Next Generation and Domestically Produced Active Materials for Lithium-Ion Cells for Military and Aerospace Applications

R. Gitzendanner[1], F. J. Puglia, Jr.[2], M. Gulbinska[3], S. Santee[4], B. Ravdel[5], and J.Gnanaraj[6]
Yardney Technical Products, Inc., 82 Mechanic St., Pawcatuck, CT 06379

Abstract

Yardney Technical Products (YTP) has established comprehensive programs to develop and test next generation and domestically produced, high energy, high power and long life anode and cathode materials. This effort was undertaken to support Yardney's diverse military and aerospace customer base to ensure design heritage and provide demonstrated performance enhancements for new applications. The initial effort includes partnering with several domestic partnerships, focusing on both anode and cathode efforts, as well as investigations into electrolyte and separator materials. The initial effort has focused on the development of mixed metal oxide cathode materials along with cathode materials that include surface stabilizing coatings. The cathode surface stabilization benefits from YTP's extensive high voltage cathode development efforts in which various high voltage cathodes are being evaluated. The initial testing is demonstrating stability at very high discharge rates (100C continuous, 400C pulses) and low and high temperatures (from -30°C to 85°C). In addition, the cathode materials are being tested in high specific energy designs to support lower rate, moderate temperature applications such as Unmanned Underwater Vehicles (UUVs). This paper presents the results of these initial material developments with comparisons to the state of the art commercial (foreign produced) materials.

I. Introduction

Lithium-ion battery technologies continue to demonstrate the high level performance parameters that make them very attractive for many military and aerospace applications. Compared to historically utilized chemistries such as Ni-Cd, Ni-H, and NiMH, Lithium-ion cells and batteries offer higher energy and power density, broader temperature operation, and excellent cycle and calendar life. Lithium-ion technologies have also proven to be reliable and safe, as long as treated appropriately. Many applications, including the B2 Stealth Bomber, Global Hawk UAV, Martian rovers and landers, many satellites and next generation launch vehicles rely on Lithium-ion batteries, often as a mission enabling technology as other battery chemistries could not provide the performance needed to meet the mission requirements. Continued development and production of these batteries are critical to meeting national defense and scientific exploration goals and objectives. Historically, the key active materials utilized in nearly all Lithium-ion batteries were foreign-sourced, often from Asia. In addition, the manufacturers and suppliers of these key materials are driven by the larger volume demand of consumer electronics, leaving military and aerospace battery manufacturers limited to the materials that met the requirements of typical cell phone and laptop markets.

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[1] Director, Executive Director, Lithium Engineering, Lithion, non member
[2] Director, Research and Development, Lithion, non member
[3] Lead Materials Scientist, Lithion, non member
[4] Senior Research Engineer, Lithion, non member
[5] Research Scientist, Lithion, non member
[6] Senior Scientist, Lithion, non member

The consumer electronics market is driven not by long life and high reliability, but by cost. Thus the materials developed for these Lithium-ion applications are not ideally suited to aerospace needs, and the formulations can change at a moment's notice as cheaper materials or less involved synthesis procedures are discovered or developed. Faced with this concern, YTP began a comprehensive effort several years ago to identify domestic source and/or Next generation materials that would continue to support the needs of the military and aerospace markets.

II. Anode and Cathode Development Efforts

The focus of the efforts has been to identify and qualify appropriate replacement materials for the heritage materials utilized in many Yardney batteries, and to identify and incorporate specific performance improvements to enhance next generation battery performance.[1] The cathode and anode development efforts were initially established with the following specific enhancements relative to the current state of art materials (in order of importance):

1. Improved Stability and Life for 100% DoD cycling
2. Improved High Rate Performance (up to 60C continuous)
3. No Reduction in Battery level Energy Density
4. Improved Safety

Efforts to date have focused on the first three areas, specific improvements to safety have not been fully addressed, however testing of the thermal stability, cycling and life stability, and Differential Scanning Calorimetry (DSC) heat generation tests have indicated potential improvements in overall safety; these tests will not be discussed in this paper as the results are still preliminary.

It was especially important that new materials be reliably and repeatedly manufacturable in commercially viable quantities (typically a minimum of 1-2 metric tones per batch), and be able to achieve a Technology Readiness Level (TRL) of 9 within 2 years, indicating that they had been fully qualified and fielded in an application. These needs quickly eliminated some of the newest development materials from this initial effort as they would not support the race to market needs. Several mixed metal oxide cathode materials (such as $LiNiCoO_2$ and $LiNiCoAlO_2$) and graphite-based Anode materials were selected for evaluation and demonstrated viability as future replacement candidates. These early investigations identified specific materials that could be used as replacements for heritage programs, and efforts are currently underway to test these materials to program-specific performance profiles and fully qualify them for future procurements. In addition to identifying reliable materials with a good source of supply for heritage programs, these studies helped identify key material characteristics and how they relate to battery performance; thus facilitating material selection to support specific program needs. While this effort continues at the program-specific level, recent efforts have focused on developing the next generation materials that will continue to provide enhanced performance of Lithium-ion batteries for future applications.

A. High Power Materials:

Increasing the rate capability of a cell or battery can be achieved by improvements to the mechanical design (typically focusing on reducing ohmic resistance contributors) and by chemical modifications (typically focusing on improving the ionic transport capabilities). Such enhancements combine to reduce overall cell/battery impedance and, ideally, reduce the power loss due to repeated cycling. Some power fade can be attributed to high temperature effects, so reducing the cell's ohmic resistance (thus heat generation and the cell's internal operating temperature) typically improves cyclability. However, improvements to the stability of the active materials are also needed to ensure they can sustain repeated high rate charge and/or high rate discharge cycling. High power capability has long been demonstrated in Lithium-ion technologies. Yardney has demonstrated continuous discharge rates up to 200C, Fig. 1. In this test high rate experimental 7Ah cells were discharged at C/5 rate to establish a baseline capacity, then discharged in the order indicated in the legend, an initial 200C rate discharge, followed by 5.2C, 10.4C, 20.8C and so on, ending with a final 200C rate discharge. As shown in the figure, the cell capacity and voltage performance under load was not significantly affected by the numerous high rate cycles, demonstrating low power fade over this limited number of cycles.

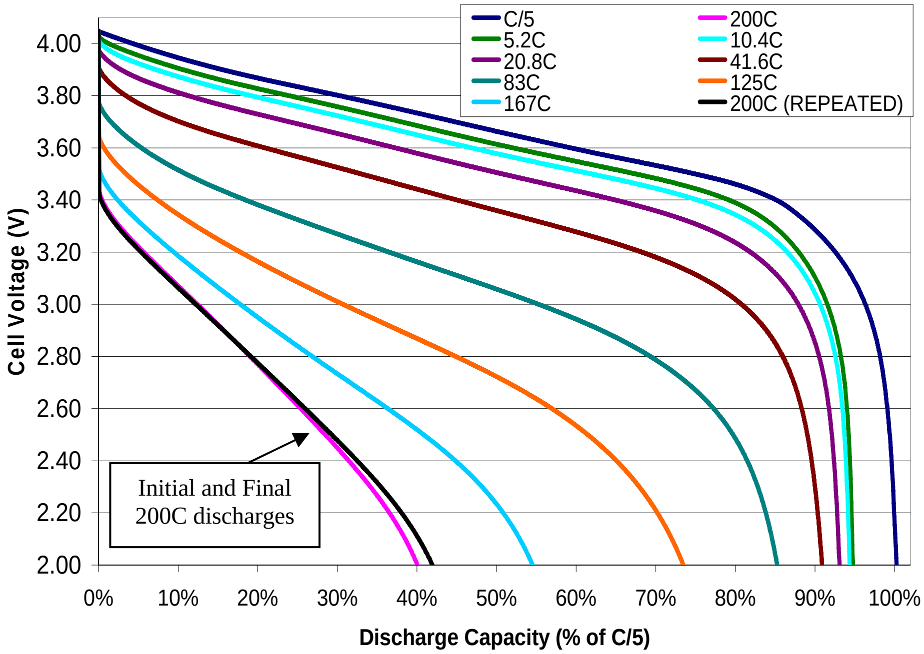

Figure 1. Rate capability of High Rate Lithium-ion cell

Improvements to the rate capability of cathode materials, by reducing primary particle size and improving ionic conductivity, have shown further reductions in cell polarization. Fig. 2 demonstrates the voltage response for 7Ah test cells discharged at a 20C rate (discharge starts at t=1 minute), cells with the higher rate cathode material (top/blue line) show approximately 100mV less polarization at a given depth of discharge than the baseline cells (bottom/pink line). In this case, the reduced impedance would result in a 7.2V higher operating voltage in a high power 270V battery application. And at a 250A discharge rate, this corresponds to almost 2kW less heat generation, significantly reducing the operating temperature and improving performance.

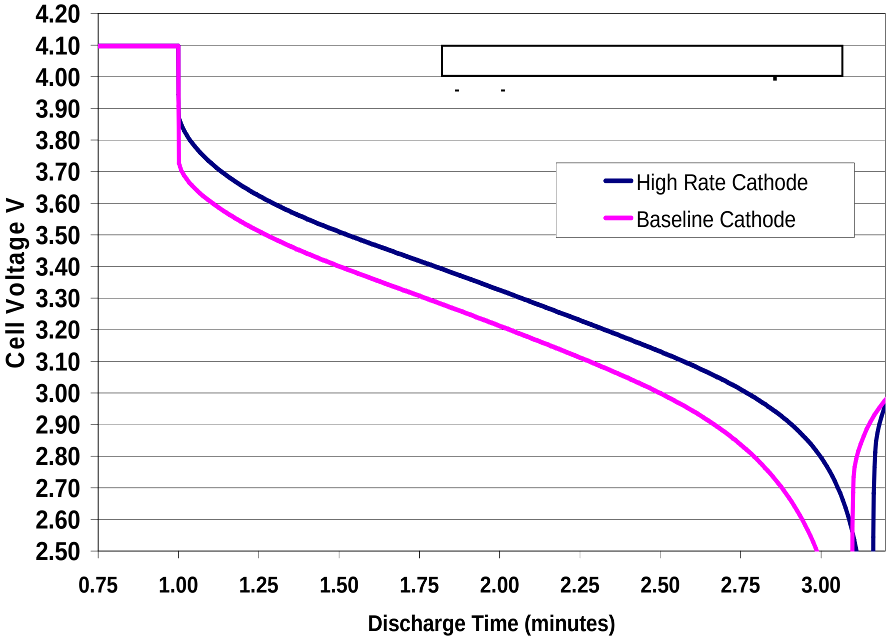

Figure 2. Cathode polarization at 20C discharge.

Further improvements to cathode coatings, aimed at improving current distribution throughout the coated material and increasing ionic conductivity, also show improvements in impedance and power fade, Fig.3. In this pouch cell comparison Lot 1 and Lot 2 have the same mixed metal oxide cathode material, but the electrode formulation of Lot 2 utilized different conductive diluents, designed to improve electronic conductivity throughout the electrode coating. Lot 4 takes advantage of both improved conductive diluents and a new cathode material for decreased power fade over 200 high rate cycles.

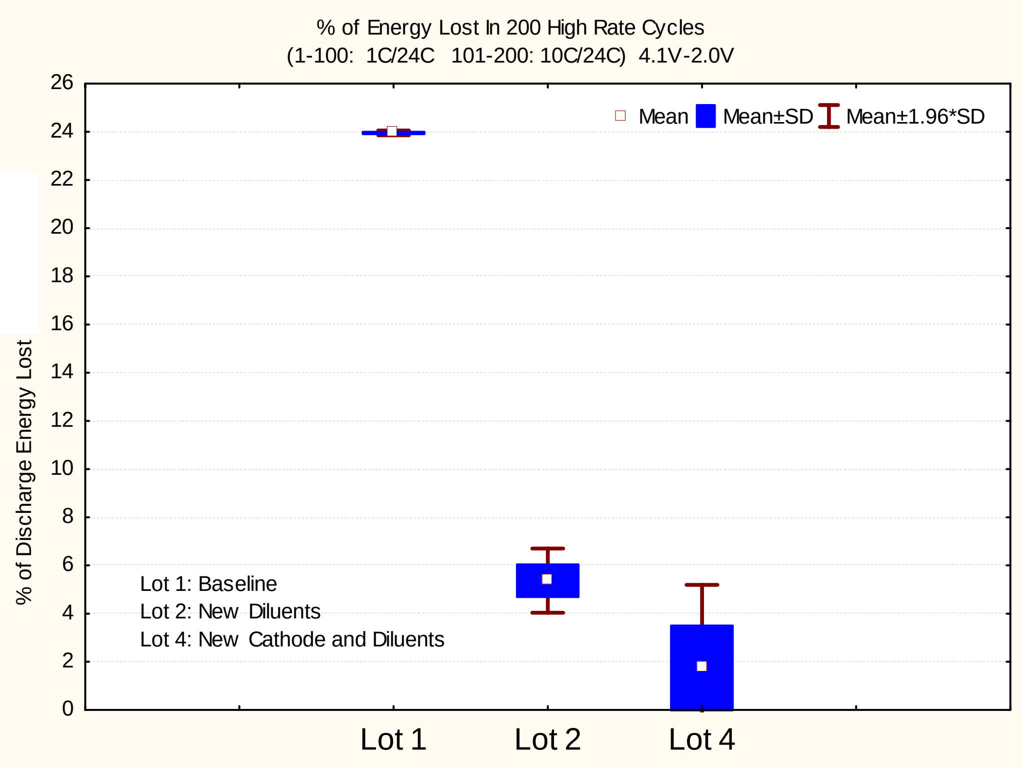

Figure 3. Comparison of Fade Rates after 200 high rate cycles (1C charge rate, 24C discharge rate). Mean and Standard Deviation were calculated from Lot size of 5 cells each.

B. High Energy Materials:

With ever increasing energy demands of future applications, and the need to keep overall size and weight to a minimum, many aerospace customers are looking for Lithium-ion batteries that provide increasingly higher energy density. NASA is especially interested in such materials for various lunar missions and applications, and also interested in the very low temperature performance of these chemistries. Through simple processing modifications and selection of new binders, Yardney has delivered to NASA JPL test cells with approximately 15% greater energy density in comparison with the baseline chemistry utilized for the Mars Lander and Mars Exploration Rover (MER) applications, Fig. 4. The cells, size/type designation “NCP7”, delivered 9Ah capacity at a C/5 rate at 20°C with the improved electrode formulation; mixed metal oxide cathodes and graphite-based anode materials were utilized in all cells. These cells have also been filled with new electrolytes developed by NASA Jet Propulsion Laboratory (JPL) for very low temperature operation consisting of a volume ratio of 20% Ethylene Carbonate (EC), 20% Dimethyl Carbonate (DMC) and 60% Ethyl Methyl Carbonate (EMC). These cells have demonstrated performance at temperatures as low as -50°C and -60°C, Fig. 5; far below temperatures standard Lithium-ion chemistries are operational.

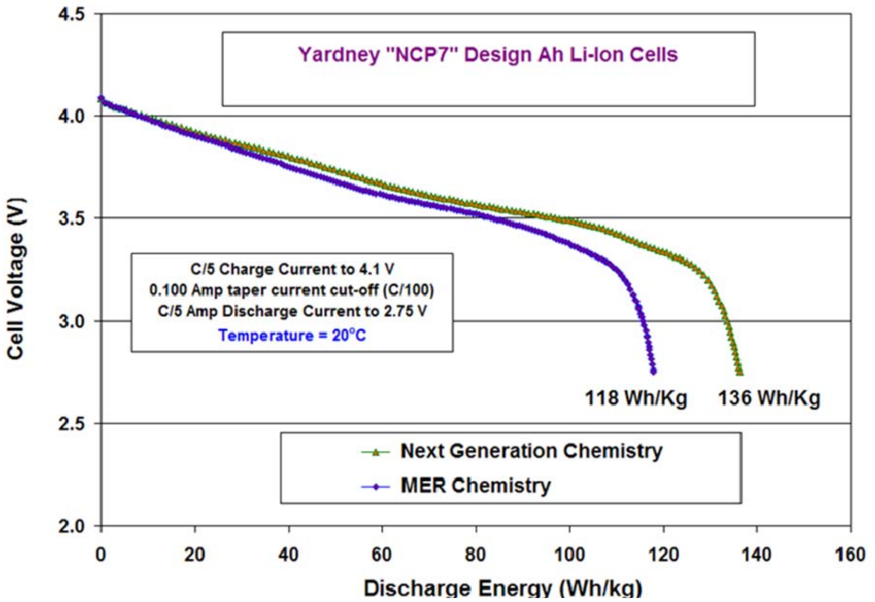

Figure 4. Comparison of Energy Density in experimental "NCP7" or 9Ah cells. *Note low temperature electrolyte in both cells and cell design not optimized for energy density.*

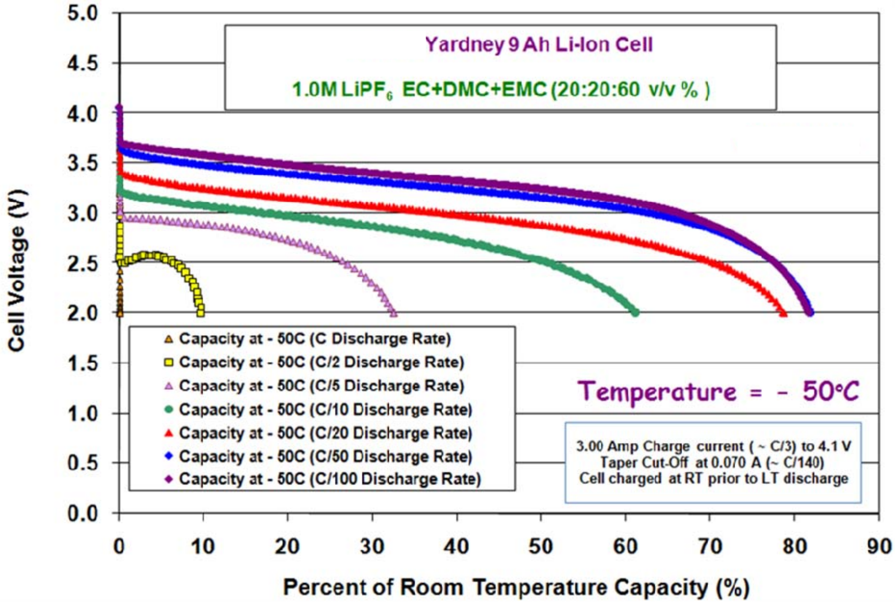

Figure 5. Discharge of high energy test cell with low temperature electrolyte at -50°C

C. High Voltage Materials:

Lithium-ion cells typically operate with a maximum cell voltage of approximately 4.1V to 4.2V. Operation at higher voltages typically leads to material degradation and performance loss, or even unsafe conditions. However, increasing the operating voltage of a cell or battery is one way to enhance the system's energy density. Several Next generation materials have higher redox potentials, and can be operated safely as Lithium-ion batteries with some surface modifications and electrolyte stabilization.

Lithium Iron Phosphate ($LiFePO_4$) has been widely studied, and utilized, as a new cathode material, however, one of its disadvantages is the low operating voltage of 3.2V[2]. Other olivine phosphates have much higher redox potentials[3] and can be utilized as cathode materials with careful synthesis and appropriate treatments, Table 1. As with $LiFePO_4$, these materials are relatively poor electrical conductors, and so need to be produced as nano-sized particles and/or with appropriate dopants to provide sufficient conductivity for Lithium-ion battery applications.

Table 1. Reduction/Oxidation Potentials of various metal phosphates

Li**M**PO_4	Redox Potential vs. Li
Mn^{3+} / Mn^{2+}	4.1V
Co^{3+} / Co^{2+}	4.8V
Ni^{3+} / Ni^{2+}	5.1V

$LiCoPO_4$, synthesized via a modified solid state synthesis has demonstrated reasonable cyclability and capacity, Fig. 6 shows the discharge capacity (in mAh/g active cathode) of six test cells fabricated with this cathode. True benefits of these higher voltage cathode materials come when combined with anodes such as Lithium Titanate that operate at a much higher voltage relative to graphite-based anodes. Cells manufactured with these combined high voltage cathode and anode materials would still have a useful operating voltage, Fig. 7, note not all combinations have been tested to date, dashed voltage profiles are theoretical.

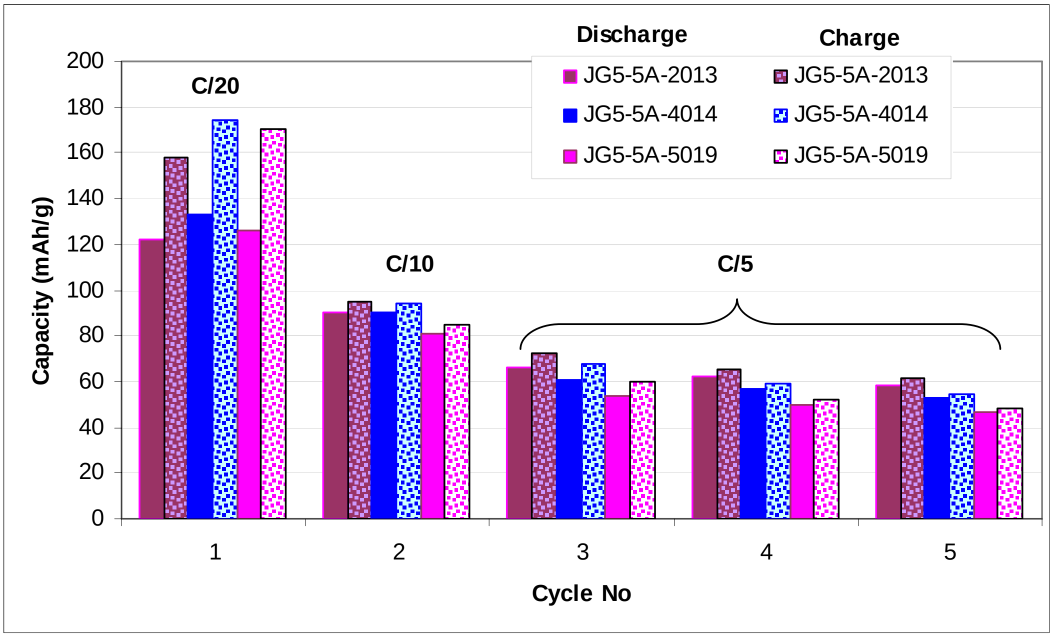

Figure 6. Cycling of $LiCoPO_4$ coin cells.

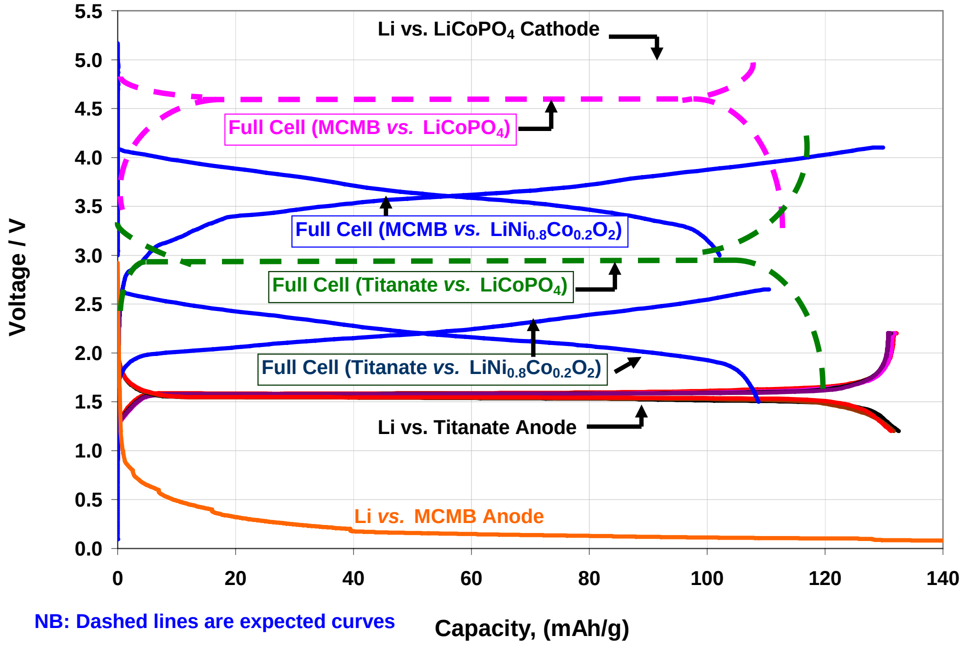

Figure 7. Relative operating voltages of cells with different anode and cathode combinations.

III. Conclusion

Lithium-ion technology continues to provide an energy and power dense solution for many military and aerospace applications. Suitable heritage replacement and next generation active anode and cathode materials have been identified and are now being demonstrated and qualified on a program-specific, case-by-case, basis. These efforts provide not only assurance that materials will be available to support future systems, but also provide an understanding of the key characteristics that drive performance parameters, allowing for specialized tailoring for new applications. Specific safety improvements from these materials are still being evaluated, but initial testing has been positive. High rate improvements have been demonstrated in not only modifications to the base materials, but also through improved engineering of the electrode coatings themselves. And high energy improvements can be realized with standard materials and newer high voltage materials with appropriate modifications to the overall chemistry. Continued developments in these areas provide assurance that military and aerospace applications will be supported by high performance Lithium-ion batteries for years to come.

Acknowledgments

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