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Design and development of A 20 Ah Li-ion prismatic cell

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Abstract

Yardney Technical Products has undertaken a program to develop large scale, 20 Ah size, lithium-ion cells for military and aerospace applications. A space efficient and adaptable parallel-plate prismatic design has been chosen for this program. Using advanced, energy dense materials, 20 Ah cells with a specific energy of 123 Wh/kg and energy density of 326 Wh/1 have been produced. Many of the design parameters for these cells were optimized using statistical design experiments with smaller test cells. These design experiments allowed the identification and optimization of important parameters in far less time than would have been required by standard, iterative, experimentation. Optimization of rate capability and extended life cycling were the primary objectives for these experiments. High discharge rates up to 2 C and extended, 100% DOD, life cycling to greater than 2000 cycles have been achieved.

Keywords: Lithium-ion batteries; $LiNi_{1-x}Co_xO_2$; Mesocarbon microbeads

1. Introduction

Continued growth in the commercial market for lithium-ion batteries demonstrates the range of options for these high energy density power sources. This success has contributed to the increasing interest in the development of similar technologies for military and aerospace applications. Such applications have much more demanding requirements in terms of reliability, total capacity, power delivery, battery life, and operating temperatures than found in the commercial arena.

Yardney Technical Products has begun a program to design and develop 20 Ah Li-ion battery technology for evaluation in numerous USAF and aerospace applications. The goal of this program was to develop a technology that delivered, at the cell level, a specific energy > 150 Wh/kg and energy density > 300 Wh/l. The desired operating temperatures for the system ranged from -40°C to $+65$°C. High rate capability was a prime consideration with the battery operating at a normal charge rate of C/3 and discharge at a 2 C/3 rate; a maximum discharge rate of 2 C was also required. For utilization in many long-life applications it was desirable that the battery could deliver > 80% of its initial capacity for more than 1000, 100% DOD cycles.

A parallel plate prismatic design was chosen for this development project as it offers a number of advantages over other designs such as cylindrical or flat-mandrel wound construction. A true prismatic design utilizes available space more efficiently and is easily scaleable for different size requirements. Thermal management in larger cells is simplified in this design, as the high heat conductivity of the electrode substrates allows the plates to act as fins, drawing the generated heat out to the edges of the cell stack. The uniformity of current density is also better in a prismatic design, thus lowering the polarization of the electrodes. Due to the high rate requirements of this program, both thermal management and current distribution were important considerations.

The chemistry for those cells was specially developed to achieve the performance goals. Standard commercially available cells typically use either $LiCoO_2$ or a $LiMn_2O_4$ cathode active material. $LiNiO_2$, which is iso-structural with $LiCoO_2$, has been widely investigated as well, but problems with stability and synthesis have precluded its full commercial development [1]. To reduce the cost factors associated with $LiCoO_2$ and the stability and synthesis problems of the $LiNiO_2$, solid solutions of these materials

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Table 1
Design experiment matrix layout for determining effects of separator choice, electrode porosity, and C:A ratio

Standard run	Separator	Cathode porosity	Anode porosity	C:A ratio
1	Celgard	Low	Low	1.25
2	2400			1.5
3			High	1.25
4				1.5
5		High	Low	1.25
6				1.5
7			High	1.25
8				1.5
9	UHMW-PE	Low	Low	1.25
10				1.5
11			High	1.25
12				1.5
13		High	Low	1.25
14				1.5
15			High	1.25
16				1.5
17		Low	Low	1.50
18				2.00
19			High	1.50
20				2.00
21		High	Low	1.50
22				2.00
23				1.66
24			High	1.50
25				2.00
26				1.66

have been developed and shown to provide excellent performance [2]. These cells utilize a commercially obtained advanced $LiNi_{1-x}Co_xO_2$ cathode material that provides a high specific capacity of greater than 150 mAh/g. A commercially produced mesocarbon microbead (MCMB) graphitized carbon material was chosen for the anode as it has demonstrated a flat discharge potential, high capacity and excellent rate capability [3]. Other important design considerations, such as C:A ratio, electrode porosity, and separator material were investigated in a partial factorial design experiment. Design experiment methods allowed for the statistical analysis of the effects and interactions of important factors not possible with standard, iterative, experimentation [4]. Such interactions are increasingly important for complex systems such as Li-ion batteries. This type of experimentation therefor, reduces the number of experiments needed and improves the robustness of the design. For reasons of cost and convenience, design development testing was carried out using ~3.5 Ah size cells in sealed polypropylene cases. To improve hermeticity and structural strength, the 20 Ah prototype cells were manufactured in welded stainless steel cases with Glass to Metal seal terminal feedthroughs and a fill port designed to allow vacuum filling with the electrolyte.

2. Experimental

2.1. Test cell construction

Test cells of ~3.5 Ah capacity in polypropylene cases were manufactured for the design experiment. Anode and cathode material slurries were coated on to substrate foils, copper and aluminum respectively, using a continuous coating machine by the knife-over-roll method. Cells were vacuum filled with a predetermined amount of 1 M $LiPF_6$ in 1:1 EC/DMC electrolyte.

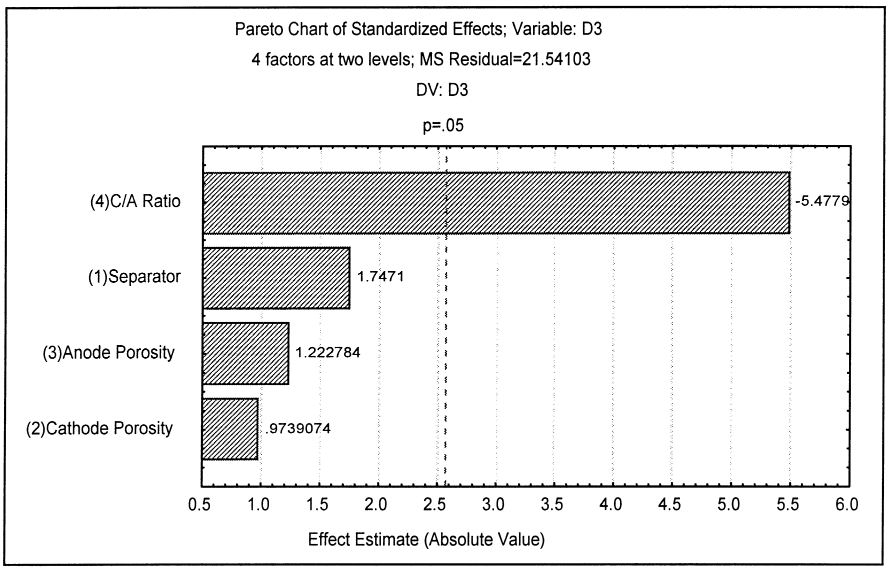

Fig. 1. Pareto chart of effects with respect to discharge capacity at 3 mA/cm^2. Effects with a p value greater than 0.05 are statistically significant, in this case only the C:A ratio shows a statistical significance.

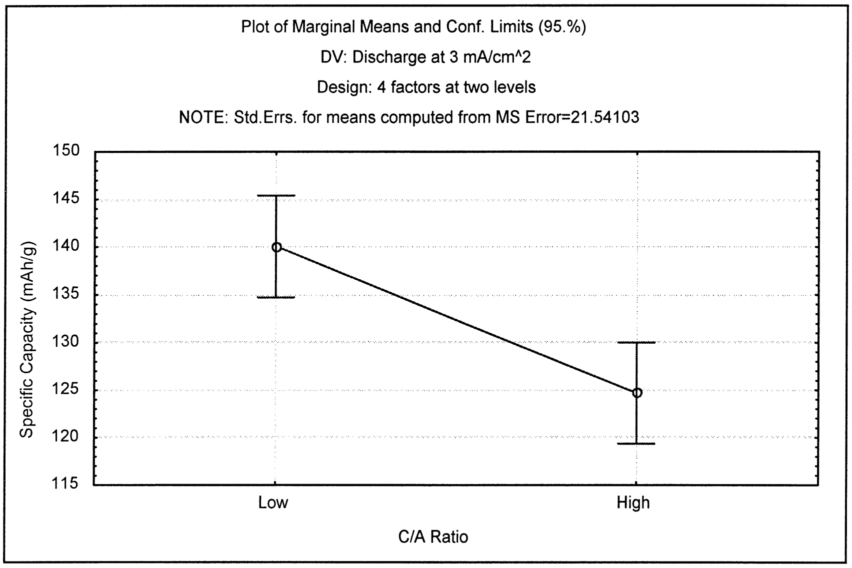

Fig. 2. Marginal means plot of C:A ratio showing improved performance with lower C/A ratio.

2.2. Design experiment

The experiment was designed to investigate three factors at two levels each (2 × 3 design) (Table 1). Celgard 2400 and an ultrahigh molecular weight polyethylene (UHMW-PE) were the candidate separator materials. The UHMW-PE material has a much higher porosity and electrolyte wettability than the Celgard, however, the puncture resistance of the two materials is similar. The UHMW-PE is also mechanically favorable due to improved heat-sealing properties. Two levels of both anode and cathode porosity were investigated. Weight loading of the electrodes was held constant and porosity was adjusted by compression. The third factor of interest was the C:A ratio. Two levels were initially investigated, with three other levels subsequently added. In all cases, the weight loading of the anode was maintained constant, the weight loading of the cathode was varied to obtain the desired ratios.

2.3. Design matrix testing

Cell formation involved one cycle at a C/20 rate charge and discharge, followed by three cycles at C/10 rate charge and discharge, all charge steps included a

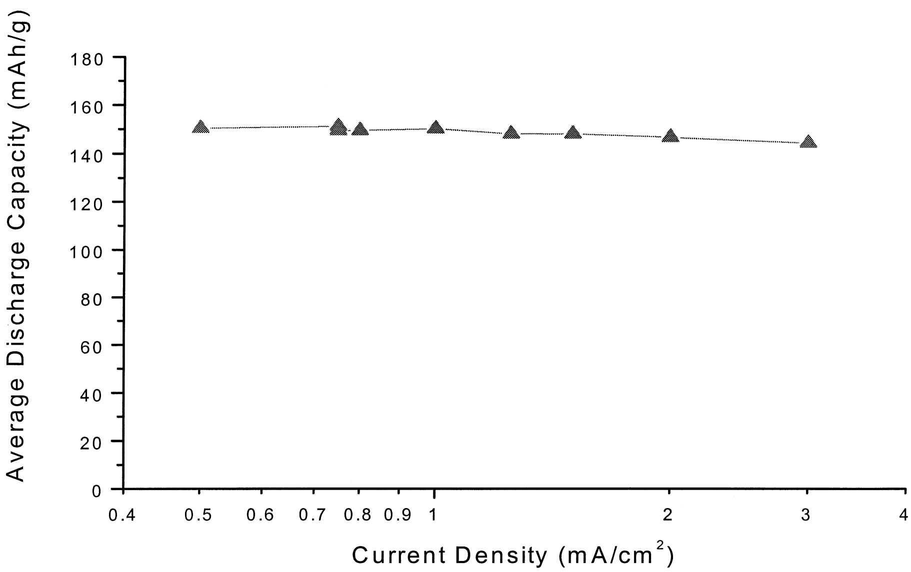

Fig. 3. Rate capability cycling of a cell with the statistically preferred low C:A ratio. Points are average values of 3 cycles at each current density.

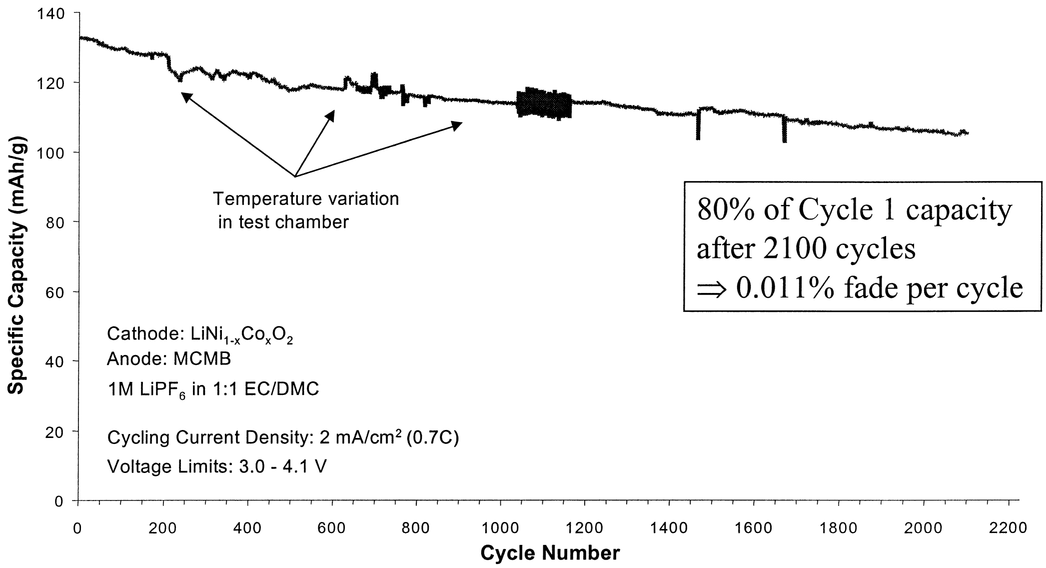

Fig. 4. Life cycle testing of 3.5 Ah developmental cell at charge and discharge current density of 2 mA/cm^2.

constant voltage taper charge to C/100. All cycles were charged to 4.1 V and discharged to 3.0 V. The cells were in a vented state during formation. After formation, the cells were sealed and underwent rate capability testing. Cells were charged at a C/5 rate to 4.1 V with no taper charge, then discharged at current densities of 0.5, 0.75, 0.8, 1.0, 1.25, 1.5, 2.0, and 3.0 mA/cm^2 to 3.0 V. Three cycles at each current density were performed. Cells were also evaluated for life cycle performance. The cells were cycled at a current density of either 1 or 2 mA/cm^2 for both charge and discharge, with no taper charge or OC rest between cycles.

2.4. Ah cell construction and testing

The final design of the 20 Ah Li-ion prismatic cells was refined after examination of the data from the test matrix. Electrode composition, porosity and C:A Ratio were all determined from the test cell data discussed below. These cells were sealed in welded stainless steel cases and vacuum filled with the same electrolyte. Again, the cells were

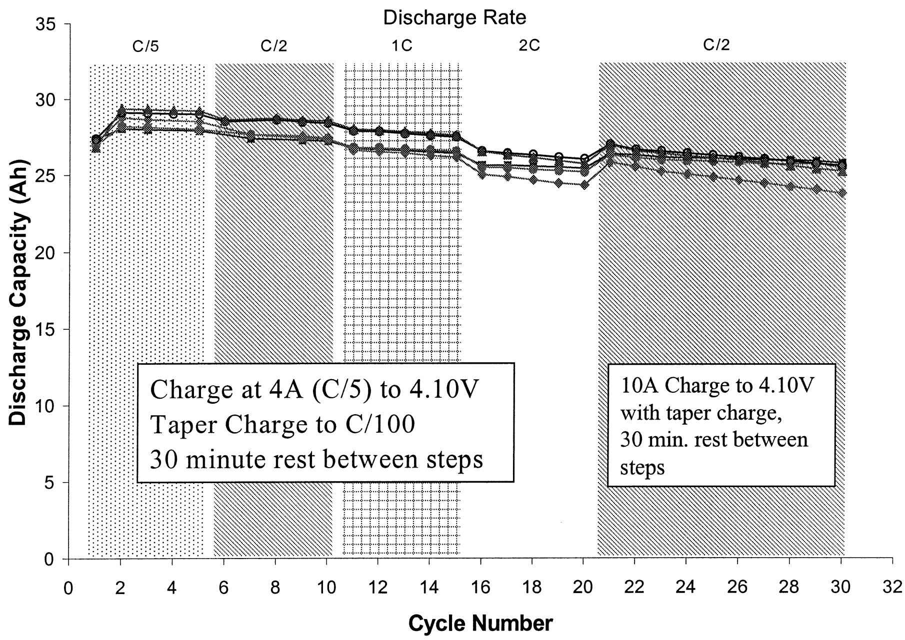

Fig. 5. Rate performance of 20 Ah Li-ion prismatic cells.

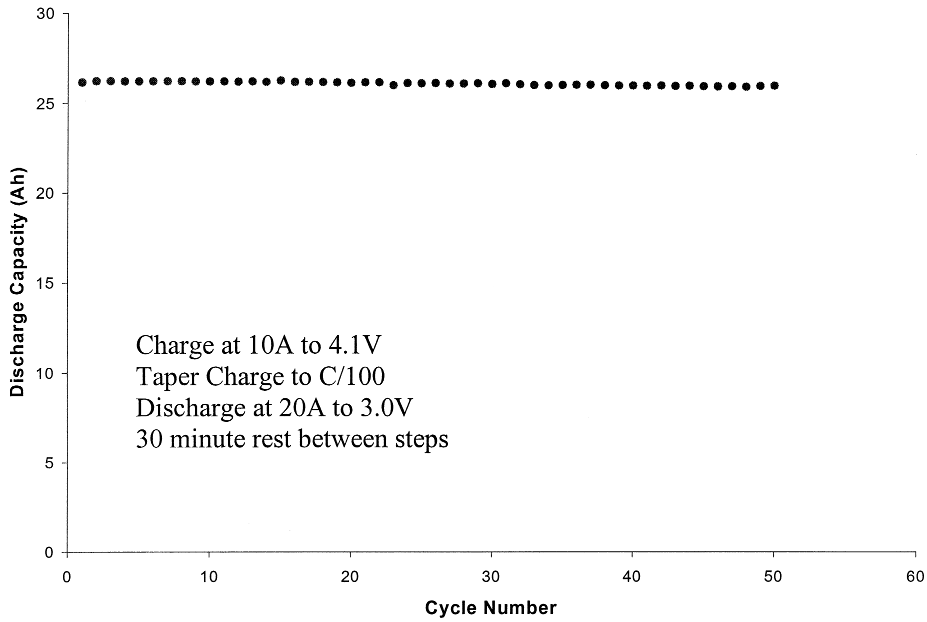

Fig. 6. Life cycle testing of 20 Ah Li-ion prismatic cell.

formed in a vented state, following the procedure described above. Selected cells then underwent rate capability and life cycle testing. For rate capability testing, the cells were charged at a C/5 rate to 4.1 V, with a follow on taper charge at a constant 4.1 V until the current fell below 0.25 A. They were then discharged at rates of C/5, C/2, 1 C and 2 C; five cycles were performed at each rate. The charge rate was also increased for the last 10 cycles with both charge and discharge at a C/2 rate. All cycles were discharged to 3.0 V, 100% DoD. Accelerated life cycle testing was performed by charging at the C/2 rate, with a taper charge at 4.1 V, followed by a C-rate discharge to 3.0 V.

3. Results and discussion

Statistical analysis of the design experiment data revealed that the C/A ratio was the only statistically significant factor in the cell performance (Fig. 1). A lower C:A

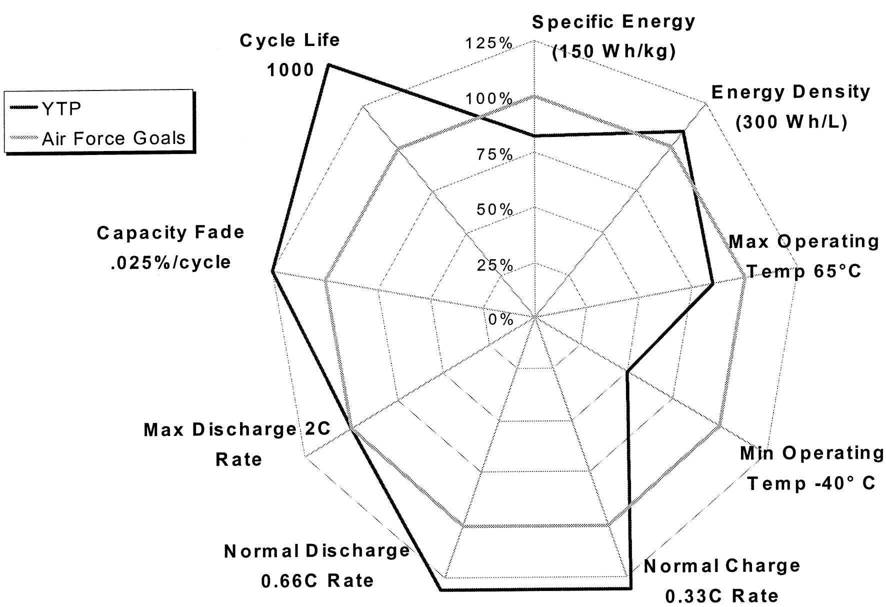

Fig. 7. Comparison of USAF program goals with demonstrated achievements.

ratio was preferred (Fig. 2). Rate capability testing showed practically no decline in the delivered capacity up to a discharge current density of 3 mA/cm^2 (Fig. 3). The other factors, such as electrode porosity and separator material, had no statistically significant effect on the overall cell performance. However, slight differences can be discerned and used in the final cell design. For primarily mechanical processing reasons, the UHMW-PE material was chosen for the construction of the 20 Ah cells; and, based on other experimental data, a high cathode porosity, and moderate anode porosity were used for the electrode fabrication. The overall performance of these design experiment cells was encouraging, with several cells delivering more than 2000 cycles with greater than 80% capacity retention (Fig. 4).

Prototype 20 Ah Li-ion prismatic cells were constructed using the refinements determined from the designed experiment, they also underwent rate capability and life cycle testing. Fig. 5 shows the discharge capacity of selected cells. These cells demonstrated good capacity retention up to discharge rates of 2 C. Capacity was also not significantly effected by increasing the charge rate to C/2. This performance exceeds the rate capability goals set out by the USAF for this program. Life cycle testing of the 20 Ah cells also demonstrated exceptional performance. Over 50 cycles of high rate charge (C/2) and discharge (C) cycling have been completed to date, these cells show practically no capacity fade (Fig. 6). These life-cycling tests are continuing; however, based on the performance of the 3.5 Ah test cells, which provided more than 2000 cycles with this chemistry, we predict that these cells should exceed the 1000-cycle requirement.

4. Conclusions

YTP has successfully undertaken a program to design and develop a 20 Ah Li-ion prismatic cell; the current prototype has succeeded in meeting or exceeding many of the initial goals set out by the USAF, see Fig. 7. These cells demonstrate high energy density, 326 Wh/l, and specific energy, 123 Wh/kg. It should be noted however, that, in the interest of expediting the manufacture of these cells, several of the construction components have not yet been optimized. Both the cell case and cover are currently being redesigned to minimize weight and volume; the glass to metal seals are similarly being refined. Further, with the recent addition of a production-size coating line, YTP has acquired the ability to coat electrodes onto much thinner substrate foils. Using a thinner copper foil alone would reduce the total weight of the cell by almost 10%. It is also important to note that extensive testing of performance at high and low temperatures has not yet been carried out. YTP is currently investigating several candidate electrolytes reported to have improved temperature performance, and work is continuing to determine the full temperature window for required performance.

Acknowledgements

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