SBIR Integrates Basic Research into Cost-effective Manufacture of Li-ion Batteries

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Introduction

Behind cost and performance, the major stumbling block to commercial application of Li-ion battery to HEV (high-mileage, Hybrid Electric Vehicles) is the combined issues of thermal management and safety**.** Unique thermal properties of the InvenTek cell for internal heat rejection combined with a flame retardant (FR) additive to the electrolyte for self extinguishing cell incineration (1) promise to provide a cost-effective battery for HEV. The research of Prof. Jai Prakash at the Illinois Institute of Technology (IIT) identified FR materials that can be used as additives to Li-ion batteries. The NSF SBIR has proven to be a valuable and possibly unique avenue to make application of his innovative basic research.

The NSF-funded SBIR focuses on a new method of Li-ion battery manufacture that can reduce the cost of a battery for hybrid electric vehicle (HEV) by 50%. The unique disc-shape of InvenTek rolled-ribbon Li-ion cell (7.5Ah) enables creation of a compact, high power density, stacked-cell battery (2). The specific energy of a high-performance battery (90-135 Wh/kg) is coupled with the specific power of an ultracapacitor (2.5kW/kg). Intrinsic internal heat dissipation of the cells improves battery stability, as well as safety. A fire-retardant (FR) additive to the flammable organic electrolyte limits the consequences of overheating and overcharge. Passive thermal management of the cell design and inherent safety offered by the FR additive provide further cost advantages for the InvenTek Li-ion battery.

This paper will describe the levels of interaction of basic research at IIT with InvenTek and its industrial partners that are made possible by the SBIR. Through the SBIR, students have hands-on exposure to HEV technology that addresses a critical national need of energy independence and environmental stewardship.

Background

The cost savings of the Inventek HEV battery was compared to a conventional prismatic Li-ion battery. First, the cost of electrode materials was assessed in Inventek's stackable 6.5-8.5Ah, disc-shaped cells. As in Fig.1, these button cells can minimize performance loss at a "20 C" pulse rate due to its large-area cell/battery hardware connections. High cell current capability for the rolled-ribbon design doubles power output for the HEV application. These prototype Li-ion cells were tested to meet PNGV specifications. Tests so far have shown that the rolled-ribbon cell design can approximately double the power density of any given cell chemistry, -- a significant economic benefit. Specific power of cells exceeds 1500W/kg for HPPC (high pulse power characterization, specific for hybrid vehicles) over a broader range of SOC, 10-70% SOC, whereas 40-60% is typical. Further cell capacity is generally doubled to accommodate the significant loss of power and capacity at -30C. But tests at Inventek's commercial partner show that the added capacity to meet power requirements at the low temperatures is not necessary with the rolled-ribbon cell configuration. In essence only 33-50% of the projected 15.4 Ah would be required; that's at least a $200/battery savings. (Disposal/recycle cost are also proportionally reduced.) Reduced manufactured cost of a Li-ion cell also results from the low-cost button-cell enclosure (two stamped cups). Because these cells eliminate costly header components and have a no-weld assembly, a Li-ion battery can be assembled at a significantly lower cost. Flexibility of design is accomplished by varying cell diameter and cell width to package a range of power/energy objectives. High pulse power objectives are met by changes in electrode thickness, foil thickness, and separator area. The rolled-ribbon design, as will be explained, captures optimum performance from the Li-ion chemistry to allow a reduction of all materials to fulfill high power/high energy application.

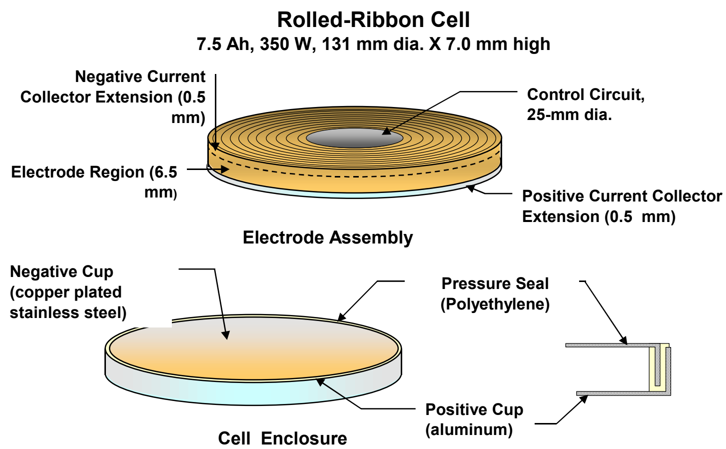

Fig.1, Rolled-ribbon Cell and Button Hardware

In addition active material costs, the cost of production (and, attrition) and battery hardware materials must be considered to give a realistic cost of the HEV battery. Cost includes estimates of all essential battery hardware materials that will be necessary to complete the build. The costs cover the materials necessary to build 100 cells each of the ribbon rolled design and the prismatic design. The rolled-ribbon cell hardware has design feature that integrates most all of the costly add-ons required of the prismatic design. The can, cover, terminal, rupture disc are all features of the button enclosure of the rolled-ribbon cell. Metal stamping capability for cell hardware was developed to meet greater demands in a battery prototype phase. The simplicity of this hardware makes it conducive to automated metal forming and plastic molding processes; these can be very low unit cost at $0.10 in large volume, millions of units. For this study, a pilot-plant level of production, 10-100K units, is costed. So, on a materials basis alone, the total cost of the ribbon rolled cell is $1000/battery (assume 100 cells per battery) and that of the prismatic design is $3400/battery.

Thus, the overall cost of a hybrid EV battery in a prismatic design including hardware is $5000/battery compared to $1000/battery for the ribbon rolled design. The hardware and manufacture costs for the Li-ion rolled-ribbon battery are negligible by comparison. A manufacturing cost of $20/kW for the ribbon rolled design, as opposed to $64/kW for the prismatic design presents the real potential advantage of this design in high volume production. This $20/kW low production would almost certainly be reduced by 75% to $5/kW in higher volumes due to savings associated with large batch processing. The materials cost of about $150/battery is the only significant residual cost in a mass-produced HEV battery. The rolled-ribbon Li-ion may be unique in providing high power density at low cost, because of its enhanced performance and low-cost hardware.

Much-enhanced thermal management over conventional spiral-wound and prismatic battery cells is a further benefit of the disc-shaped button cells. Management of internal pressure is an integral feature of the button-cell seal design. The SBIR will demonstrate the outstanding performance and safety aspects of the rolled-ribbon Li-ion battery. A group of a dozen cells were built and tested with the same electrode materials to permit direct comparison of cell design. Electrode ribbons act as cooling fins to remove heat from the Celgard separator interface. Heat is transferred to the heat-conducting metal cell hardware that acts as heat sink. As illustrated in Fig.2, heat removal is further augmented by large area contact between electrode and cell hardware and also by the short path length from electrode interface and cell hardware. An inherent thermal management feature of rolled-ribbon cells is that no heat must exit the cell by crossing a Celgard separator layer. Excessive internal pressure from external heating is an added safety concern. The cell has a pressure regulating, "burping" seal to limit internal pressure.

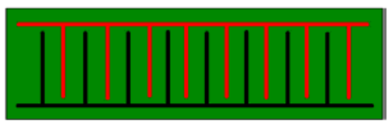

Fig.2, Cross-sectional schematic; Outstanding heat removal by interdigitated fins of electrode, negative (Black) and positive (Red)

The cells were evaluated at extremes of cell power and energy demand. The continuous discharge test was pushed from 30A up to 75 A. For an average discharge of 1000 W/kg, cell specific energy exceeds 70Wh/kg. This level of continuous power is about double that of our earlier power levels and conventional spiral wound cells having about 35hW/kg at 500W/kg. Therefore, the rolled-ribbon cell is showing about a 4-fold advantage in specific power. At high specific power, the internal heating of Li-ion cell can be a commercial drawback. Outstanding heat rejection was demonstrated by rolled-ribbon cell with constant full-capacity discharge at 15C rate, or 75 A. Under high power discharge, only a modest temperature rise results. Power pulses gave a temporary 2-3 ^{o}C rise and high rate discharge gave a 10 ^{o}C rise. The temperature differential from center to edge of cell never exceeded more than 1 ^{o}C. Passive thermal management is sufficient even under extreme power demands.

To enhance safety, addition of flame retardant (FR) electrolyte additive (eg., hexaethoxy-triaza-phosphazene) is used to suppress thermal runaway and for self extinguishing cell incineration (1). Addition of FR cannot reduce cell performance relative to cell operating temperature. The effect of temperature on the lithium–ion cells performance is evident especially when the battery is operating at low temperature (<10^{o}C). At such low temperatures a considerable loss of the cell capacity is observed mainly due to the decrease of ionic conductivity, electrochemical reaction rates, electrical conductivity, and solid lithium diffusion at low temperature (3,4). On the other hand, although a better performance is expected at higher temperature, most lithium-ion cell manufacturers recommend operation below 65^{o}C to avoid thermal runaway and hence cell rupture (5). Exothermic reactions of electrodes with the electrolyte can cause the Li-ion cells to undergo thermal runaway (6-8) at relatively low temperatures especially at increasing state of charge.

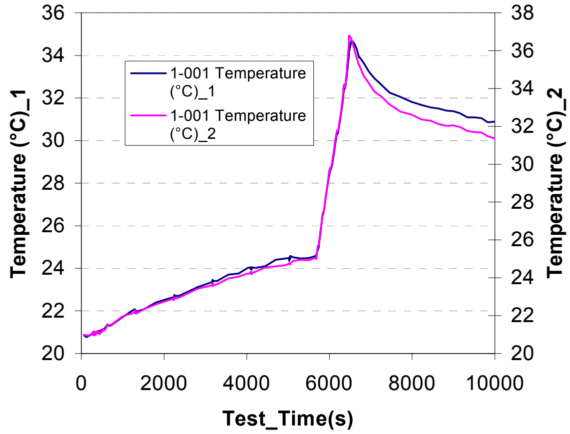

Fig.3, Temperature at Center and Edge (blue) of Rolled-Ribbon Cell during a 30 amp, 5C rate discharge in the adiabatic chamber

SBIR to Enhance HEV Battery Safety

Li-ion battery safety is a priority of most commercial applications. Heat dissipation becomes a special concern for high power batteries. Especially to be cost competitive for the hybrid vehicle application, the battery design requires inherent reliability and safety. InvenTek is applying an FR electrolyte additive through the support of the Center for Electrochemical Science and Engineering research laboratories at the Illinois Institute of Technology. Some companies are now offering larger, 5-10Ah flat-wound, or other variations of a spiral-wound cell, as the Saft hollow jelly-roll. The issue of heat rejection is exacerbated. This proposal applies advanced materials to a cell design that has inherent advantages for high power battery with enhanced thermal management. Electrolyte stability is improved by modifying with phosphazene additives (a fire retardant). This approach has proven to improve safety of Li-ion cells.

Application and testing is critical for commercial acceptance of advanced technology. Proper application requires the FR incorporation results in a net benefit to the system. The FR must not only exhibit increased system stability (reduce exothermal reaction from overheating and flame arresting), but must also improve the economics applying the FR containing battery to the hybrid electric vehicle. The extent of the stability improvement can be examined by cell tests and more specifically by DSC (differential scanning calorimetry). IIT graduate student Hyun-Joo Bang used DSC to examine the reactivity of electrolyte and individual cell components. These thermodynamic evaluations require some history of such measurements to gauge relative impact. The FR can use different functional groups to adapt. The FR must not significantly reduce cell/battery performance. Many times the performance is affected at extremes in the application environment.

Modifying the electrolyte with phosphorous nitride base compounds demonstrate significantly a reduced self-heat rate for the Li-ion cell (8). This project looked at hexaethoxy-triaza-phosphazeneas, 5% HMTP, as the flame-retardant additive for the Li-ion cell. As in Figs.4, laboratory-scale half-cells show delayed and reduced self-heat rate. This in turn, helps the thermal stability and hence the nonflammability of the electrolyte. Coin cells (2016) Fig.5 looked at the electrochemical performance of a cell with the 5% HMTP and shows no diminished cell energy. Cold performance is a key factor in sizing the battery for HEV application. Low temperature performance, Fig.6 side by side cell tests, at –30 °C for two cells, one with and one without the FR, showed not only the same Ah capacity, but cell resistance was unchanged, or the cell power was not affected by the FR. Also, the electrochemical performance in terms of rate capabilities, overcharge, over-discharge characteristics, and self-discharge at elevated temperatures was evaluated in these coin cells. Thermal abuse tolerance was addressed with the application of fire retardant additive, FR, to the electrolyte. A key development was the identification and supply of FR from a commercial source, Bridgestone. Sufficient supply can be obtained such that our development partners can also access the material for their future use.

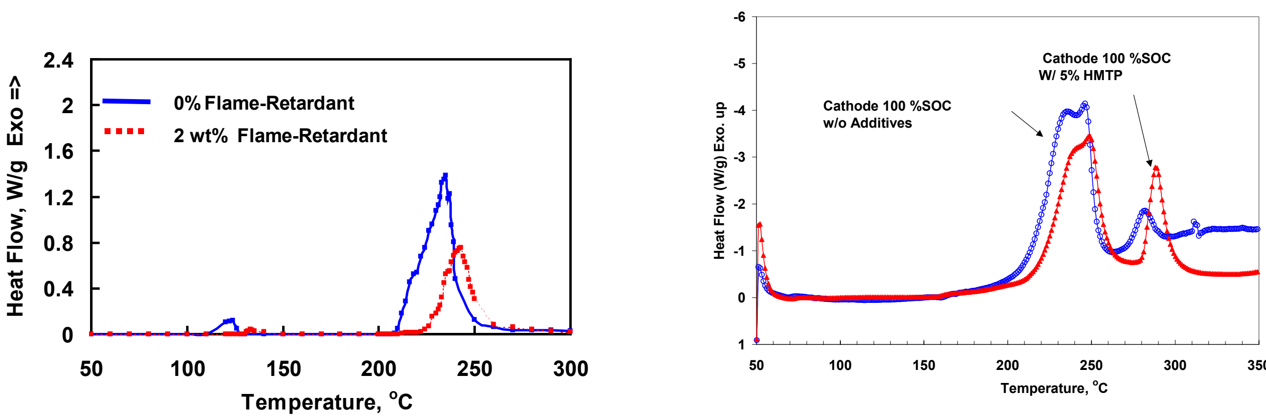

Fig.4, Differential Scanning Calorimetry DSCs of laboratory-scale half-cells. The cathode/electrolyte couple on the left and the anode/electrolyte couple on the right both show delayed and reduced self-heat rate. This indicates an improved safety factor for the Li-ion chemistry with the FR additive.

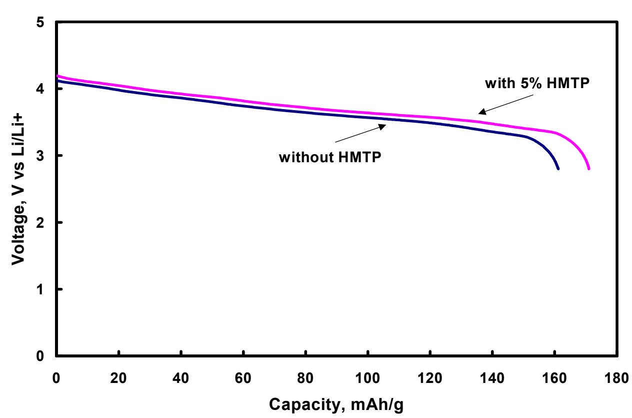

Fig. 5, The voltage/capacity of two cells; one with the 5% HMTP FR and one without the FR. The FR does not reduce cell specific energy.

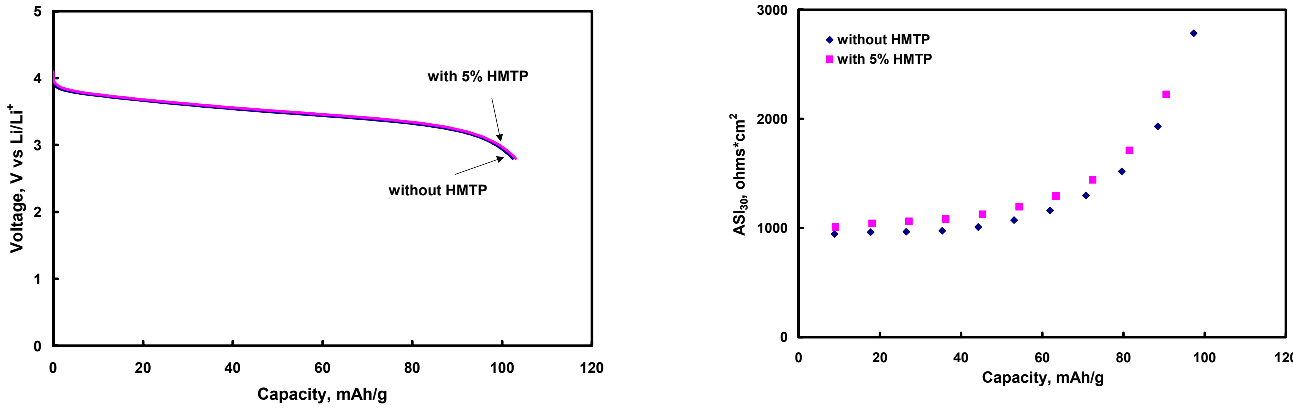

Fig.6, Voltage/capacity and Area Specific Impedance (right)Measured for full cells with and without 5% HMTP at -30^{o}C.

Finally, Accelerated Rate Calorimetery (ARC) is used to investigate the performance of these cells at elevated temperature, thermal stability and thermal runaway as a function of temperature and state-of-charge. The fire retardant, FR, is evaluated using accelerated rate calorimetry, ARC, with a special spiral wound cell, similar to a "D" cell size. It was necessary to develop a cell of greater than 1 Ah capacity that would fit within the ARC test chamber. This evaluation is a collaborative effort with Prof. Jai Prakash and graduate student Humberto Joachin at IIT. The results thus far support the expectation of FR reducing the autothermal reactivity of the Li-ion cell under incineration conditions. The results show a significantly reduced exotherm due to the addition of FR to the electrolyte. The typical ARC for a Li-ion would show a self-heating spike at 180^{o}C. As in Fig. 7, the ARC for the cell containing the 5% HMTP flame retardant additive has self-heating delayed to beyond 250^{o}C, a safety improvement.

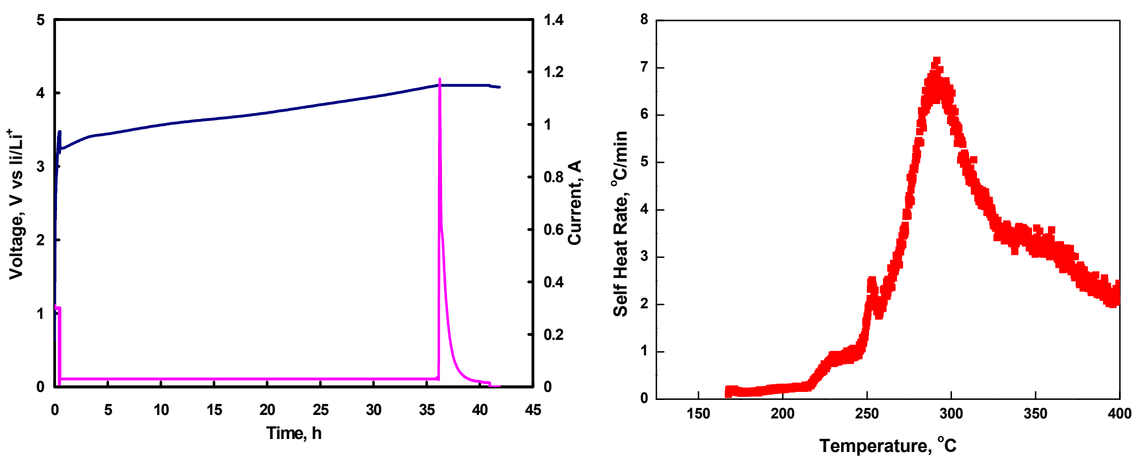

Fig.7, Thermal Study by ARC overall diminished and delayed heat generation from electrode/electrolyte reaction and cell component combustion, At the left is the preparation of the fully-charged state cell; right is the ARC data of the special rolled-ribbon cell without hardware.

Reduced cost associated with thermal management and safety was indicated from systems modeling. Temperature related cell data was collected over the course of six months, impedance vs. DOD in both charge and discharge vs. temperature. ChE graduate student Siddique Ali Khateeb Razack used this data in an HEV system design model ADVISOR. Unlike the commercial Ni/MH battery, the ADVISOR model indicated that the rolled-ribbon Li-ion battery would not require an active cooling system for the HEV vehicle application. The inherent safety of the battery is increased. The energy efficiency of the HEV drive system is also improved by relying on passive thermal management. The system is safer without dependence on a cooling system. Without active cooling (such as a blower), a parasitic energy loss is eliminated. Due to the enhanced safety afforded by the FR, the system could rely on cost saving, passive thermal management.

Conclusions

Academic research can provide fresh approaches for solving problems and industry must apply them cost effectively to survive in the competitive market place. To this end, the development of high power, larger capacity Li-ion cells for next generation batteries offer challenges for safety and thermal management. With these issues in mind, Inventek has integrated its NSF Phase II project with the research and educational activities in the Center for Electrochemical Science and Engineering research laboratories at the Illinois Institute of Technology. Participation in the development of next generation batteries requires highly-trained scientists and engineers with hands-on experience. The SBIR program has been very helpful to students wanting to learn about Li-ion batteries. The active participation of IIT students in the InvenTek project has helped them a great deal in understanding the critical issues of high power Li-ion batteries from the perspective of both fundamental and applied science. The following research tasks have involved students who are mentored and have gained hands-on experience:

- Understanding the design and fabrication of high-power Li-ion cells
- Electrochemical performance analysis using specialized testing protocols such as HPPC and pulse charge-discharge
- Understanding and analyzing the thermal behavior of high-power Li-ion cells using Accelerated Rate Calorimetery (ARC)
- Use of flame retardant (FR) additive to improve the thermal run away characteristics of high power Li-ion cells (In Collaboration with Inventek and Bridgestone Company, Japan)
- Understanding the issues related with the scaling up of the laboratory size cells.

The SBIR not only makes application of the FR additive to a commercial product, but serves as forum for faculty and students to participate in product commercialization. Emphasis on economic alternatives helps gauge commercial value of the improved technology. Research methods can be applied to problem solving. The ultimate objective of failsafe operation of a large capacity Li-ion HEV battery is to provide a significant marketing advantage. Cost-effective HEV battery to save imported oil, reduce air pollution, improve industrial competiveness in a key technology that is dominated by Japanese and Chinese companies.

Inventek's NSF Li-ion battery project has its significant relevance and impact on both research and development and public policy over the next decade.

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