous 100% depth of discharge (DOD) cycling was performed on Battery 1 at a C/2 (4.5A) discharge rate to a minimum cell voltage of 2.8V. Each discharge is followed by charge at the C/2 rate. Figure 4 presents the cycling data. There are over 500 cycles with a minimum capacity of 80% of the BOL capacity or 7.0 Ah.

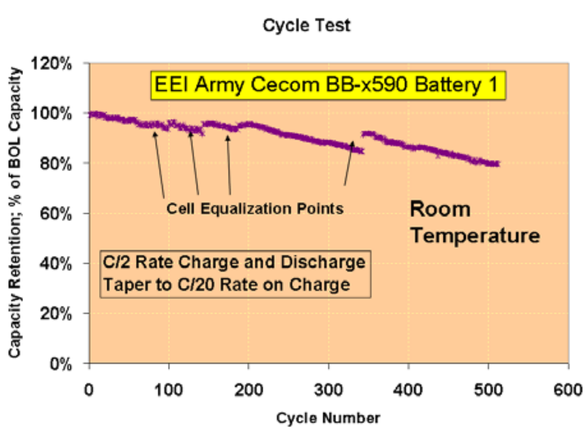

Figure 4. Cycle Test

The cycling was periodically interrupted to perform a cell balancing. The cell balancing consisted of a constant voltage (4.2V) top-off to C/20 charge on each individual cell.

Figure 5 shows the same data with the projected capacity retention had the cell balancing not taken place prior to 224 cycles. The projected capacity without cell balancing is 7.5 Ah, significantly above the 5.4 Ah requirement. Keep in mind, the above discharge rate was at 4.5A, exceeding the 2A requirement.

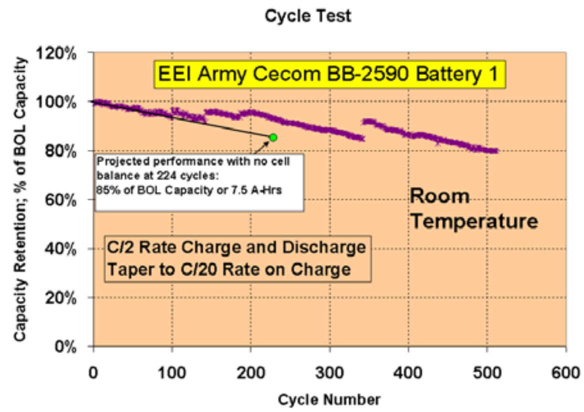

Figure 5. Projected 224 Cycle Capacity

HIGH RATE DISCHARGE

The high rate discharge was performed as described in the MIL-PRF-BBx590 specification. The 28 V volt battery was discharged at 10 A until the battery voltage reached 20 V. The battery yielded 9.0 Ah (97.8% of C/10 the discharge capacity) to a battery cut-off voltage of 21.7V (the electronics would not allow for a discharge below 21.7V), well above the 5.2 Ah requirement. Figure 6 shows the data for the high rate discharge.

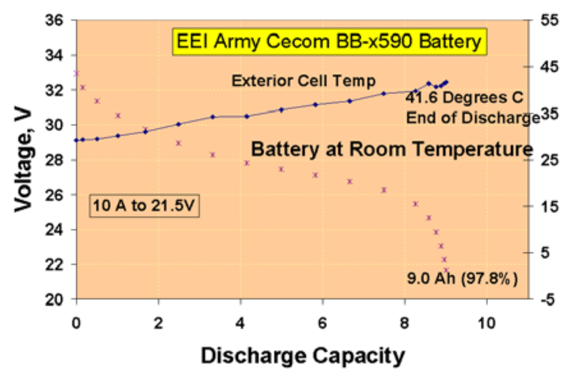

Figure 6. High Rate Discharge

The battery heats up very quickly at a 1C discharge rate. The end of discharge temperature for the battery was 41.6 degrees Celsius at the exterior of the cells. The rapid rise in temperature is due to resistance within the cell and the confined space of the cell in the container. The internal resistance of the cell is largely due to the thick electrodes creating a very large concentration polarization within the cell. The data in Figure 6 shows the temperature rise of the cell over the 1C discharge.

LOW TEMPERATURE DISCHARGE

The low temperature discharge was performed as described in the MIL-PRF-32052 specification. The ambient temperature was reduced to -30ºC and held until the battery also reached -30ºC (+/-1C).

Two low temperature discharges were performed at C/5 rate until the first cell reached 2.25V. In the first case the battery was un-insinuated from the -30ºC environment. Figure 7 shows the data for this case.

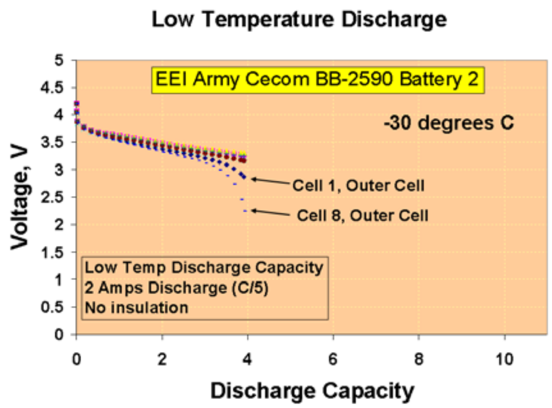

Figure 7. Un-insulated -30C Discharge Test

In the second case the cell was wrapped in insulation. The discharge curves are shown in Figure 8 along with the uninsulated discharge curves.

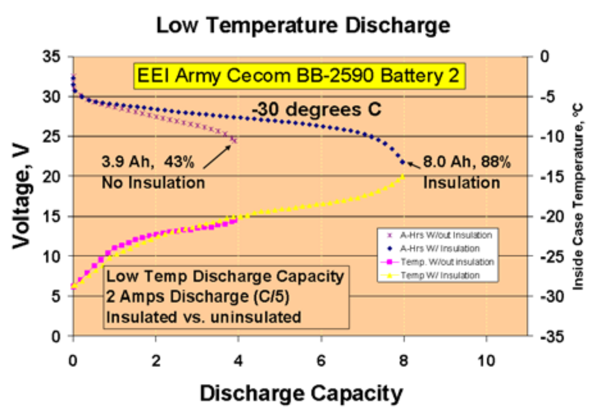

Figure 8. Insulated -30C Discharge Test

Some of the significant difference in capacity is a result of terminating the discharge based on cell voltage as opposed to overall battery voltage. Based on individual cell voltages, it is clear the cell-to-cell temperature variation was significantly greater in the uninsulated case. Figure 9 shows the individual cell voltage during the discharge. Cells# 1 and 8 are on the outside of the pack, adjacent to the un-insulated case wall and are unable to take full advantage of internal heating due to self-heating from the discharge.

Figure 9 shows the cell voltages during the insulated discharge. The insulation results in a more uniform cell-to-cell temperature, allowing the exterior #1 and 8 cells to retain more heat and continue the discharge to 8.0 Ah's.

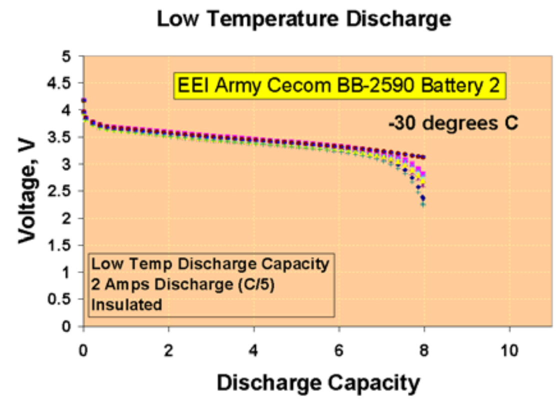

Figure 9. Insulated Cell Voltages

PULSE DISCHARGE

The pulse discharge test was performed as described in the MIL-PRF-32052 specification. The 28 V battery was discharged at 18 Amperes for 5 seconds and then allowed to rest for 25 seconds as shown in Figure 10. This cycle was repeated until the battery reached 18V (tests at EEI were stopped due to the electronics board, which did not allow the battery voltage to drop below 23.1 Volts).

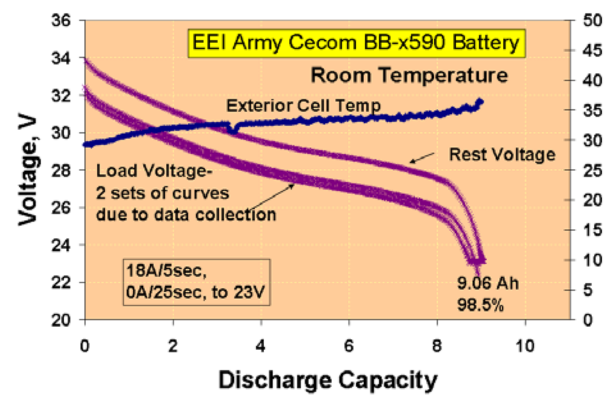

Figure 10. Pulse Discharge

HIGH POWER BATTERY

Initial cells have been constructed for design of a high power lithium ion battery. NMC was chosen as the cathode material because it is capable of very high rates, safer compared to $LiCoO_2$, and is a high energy material. High capacity, 5.5 Ah, cells were tested for power, energy and cycle life. Figure x shows the discharge of a 5.5 Ah high power cell. Cells had a specific energy of 120 Wh/kg, and were capable of 20C continuous rates and 5 second pulses of 40C.

Figure 11 shows the discharge curves of EEI's 5.5 Ah cell. Cells were capable of 2.5 kW/kg continuous power with pulse power greater than 4 kW/kg. With further engineering, EEI hopes to build cells exceeding 4 kW/kg of continuous power while in a cell greater than 120 Wh/kg.

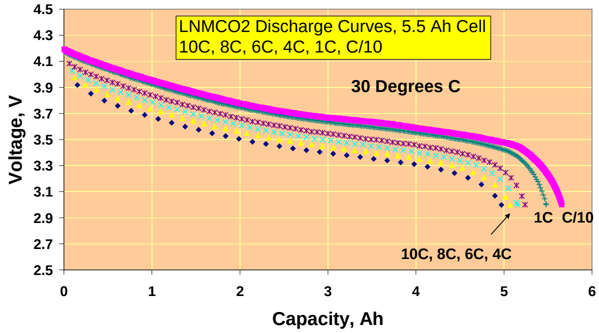

Figure 11. Discharge Curves of High Power 5.5 Ah Cell

Figure 12 shows the C-rate cycle life of Electro Energy's high power cell. Cells cycle over 1500 cycles before reaching 80% of initial capacity.

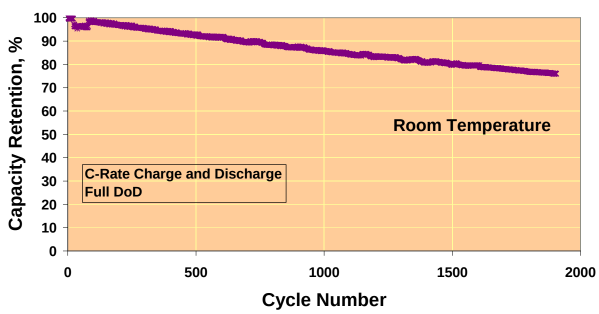

Figure 12. Cycle Life of EEI's 5.5 Ah cell

CONCLUSIONS

The BB-x590 developed by EEI showed a battery with an energy density of 271 Wh with the possibility of further improvement. The battery proved to have high rate capability, good low temperature performance, improved cycle life and have good safety characteristics. All electrochemical tests exceeded Army's requirements by a substantial margin.

Electro Energy's power cell gave greater than 2.5 kW/kg of continuous power with cells that were greater than 120 Wh/kg. With further development, Electro Energy hopes to exceed 4 kW/kg of continuous power in a cell that is greater than 120 Wh/kg and implement this into a high performance aircraft battery.

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