ADVANCED LITHIUM-ION POLYMER BATTERY DEVELOPMENT

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Abstract

The team of Ultralife Batteries, Inc. (UBI), Eagle-Picher Technologies, LLC., Lockheed Martin Missiles & Space (LMMS), Sandia National Laboratories (SNL), and Argonne National Laboratories (ANL) have been advancing the development of lithium-ion polymer batteries. Under the National Institute for Standards and Technology's Advanced Technology Program SNL and ANL have developed and produced high energy density anode and cathode active materials that will increase the specific energy of battery cells to 200 Wh/kg. UBI has incorporated these new materials into electrode laminate and cells. Using this new laminate, EPT worked to develop cells and batteries for aerospace applications while LMSS tested the cells and designed and developed advanced battery charge management controller technology to apply this use in launcher and satellite applications. This paper reviews the battery cell material and battery charge management technical advances of this program and identifies significant areas for further engineering and manufacturing development.

Introduction

Ultralife Batteries, Inc., Eagle-Picher Technologies and Lockheed Martin Missiles & Space were awarded a Joint Venture Advanced Technology Program (ATP) entitled "Advanced Lithium Solid Polymer Battery Development" from the U.S. Department of Commerce National Institute of Standards and Technology in 1998. The main objective was to develop, manufacture, and market a new generation of lithium-ion polymer cells and battery packs for portable electronic and aerospace applications. Objectives for consumer applications such as wireless communications devices and mobile computers were a specific energy greater than 200 Wh/kg, energy density greater than 350 Wh/l, and cycle life greater than 2000 cycles at 100% depth of discharge. Objectives for aerospace applications were a specific energy greater than 200 Wh/kg, energy density greater than 475 Wh/l, and cycle life greater than 35,000 cycles at 25% depth of discharge typical of the requirement for a low earth-orbit satellite. Objectives were at the cell level and significantly greater than then current commercial technology for lithium-ion cells. Most offerings were cylindrical and prismatic $LiCoO_2$-based chemistry using a liquid electrolyte system and metal housings averaging about 125 Wh/kg and 300 Wh/l [1]. Ultralife was the first company to supply commercial quantities of lithium-ion polymer cells in 1997 [2]. Those cells used $Li_{1+x}Mn_{2-x}O_4$ chemistry and foil laminate packaging and had energy densities of about 120 Wh/kg and 200 Wh/l.

The overall ATP development program consisted of four components: materials technology, cell and process engineering, battery engineering, and charge management and integration. Each joint venture partner brought unique strengths to the program. Ultralife is a leader in the development, manufacturing and marketing of lithium battery technology. Ultralife planned to subcontract development and scale-up of new high capacity cathode and anode active materials, then apply and expand its expertise in battery design, processing and manufacturing of lithium-ion polymer products for consumer and military markets. Ultralife used this approach successfully in 1998 to develop experimental cells based on $LiNi_xCo_yAl_{1-x-y}O_2$ cathode active with specific energy and energy density of about 150 Wh/kg and 260 Wh/l, respectively [3]. Eagle-Picher brought expertise in battery engineering and manufacturing for aerospace markets. Lockheed Martin is a system integrator and end-user of high technology launcher and satellite systems. Lockheed Martin had developed a state-of-the art charger for lithium-ion cells [3] and planned to reduce its size and weight using ASIC with power high density interconnect technology.

Materials and Cell Development

Ultralife's current line of lithium-ion polymer products uses $LiCoO_2$ cathode active and MCMB graphite anode active [4]. Specific energy and energy density up to 160 Wh/kg and 305 Wh/l have been achieved at the cell level [5]. New cell materials and cell designs are needed to increase realized energy content, especially for higher rate applications. Advances in both anode and cathode active materials are needed for maximum effect due to cell balancing requirements. Important active material considerations are reversible specific capacity, voltage profile, intrinsic stability and reactivity with the electrolyte which are largely determined by composition and structure and are often sensitive functions of temperature and cycle history. Ability to process the materials into electrodes compatible with the cell manufacturing process and suitable for the specific application are also required.

Anode active materials for lithium-ion cells can be broadly divided into two categories, carbonaceous and non-carbonaceous materials. The focus was on carbonaceous materials because of the long cycle life requirement and time frame for the program. Both Sandia National Laboratory and Argonne National Laboratory participated in the development and delivery of carbonaceous materials to Ultralife. The focus was on carbon-carbon composite materials, primarily taking a core carbon material and coating the surface with another carbon material. Goals were to try and capitalize on the higher capacity of disordered carbons with respect to graphite while trying to mitigate high irreversible losses and lower density. In parallel, Ultralife worked with a number of vendors to evaluate natural and synthetic flaky graphites, mesophase pitch-based carbon fibers, and disordered carbons, many with various dopants and surface treatments. None of the sources evaluated by Ultralife were found to be better than MCMB materials when both reversible capacity and anode processing are considered together. Tin-metal carbide composites were also investigated but showed poor cycle life and a decrease of 0.3 V in average cell voltage.

A series of new spherical carbon-carbon composite materials named GDR did result from developments at Argonne and elsewhere. The materials consist of a disordered carbon surface on a graphitic core as shown in Figure 1. First cycle reversible specific capacity of these carbons measured at Ultralife in coin cells versus lithium metal ranged from 315-335 mAh/g versus 303 mAh/g for MCMB. Kilogram quantities of material were delivered to Ultralife for scale-up and were found to process well. One material was incorporated into the final polymer cell build for this program. Cells using these new anode materials appear to cycle similar to cells using MCMB as shown in Figure 2. Expected advantages of these new carbons are lower cost and stability in a wider range of electrolytes. Stability in propylene carbonate is shown in Figure 1. No gains in cell capacity were obtained in these initial trials because lower anode density countered the higher specific capacity. Calendering the material was not performed at Ultralife, but is expected to help. Particle morphology of GDR remains unchanged under a calendering pressure of $0.2 t/cm^2$, taking an electrode of density 0.95 g/cc to 1.58 g/cc. Indications are these new carbons are a superior and commercially viable alternative to MCMB and are one of the successes of this program slated for further development.

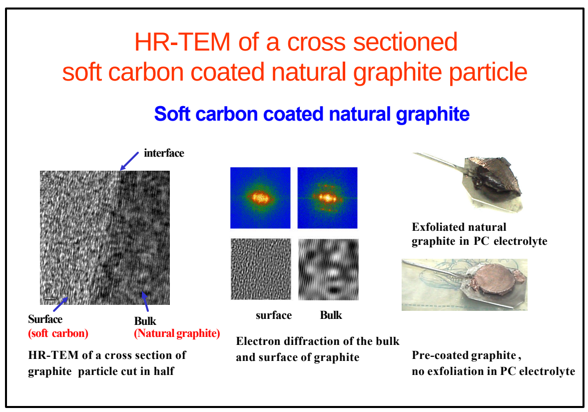

Figure 1: *HR-TEM of a cross sectioned soft carbon coated natural graphite particle*.

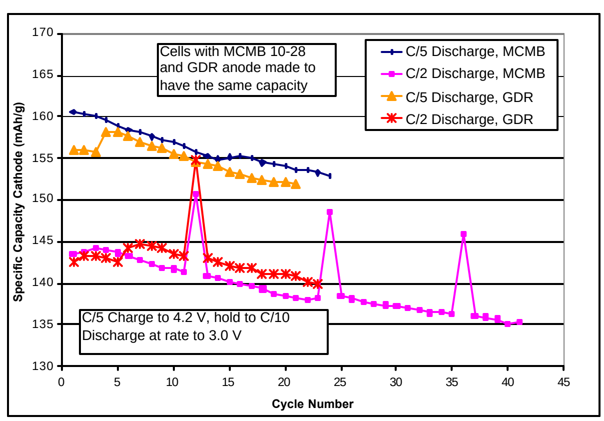

Figure 2: *Cycle data for $LiNi_{0.95}Ti_{0.05}O_2$.*

Cathode development focused on transition metal oxides. During the first year of the program Rentech, Inc. investigated a series of novel vanadium oxides. While these materials had very high specific capacity, some near 400 mAh/g, voltage windows were wide, some as wide as 1.6 V-4.0 V with average voltages below 3.0 V. Model calculations showed that effort would be better directed towards later transition metal oxides with lower specific capacity but higher voltage. In parallel, Ultralife worked with a number of vendors to evaluate doped nickel oxides and demonstrated full-scale manufacturing capability using $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$. Ultralife discussions with Argonne National Laboratory suggested there was still significant opportunity to increase the capacity of doped nickel oxides by going to the compositions $LiNi_xTi_yAl_{1-x-y}O_2$, and mechanisms were in place between Argonne and several companies for scale-up.

Argonne developed a method for making these compositions and had several kilograms of $LiNi_{0.95}Ti_{0.05}O_2$ prepared by a spray drying process at Fuji Chemical Company. A uniform spherical particle morphology was obtained with a particle size of 12 µm. Test results at Argonne showed reversible capacity of 200 mAh/g at C/3 rate with no capacity fade after 40 cycles, and no impedance growth for cells stored at 90% state-of-charge at 50°C for 25 days, and much lower reactivity at >200°C by DSC. Kilogram quantities of material were delivered to Ultralife where it was found to process well through all steps of the manufacturing process. Polymer cells were built and tested in several cell designs, one where only the cathode was changed from standard product, one where the cathode, separator, and electrolyte were switched, and one where cathode, separator, anode, and electrolyte were switched. The separator and electrolyte were also developed at Ultralife under this program. Cycle results for the latter two designs are shown in Figure 2. Specific energy and energy density for the MCMB cells are 142 Wh/kg and 267 Wh/l at C/5 discharge, respectively. Corresponding model results for the cells as built are 146 Wh/kg and 255 Wh/l. The GDR cells are 120-130 Wh/kg and 210-230 Wh/l, versus 139 Wh/kg and 223 Wh/l modeled as built. An aggressive cathode formulation with lower carbon and higher actives content than commercial Ultralife product, and much lower than the Argonne formulation, was used which may be limiting full utilization of the material. Time did not permit any formulation or engineering development, or extensive testing, but results are still impressive for an initial trial. Models indicate energy values of 185 Wh/kg and 360 Wh/l are possible with reasonable changes to the cell design; likely higher for low rate applications. The cathode development project is considered a success and warrants further development.

Various cell designs are being tested on low-earth orbit and geosynchronous-earth orbit satellite protocols. The details of the cell designs and test protocols have been described previously [6]. These cells are still on test after 20 and 26 months, respectively. Cells designs used for portable electronic applications are out about 6000 (LEO) and 700 (GEO) cycles with no fade in capacity or end-of-discharge voltage. This suggests that $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ and MCMB graphite may cycle well enough for satellite applications. The new materials developed in this project are also expected to cycle well long term.

Cell and Battery Engineering

Using Li-ion polymer laminate developed early in the program by UBI, EPT assembled nominal 20 Ah cells as previously reported [6]. Since then, LMMS has performed characterization, thermal, safety and abuse tests of these cells as well as launcher and satellite battery functional cycling tests.

Battery Charge Management

LMMS has developed several basic strategies for Li-ion battery cell charge balancing [7]. As previously reported [8], portable and short-duration aerospace applications testing has shown that commercially available charge controlling chips are more than adequate provided the battery package is properly thermally managed so as to prevent diverging impedance growth of initially well balanced cells. For initial space applications, multiply redundant cell charge management schemes will be utilized. Charge management circuitry has been designed, fabricated and tested using discrete surface mounted electronic components on a printed circuit board. Multiple boards are needed for each battery and the challenge of this program has been to implement the circuits on multi-chip modules and analog/digital ASICs that reduce the packaging requirements for a single system so as to use only a single board. The results of this development have led to the advanced balancer packaging design shown in Figure 3 which utilize opto couplers to provide voltage isolation thereby eliminating bulky magnetics. It locates the A/D converter at the cell pack and utilizes hybrid packaging techniques to produce compact space qualified radiation hard packaging. The resulting A/D ASIC is in foundry fabrication design and its use will reduce the packaging cost, volume and mass for satellite applications by 75%.

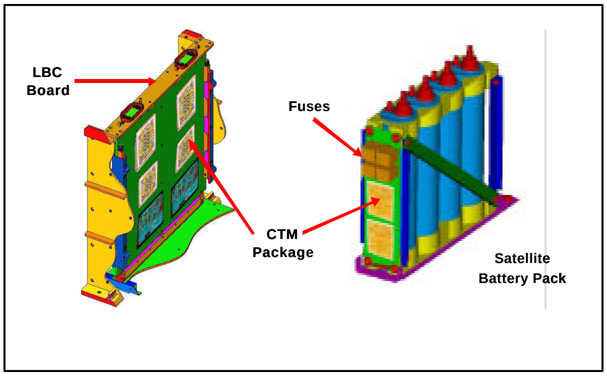

Figure 3: *Advanced Balancer Packaging*

Summary and Conclusions

New anode and cathode materials have been developed that should allow lithium-ion polymer cells to come close to attaining the original objectives of this program and maintain Ultralife's leadership position in the field. Present state-of-the-art nickel-based chemistry is likely capable of supporting LEO and GEO satellite cycling requirements with proper cell design. Advanced Li-ion cell balancing packaging has been developed that will allow the early introduction of Li-ion satellite batteries in space applications with minimal cost and mass impacts.

Acknowledgements

This work was performed under Advance Technology Program award 70NANB8H4073 supported jointly by the U.S. Department of Commerce National Institute for Standards and Technology, Ultralife Batteries, Inc., Eagle-Picher Technologies, and Lockheed Martin Space Systems. Financial support from NIST is gratefully acknowledged.

The authors also wish to thank all of the many dedicated individuals who worked on this program, including those listed in references 4 and 7, Curtis Martin (EPT), Dan Doughty (SNL), Ron Guidotti (SNL), Dale Shackle (Rentech) and all the other technical and engineering support staffs.

References

1. Boone B. Owens, "Survey of Rechargeable Lithium Battery Technology", Technical Report 970228-TR/BBO prepared for the Electric Power Research Institute (EPRI), 1997.

2. J.S. Xue, R.D. Wise, X. Zhang, M.E. Manna, Y. Lu, G. DuCharme, and E.A. Cuellar, "Performance Characteristics of Ultralife's Solid Polymer Rechargeable Batteries", J. Power Sources, 80(1999) 119-127.

3. Developed under the "High Capacity Solid Polymer Technology Reinvestment Project (TRP) supported jointly from 1995-1998 by the Defense Advanced Research Project Agency, Lockheed Martin Corp. and Ultralife under a Cooperative Agreement between Lockheed Martin Missiles and Space, Ultralife Batteries, Inc., and NASA Lewis Research Center dated February 2, 1995.

4. E.A. Cuellar, M.E. Manna, R.D. Wise, A.B. Gavrilov, M.J. Bastian, R.M. Brey, and J. DeMatteis, "Ultralife's Polymer Electrolyte Rechargeable Lithium-Ion Batteries for Use in the Mobile Electronics Industry", J. Power Sources, 96 (2001) 184-198.

5. For the most current information on product specifications, see Ultralife's website at www.ulbi.com or www.ultralifebatteries.com.

6. V.L. Teofilo, R. Brown, and E.A. Cuellar, "Advanced Lithium Ion Solid Polymer Electrolyte Battery Development" Proc. of 39th Power Sources Conference, Cherry Hill, NJ, June 2000.

7. M. J. Isaacson, R. P. Hollandsworth, P. J. Giampaoli, F. A. Linkowsky, A. Salim, and V. L. Teofilo, Proc. 15th Annual Battery Conf. on Applications and Advances, p. 193, CSU Long Beach, CA, Jan. 2000.

8. M. J. Isaacson and V. L. Teofilo, "Li-ion Battery Cell Balancing Requirements" in NASA Aerospace Battery Workshop, Huntsville, AL, Nov. 14, 2000.