

Development of Lithium-Ion Batteries for Naval Aviation Applications

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ABSTRACT

Experimental Lithium-ion (Li-ion) cells were constructed with three different types of Li-ion cathode materials and two different graphitic anodes. The cathode materials were lithium nickel cobalt aluminum oxide, $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA), lithium nickel cobalt manganese oxide, $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM), and lithium iron phosphate, LiFePO_4 (FEP). The two graphitic anodes differed only in particle size. The cells were built in lots identified by their cathode and anode materials. The goal was to develop a battery for Naval Aviation applications. Initial testing favored the cells built with an NCM cathode. Further testing was per MIL-PRF-8565/14(AS) with Amendment 1, which resulted in a reduced voltage range during testing favoring the NCA lots. The cells were tested under two different types of cycle life conditions. In both cases, the NCA lots fared best. The NCA lots also had the lowest DC Resistance (DC Res) results (both $\leq 10 \text{ m}\Omega$). One NCA lot experienced no loss in discharge capacity at -20°C after cycling at 70°C , and little loss (-6.5%) after storage at 85°C . That NCA lot was selected for the developmental battery build.

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INTRODUCTION

Lithium-ion (Li-ion) batteries continue to be selected as the battery of choice for a wide variety of applications, both military and commercial. Of the many reasons, the fact that Li-ion refers to a class of battery chemistries that utilize the energy resulting from the shuttling of a Li^+ between the anode and cathode materials, instead of the elementary redox reactions present in battery systems with pure metallic electrodes, leads to a wide variety of performance characteristics that can be tailored to specific applications. High power, high energy, safety, long cycle life, thermal stability, low temperature performance, and operating voltage range are all dependent upon the selection of the electrode materials, separator and electrolyte.

Li-ion batteries being developed for naval aircraft need to have all of the above characteristics, but some characteristics are more important than others. The specific battery being developed is Navy part number D8565/14-1, a medium rate, maintenance-free, 24 V, 15 Ah aircraft storage battery. It is roughly 40 lbs. and ~11 inches long, ~6 inches tall and ~7 inches wide. Per its description, mass and dimensions, the battery requires neither the highest power nor the highest energy density, gravimetric or volumetric. The battery does have a wide operating temperature range of -40°C to $+68^\circ\text{C}$.

Operation at either end of the temperature range is not difficult for many battery systems. Maintaining good low temperature performance after extended cycling at high temperature is a more difficult task for any battery system.

To develop, test and select the most ideal Li-ion chemistry, a number of different cathodes and anodes were manufactured and constructed in experimental stainless steel hardware, designated NCP7. Previous work had been completed in earlier programs with the Navy that developed more thermally stable electrode formulations with mixed metal oxide cathodes and graphitic anodes [1]. Those electrode formulations were applied to three different Li-ion chemistries for the current development effort: NCA, NCM, and FEP.

EXPERIMENTAL

Hardware

The NCP7 hardware used to construct cells designated INCP 53/26/92 normally ranges in capacity from 9 Ah for high energy applications to 5 Ah for high power applications. In this experiment, a reduced number of electrodes were used to construct the cells, detailed below in [Table 1](#). Polypropylene shims were used to fill the void volume in the cell case and allow proper stack pressure to be applied to the

cells during testing. All cells utilized the same commercial polyolefin separator. All cells had the same number of pairs of electrodes and were filled with the same amount and type of electrolyte. The NCA and NCM cells used the same percentages of cathode active material, binder and diluents. The NCM cells had a heavier cathode plate weight compared to the NCA cells to account for the lower cathode utilization of NCM. The FEP cells had a heavier weight loading than NCM, a higher percentage of active material and binder, and used more of the higher surface area conductive diluents to account for lower cathode utilization and poorer intra-electrode conductivity of FEP. This was all done in an attempt to normalize the capacity of the cathode plates. There were two types of graphitic anodes manufactured. The only difference was the mean diameter of the anode active material particle size. The cells were rated at 2 Ah for purposes of establishing the 1C rate. Five cells were constructed and tested for each lot. The cathode materials identified as NCM#1 and NCM#2 represent materials with the same chemical formula from different manufacturers. Anode material A1 has a larger particle size than material A2.

Table 1. Cell Lot Identification.

Lot	Cathode	Anode
1	NCA	A1
2	NCM#1	A1
3	NCM#2	A1
4	FEP	A1
5	NCA	A2
6	NCM#1	A2
7	NCM#2	A2
8	FEP	A2

Initial Testing

All of the cells performed the same initial testing to characterize cell performance. Afterwards, the cell lots were split into two groups to test according to two different styles of cycle life testing. The initial formation and cell acceptance testing (CAT) were at the same C-rates and temperatures listed below in [Table 2](#), but the voltage ranges were tailored to the specific chemistries of the cell lots. Lots 1 and 5 (NCA) were cycled from 4.1 V to 3.0 V. Lots 2, 3, 6 and 7 (NCM) were cycled from 4.2 V to 3.0 V. Lots 4 and 8 (FEP) were cycled from 3.65 V to 2.5 V. All charges were constant current up to the voltage limit where the charge was switched to constant voltage and the current was allowed to taper to C/50 before ending the charge. A DC Res test was performed during Cycles 5 and 16. After 50% of the rated capacity is removed at the C/5 rate, a one second, 1C pulse is applied to the cell. Using Ohm's Law ($V=IR$), the effective resistance is calculated by dividing the change in the voltage by the change in the current at the end of the one second pulse. DC Res tests were used throughout testing to track the increase in resistance of the cell during its life. A 72 hour Stand Test was

performed during Cycle 17. Cells rest for 72 hours between charge and discharge to assess the self discharge rate of the cell.

Table 2. Formation and CAT.

Cycle	Regime Charge - Discharge	Temp. °C	Description
1	C/20-C/20	25	Formation
2 - 3	C/10-C/10	25	Formation
4	C/5-C/5	20	CAT
5	C/5-C/5	20	DC Res
6 - 9	C/5-C/5	20	CAT
10 - 12	C/5-C/2	20	CAT
13 - 15	C/5-1C	20	CAT
16	C/5-C/5	20	DC Res
17	C/5-C/5	20	72 hour Stand

Following formation and CAT, all cells performed a number of tests per MIL-PRF-8565/14(AS) with Amendment 1, "Figure 3: Aircraft battery discharge profile requirements." The discharge currents in the test were scaled for testing the NCP7 cells, which are 1/15th of the predicted capacity of the battery, and presented below in [Table 3](#). The testing also included Step 14, an additional 37 seconds at the end of the test called out for all qualification testing. Step 10, at 5 A for 10 seconds, was consistently the step for which the cells experienced the largest voltage drop. For that reason, all test data per [Table 3](#) above presented in this paper will consist of only the cell voltage at the end of Step 10, multiplied by the number of cells in series that would be used to make a battery from that given lot, i.e. seven cell for lots 1, 2, 3, 5, 6, and 8 and eight cells for lots 4 and 8. For cycle 18, the cells were charged at C/5, rested for 15 minutes, and discharged per [Table 3](#), all at 20°C. For cycle 19, the cells were charge at C/5 and 20°C. The temperature chamber was set to -20°C, and the cells equilibrated for 8 hours at -20°C before discharging per [Table 3](#).

Table 3. 8565/14 Fig. 3 Scaled Testing Profile.

Step	Current (A)	Time (s)
1	4.33	15
2	5.00	10
3	2.00	35
4	0.20	290
5	2.00	50
6	0.20	60
7	2.00	60
8	0.20	320
9	2.00	30
10	5.00	10
11	2.00	30
12	2.33	60
13	2.67	73
14	2.67	37

Modified Qualification Testing (Qual)

Following the testing per [Table 3](#), the cell lots were split into two groups for further testing. Three cells from each lot were assigned to perform testing based on MIL-PRF-8565/14(AS) with Amendment 1, "[Table I](#): Qualification inspection and conformance inspection of batteries." The testing for full batteries includes a large amount of dynamics testing to qualify hardware that is not applicable to individual cell testing. The testing of the NCP7 cells focused on the 400 cycles of discharge-charge-rest at three temperatures: 24°C, 43°C and -18°C. From this point on, the cells were cycled according to the battery voltage limits set out in MIL-PRF-8565/14(AS) with Amendment 1, 28.25 V to 20.00 V. The NCA and NCM cells would be used to make a battery with seven cells connected in series. Each cell could cycle from 4.036 V to 2.857 V. The FEP cells would be used to make a battery with eight cells connected in series. Each cell could cycle from 3.531 V to 2.50 V. Prior to starting the 400 cycle qualification cycles, the cells performed a capacity check cycle at 24°C. The cells were charged for 2 hours at 3.33 A to their upper voltage limit where the current was allowed to taper, in many cases to 0.0 A, until the two hours was complete. This is how charges were conducted during all subsequent testing. The cells were discharged at 1 A to their lower voltage limit. Afterwards, the cells performed a number of cycles based on aircraft loads and some high and low temperature charge testing. Once those tests were complete, the cells were equilibrated at 24°C and charged. The cells then began the 400 cycle testing. Each cycle begins with the cell discharging per [Table 3](#) above (18 minutes). The cells were charged (2 hours). The cells rested for one hour and 42 minutes. This four hour cycle was repeated for a total of 25 cycles at 24°C. The cells were then equilibrated at 43°C before another 25 cycles were completed. The cells were then equilibrated at -18°C before another 25 cycles were complete. This sequence of 25 cycles at each of the three temperatures was repeated until 400 cycles were complete, ending at 24°C. The cells were then discharged at 1 A to their lower voltage limit. To complete the testing, a final capacity check cycle was performed identical to the cycle performed prior to the start of the 400 qualification cycles.

Variable Temperature Cycle Life Testing

The remaining two cells from each lot were assigned to perform variable temperature cycle life testing. These cells were also cycled according to the battery voltage limits set out in MIL-PRF-8565/14(AS) with Amendment 1, as stated in the paragraph above. All charges were constant current up to the voltage limit where the charge was switched to constant voltage and the current was allowed to taper to C/50 before ending the charge. Variable temperature cycle life testing is described below in [Table 4](#). Cycle 22 was a DC Res test to establish the initial DC Res prior to life testing. After 50% of the rated capacity is removed at the C/2 rate, a one

second, 2C pulse is applied to the cell. Every time the temperature was changed, the cells were equilibrated for eight hours at the new temperature before testing was resumed. The repetition of three cycles at -20°C allows data for comparison of low temperature performance before and after each excursion at higher temperatures. Life testing at 25°C or 70°C consists of rounds of five cycles. The first four cycles are at C/2. The fifth cycle is a DC Res test as described earlier in this paragraph. Cycle 135 is a stand test similar to the 72 hour test performed during CAT. The cells were equilibrated at 85°C, charged, allowed to rest for 168 hours, and discharged. The final five cycles are the same as a round of five life cycles described earlier in this paragraph.

Table 4. Variable Temperature Cycle Life Testing.

Cycle	Regime Charge - Discharge	Temp °C	Description
22	C/2 & DC Res	25	Baseline
23 - 25	C/5-C/2	-20	Low Temp
26 - 75	C/2 & DC Res	25	25°C Life
76 - 78	C/5-C/2	-20	Low Temp
79 - 103	C/2 & DC Res	70	70°C Life #1
104 - 106	C/5-C/2	-20	Low Temp
107 - 131	C/2 & DC Res	70	70°C Life #2
132 - 134	C/5-C/2	-20	Low Temp
135	C/5-C/5	85	1 week Stand
136 - 138	C/5-C/2	-20	Low Temp
139 - 143	C/2 & DC Res	25	End

RESULTS

Initial Testing Results

Below is a plot of the mean discharge capacity for each lot of five cells during formation and CAT. Lots 1 and 5 (NCA) exhibit the highest capacity. Lots 2, 3, 6 and 7 (NCM) deliver slightly less capacity. Lots 3 and 7 (NCM#2) delivers less capacity compared to NCM#1 at the 1C rate. Lots 4 and 8 (FEP) deliver the least capacity. Although attempts were made to match the utilization of the cathode materials to normalize the capacities of the cells, the fact that FEP electrodes have a lower specific capacity, both gravimetric and volumetric, means that FEP cells with the same volume or mass compared to either NCA or NCM will have a lower capacity.

The capacities of cycles 5 and 16 are not reported in the figure above. Instead, the DC Res of the cells is determined during those cycles. Below is a chart of the mean DC Res, including error bars that represent one standard deviation. Lots 1 and 5 exhibit the lowest resistance. Lots 2, 3, 6 and 7 have slightly higher resistances. Lots 4 and 8 have the highest mean resistances. The cell lots with the smaller anode particle (5, 6, 7 and 8) have lower resistances, as expected, compared