Considerations Regarding Electric and Hybrid Vehicle Safety

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ABSTRACT

Lithium-ion batteries are often the preferred choice for powering rechargeable-battery-operated consumer products due to their high value proposition for cost and energy density. Lithium-ion batteries are also highly reliable. Therefore, lithium-ion battery packs are now finding their way into very complex consumer products including hybrid and electric vehicles. The utilization of lithium batteries in small consumer products is increasing rapidly. However, lithium-ion battery failures can be substantially more energetic than failures of conventional battery units traditionally used in the automotive market, due to higher quantities of stored electrical and chemical energy within lithium-ion cells.

The large and complex battery configurations needed for electric and hybrid vehicles and the applications to very demanding automotive operational conditions present new challenges in areas of safety, durability, reliability, and performance. Thus, the risk potential and exposure to new potential technical challenges in a new and demanding operational environment should be considered in the vehicle development process. As new uses are explored, this battery technology must be well understood and thoroughly considered in the context of the new application.

INTRODUCTION

The community of individuals and institutions with interests in motor vehicle safety is very large, including but not limited to:

- Vehicle drivers/ roadway users
- Motor vehicle manufacturers
- Safety researchers and practitioners
- Government institutions:
    - Legislative
    - Administrative
    - Judicial
    - Law enforcement
    - Transport officials
- Health officials
- Non-government organizations/institutions (NGOs)
- Emergency responders
- Roadway designers and builders
- Taxpayers

Historically, the role of vehicle safety could be defined by a Haddon matrix that plots the injury triangle elements of driver, environment and vehicle against timeframes before a crash, during a crash, and after a crash. The advent of electric vehicles (EVs) and hybrid electric vehicles (HEVs), both of which come in a variety of categories defined by their operating mechanism configurations, has added a new layer of health and safety concerns.

New elements to be considered include:

- Energy storage methods
- High voltage sources
- High power electrical connections and lines
- Battery chemistry
- Battery crashworthiness
    - Battery structure robustness
    - Battery protection within vehicle
- Service considerations
- Energy recharging
    - Vehicle manufacturer
    - End user
- Battery handling and shipping
- Battery storage at vehicle test and assembly facilities
- Information and knowledge transfer to affected parties

Due to energy density characteristics, lithium-ion cells are currently an attractive choice for assembling into high voltage rechargeable batteries for EV and HEV use. What is not so quick to penetrate, particularly in the view of the public and of non-technical but interested government entities as expressed in public media and blogs, is that the shift to lithium-ion batteries as a rechargeable power source is a major paradigm shift, and the learning curve for new applications can be both steep and challenging. An understanding of the cell chemistry, reliability safety performance and potential failure

modes and by-products form part of this learning curve.

DISCUSSION

While battery cells have been with us for hundreds and even thousands of years, most significant battery development for consumer products before the lithium-ion has been based on an aqueous electrolyte.

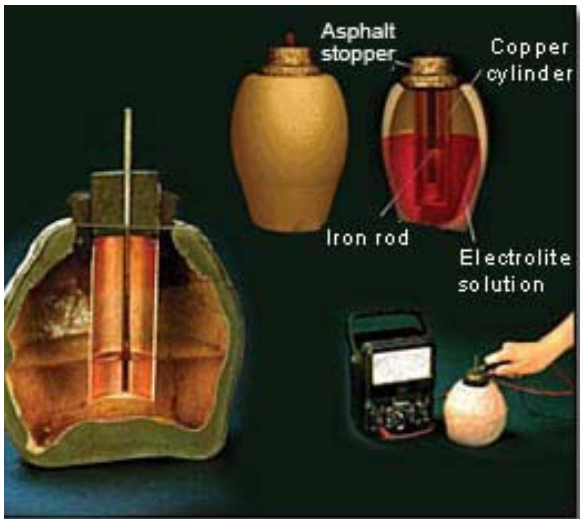

Figure 1. The "Baghdad Battery", from 200 BC Persia (speculated use)

Aqueous-based cells and batteries can produce flammable gases, usually hydrogen gas produced by electrolysis of water, during charging and operation, and can be consumed in a fire. Lithium-ion batteries, however, contain flammable organic electrolyte that can release significant chemical energy upon combustion.

Lithium-ion batteries have been commercially available since the early 1990s. Since that time lithium-ion chemistry has become the dominant battery chemistry in a wide variety of consumer electronic devices. Adopting lithium-ion technology to automotive applications can appear, in many respects, to be a straightforward problem of scaling up an existing technology. However, there are a number of factors related to actual experience with lithium-ion cells compared to automotive industry performance requirements, current lithium-ion battery technology itself, as well as various potential issues with scale-up that may prove problematic.

Automotive requirements are significantly more demanding than those imposed on today's consumer electronics lithium-ion battery packs. Consumer electronics devices range in size and complexity from very small single cell devices (e.g., Bluetooth headsets, hearing aids) to multi-cell devices with elements connected in series. Very small cell devices run at nominal voltages of 3.7 V, with capacities in the range of 0.05 Ah (0.19 Wh), with rudimentary protection electronics.

Multi-cell devices such as notebook computer battery packs run at nominal voltages of up to 14.4 V with capacities up to 6.6 Ah (95 Wh) and higher, and implement complex protection electronics. Notebook computers arguably represent the largest population of relatively complex lithium-ion batteries in the commercial market. Most of these packs contain between three and sixteen individual cells connected in combinations of series and parallel cell stacks. It is therefore not un common to find pack configurations involving three- or four-series cell blocks with each block consisting of two or more cells connected in parallel. There are some notebook computer battery packs and power tool battery packs, which include larger cells or higher cell counts.

The maximum size of commercially available portable product battery packs has been effectively limited by international shipping regulations (ref. 1). Exemptions to hazardous materials transport rules for lithium-ion cells smaller than 20 Wh (effectively a 5 Ah cell with a nominal voltage of 3.7 V) and lithium-ion batteries smaller than 100 Wh (e.g., a battery pack with twelve 18650 cells of 2.2 Ah capacity each) are listed. Cells or battery packs that fall outside of the exemption limits must be transported as Hazardous Materials. Due to the generally smaller size of consumer products and their batteries, it can be argued that small form factor batteries make up the bulk of the market. The consumer products industry now has more than 20 years experience with small form factor cells, such that cell quality (manufacturing) and protection electronics (battery pack design) interact to generally result in adequate cell performance.

In comparison, based on the total number of vehicle manufacturers utilizing large-format lithium-ion cells in service, it can be argued that there is very limited experience with high volume large format (ref 2) Lithium ion cells or large parallel arrays of cells. A

small number (relative to typical consumer product battery pack populations) of larger lithium-ion battery packs have been manufactured for certain low volume (at the time of this writing) applications such as electric vehicles, satellites, grid stabilization applications, and military applications. Some of these large battery packs have been constructed using cells common to commercial applications. These designs involve connecting more than one cell in parallel to form elements or blocks that are then connected in series. Other large battery packs have been constructed from "large format cells" that have capacities in the range of 10 Ah to 100 Ah.

There is a whole lithium-ion cell family to consider; consisting of numerous lithium-ion cell chemistries being developed and deployed in consumer products of all kinds, ranging from tiny single-cell button batteries used in small consumer products such as wireless headsets to large EV batteries consisting of thousands of cells and producing hundreds of volts. What all practical or currently commercially available lithium-ion batteries have in common in varying degrees is: 1) Organic electrolyte; 2) Strong oxidizers and reducers, and; 3) No ion recombination rate ability. Due to their chemistry, all commercially available lithium-ion batteries exhibit a sensitivity to heat which can trigger a self-supporting exothermic chemical reaction and thermal runaway. Therefore, during normal operation, fail-safe controls applied directly to the batteries are required to control and limit such reactions during foreseeable use and abuse conditions.

Cell chemistry affects the stability and volatility of the cells. In very general terms, more volatile cell chemistries provide a greater energy density by mass, but can present a higher risk of a thermal runaway event. More stabile cell chemistries provide a higher threshold to thermal runaway, but generally also have lower energy density, which requires a bigger battery for equivalent energy - thus potentially more chemical fuel if a fire does occur.

Severe battery failures (failures that can cause injury; e.g., thermal runaway, cell venting, venting with flames) are rare events: it has been Exponent experience that a 1-in-1-million failure rate (for severe failures) has historically been considered a minimally acceptable rate by the US Consumer Product Safety Commission (CPSC). Batteries have been recalled if a defect in the battery that has injury potential was identified. A typical severe consumer electronics device battery failure is generally limited to the device and its immediate surroundings. Most resulting fires, if they occur, can be controlled with a hand extinguisher or equivalent, unless, for instance, undetected and allowed to progress into a house or building fire. Severe failure of a large format battery will likely pose a significantly greater hazard simply due to the increased volume of potentially hazardous and flammable vent gas produced by reacting cells and increased electrical energy available.

Note that severe cell failures can be caused by a multitude of failure modes (ref. 3) associated with deficient cell design, cell manufacturing defects, mechanical or thermal damage, user abuse, or other issues. Relative to consumer electronics applications, the automotive environment poses increased risk of mechanical damage to batteries due to operation in a highly dynamic environment, and the potential for direct or indirect collision-related insult. Additionally, thermal stress subsequent to a collision and ignition of non-battery components of the vehicle could occur. Thus, even if they had comparable cell and battery pack designs and manufacturing defect rates, the automotive industry might experience an increased rate of severe cell failures, greater than that seen in consumer electronics. Therefore, vehicle manufacturers must forecast these potentials and act to reduce the likelihood of occurrence. To maintain comparable severe failure rates, automotive battery designs must be designed to be even more robust and tolerant to factors such as internal faults and external damage than current commercial battery designs.

In many cases, the cells are produced by one independent company, which provides them to a second independent company which packages them together into a battery or power unit, perhaps with built-in electronic thermal sensors and other controls, which are then provided to a final manufacturer for assembly into a vehicle or other product. This can make root cause analysis and application of production system corrections challenging, particularly in a rechargeable battery environment where a fault may not propagate itself until years after fabrication. Systems for accurately back-tracking manufactured cell lots used in battery pack assembly will be critical. Motor vehicle manufacturers are already accustomed to this supply chain sequence and have sophisticated tracking mechanisms to look down the supply chain to locate original sources.

A subset of this paradigm shift is also to understand how to respond to an emergency situation involving lithium-ion batteries, particularly as envisioned for use in automotive products. Something as straight forward as fire suppression becomes a difficult

question to which there is common consensus opinion. Historical experience with consumer product lithium-ion batteries, does not necessarily apply. There is little field experience with fire suppression of large-format lithium-ion batteries. In general, the best way to extinguish a lithium-ion battery fire is to extract the heat from the chemical reaction. Water has good cooling properties, yet to flood a high-voltage battery with water has potential hazards and limitations of its own, and it is not known how these concerns are addressed in current rescue/firefighting codes and protocols.

Analysis and testing is also required to understand the potential organic by-products of a runaway chemical reaction for a specific cell chemistry, what potentially harmful gases may be vented and in what quantities.

There are many areas of concern where there is very limited public field experience with lithium-ion batteries as a power source in volume automotive production, and issues tend to change as production moves from low-volume prototype testing, where batteries are typically manufactured and assembled with temporary tooling or by hand, to high-volume production with many automated operations. The risk tends to evolve, and the lack of a product failure modes knowledge base hinders facilitation of mitigating actions.

Failures of cells/batteries can have various effects of various severities, but that could include: loss of function of the product or vehicle; property damage to the device or vehicle itself; property damage to a manufacturing plant or test facility; property damage to the house or building where the product or vehicle is being used or stored and/or charged; and personal injury or death due to combustion and/or chemical reaction by-products such as harmful gases.

Lithium-Ion Battery Technology

Although scaling-up existing lithium-ion technology may seem to be relatively straightforward, as noted earlier, various potential issues may be problematic. As an illustration we present two examples of the difficulties involved in scaling up lithium-ion technology for application in EVs and HEVs; maintaining cell electrode coating quality, and adopting battery protection approaches from consumer electronic devices.

The term lithium-ion battery refers to a family of battery chemistries where the negative electrode and positive electrode materials serve as a host for the lithium-ion (Li^+). Like a lithium metal battery (lithium metal negative electrode), a lithium-ion cell provides a high-energy density and a high-voltage potential. These batteries differ from lithium metal batteries in that lithium-ion cells use lithium intercalation compounds as the negative electrode material rather than metallic lithium. Use of intercalation compounds for electrodes does reduce energy density relative to lithium metal systems, but it possible to recharge the battery over hundreds of cycles (ref. 4). The lithium intercalation sites in the negative and positive electrodes are at different chemical potentials; therefore, discharge is spontaneous and limited by diffusion. In this system, the useful energy comes from electrons moving to a lower electrical potential while compensating for the transfer of positively charged lithium from the high chemical potential intercalation material to the lower chemical potential intercalation material.

The four primary functional components of a practical lithium-ion cell are the negative electrode (anode), positive electrode (cathode), separator, and electrolyte. Additional components of lithium-ion cells such as the current collectors, case or pouch, internal insulators, headers, and vent ports can also impact cell reliability and safety. The chemistry and design of all of these components can vary widely across multiple parameters. The market is currently dominated by lithium-ion cells that have similar designs: a negative electrode made from carbon/graphite coated onto a copper current collector, a metal oxide positive electrode coated onto an aluminum current collector, a polymeric separator, and an electrolyte composed of a lithium salt in an organic solvent. For the purposes of this paper, the discussion will be limited to these types of lithium-ion cells.

The lithium-ion cell negative electrode is composed of carbon/graphite powders combined with a binder material that is coated in thin layers onto a metal foil current collector. The nature of the carbon can vary considerably: in particle size, particle size distribution, particle shapes, particle porosity, crystalline phase of carbon, etc. The negative electrode material mixing and coating process is often proprietary as variations in processing parameters will affect the resultant coating, and have a strong effect on cell capacity, rate capability, and ageing behavior.

There are varieties of positive electrode materials used in traditional lithium-ion cells – as with the negative electrode, these materials are powders that are combined with conductivity enhancers (carbon) and binder, and coated in a thin layer onto a foil current collector. The most common material is lithium cobalt dioxide (a layered oxide). However, various other materials are used such as lithium iron

phosphate, spinels, such as lithium manganese (Mn) oxide, or mixed metal oxides that include cobalt (Co), nickel (Ni), aluminum (Al), and manganese oxides.

The electrolyte in a traditional lithium-ion cell is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate. These solvents contain solvated lithium-ions, which are provided by lithium salts such as lithium hexafluorophosphate ($LiPF_6$).

In a cell thermal runaway, electrolyte vents from a cell. The resulting vent gases are flammable due to the organic solvents, and may also be toxic due to the dissolved lithium salts. Much of the discussion surrounding safety of lithium-ion cells is directly related to the flammability of the electrolyte. Discussions of electrode stability, self-heating rate, resistance to over-charge, resistance to cell internal shorts, resistance to external shorts, resistance to crush (e.g., from automotive collisions), resistance to thermal abuse, and reliability of pack protection electronics are primarily driven by concern over the likelihood of cells undergoing thermal runaway reactions that cause venting of a flammable electrolyte. Ignition can also occur if the vent gases come into contact with any number of possible competent ignition sources including hot surfaces (possibly heated cell cases), sparks, or open flames. For example, garage spaces often contain heaters with pilot lights. Furthermore, the automotive industry must plan for severe vehicle collisions where numerous ignition sources exist such as sparks from metal scraping on pavement, lamp filaments, arcing of electric systems, etc.

The use of copper as the current collector for the negative electrode has particular reliability and safety implications. At severe levels of battery discharge, usually ~ 1 V for the cell, the copper current collector will begin to oxidize and dissolve. On subsequent recharge, the dissolved copper plates onto negative electrode surfaces, reducing their permeability and making the cell susceptible to lithium plating and capacity loss. Usually, once a severe over-discharge event has occurred, cell degradation accelerates because once the negative electrode has become damaged by copper plating it will no longer be able to uptake lithium under "normal" charge rates. In such an instance, "normal" charge cycles cause lithium plating, which result in a greater loss of permeability of the surfaces. Ultimately, over discharge of cells can lead to cell thermal runaway.

Most consumer electronics devices set specific discharge limits for their lithium-ion battery packs to generally prevent over-discharge. The protection electronics disconnect the pack from the discharge load, but they cannot prevent over-discharge resulting from self discharge of cells. Thus, if a device is fully discharged and then stored for an extended period, the cells may become over-discharged, or if a mild short exists within the battery, the cells may become over-discharged within a short time. Most pack protection electronics will allow recharge of over-discharged cells, despite the potential for the negative electrode to have become damaged. In single cell consumer applications (e.g., cell phones), the resulting capacity fade, and elevated impedance of the battery will generally drive a user to replace the battery pack. Nonetheless, over-discharge does periodically cause thermal runaway of single cell battery packs. In multi-series element battery packs (e.g., notebook computers), the capacity fade, and elevated impedance will usually cause a severe block imbalance that drives permanent disabling of the battery pack.

Electrode Quality

Practical lithium-ion cell and battery pack lifetimes are strongly related to electrode coating uniformity. A uniform electrode coating will ensure that electrode material from all parts of a single cell performs in the same way: that one portion of the electrode is not being over-charged or over-discharged, while another portion of the electrode remains within an acceptable operational envelope, particularly as the cell ages. Localized overcharge or over-discharge within a cell could lead to reliability and safety problems.

Uniform electrode coatings also result in cells that have well matched capacities and internal impedances that will perform well when assembled into large battery packs. On commercial cell production lines, after cells are manufactured (and also sometimes before they are assembled into battery packs), cells are tested for capacity and impedance, and then graded based on these parameters. Severe outliers are rejected. This grading and matching process serves to group together cells with uniform qualities "as tested" in 2 to 3 Ah segments. As long as the cells are properly matched, batteries produced from them will perform well even with tight cut-off voltages.

If an electrode coating process produces variability; for example, coating thickness increases steadily from one end of a roll to another, small cells produced from the beginning of a roll will likely match each other and internally contain fairly uniform electrodes, while small cells produced from the end portion of the roll will likely match each other and internally contain fairly uniform electrodes,

but small cells produced from the beginning of the roll will likely not match small cells produced from the end of the roll (Figures 2 and 3). Large cells produced from the same roll would likely be more difficult to match, and in addition, their internal electrodes could exhibit more significant variability. The presence of this greater variability would require the application of more gracious cut-off voltages – effectively "derating" a battery pack and increasing cost per capacity.

When impedance is measured across a large format cell or a large parallel array of cells, the resulting values are the average of values across all of the electrodes and parallel cells. Similarly, the capacity of a large format cell or a large parallel array of cells is an average of the capacity of the entire electrode area. Thus, a zone of high impedance (or low capacity) on a small part of an electrode or within a single cell in a large parallel array, will appear identical to a modest impedance increase (or a modest capacity decrease) over the entire electrode or all cells within a parallel array.

In consumer electronics battery packs, independent voltage sensing (and thus, calculated capacity and cell impedance) occurs at each block element resulting in approximately one voltage sensor per 5 Ah of installed capacity. In comparison, for a ten 18650 cell block there will be one voltage sensor per 25 Ah of capacity, and for a large format cell there might be one sensor per 50 Ah of capacity: a reduction of sensor "density" by a factor of 10. Should a relatively high impedance (or low capacity) zone form within a larger cell or a large parallel array of cells, it will be undetectable via this measurement approach. However, the presence of even small high impedance or low capacity zones may result in electrode degradation that can accelerate cell aging, and possibly cell thermal runaway.

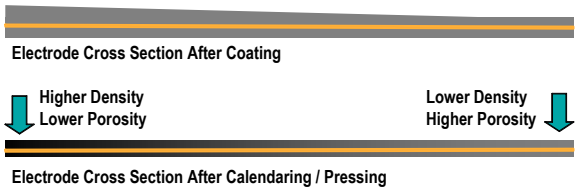

Figure 2. Effects of non-uniform coating on electrode density and porosity

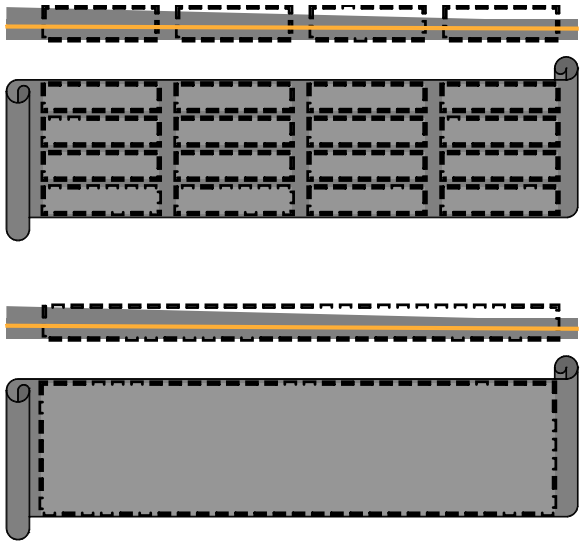

Figure 3. Schematic depiction of an electrode roll with large-scale coating thickness variation, and the effect of that variation on small and large format electrodes cut from the roll.

Beyond the challenges associated with large scale coating variation, defects in coatings that can cause cell failures (Figure) are more likely to be detected during grading of small cells as the size of defect that is detectable scales more favorably with the area of electrode that is being tested. Thus, production of large format cells with quality comparable to typical commercial cells requires tighter control of a range of coating processing parameters than for production of small commercial cells.

If an internal short occurs within a cell, the shorting location can draw energy from the entire cell, as well as any cells connected in parallel. Thus, a short that may result in a very mild failure in a small single cell, may result in a severe failure in a multi-cell configuration or in a large format cell. To date, Exponent is unaware of any testing conducted to assess the potential effect of cell capacities or high parallel cell counts on internal cell faults. There is also insufficient field data available to assess this issue.

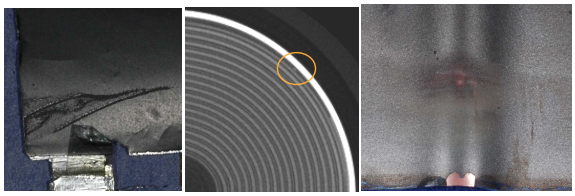

Figure 4. Three examples of coating defects: scratch, contaminant, delamination or void.

Battery Safety Devices

Consumer electronics battery packs rely on a number of safety devices to disable cells and battery packs that may have become degraded and could pose a risk of thermal runaway. Not all of these devices are compatible with large battery packs. For example, some small commercial cells, such as 18650s, integrate charge interrupt devices (CIDs).

On activation CIDs physically and irreversibly disconnect the cell from the circuit. Although CIDs are usually described as overcharge protection devices, they will activate if anything causes cell internal pressure to exceed the activation limit. This could include overcharge, cell overheating, significant lithium plating, mild internal shorting, and/or significant cell over-discharge. Should a CID activate in a large parallel array of cells, it will cause redistribution of the full current to other cells in the array. In two or three cell parallel arrays, CID's generally work as expected and facilitate a graceful failure of a battery pack. Ideally, if a significant fault condition were encountered, all CIDs in a parallel array would activate simultaneously.

In practice, however, these devices do not activate simultaneously, which can result in high current application to a small subset of array cells with non-activated safety devices, leading to over-current over-charge conditions that can cause cell thermal runaway (Ref. 8).

In most consumer electronics applications, a benign battery failure (e.g., loss of capacity, or inability to recharge) is viewed as a nuisance rather than a critical failure. Thus pack protection electronics in notebook computers generally are capable of permanently disabling a battery pack if certain conditions are detected including a variety of out-of-range conditions such as excessive pack temperature, as well as when the functionality of various components is in doubt, in order to produce graceful failure of a battery pack rather than a severe failure.

The permanent disable features in notebook computers also effectively provide a mechanism for acceptable premature end-of-life of these battery packs. For example, one of the conditions that will cause permanent disabling of a notebook computer battery pack is a severe block imbalance: the pack is disabled if there is a significant voltage divergence between series elements (blocks) within the pack. Block imbalance detection is often discussed in literature as a redundant method for preventing cell over-charge. However, in practice, block imbalance detection serves to detect cells that have become damaged, for example, by severe over-discharge, internal shorting, electrolyte leakage, etc. Continued cycling of cell blocks containing damaged cells could result in thermal runaway reactions. In automotive applications, with many blocks in series and many series strings in parallel, permanent battery pack disabling may be required if block voltages become too unbalanced.

CONCLUSIONS

Despite a long and largely successful history in consumer electronics devices, the use of lithium-ion cells in automotive applications continues to pose a range of challenges, a few of which have been discussed here. There is very limited public field experience with lithium-ion batteries as a power source in automotive products. Protocols for shipping and handling large format batteries in various states of charge are in their infancy, as well as those for emergency response to large format battery fires. One of the main challenges in solving the technical issues will be to identify and fully address risk elements that attach to use of lithium-ion technology batteries in the automotive environment. Prior experience with smaller scale consumer product applications can serve as guidance to these risk considerations and other analytical techniques may assist in identifying and evaluating risks to be addressed.

REFERENCES

1. UN Transport of Dangerous Goods – Model Regulations, ICAO Technical Instruction for the Safe Transport of Dangerous Goods by Air, IATA Dangerous Goods Regulations, etc.
2. The term "large format" is often loosely applied in the lithium-ion battery area, as the definition is linked to transport regulatory requirements that have been subject to change. Based on recent UN Model Regulations, a large format cell contains more than 20 hr of energy (for example, more than 5 Ah capacity with a 3.7 nominal voltage), while a large format battery pack contains more than 100 Wh of energy (for example, a battery pack containing more than twelve 2.2 hr cells).
3. Mikolajczak C, Stewart S, Harmon, J, Horn, Q, White K, Wu M, Mechanisms of latent internal cell fault formation and opportunities for detection, Proceedings, 2008 NASA Aerospace Battery Workshop, Huntsville, AL, November 18–20, 2008 and Mikolajczak C, Stewart S, Harmon, J, Horn, Q, White K, Wu M, Mechanisms of latent internal cell fault formation, Proceedings, 9th BATTERIES Exhibition and Conference, Nice, France, October 8–10, 2008.

4. Attempts to manufacture practical rechargeable lithium metal batteries with cycle life greater than 300 cycles have generally proven unsuccessful to date due to uneven lithium plating (dendrite formation) during charging.
5. Kishiyama C, et al, "Improvement of Deep Discharge Capability for Lithium Ion Batteries," Abs. 425, 204th Meeting, The Electrochemical Society, Inc., 2003.
6. Zhao M, et al., "Electrochemical Stability of Copper in Lithium-Ion Battery Electrolytes," *Journal of the Electrochemical Society*, **147** (8) (2000) 2874-2879.
7. A PTC device may serve to limit the current available to a shorting cell.
8. Jeevarajan J, "Performance and Safety Tests on Lithium-Ion Cells Arranged in a Matrix Design Configuration," Space Power Workshop, April 2010.