Vehicle Battery Safety Roadmap Guidance

Daniel H. Doughty, Ph.D.
Battery Safety Consulting, Inc.
Albuquerque, New Mexico

Technical Monitor:
Ahmad A. Pesaran, Ph.D.
National Renewable Energy Laboratory

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Foreword

In 2010, the National Renewable Energy Laboratory (NREL) entered into a subcontract agreement with Dr. Daniel Doughty, the principal of Battery Safety Consulting Inc. At NREL, we perform battery research and development (R&D) in areas of materials, modeling, testing, and system analysis, particularly as they relate to the lithium-ion (Li-ion) battery safety modeling and testing for electrified vehicles. This work was supported by the U.S. Department of Energy's (DOE) Energy Storage R&D Vehicle Technologies Program in the Office of Energy Efficiency and Renewable Energy under DOE/VTP Agreement 16378 of the 1102000 B&R, NREL Task Number FC086200.

The purpose of the subcontract was to investigate the research, development, and other activities related to the safety of Li-ion batteries for electric drive vehicles and to provide recommendations for developing a DOE roadmap for the safety of Li-ion batteries for electric drive vehicles. Dr. Doughty has a long, distinguished career in battery R&D, particularly at Sandia National Laboratories (SNL), where he was responsible for the safety and abuse tolerance testing of batteries for more than 15 years. Dr. Doughty has chaired the Society of Automotive Engineers (SAE) committee that revised and updated SAE Recommended Test Procedure J2464, "Electric and Hybrid Electric Vehicle Rechargeable Energy Storage System (RESS) Safety and Abuse Testing," published November 2009. With his strong experience in battery safety and involvement with safety committees, Dr. Doughty was in a unique position to perform this work by collecting the necessary information, interacting with key players in the community, and providing recommendations.

This document is divided into two sections: (1) the synopsis, which discusses high-level findings of the work, and (2) the full report, which provides a comprehensive, in-depth review of the state of the art and also discusses interactions with experts, users, researchers, and developers from different organizations interested in the safety of vehicle batteries.

The findings and recommendations in this document will be taken into consideration by the Energy Storage R&D Program at the DOE Vehicle Technologies Program for further defining the R&D roadmap for developing safer batteries for electric drive vehicles. We appreciate the support provided by Dave Howell and Brian Cunningham of DOE's Vehicle Technologies Program.

Ahmad A. Pesaran, Ph.D.
Energy Storage Team Lead
Subcontract Technical Monitor
National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, CO 80401

ahmad.pesaran@nrel.gov

Synopsis

The safety of electrified vehicles with high-capacity energy storage devices creates challenges that must be met to ensure commercial acceptance of electric vehicles (EVs) and hybrid electric vehicles (HEVs). One of the most important objectives of DOE's Office of Vehicle Technologies is to support the development of Li-ion batteries that are safe and abuse tolerant in electric drive vehicles.

Batteries for EVs and HEVs, which in this document includes plug-in hybrid electric vehicles (PHEVs), are different from batteries developed for other applications. The environment that vehicle traction batteries experience during their life is more difficult than for applications such as portable computers, cell phones, or stationary applications. High-performance vehicular traction energy storage systems must be intrinsically tolerant of abusive conditions, including overcharge, short circuit, crush, fire exposure, overdischarge, and mechanical shock and vibration.

Battery safety and failure modes of state-of-the-art cells and batteries are reviewed and analyzed. Using this information, the roadmap presents recommendations on future investments in three areas:

- Improving our understanding of failure modes

- Developing better characterization tools

- Improving the safety of energy storage technologies.

Mission
The safety of electrified vehicles with high-capacity energy storage devices creates challenges that must be met to ensure commercial acceptance of EVs and HEVs. High-performance vehicular traction energy storage systems must be intrinsically tolerant of abusive conditions: overcharge, short circuit, crush, fire exposure, overdischarge, and mechanical shock and vibration. Fail-safe responses to these conditions must be incorporated into the design at the materials and system levels through selection of materials and safety devices that will further reduce the probability of single cell failure and preclude propagation of failure to adjacent cells.

Objectives
One of the most important objectives of DOE's Office of Vehicle Technologies is to support the development of Li-ion batteries that are safe and abuse tolerant in electric drive vehicles. This roadmap analyzes battery safety and failure modes of state-of-the-art cells and batteries and makes recommendations on future investments that would further DOE's mission.

Safety criteria for EV and HEV traction batteries may be viewed from different perspectives, and each original equipment manufacturer will have a unique safety approach tailored for its vehicle platform. However, two objectives will be fundamental to all efforts:

- Failure rate of cells that leads to thermal runaway will need to become exceedingly rare.

  o Note that the failure rates have been developed *for mass-produced cells such as the 18650*. The influence on failure rates of cell manufacturing techniques (wound versus

prismatic or z-fold design) as well as the effects of cell size/geometry on large format cells are largely unknown because of scant manufacturing history/experience. The relevancy and scaling of known failure rates are problematic; therefore, measuring achievement toward the objective is challenging.

- Propagation of thermal runaway from cell to cell leading to a cascading failure of a battery module or pack cannot be allowed to occur.

Background

Batteries for EVs and HEVs are fundamentally different from batteries developed for other applications. In addition to the scale difference—EV batteries store up to three orders of magnitude more energy than laptops—the environment that vehicle traction batteries experience during their life is more difficult than in other applications, such as portable computers or cell phones. The demanding environmental conditions include exposure to wide temperature extremes, vibration, high rates of discharge, and high rates of charge. High rates of both discharge and charge can occur at extreme temperatures. To increase an all-electric vehicle's driving range, the vehicle traction application will require high voltage, which in turn requires long strings of cells, long life, and high energy. Finally, because the focus of this study is on EVs and HEVs that are passenger vehicles, fire safety is a primary concern. Batteries with flammable electrolytes present challenges when designing the safety of a vehicle's energy storage device. These safety concerns are especially acute for PHEV and EV applications where vehicles may be charged in confined garage spaces of private residences and commercial businesses.

Safety cannot be determined or evaluated by one criterion or parameter. Rather, enhanced safety is determined by the implementation of several approaches that work synergistically, such as:

- Reducing the probability of a battery failure event

- Lessening the severity of outcome if an event occurs.

As this safety approach applies to vehicle batteries, thermal stability is perhaps the most important of several parameters that determine safety of Li-ion cells, modules, and battery packs.

When discussing battery safety, it is important to understand that batteries contain both an oxidizer (cathode) and fuel (anode as well as electrolyte) in a sealed container. Combining fuel and oxidizer is rarely done due to the potential of explosion (other examples include high explosives and rocket propellant), which is why the state of charge (SOC) is a very important variable. Lower SOCs reduce the potential of the cathode oxidizing and the anode reducing. Under normal operation, the fuel and oxidizer convert the stored energy electrochemically (i.e., chemical to electrical energy conversion with minimal heat and negligible gas production). However, if electrode materials are allowed to react chemically in an electrochemical cell, the fuel and oxidizer convert the chemical energy directly into heat and gas. Once started, this chemical reaction will likely proceed to completion because of the intimate contact of fuel and oxidizer, becoming a thermal runaway. Once thermal runaway has begun, the ability to quench or stop it is nil.

The energy content of batteries continues to increase as new electrode materials are developed with increased capacity and higher voltage operation. With these developments, new high-energy

cell designs are appearing in the marketplace. Electrode materials represent some of the most reactive materials known and operate at high voltage (4.2 V to 4.6 V).

Different battery chemistries have various failure modes, but several events are common among all types of batteries. A typical response of a cell to abusive conditions is generation of heat and gas. While they may be linked (i.e., gas and heat are produced by the same chemical reactions), there are occasions where heat and gas are produced independently.

Abuse tests are intended to emulate abnormal conditions or environments or when a battery pack is used in a manner outside the design parameters or beyond useful life. Abuse tests can be grouped into three major categories:

1. Thermal Abuse (includes thermal stability, simulated fuel fire, elevated temperature storage, rapid charge/discharge, and thermal shock cycling)

2. Electrical Abuse (includes overcharge/overvoltage, short circuit, overdischarge/voltage reversal, and partial short circuit)

3. Mechanical Abuse (includes controlled crush, penetration, drop, immersion, roll-over simulation, vibration, and mechanical shock)

Heat generation within battery cells (termed "self-generated heat") underlies many abuse responses and can make failures more hazardous. For example, a short circuit will heat up a cell because of Joule heating, which depends on the current and resistance of the cell ($I^2 R$). As the temperature increases, the cell begins to produce heat by internal chemical reactions (i.e., above the temperature where onset of self-heating reactions begin). Overcharge can also generate heat within the cell due to other chemical reactions that may trigger thermal runaway. In both of these cases, a comprehensive approach is essential to understand cell response and design of thermal management of the battery pack that incorporate cell thermal environment, heat capacity, and self-heating rate as a function of temperature.

In addition to safety incidents, which can arise when batteries are abused, spontaneous internal failures (called field failures) are observed in battery-powered equipment. Abuse tests in use today cannot predict or screen for field failure, as evidenced by the fact that:

- All battery recalls involve cells that have passed Underwriters Laboratories safety tests.

- Battery companies carry out 100% machine vision X-ray inspection.

- All battery manufacturers use high-potentiometer testing designed to find cells with internal short circuits.

Field failures arising from manufacturing defects that cause *internal short circuits* have very low probabilities of occurrence (estimates for 18650-size cells that fail catastrophically are 1 in 10 million cells to 1 in 40 million cells). While this may be reassuring for manufacturers of portable electronics, EV and HEV battery packs may have thousands of cells and up to 1,000 times more stored energy, making even this small failure rate unacceptable. The development of an internal short circuit test is an important objective and is being explored by several laboratories. Experimental simulation of internal short circuit field failure is also an important objective in

understanding failure mechanisms and mitigation. Several laboratories are pursuing approaches for these purposes and for validation of thermal models of field failure.

To characterize heat and gas generation that might occur during off-normal conditions, cells and packs are exposed to elevated-temperature abusive conditions that resemble conditions that might be seen in the field, if only rarely.

The materials comprising the cell have a profound influence on the safety and abuse tolerance of the cell and battery pack. The choice of cathode has a very significant influence on cell safety. New, high-energy cathodes are being used in commercial cells or are in development. Lithium cobalt oxide ($LiCoO_2$, or LCO) has been the cathode of choice for the majority of consumer-level Li-ion cells produced today. Although it delivers good capacity, it is the most reactive and has poorer thermal stability than other cathodes. Much progress has been made in commercializing safer cathodes. A comparison of the thermal stability of cathodes is shown in Figure S-1.
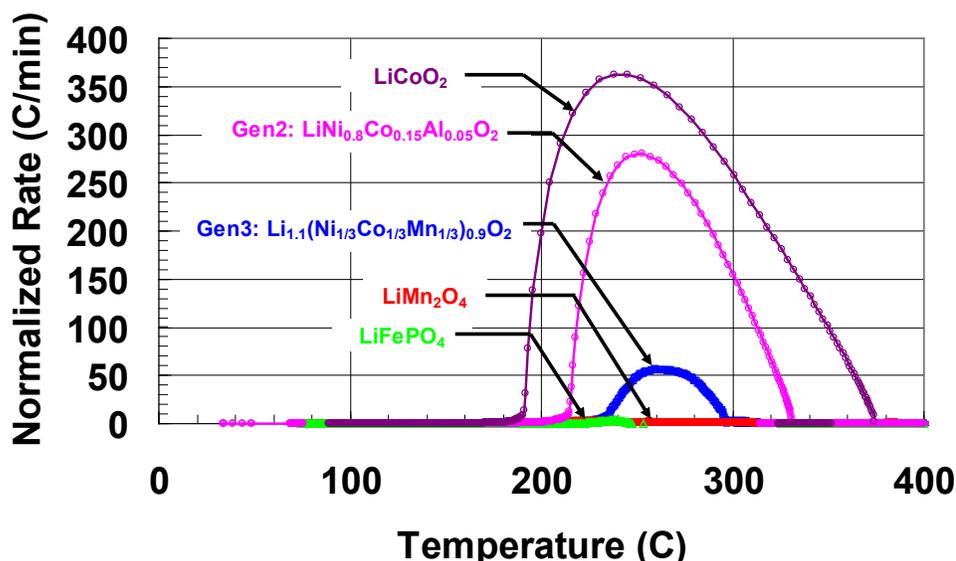
Figure S-1. Self-heating rate of the 18650 full cell as measured by accelerating rate calorimetry (ARC). Improving cathode stability results in a higher thermal runaway temperature (increased stability) and a reduced peak heating rate.

Source: E. P. Roth, D. H. Doughty, Proceedings of AABC 15-19 May 2006, Baltimore, MD.

Anode materials are chosen to have a high capacity, high rate capability, and low irreversible loss on formation cycling and stability with respect to cycling and high-temperature exposure. All of these material properties affect the thermal response of the anode under abuse conditions. The relative contribution of the anode and cathode material to the full cell response depends on the specific reactivity of the active materials and the mass loadings of each (the thermal stability of each electrode is important).

Shutdown separators are intended to stop current flow in a cell above a certain temperature limit. An ideal shutdown separator will have a sharp transition to a very high resistance at a relatively

low temperature, an ability to block high voltage, and a wide temperature window of stability. Separators generally are classified into three groups: (1) microporous polymer membranes, (2) non-woven fabric mats, and (3) inorganic composite membranes. The separators enhance cell safety by having properties of high mechanical strength (puncture resistance), high thermal stability, and desirable shutdown properties. However, less-than-ideal shutdown separators can be the source of internal shorts and cell failure above the shutdown temperature, especially in high-voltage, series-connected strings. Non-shutdown separators, even though not offering current-limiting protection, can offer a wider range of temperature stability.

The organic-based electrolytes used in Li-ion batteries have a unique characteristic compared to other electrochemical storage systems. Li-ion electrolytes are almost universally based on combinations of linear and cyclic alkyl carbonates. These electrolytes make possible the use of lithiated graphite (LiC_6) as the anodic active component, resulting in the high power and energy densities characteristic of the Li-ion chemistries. However, organic electrolytes have high volatility and flammability that pose a serious safety issue if the electrolyte is released during an abuse event and begins to burn. Under extreme conditions of voltage and temperature, electrolytes can react with the active materials of both anode and cathode to release significant heat and gas.

Technology Development Issues

The design of abuse-tolerant energy storage systems begins with specification of relevant abuse conditions and the desired responses to those conditions. Development programs sponsored by the U.S. Advanced Battery Consortium (USABC) [http://www.uscar.org] include characterizations of the candidate technologies in abuse tests. Uniform standards of characterization testing in this area have been established.

Abuse-tolerant subsystems will need to provide robust controls at several levels, up to and including the vehicle controller. These controls should include detection and management of the SOC, temperature, and electrical faults. Controls at the cell level will likely include devices for relief of internal pressure buildup and for external short circuit interruption. This latter approach must be compatible with the subsystem's functional and performance requirements.

In parallel with lithium battery developers' efforts to provide abuse-tolerant systems, the DOE has two strong battery R&D programs, Batteries for Advanced Transportation Technologies (BATT) [http://batt.lbl.gov] and Applied Battery Research (ABR) [www1.eere.energy.gov/vehiclesandfuels/technologies/energy_storage/applied_battery.html]. These DOE programs fund projects to improve the intrinsic chemical stability of Li-ion rechargeable battery chemistries through development of new materials, characterization of advanced commercial materials, and development of standard abuse test protocols.

The programs that are focused on safety and currently funded by DOE and USABC are grouped below according to topic of investigation (funding source and principal investigator's last name are included):

- Development of safer electrolytes (including non-flammable electrolytes)
  - Argonne National Laboratory: BATT – Electrolyte Degradation Modeling (Curtiss, Amine) [http://www.anl.gov/]

- o Arizona State University: BATT – Thermally Stable Electrolytes (Angell) [http://www.asu.edu/]

- o Brookhaven National Laboratory: ABR – Thermally Stable Electrolytes (Yang) [http://www.bnl.gov]

- o Case Western Reserve University: BATT – Nonflammable Electrolytes (Scherson) [https://www.case.edu/]

- o SNL: ABR – Non-Flammable Electrolyte Development (Orendorff) [http://www.sandia.gov]

- Electrolyte additives

  - o Argonne National Laboratory: ABR – SEI Electrolyte Additives (Zhang, Abraham)

  - o Idaho National Laboratory: ABR – Phosphazene-Based Electrolytes (Gering) [http://www.inl.gov]

  - o University of Rhode Island: BATT – Electrolyte Additives (Lucht) [http://www.uri.edu/]

- Development of safer cathodes

  - o Argonne National Laboratory: ABR – Gradient Cathodes (Amine)

- Development of safer separators

  - o Celgard: USABC – Separator Development (Ramadass) [http://www.celgard.com/]

  - o Entek: USABC – Separator Development (Pekela) [http://www.entek-international.com]

- Analysis of electrochemistry materials developed to improve safety

  - o SNL: ABR – Materials Evaluation (Orendorff)

- Overcharge protection

  - o Argonne National Laboratory: ABR – Overcharge Shuttle Development (Amine)

  - o Lawrence Berkeley National Laboratory: ABR – Overcharge/Redox Polymers (Richardson) [http://www.lbl.gov/]

- Abuse test method development

  - o NREL: ABR – Internal Short Circuit (Keyser) [http://www.nrel.gov]

  - o SNL: USABC – Internal Short Circuit, Electrolyte Flammability, Abuse Testing (Orendorff)

- System safety modeling

  - o NREL: ABR – Chemicals Reaction and Thermal Modeling (Kim, Santhanagopalan)

  - o NREL: Computer-Aided Engineering for Electric Drive Vehicle Batteries – Internal Short Circuit Modeling (Kim)

Proposed Path Forward

The projects mentioned above have made progress, but more work needs to be done to improve the safety of automotive traction batteries. The challenges of large-format energy storage applications should be addressed in a systematic manner through R&D. Based on an analysis of existing programs, the following three topical areas have the highest impact in addressing the gaps to improved safety and removing the sources of concern that could impede commercial success of EVs and HEVs.

1. Improve our understanding of failure modes

   A. Failure modes such as an internal short circuit have substantial negative consequences and are difficult to characterize.

      i. Elucidate the details and provide a better understanding of initiation and propagation of internal short circuits.

      ii. Develop a standardized test method that would determine cell susceptibility to this failure mode.

   B. Propagation of failure from cell to cell, which leads to catastrophic failure, cannot be tolerated.

      i. Build an easy-to-use, validated cell and battery pack abuse model that realistically captures propagation.

2. Develop better characterization tools

   A. Failures often have an incubation period of several hours, but when a "tipping point" is reached, a failure happens very fast.

      i. Develop diagnostic methods that could alert the Battery Management System (BMS) to an incipient failure and trigger early intervention, thus preventing a major incident.

   B. Understanding and improving safety of large battery packs is a priority.

      i. Develop models for cell, module, and battery pack safety and abuse tolerance.

3. Improve the safety of energy storage technologies

   A. Since cathodes continue to be a source of failure in Li-ion rechargeable batteries, invest in R&D for:

      i. Coated cathodes

      ii. Novel cathode discovery methods

      iii. Cathode conversion reactions.

   B. Develop non-flammable electrolytes. The flammability of the vented electrolyte is a significant unresolved safety issue for Li-ion batteries.

      i. Make a concerted effort toward reducing gas generation at elevated temperature as well as investigate ionic liquid electrolytes or other non-flammable solvents that could permanently solve the electrolyte flammability issue.

   C. Develop methods to prepare a "permanent solid electrolyte interphase (SEI)"

D. Develop new separators (and/or ceramic coatings applied to separator or electrode) as they can provide protection from internal short circuits and other abusive events.

    i. Answer questions such as "what method of application of a ceramic heat resistant layer provides the best safety result?"

    ii. Are shutdown separators necessary for high-voltage, series-connected cell strings?

E. Better understand the safety performance of batteries containing anodes made with silicon or other alloys. Currently the failure modes in Li alloy anodes (e.g., lithium dendrite formation on repeated cycling) occurring in these systems are not known. Fundamental understanding as well as more test data are needed.

Technical Report: Vehicle Battery Safety Roadmap Guidance

Prepared for:

National Renewable Energy Laboratory
15013 Denver West Parkway
Golden, CO 80401

Prepared by:

Daniel H. Doughty, Ph.D.
President

Battery Safety Consulting Inc.
139 Big Horn Ridge Rd. NE
Albuquerque, NM 87122 USA

dhdoughty@batterysafety.net

http://www.batterysafety.net

NREL Technical Monitor: Ahmad A. Pesaran, Ph.D.
Energy Storage Team Lead
Subcontract Technical Monitor

ahmad.pesaran@nrel.gov

Executive Summary

The most important objectives of the U.S. Department of Energy's Office of Vehicle Technologies is to support the development of lithium-ion batteries that are safe and abuse tolerant in electric drive vehicles. This roadmap analyzes battery safety and failure modes of the state-of-the-art cells and batteries and makes recommendations on future investments that would further DOE's mission.

Safety criteria for electric vehicle (EV) and hybrid electric vehicle (HEV) (including plug-in hybrid electric vehicles) traction batteries will be viewed differently, and each original equipment manufacturer will have a unique approach tailored for its vehicle platform. However, two objectives will be fundamental to all efforts:

- The failure rate of cells that leads to thermal runaway will need to become exceedingly rare (even lower frequency than today's estimated failure rate of 1 in 5 million cells)

- Propagation of thermal runaway from cell to cell, which leads to a cascading failure of a battery module or pack, cannot be allowed to occur.

Past efforts have traded increased battery safety for lower energy. The goal of this roadmap is to identify opportunities where high energy and safety can be simultaneously met—i.e., research and development (R&D) priorities that, if achieved, will enable development of cells and batteries that can support long-driving range and have sufficient safety to be used in EVs and HEVs.

The following topics are identified as needs that are not being met and for which additional funding would have the greatest impact on enabling safe, high-energy vehicle batteries.

This roadmap provides recommendations in three areas:

1. Improve our understanding of failure modes.

    A. Failure modes such as an internal short circuit have substantial negative consequences and are difficult to characterize. We recommend a systematic R&D program that would:

        i. Elucidate the details and provide a better understanding of initiation and propagation of internal short circuit

        ii. Develop a standardized test method that would determine cell susceptibility to this failure mode.

    B. Propagation of failure from cell to cell that leads to catastrophic failure cannot be tolerated. Building an easy-to-use, validated cell and battery pack abuse model that realistically captures propagation is essential.

2. Develop better characterization tools.

    A. Failures often have an incubation period of several hours, but when a "tipping point" is reached, they happen very fast. Diagnostic methods that could alert the BMS to an

incipient failure and trigger early intervention could pay big dividends by preventing major incidents.

    B. Models for cell, module, and battery pack safety should be a priority because they will drive understanding and improvements in safety of large battery packs.

3. Improve the safety of energy storage technologies.

    A. Cathodes continue to be source of failure in Li-ion rechargeable batteries. Three areas are recommended for R&D investments:

        i. Coated cathodes

        ii. Novel cathode discovery methods

        iii. Cathode conversion reactions.

    B. Develop non-flammable electrolytes. The flammability of the vented electrolyte and the amount of flammable gas ejected from a cell during abusive failure are significant unresolved safety issues for Li-ion batteries. The roadmap recommends a concerted effort in ionic liquid electrolytes that could permanently solve the electrolyte flammability issue.

    C. The stability of the anode/electrolyte interface needs to be durable and tolerant of excursions in temperature. SEI stability is a continuing problem. The roadmap recommends a concerted effort to prepare a "permanent SEI."

    D. New separators (and/or ceramic coatings applied to separator or electrode) can provide protection from internal short circuit and other abusive events. Many questions remain to be answered, such as what method of application of ceramic heat-resistant layer provides the best safety result?

    E. Understand the safety performance of batteries containing anodes made with silicon or other alloys.

Acknowledgements

List of Acronyms and Abbreviations

ABR	Applied Battery Research (DOE program)
ARC	accelerating-rate calorimetry
BATT	Batteries for Advanced Transportation Technologies (DOE program)
BMS	battery management system
Cu	copper
DEC	diethyl carbonate
DMC	dimethyl carbonate
DOE	U.S. Department of Energy
DSC	differential scanning calorimetry
EC	ethylene carbonate
ECS	The Electrochemical Society
EMC	ethyl methyl carbonate
EV	electric vehicle
Fe	iron
H_2	hydrogen
HEV	hybrid electric vehicle
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronics Engineers
IL	ionic liquid
ISO	International Organization for Standardization
LCO	lithium cobalt oxide
Li	lithium
$Li_4Ti_5O_{12}$	lithium titanate
LiC_6	lithiated graphite
$LiCoO_2$	lithium cobalt oxide
$LiFePO_4$	lithium iron phosphate
$LiMn_2O_4$	lithium-manganese oxide
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	nickel-cobalt-aluminum oxide
$LiPF_6$	lithium hexafluorophosphate
LTO	lithium titanate
MCMB	meso-carbon micro beads
MJ/kg	megajoules per kilogram
NASA	National Aeronautics and Space Administration
NiMH	nickel metal hydride
NMC	$LiNi_{1-x-y}Mn_xCo_yO_2$
NMP	N-methyl-2-pyrrolidone
NREL	National Renewable Energy Laboratory
O_2	oxygen
PC	propylene carbonate
PEO	poly(ethylene oxide)
PHEV	plug-in hybrid electric vehicle
R&D	research and development
SAE	SAE International
SEI	solid electrolyte interphase

SNL	Sandia National Laboratories
SOC	state of charge
UL	Underwriters Laboratories
USABC	U.S. Advanced Battery Consortium
VC	vinylene carbonate
VEC	vinyl ethylene carbonate
Wh/kg	watt-hour per kilogram

Table of Contents

List of Figures

9

List of Tables

1 Introduction

Batteries for electric vehicles (EVs) and hybrid electric vehicles (HEVs), which in this document include plug-in hybrid electric vehicles (PHEVs), are different from batteries developed for other applications. The environment that vehicle traction batteries experience during their life is more difficult than in other applications such as portable computers, cell phones, or stationary applications. The demanding environmental conditions include exposure to wide temperature extremes, vibration, high rates of discharge, and high rates of charge. The vehicle traction application will also require high voltage (which will require long strings of cells), high energy (which allows increased all-electric vehicle driving range), and long life. Finally, since the focus of this study is on EVs and HEVs that are passenger vehicles, fire safety is a primary concern. Batteries with flammable electrolytes present challenges when designing the safety of a vehicle energy storage device. These safety concerns are especially acute for PHEV and EV applications where vehicles may be charged in confined garage spaces of private residences and commercial businesses.

Safety cannot be determined or evaluated by one criterion or parameter. Rather, safety is determined by the implementation of several approaches that work together to enhance safety, such as:

- Reducing the probability of an event

- Lessening the severity of the outcome if an event occurs.

As this approach is applied to batteries, thermal stability is perhaps the most important of several parameters that determine safety of lithium-ion (Li-ion) cells, modules, and battery packs.

When discussing battery safety, it is important to understand that batteries contain both the oxidizer (cathode) and fuel (anode) in a sealed container. Combining fuel and oxidizer is rarely done due to the potential of explosion (other examples include high explosives and rocket propellant). Under normal operation, the fuel and oxidizer convert chemical energy to electrical energy with minimal heat and negligible gas. If allowed to react chemically in an electrochemical cell, the fuel and oxidizer convert the chemical energy directly into heat and gas. Once started, this chemical reaction will likely proceed to completion because of the intimate contact of fuel and oxidizer, becoming a thermal runaway. Once thermal runaway has begun, the ability to quench or stop it is nil.

The energy content of batteries continues to increase as new electrode materials with larger capacity and higher voltage are developed and new designs appear in the marketplace. Electrode materials represent some of the most reactive materials known and operate at high voltage (4.2 V to 4.6 V). The maximum theoretical voltage that can be obtained from known electrode materials is 6.5 V [lithium anode and copper (II) fluoride cathode].[1]

The highest specific energy available in today's commercial Li-ion rechargeable batteries is approximately 240 watt-hours per kilogram (Wh/kg), nearly 20% of the energy content of TNT

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[1] Linden, D.; Reddy, T. B. (2011). "Basic Concepts." Reddy, T. B., ed. *Linden's Handbook of Batteries, 4th edition*. McGraw Hill, 2011, ISBN 978-0-07-162421-3; pp 1.10–1.11.

at 4.61 megajoules per kilogram (MJ/kg) (1,282 Wh/kg).[2] Batteries are continuing to increase in energy density. Figure 1 compares gravimetric energy (specific energy) of various battery chemistries as well as liquid fuel for internal combustion engines.
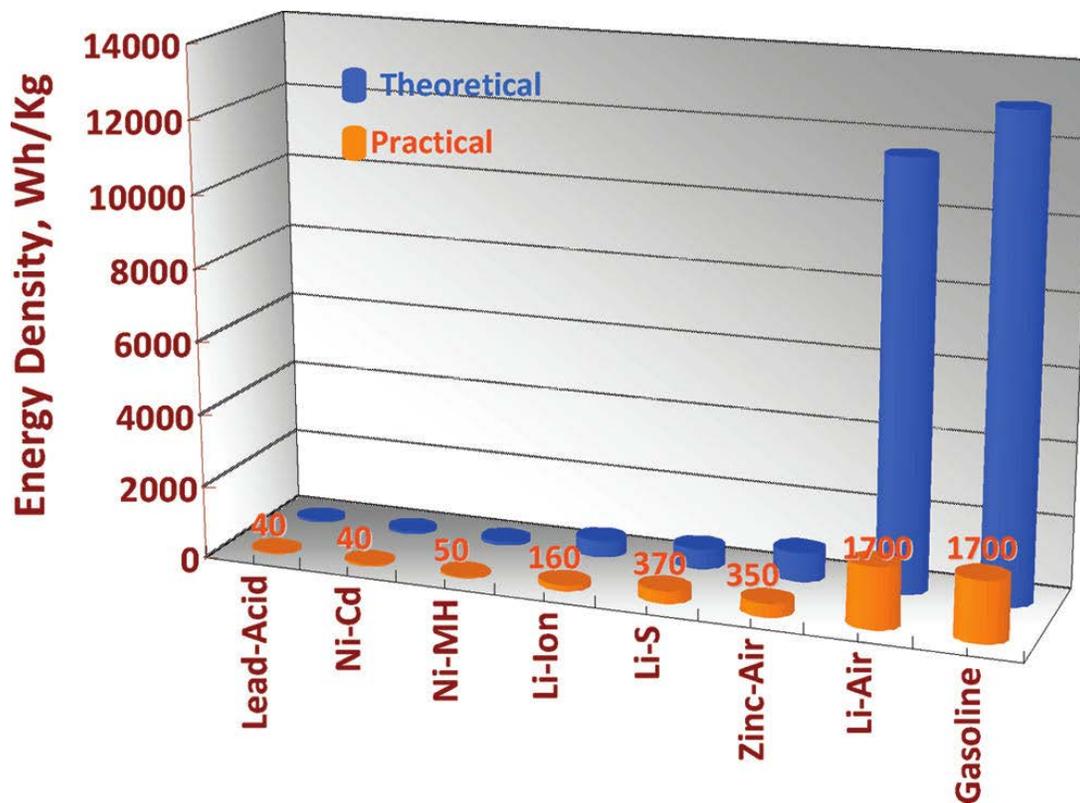
Figure 1. The gravimetric energy densities (Wh/kg) for various types of rechargeable batteries compared to gasoline.[3]

The theoretical density is based strictly on thermodynamics and is shown as the blue bars while the practical achievable density is indicated by the orange bars and numerical values. For lithium-air, the practical value is just an estimate. For gasoline, the practical value includes the average tank-to-wheel efficiency of cars.[3]

[Note: Comparisons of this type need to be regarded with caution, because the battery cell is a complete energy storage unit and can deliver electricity without additional equipment. Fuels, whether they are delivered to an internal combustion engine or fuel cell, are not complete and always require conversion equipment (i.e., the engine or fuel cell stack) as well as an oxidizer.]

[2] Kinney, G. F.; Graham, K. J. (1985) *Explosive Shocks In Air*, 2nd edition. Springer-Verlag.

[3] Girishkumar, G.; McCloskey, B.; Luntz, A. C.; Swanson, S.; Wilcke, W. (2010). *Journal of Physical Chemistry Letters*. 2010, 1, pp 2193–2203.

1.1 Characteristics of Battery Failures

Safety incidents can arise when batteries are abused (i.e., used in a manner outside design parameters or beyond useful life) or from spontaneous internal failures (called "field failures"[4]). Abuse failures can result during assembly, operation, or maintenance and are a much more likely occurrence.

Field failures usually arise from manufacturing defects and have very low probabilities of occurrence. The failure rate has been estimated between 1 in 10 million[4] and 1 in 40 million cells.[5] Tests in use today cannot predict field failures, as evidenced by the fact that:

- All battery recalls involve cells that have passed Underwriters Laboratories (UL) tests.

- Battery companies carry out 100% machine vision X-ray inspection.

- All battery manufacturers use high-potentiometer testing designed to find cells with internal short circuits.

The most serious consequences occur when the stored energy is rapidly released in an unintended manner, producing large quantities of heat and gas. The fact is that, because failures will occur, however infrequent, the challenge for cell and battery pack designers is to achieve a "*graceful failure*," (i.e., a failure that only has minor consequences and avoids a catastrophic failure). The goal of graceful failure can be realized by:

- Reducing the severity of response of individual cells to abusive events

- Implementing engineering approaches that keep individual cell failures from propagating to adjacent cells, thereby isolating the damage and reducing the risk of injury.

As we discuss in this roadmap, heat and gas generation are the key parameters that must be controlled to improve the safety of Li-ion rechargeable batteries. Heat generation increases exponentially with temperature while heat dissipation only increases linearly.[6] The response to any abuse scenario arises from the dynamics of heat generation and heat dissipation. Below we present three possible outcomes of an event that could lead to a safety incident.

Case #1 – An abuse event that leads to graceful failure at the cell level (*the preferred outcome*):

1. ONSET: An abuse event occurs within a cell that leads to an increase in temperature.

    A. Event can be an internal short circuit or an externally driven short circuit, adjacent cell heating, or overcharge.

2. ACCELERATION: Decomposition of reactants creates additional heat and gas. Reaction zone expands.

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[4] Barnett, B. M.; Roth, E. P.; Thomas-Alyea, K. E.; Doughty, D. H. (2006). "Abuse Tolerance versus Field Failure: Two Different Issues for Lithium-Ion Safety." Prepared for the *International Meeting on Lithium Batteries*, June 2006.

[5] Dahn, J.; Erlich, G. M. (2011). "Lithium Ion Batteries." Reddy, T. B., ed. *Linden's Handbook of Batteries*, 4th edition. McGraw Hill, 2011, ISBN 978-0-07-162421-3; pp 26–68.

[6] Levy, S. C.; Bro, P. (1994). *Battery Hazards and Accident Prevention*. Plenum Press, New York, NY.

3. NO RUNAWAY: Heat dissipation rate exceeds heat generation rate and cell is cooled, preventing thermal runaway.

Case #2 – An abuse event results in cell explosion but leads to graceful failure at the pack/module level (*an acceptable outcome*):

1. ONSET: An abuse event occurs within a cell that leads to an increase in temperature.

   A. Event can be internal short circuit or externally driven short circuit, adjacent cell heating or overcharge.

2. ACCELERATION: Decomposition of reactants creates additional heat and gas. Reaction zone expands.

3. RUNAWAY: Heat dissipation rate is less than heat generation rate, and cell enters thermal runaway.

   A. Additional heat and gas are produced.

   B. Decomposition of electrolyte proceeds to completion.

   C. Cell vents violently or explodes.

Adjacent cells heat up, but are not driven into thermal runaway. Propagation of failure is stopped after the initial cell failure.

Case #3 – An abuse event that leads to catastrophic failure at the pack/module level (*an unacceptable outcome*):

1. ONSET: An abuse event occurs within a cell that leads to increase in temperature.

   A. Event can be internal short circuit or externally driven short circuit, adjacent cell heating, or overcharge.

2. ACCELERATION: Decomposition of reactants creates additional heat and gas. Reaction zone expands.

3. RUNAWAY: Heat dissipation rate is less than heat generation rate and cell enters thermal runaway.

   A. Additional heat and gas are produced.

   B. Decomposition of electrolyte proceeds to completion.

   C. Cell vents violently or explodes.

4. Adjacent cells are driven into thermal runaway and explode. Cascade of cell failures consumes the entire battery module/pack.

Another way to analyze failures is to examine the cause(s) and to evaluate the efficacy of current control methods. A TIAX battery safety presentation included a slide that is a useful starting point for analysis.[7] The analytical approach identifies a trigger for a failure and asks the questions: "What is the cause and is it adequately being managed?" The analysis presented at

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[7] Stringfellow, R.; Ofer, D.; Sriramulu, S.; Barnett, B. (2010). "Lithium-Ion Battery Safety Field-Failure Mechanisms." Presented at the 218th Meeting of the ECS, Las Vegas, NV, Oct. 12, 2010 (Abstract #582).

The Electrochemical Society's (ECS) 218th Meeting in Las Vegas (see Figure 2) highlighted two areas that need attention:

1. Internal short circuit
2. Propagation of cell failures in pack or module.

In our discussion below, we will identify the mechanisms that underlie this sequence of events and highlight the methods that will make cells and battery packs more abuse tolerant to minimize the possibility of catastrophic failures.

Trigger	Why can this occur ?	Is this managed ?
Overcharge	Defective connections, failure of charging circuit	Yes, battery management system Yes, cell-level safety devices
Overheating from external sources	Battery pack placed too close to a heat source	Yes, cell-level safety devices open the cell at suitable internal pressure
Cell crushing creating massive internal shorts	Physical abuse of battery pack	Yes, design enclosures are built more tolerant to specific abuses
Internal short-circuits (a.k.a., field failures)	Internal-short caused by manufacturing defects	No, new technologies needed
Cascading of thermal energy release	Affected cell can raise the temperature of surrounding cells	No, new technologies needed

Figure 2. Managing Li-ion battery safety can be approached by analyzing the triggers of failures and how effectively they can they be managed.[7]

1.2 Approach

Information gathered for this roadmap came from several sources. A comprehensive literature search was conducted. Published results from existing U.S. Department of Energy (DOE) programs—Advanced Battery Research (ABR) (previously named Advanced Technology Development) and Batteries for Transportation Technologies (BATT)—were particularly valuable because detailed information about cell materials and construction was available.

Information presented at recent international meetings dealing with battery safety was included. These meetings were:

- ECS Symposium B2, *Battery Safety and Abuse Tolerance,* at the 218th Meeting of the ECS in Las Vegas, Nevada, October 10–15, 2010. D. H. Doughty was the lead organizer of this symposium.

- Knowledge Foundation's *Battery Safety 2010* and *Lithium Mobile Power 2010* in Boston, Massachusetts, November 3–5, 2010.

- *51st Battery Symposium* in Nagoya, Japan, November 9–11, 2010.

- *Pacific Power Source Symposium 2011,* Hilton Waikoloa Village, Hawaii, January 10–15, 2011.

Finally, input was solicited from many representatives of industry, academia, and national laboratories who have experience and expertise in safety and abuse tolerance testing. The list of individuals and organizations is presented in Table 1. All points of contact invited to participate were sent a list of questions (see Appendix A). Responses were obtained from slightly over half of the people on the list.

Table 1. Battery Safety Roadmap Points of Contact

	No.		
Battery Safety Roadmap Points of Contact.			
1. Scientists and Battery Research Programs.			
	No.		
US National Labs:	1	Argonne National Laboratory	Michael Thackeray
	2	Argonne National Laboratory	Khalil Amine
	3	Brookhaven National Laboratory	Xiao-Qing Yang
	4	Lawrence Berkeley National Lab	Venkat Srinivasan
	5	National Renewable Energy Lab	Ahmad Pesaran
	6	Oak Ridge National Laboratory	Nancy Dudney
	7	Sandia National Laboratories	Chris Orendorff
Universities and individual experts.			
	8	Dalhousie University	Jeff Dahn
	9	IIT	Jai Prakash
	10	SUNY-Binghamton	Stan Whittingham
	11	Battery Design Co.	Bob Spotnitz
	12	CNRS	Dominique Guyomard
	13	Univ. Munster	Martin Winter
	14	Broddarp of Nevada	Ralph Brodd
	15	Consultant	Rick Howard
2. Commercial Battery Companies and Material Suppliers			
US Battery developers and materials suppliers			
	16	A123	Tom De Lucia
	17	Ener1	Cyrus Ashtiani
	18	Johnson Controls-SAFT	Jim Symanski
	19	Yardney/Lithion	Rob Gitzendanner
	20	Amperex Technology Limited	Anthony Wong
	21	Celgard	John Zhang
	22	Entek Membranes	Rick Pekala
	23	Hydro Quebec	Karim Zaghib
	24	Quallion	Hisashi Tsukamoto
3. Battery Users – automotive.			
US Industry users (Detroit original equipment manufacturers & other car makers)			
	25	General Motors	Galen Ressler
	26	General Motors	Joe LoGrasso
	27	Ford	Ted Miller
	28	Chrysler	Ron Elder
	29	Tesla	Kurt Kelty
	30	Continental Powertrain Corp.	Olaf Bose
	31	Mitsubishi Motors	Gerry Wing
	32	United States Advanced Battery Consortium	Ahsan Habib (GM) or
	33	United States Advanced Battery Consortium	Kent Snyder (Ford)
4. Battery Users and other.		.	
Commercial Companies:	**US Industry users (Portable Electronics Manufacturers)**		
	34	Dell	Warren Payne
	35	Motorola	Jason Howard
	36	Materials Handling Group, Inc.	Laurence Dunn
Government agencies.			
	37	Naval Surface Warfare Center	Clint Winchester
	38	Naval Surface Warfare Center	Julie Banner
	39	ARL	Richard Jow
	40	NASA	Judy Jeevarajan
	41	NASA	Eric Darcy
	42	Department of Transportation	Spencer Watson
	43	NHTSA	Phil Gorney
Regulatory Agencies and Test Organizations.			
	44	Underwriters Laboratory	Lorie Florence
	45	Engineering Laboratory, Inc.	Jae-Sik Chung
	46	SGS U.S. Testing Company Inc.	Jody Leber
	47	Intertek	Rich Byczek
	48	Detroit Testing Laboratory, Inc.	Earl L. Smith

Much of the research that has been performed in the area of Li-ion abuse tolerance, which is the main subject of this Battery Safety Roadmap, has been performed under DOE's Vehicle Technologies Program.[8] The DOE's Vehicle Technologies Program office works with industry, universities, and national laboratories to develop advanced transportation technologies that would reduce the nation's use of imported oil (almost 96% of the U.S. transportation fleet uses oil). The Vehicle Technologies Program encompasses multiple activities: hardware development with industry [U.S Advanced Battery Consortium (USABC)], short-term research and development (R&D) (ABR), and focused fundamental research (BATT). The abuse tolerance work that has been performed is part of the ABR program, which encompasses the efforts of seven national laboratories and other government agencies. The program covers several interrelated areas, many of which impact abuse tolerance of the Li-ion cells (see Figure 3). Although this roadmap covers many of these topics, there are many areas of ABR- and BATT-supported research that are not explicitly covered. Please refer to the DOE website, particularly the "2010 Annual Progress Report for Energy Storage R&D" (http://www1.eere.energy.gov/vehiclesandfuels/resources/vt_es_fy11.html), for a more detailed listing of the many applicable areas of research.
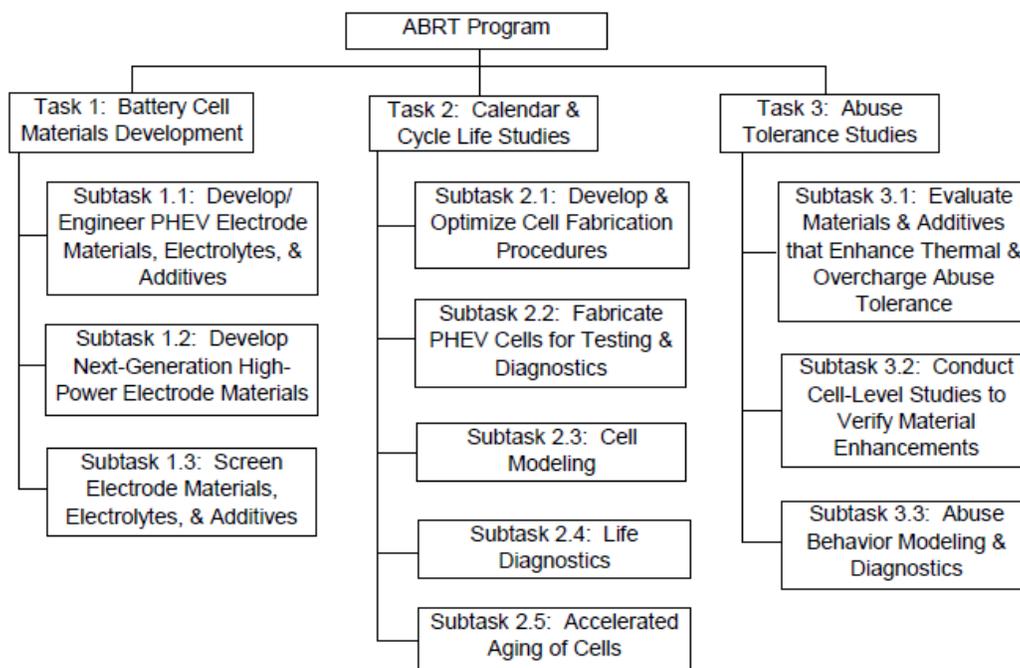
Figure 3. Structure of the DOE ABR program.[8]

1.3   Li-ion Rechargeable Batteries

The demand for high-energy rechargeable batteries has fueled remarkable growth of lithium secondary (rechargeable) batteries over the last 20 years. These advances are gradual, resulting in increases of specific energy in watt-hours per kilogram of a few percent per year for mature technologies, but up to 10% per year for new technologies, such as Li-ion (see Figure 4). Li-ion batteries have the advantage of high energy density, high cell voltage, and long shelf life. In

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[8] "Vehicle Technologies Program." http://www1.eere.energy.gov/vehiclesandfuels. Accessed March, 2012.

addition, they are relatively lightweight compared with lead-acid and nickel metal hydride (NiMH) technologies. Projections of higher energy Li-ion cells are impressive. For example, Hosoki presented plans for Panasonic to develop 18650-size cells up to 3.4 Ah within the next few years.[9] He also stated that a silicon-alloy anode with a modified $LiNi_{0.8}Co_{0.15}Al_{x0.05}O_2$ cathode will produce a 4.0-Ah cell in 2012. He stated that the separator is coated with ceramics on only one side (presumably the anode side).

Energy Trends in Commercial Li Ion Cells
Energy Density 18650 Cells
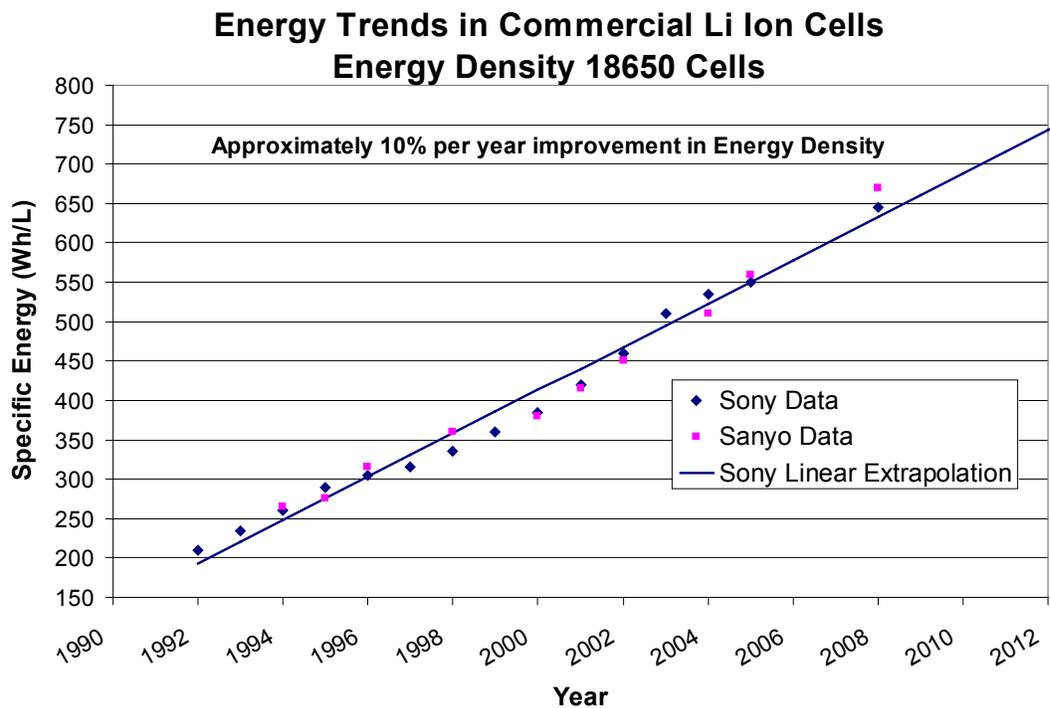
Figure 4. Energy density trends for commercial Li-ion cells.[9]

The use of lithium-containing anodes is associated with high energy density, high battery voltage, and good shelf life, but also may be associated with safety problems (e.g., fires) that are a consequence of the high energy content and flammable electrolyte that often is used in lithium systems. These attributes strongly depend on the choice of electrode and electrolyte materials.

There are many concerns with Li-ion chemistries, such as their sensitivity to overcharging and overdischarging, the flammability and toxicity of the materials, and thermal runaway. Because of these concerns, a variety of protection mechanisms are frequently employed in Li-ion batteries, such as internal cell safety shutdown separators, fuses, external contacts, advanced charging algorithms, and monitoring.

In well-designed and well-engineered battery assemblies with redundant control systems, failures are relatively rare. However, with the ever-increasing presence of battery-powered devices, from laptops and cellular phones to HEVs, even rare events can attract attention.

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[9] Hosoki, K. (2010). "Panasonic's Advanced Li-ion Batteries." Presented at Knowledge Foundation's *Lithium Mobile Power 2010 Conference,* November 4–5, 2010.

There are common failure modes that occur among all types of batteries. Cells with a flammable electrolyte or other flammable materials that could escape when the containment is compromised during a crush could present a fire hazard.[10] Heat generation and gas generation are the most common responses of batteries to abusive conditions.[3] While they may be linked (i.e., gas and heat may be produced by the same chemical reactions), there are examples where heat and gas are produced independently.

1.4   Li-Ion Polymer Batteries

An alternative to the liquid electrolytes is a solid polymer electrolyte formed by incorporating lithium salts into polymer, glassy, or ceramic matrices and forming them into thin films. The polymer may serve the function of separator as well as electrolyte, depending on the cell design.

Unlike Li-ion cylindrical or prismatic cells, which have a rigid metal case, polymer cells have a flexible, foil-type (polymer laminate) package but still contain organic solvent. The main difference between commercial polymer and Li-ion cells is that in the latter, the rigid case presses the electrodes and the separator onto each other, whereas in polymer cells this external pressure is not required because the electrode sheets and the separator sheets are laminated onto one another (Figure 5). Organic polymers are by far the most common type of separator in Li-ion polymer (Li-polymer) batteries.

The choice of electrode materials in Li-polymer batteries is generally similar to Li-ion batteries with liquid electrolytes, except where the electrochemical stability of the polymer used is less stable to oxidation (by the cathode) or reduction (by the anode). There are several versions of organic polymer electrolytes discussed in this section. Some of the polymers are true solid polymers without substantial amounts of additives or plasticizers, and others are gels with a large volume of liquid electrolyte (up to 70% by volume).

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[10] Roth, E. P.; Crafts, C. C.; Doughty, D. H. (2001). *16th Annual Battery Conference on Applications and Advances Proceedings*; April 2001, Long Beach, CA; p. 375.

Wound Prismatic Cell in Aluminum Laminate Package
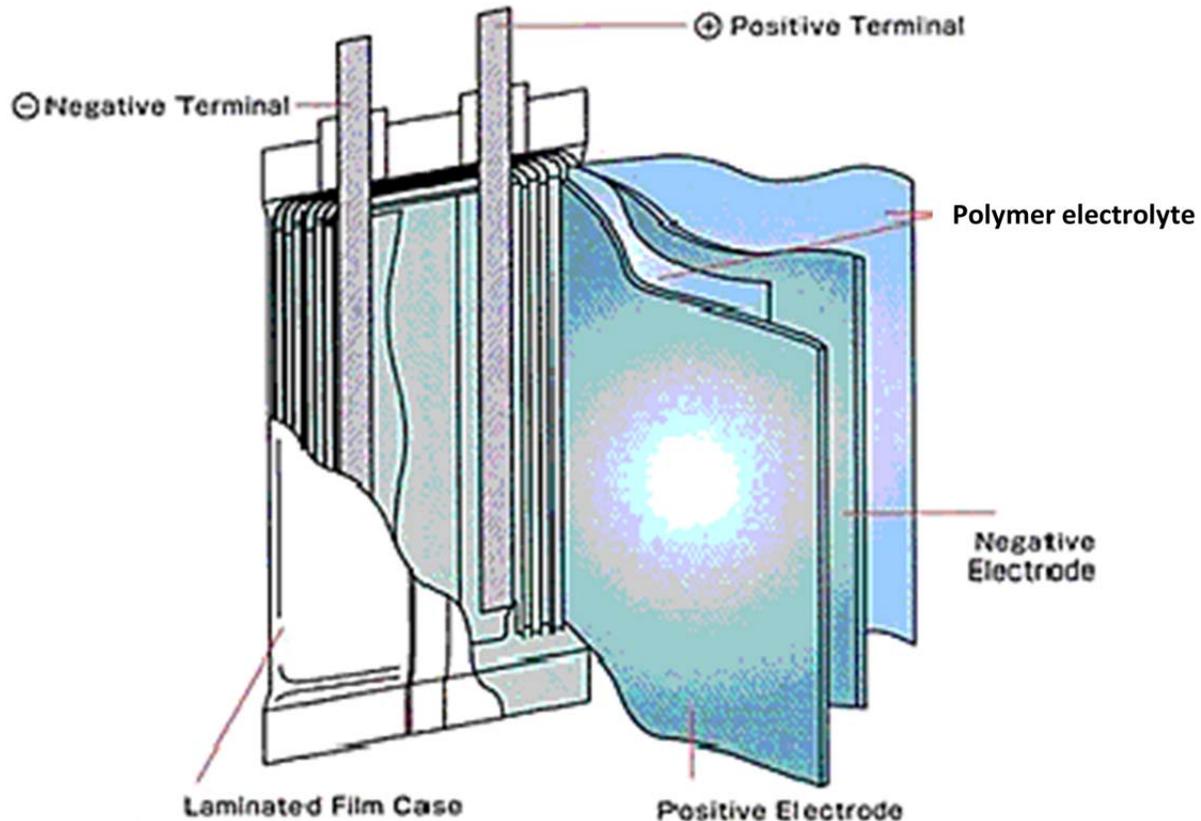
Figure 5. Illustration of Li-polymer battery.[11]

Initially, high molecular weight polymers such as poly(ethylene oxide) (PEO) and lithium salts such as $LiClO_4$ and $LiN(CF_3SO_2)_2$ (Li imide) were used in Li-ion rechargeable batteries. As "true solid polymer electrolytes," PEO-lithium salt electrolytes have good mechanical properties but low conductivities, which are about 10^{-8} S/cm at 20°C. Therefore, the batteries must be heated to 75°C–85°C to get sufficient conductivity. A significant improvement in room temperature conductivity (to $\sim 10^{-5}$ S/cm) has been achieved with the combination of modified comb-shaped PEO structures with lithium salts,[11] but these types of solid polymer electrolytes have poor mechanical properties and their conductivity is still two orders of magnitude lower than that of most organic liquid electrolytes. Further improvement in conductivity was obtained with the addition of liquid plasticizers, such as polypropylene carbonate.[12,13] The amount of plasticizer may be as high as 70%, resulting in limited chemical and mechanical stability.

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[11] http://www.mpoweruk.com/cell_construction.htm
[12] Abraham, K. M.; Alamgir, M. (1990). *Journal of Electrochemical Society*, 136 1657.

Because of the restricted high-voltage stability, many of the high-voltage Li-ion battery cathodes are not stable with PEO polymer electrolytes. PEO electrolytes will not be discussed in this roadmap, even though Bolloré in France has announced plans to commercialize the lithium metal polymer battery technology for BlueCar EVs.[14] It is the opinion of the roadmap author that the PEO-based cells are unsuited for vehicular application.

Another class of polymer electrolytes, called "gelled" electrolytes, has been developed by trapping liquid solutions of lithium salts in aprotic organic solvents [for example, $LiClO_4$ in propylene carbonate (PC)-ethylene carbonate (EC) solvent] into a solid polymer matrix, such as poly(vinylidene difluoride)[15] and poly(acrylonitrile).[16,17]

The "gel" electrolytes are made by adding liquid electrolyte solutions into the polymer porosity with an immobilization procedure, such as cross-linking, gellification, and casting. Cross-linking may be carried out by ultraviolet, electron-beam, or gamma-ray irradiation. Conductivities as high as 10^{-3} S/cm at 20°C and transference numbers around 0.6 have been obtained. However, these plasticized and gelled electrolytes have similar abuse response as liquid electrolyte Li-ion batteries.

Inorganic glasses and ceramics (e.g., NASICON conductive ceramic) can be used, but these materials are in the research phase[18] with the exception of companies trying to commercialize very thin-film, solid state batteries (15 μm or thinner and consequently low-capacity batteries) based on lithium phosphorous-oxynitride (LiPON) glass electrolytes initially developed at Oak Ridge National Laboratory by John Bates.[19] Batteries with glass or ceramic electrolytes will not be further discussed in this document because, in the opinion of the roadmap author, the likelihood of deployment of this technology for EV and HEV traction applications is remote.

The safety of polymer electrolyte cells is strongly influenced by the type of polymer electrolyte. In general, the trend of increasing safety will be (1) inorganic glass or ceramic electrolytes, (2) true solid polymers, and (3) gelled electrolytes.

In all cases, safety and abuse tolerance are still strongly influenced by the active materials that are used. The polymer electrolytes that do not contain solvents and plasticizers will have lower gas and heat production and should be more abuse tolerant. Cells made with gelled electrolytes should have similar safety performance if the organic liquids are similar or identical to those used in liquid electrolyte cells. For this reason, discussion of Li-ion rechargeable battery safety and Li-polymer battery safety are combined and treated the same in this roadmap.

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[13]Koksbang, R.; Gauthier, M.; Belanger, A. (1991) *Proc. Symp. Primary and Secondary Lithium Batteries*. Abraham, K. M.; Salomon, M. eds. The Electrochemical Society, Pennington, N.J.

[14] "The LMP Battery." Bluecar, http://www.bluecar.fr/en/pages-innovation/batterie-lmp.aspx. Accessed March 2012.

[15] Gozdz, A. S., et al. U.S. Patent No. 5,456,000, 10 October 1995.

[16] Abraham, K. M. (1993). *Applications of Electroactive Polymers*, Scrosati, B. ed. Chapman and Hall.

[17] Shen, D. H.; Nagasubramanian, G.; Huang, C. K.; Surampudi, S.; Halpert, G. (1994). *36th Power Sources Conference Proceedings*. Cherry Hills, NJ.

[18] "Advanced Lithium Battery Technology." POLYPLUS. http://www.polyplus.com/

[19] http://www.oakridgemicro.com/

2 Background

Cells are assembled into modules and battery packs for most applications. The details of the assembly are developed for the intended use. However, many structures are common. Figure 6 shows the generic relationship between cells, modules, and battery packs.
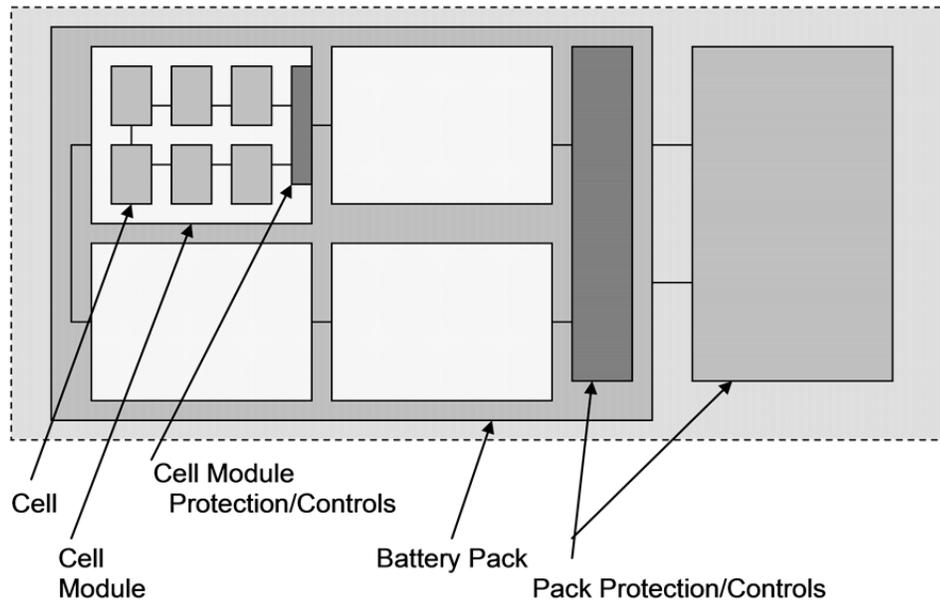
Figure 6. Schematic diagram of a battery pack, showing relationship of cells, modules, and control electronics.[20]

Safety must be addressed in the basic electrochemical cell. Safety-related issues also need to be addressed during the battery design and integration into an overall energy storage system. At the pack level, additional failure modes are possible. Careful attention to battery pack management strategies and good design principles is essential.

2.1 Cell Design

A battery is an energy storage device that functions by converting chemical energy into electrical energy by reduction and oxidation (redox) chemical reactions. Electrodes are composed of the active material, binders, conductive additives, and other materials that are in contact with (and often coated on) a current collector. As seen in Figure 7, the electrodes are held apart by a porous separator that has good ionic conductivity but poor electronic conductivity (to avoid an internal short circuit).

During discharge, the cathode active material (the oxidizer) is reduced and the anode active material (the fuel) is oxidized. The energy released during this reaction is directly proportional to the difference in the electromotive force between the two electrode materials. The highest

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[20] Diagram from UL 2580, "Standard for Safety for Batteries for Use in Electric Vehicles,"1st Edition, October 13, 2011.

voltage achievable is between the lithium anode and the copper (II) fluoride cathode, where the electromotive force is approximately 6.5 V. The stored energy is also proportional to the capacity of the electrode materials, i.e., how many electrons are released during the redox reaction per weight and volume of material.[21]
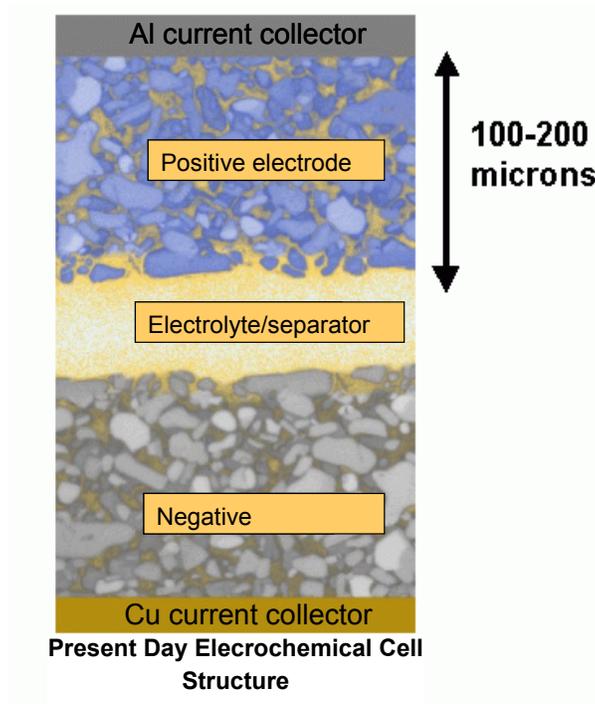
Figure 7. Electrode and cell structure of Li-ion rechargeable batteries.[24]

A schematic cutaway drawing of a cylindrical cell is shown in Figure 8. Because batteries have the fuel and oxidizer packaged together in the cell, if the energy embodied in these materials is inadvertently released in a way that triggers a rapid chemical reaction leading to thermal runaway, there is no way to interrupt the reaction since the fuel and oxidizer are in such intimate contact.

Traditional firefighting techniques that rely on separating the fuel and oxidizer cannot affect the outcome of a cell once runaway commences. The course of the reaction is exclusively dictated by the material state of change (SOC) and cell design, and it will proceed to completion within the cell. In battery packs, there is a risk that the failure of one cell will propagate to adjacent cells. Propagation of cell failure has been seen experimentally,[22, 23] as well as in accidents in the field. **The design goal for battery modules and packs should be to avoid propagation of thermal runaway from cell to cell.** This is especially true of large battery packs, such as those found in EVs and HEVs.

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[21] Levy, S. C.; Bro, P. (1994). *Battery Hazards and Accident Prevention*, Plenum Press, New York, NY.

[22] Govar, C. J.; Fuentevilla, D.; Banner, J.; Winchester, C. (2006). "Safety Lessons Learned from 18650 and D-Cell Lithium Ion Rechargeable Batteries in Unmanned Vehicles." *42nd Power Sources Conference Proceedings*, June 12, 2006, p 83.

[23] Doughty, D. H. (2005). "Li-ion Battery Abuse Tolerance Testing - An Overview." *AABC 2005 Proceedings*, Honolulu, HI, June 2005.

However, once thermal runaway has commenced within a battery pack, the best hope of traditional firefighting techniques is to cool the battery pack in such a way as to prevent a cascade of failures from cell to cell. The failure that is most difficult to guard against and typically is the most unpredictable is an internal short circuit. Internal short circuits were blamed for the well-publicized failures involving fires in laptop batteries in 2006. In 2008, HP, Toshiba, and Dell recalled over 430,000 laptops with Sony Li-ion rechargeable batteries.[25] These failures may be caused by contaminants such as metal particles inside the cells or manufacturing flaws such as burrs on the edge of current collector foils. Unlike an external short circuit or overcharge, where engineered methods and strategies can be effective at interrupting the abuse event, internal short circuits are not prevented by these safety devices.
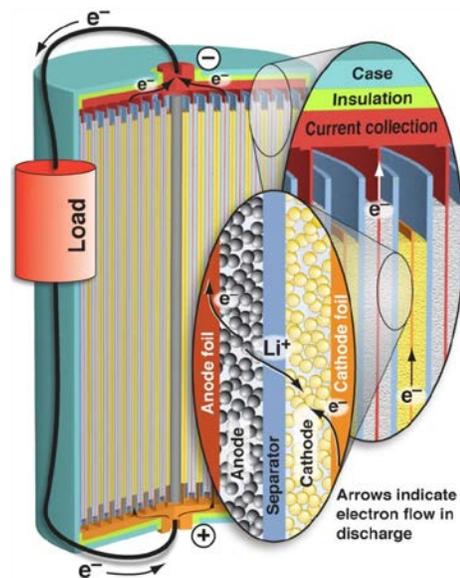
Figure 8. Cut-away drawing of cylindrical spirally wound Li-ion cell.[24]

2.2 Battery Safety Events

Safety problems can cause personal injury as well as financial loss to the battery pack suppliers and device manufacturers. In 2006, several laptop Li-ion battery fires did not result in injury but did initiate a Sony laptop battery recall that, while not the first of its kind, was the largest to date. A failure rate estimated to be 1 in 200,000 triggered an initial recall of almost six million Li-ion packs used in laptops manufactured by Dell and Apple[26] that was subsequently extended to batteries used in Sony, Lenovo/IBM, Panasonic, Toshiba, Hitachi, Fujitsu, and Sharp

If the energy contained in a battery cell is inadvertently released and results in thermal runaway, there is no way to quench the reaction because the fuel and oxidizer are in intimate contact.

R&D programs that allow original equipment manufacturers to understand the causes of these events, implement precautions, and make these failures exceedingly rare, will directly benefit EV and HEV safety.

laptops. The stated cause was contamination within the cell from metal particles created during cell manufacturing processes. Under some circumstances, after normal usage these particles can pierce the separator, creating an internal short circuit within the cell. Thus, electrical energy stored in a single cell was rapidly released, producing heat and gas from an exothermic oxidizing reaction. The cell temperature increased by several hundred degrees Celsius in a fraction of a

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[24] Colclasure, A. M.; Kee, R J. (2010). *Electrochimica Acta 55*, Society of Electrochemistry; pp 8960–8973.
[25] "Laptop Fires Prompt Sony Battery Recall — Again." *Wired* GADGET LAB, http://www.wired.com/gadgetlab/2008/10/laptop-fires-pr/. Accessed March 2012.
[26] "Lithium-ion Safety Concerns." Battery University, http://www.batteryuniversity.com/partone-5B.htm. Accessed March 2012.

second, and finally triggered thermal runaway. The high temperature of the failed cell heated up the neighboring cells, initiating a thermal runaway in other cells in the pack.

The extent of safety problems in the United States can be roughly estimated by searching the U.S. Consumer Product Safety Commission website, http://search.cpsc.gov. A search for "Battery Recalls" returned about 2,134 results that span the last 30 years. A search for "Battery Failure" gave about 580 results that span the last decade. Many of these recalls and failures were due to control circuitry rather than cell failures.

Typical Consumer Product Safety Commission recalls mention "an internal failure can cause the battery to overheat and melt or char the plastic case, posing a burn and fire hazard" as was observed in HP and Compaq notebook computer batteries (consistent with an internal short circuit). This failure seems similar to the Sony recall in 2006. However, it was based on only 20 reports of batteries overheating, including two in the United States.[27] There was a recent recall of a wireless headset with ATL Li-polymer batteries made by GN Netcom due to fire hazard in December 2008.[28] GN Netcom has received 10 reports of incidents involving overheating, including three reports of open flames and property damage to furniture on which the headsets were resting. An additional 37 reports of open flames and one report of second-degree burns that required medical attention were received from outside the United States. Laptop battery recalls seem to be recurring with regularity (e.g., HP laptop batteries were recalled again in May 2010 due to fire danger[29]).

The number of recalls and failures is small in comparison to production volumes. In 2005, 1.7 billion Li-ion and Li-polymer cells were made worldwide[30] with a projected volume of 2.2 billion cells per year by 2008. Estimates are that Li-ion rechargeable battery safety incidents occur in less than one in a million cells, and probably in less than one in 10 million cells.[2] However, even though the frequency is small based on a percentage basis, it has gained the attention of the Consumer Product Safety Commission and other consumer and transportation safety regulatory agencies.[31,32]

While rare, serious failures do occur in large packaged batteries. In November 2008, perhaps the largest single battery-related safety incident occurred to a developmental U.S. Navy electric submersible vehicle powered by fourteen 85-kWh Li-ion batteries. The Li-ion battery, a replacement for the silver-zinc battery, was both very high energy (>210 Wh/kg) and very large (>1 MWh). While under charge, one or more battery sections failed, resulting in a fire that consumed several of the battery assemblies and disabled the vehicle. There were no casualties,

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[27] "HP Recalls Notebook Computer Batteries Due to Fire Hazard." (2006). U.S. Consumer Product Safety Commission press release, 20 April 2006, http://www.cpsc.gov/CPSCPUB/PREREL/prhtml06/06145.html.

[28] "Wireless Headset Batteries Recalled by GN Netcom Due to Fire Hazard." *The Safety Review*, December 2008 edition, p 5. http://www.cpsc.gov/CPSCPUB/PUBS/tsr1208.pdf.

[29] "HP Expands Recall of Notebook Computer Batteries Due to Fire Hazard." (2010). U.S. Consumer Product Safety Commission press release, 21 May 2010, http://www.cpsc.gov/cpscpub/prerel/prhtml10/10240.html.

[30] Takeshita, H. (2005). "Worldwide Market Update on NiMH, Li-ion and Polymer Batteries for Portable Applications and HEVs," Presented at the 22nd International Battery Seminar & Exhibit, March 14, 2005.

[31] "What's New Basics." (2008). http://safetravel.dot.gov/whats_new_batteries.html Accessed March 2012.

[32] Webster, H. (2004). *Flammability Assessment of Bulk-Packed, Nonrechargeable Lithium Primary Batteries in Transport Category Aircraft*. Office of Aviation Research Report, DOT/FAA/AR-04/26. http://www.fire.tc.faa.gov/pdf/04-26.pdf.

but the repair estimate was $237 million.[33] Interestingly, thermal runaway has been documented for other chemistries, such as NiMH. In 2005, the *CMV Punjab Senator* suffered a severe explosion and fire in a cargo container containing 16 tons of HR6 NiMH cells.[34] This event appears to be combination of elevated temperatures and cargo shifting resulting in massive shorting.

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[33]"Prototype mini-sub shelved." (2009). Honoluluadvertiser.com.
http://the.honoluluadvertiser.com/article/2009/Jul/25/ln/hawaii907250321.html. Accessed March 2012.
[34] "Explosion and fire on board CMV Punjab Senator." (2007). Casualty and incident report presented to International Maritime Organization Sub-Committee on Dangerous Goods, Solid Cargoes and Containers. Report DSC 12/6/8, Published 12 July 2007. http://www.emsa.europa.eu/end185d007d003d002d004d005.html

3   Evaluation Techniques for Batteries and Battery Materials

Materials and battery assemblies may be characterized and optimized for safety by various means and techniques. The techniques evaluate the response of materials, electrode formulations, cell construction, and battery assemblies to a variety of "off-normal" conditions that simulate abusive events, such as mechanical, electrical, and thermal abuse. Characterization of cells provides baseline information on safety and abuse tolerance of a given cell chemistry. Additionally, battery packs have other failure modes, such as inter-cell shorting, inter-cell charging, and cell imbalance that can overcharge or over-discharge a cell or group of cells. Therefore, module and pack abuse tests are necessary.

3.1   Electrochemical Characterization

Electrochemical stability of materials is the basis of safe behavior of the cell and subsequent battery assemblies. Cyclic voltammetry can be used to evaluate the electrochemical stability window of materials. Thermodynamic stability of materials in intimate contact within the cell is desired but not always realized in high-voltage cells. Kinetic stability can be sufficient to design a working electrochemical cell. The solid electrolyte interphase (SEI), the passivation layer that forms on Li-ion rechargeable battery anode materials, is an example of kinetic stability being sufficient for cell operation. Another example is the lithium/oxyhalide catholyte primary battery in which the passivation layer forms on the lithium anode surfaces that provide separation between the reactive lithium anode and the liquid cathode. The reaction layer of lithium chloride crystals protects the lithium metal from continued contact and the self-discharge that would result from further chemical reaction.

3.2   Thermal Characterization

Thermal characteristics of cells and batteries are one of the most important aspects of safe cell and battery design. Individual materials as well as complete battery modules should be characterized to understand failure modes in order to develop improved abuse-tolerant cells and batteries. Thermal reactions inside the cells are extremely complex chemical interactions between the active materials and electrolyte. Characterization should include determination of individual reaction mechanisms, enthalpies, and kinetics. The effects of these material properties then need to be measured and confirmed at the materials test level as well as at the cell level for various form factors and sizes. There are a number of characterization techniques using both commercial analytical instruments and custom test fixtures that can be used to determine these cell/battery properties and performance. Calorimetric techniques have been very useful for obtaining fundamental, quantitative material properties, while laboratory-scale testing has been useful to obtain application-level performance. Several of these techniques are discussed below.

3.3   Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is used to understand the effects of thermal abuse on battery materials. This technique enables the thermal response of individual and selected combinations of cell components to be measured over a broad temperature range while scanning at a fixed temperature rate. In favorable cases, this information allows identification of the components participating in thermal activity. The DSC technique also allows qualitative measurement of the effect of the local charge state of the electrodes, which affects the cell thermal reactivity that leads to cell thermal runaway as well as cell self-discharge. DSC can be used to measure the reaction enthalpy of various active materials with different electrolyte

formulations and also determine activation energies for the observed reactions. Measurements can be made on materials from disassembled cells as well as laboratory half-cells, enabling detailed characterization of individual electrode changes under controlled conditions. DSC techniques are limited to a small sample size, but the chemical reactivity studies can be effectively applied to study high-temperature stability. For example, Aurbach and coworkers have applied DSC and other techniques[35] to clarify decomposition reactions and thermal stability of Li-ion battery electrolytes in the temperature range of 40°C to 350°C.

3.4   Accelerating-Rate Calorimetry

Accelerating-rate calorimeter (ARC) tests are conducted on full cells and cell components under adiabatic conditions[36] that allow precise control of temperature and expose the cell to more uniform conditions. Under adiabatic conditions, the cell heating rate is strictly a function of the intrinsic heat generating reactions in the cell and the thermal heat capacitance of the cell components. The reaction rate typically starts very slowly and increases through a series of accelerating stages until a final high-order thermal runaway is reached. The ARC temperature chamber tracks this cell temperature profile even up to high rates of heating. A typical experiment requires a few days rather than a few hours, as in the case of the heating block. Because of the adiabatic environment, the onset of self-heating due to chemical reactions in the interior of the cell can be detected with greater sensitivity. The experiment more closely simulates a thermal abuse environment that includes moderately high temperatures for relatively long periods.

Gas generation by the cell during the thermal runaway profile is also a critical property of the abuse response of the cell. To maintain adiabatic conditions during cell venting, sealed cell fixtures are required to confine the vent gases in the ARC chamber with a minimal expansion volume. Pressure monitoring during thermal runaway allows determination of the gas volume generation profile in conjunction with the thermal runaway profile. This information is essential to understanding the cell and cell component reactions during thermal runaway.

3.5   Thermal Ramp Test

Thermal stability of cells can be studied by linear programmed heating to cell failure, sometimes called a thermal ramp experiment.[37] In the thermal ramp experiment, cells are heated at a programmed heating rate (5°C/min was typical) from room temperature to 250°C or higher, at which temperature the cell fails by initiating thermal runaway. The cells are measured under open circuit conditions at different states of charge and are open to the atmosphere to allow unconstrained cell venting. The flammability of the vent gases and aerosolized electrolyte can be determined by placing spark ignition sources in critical locations around the cell fixture.

The design of the cell holder is crucial to obtaining relevant data. Thermocouples are placed on the cell surface and the cell is wrapped with a layer of thermal insulating material so that the cell

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[35] Gnanaraj, J. S.; Zinigrad, E.; Asraf, L.; Gottlieb, H. E.; Sprecher, M.; Schmidt, M.; Geissler, W.; Aurbach, D. "A Detailed Investigation of the Thermal Reactions of LiPF$_6$ Solution in Organic Carbonates Using ARC and DSC." *Journal of the Electrochemical Society,* 150 A1533–A1537 (2003).

[36] Thermal Hazard Technology home page, http://www.thermalhazardtechnology.com/. Accessed March 2012.

[37] Roth, E. P.; Crafts, C. C.; Doughty, D. H.; McBreen, J. (2004). *Advanced Technology Development Program for Lithium-Ion Batteries: Thermal Abuse Performance of 18650 Li-Ion Cells.* Sandia Report SAND2004-0584 March 2004.

is not closely coupled to the thermal heating block. Thermocouples are then placed between the insulating layer and the thermal block. The temperature difference between the cell and the thermal block is accurately measured and used to calculate self-heating rate (dT/dt in °C/min). The analysis of this data allows determination of the onset of self-heating, vent temperature, runaway temperature (defined as dT/dt = 10°C/min for small cells, although thermal runaway temperature will be lower for large cells since they cannot dissipate heat efficiently) and cell disassembly temperature. This method of determining cell self-heating rate data is not as sensitive as ARC data, but is more easily performed. However, heating rate data are only qualitative after cell venting due to the uncontrolled heat loss by the vent gases. A well-designed cell holder can give reproducible data that complement the quantitative ARC data.

3.6   Large-Scale Calorimetry

The use of DSC and ARC provide for characterization of the electrodes and cells and the response to thermal transients. Larger scale calorimetry (e.g., oxygen consumption calorimetry[38]) can characterize the response of a battery to sustained heating with sufficient airflow to permit full combustion of all non-electrochemical materials in addition to promoting reactions of the electrochemical couple. The result will invariably produce heat release rates in terms of sustained kilowatt and megawatt-size fire events that yield significantly more energy through collateral combustion than contained electrically. These thermal release rates provide data for fire protection system engineering suitable for production facilities, warehouses, and transportation systems.

For any system with a high prevalence of organic construction (plastic cases, separators) or organic solvent electrolytes (as in Li-ion cell technologies), the rate of oxygen consumption may be directly correlated to the heat released based on a standard of 13.1 MJ/kg oxygen consumed. A combination of radiant flux meters provides all necessary data to support large-scale battery failure analysis.

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[38] "Standard Practice for Full-Scale Oxygen Consumption Calorimetry Fire Tests." ASTM International, ASTM E2067-08, http://www.astm.org/Standards/E2067.htm . Accessed March 2012.

4 Standardized Safety and Abuse Tolerance Test Procedures

Standardization of tests is crucial to comparing safety and abuse response of batteries. For example, a change as simple as the charge current can affect the outcome of overcharge tests.[39] There are a number of standardized test procedures that evaluate the safety and abuse tolerance of cells and batteries. The test procedures are adapted to the intended applications.

4.1 Pass/Fail Battery Abuse Tests
Certain test standards classified as "Pass/Fail" type are designed to analyze and approve battery use in given environments. Examples of pass/fail tests include:

- **United Nations Testing Protocol UN 38.3** "Recommendations on the Transportation of Dangerous Goods"[40] is the international standard designed to qualify hazardous materials (including batteries) for shipment.

- **Underwriters Laboratories Standards UL 1642 and UL 2054**.[41] These standards are a collection of testing protocols that are intended to qualify lithium metal and Li-ion rechargeable cells (1642) and batteries (2054) for use in commercial products. UL is also developing a pass/fail standard for EVs and HEVs, UL 2580, "Batteries for Use in Electric Vehicles," which likely will be published in mid-2012.

- **SAE International (SAE) Standard J2929** "Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Lithium-based Rechargeable Cells" is under development at SAE. The standard defines a minimum set of acceptable safety criteria for a lithium-based rechargeable battery system to be considered for use in a vehicle propulsion application as an energy storage system connected to a high-voltage power train. It will likely be published in the first few months of 2012.

- **Institute of Electrical and Electronics Engineers (IEEE) Standards #1625-2008 and #1725-2006**[42] titled "IEEE Standard for Rechargeable Batteries for Multi-Cell Mobile Computing Devices" and "IEEE Standard for Rechargeable Batteries for Cellular Telephones," respectively.

4.2 Characterization Battery Abuse Tests
Other standards are "characterization" type standards and are designed to evaluate the response of batteries to specific "off-normal" conditions that might be expected to occur, although very infrequently, during use. Examples are:

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[39] Yoshida, T.; Kitoh, K.; Ohtsubo, S.; Shionoya, W.; Katsukawa, H.; Yamaki, J-I. (2007). *Electrochemical and Solid-State Letters*, 10 A60–A64.

[40] http://www.unece.org/trans/danger/danger.html

[41] UL 1642 Standard. "Lithium Batteries." http://ulstandardsinfonet.ul.com/scopes/scopesnew.asp?fn=1642.html

[42] IEEE Standard #1625-2008, http://standards.ieee.org/findstds/standard/1625-2008.html; IEEE Standard #1725-2006, http://standards.ieee.org/findstds/standard/1725-2006.html

- **SAE J2464**[43] "EV & HEV Rechargeable Energy Storage System (RESS) Safety and Abuse Testing Procedure" evaluates abuse tolerance of cells and battery packs for electric vehicles. The hazard severity level observed in the test is input to a risk management approach[44] that combines probability and severity of occurrence to develop a hazard risk number for vehicular applications.

- **USABC** has published safety and abuse tolerance test procedures [45] that were developed at Sandia National Laboratories (SNL) for EVs and HEVs.

- **NAVSEA S9310**[46] is a U.S. Navy-published test protocol, "Technical Manual for Batteries, Navy Lithium Safety Program Responsibilities and Procedures," that addresses the safety of any type of lithium cell or battery that would be used by Navy and Marine Corps activities on any type of vessel or aircraft. The purpose of the manual is broader in that abuse testing has the goal to "establish safety guidelines for the selection, design, testing, evaluation, use, packaging, storage, transportation, and disposal of lithium batteries."

- **IEC**[47] – The International Electrotechnical Commission has published safety and abuse tolerance test for shipping (IEC 62281) and use in portable applications (IEC 62133) and is developing a new standard for cells that will be used in vehicles (IEC 62660-02 "Secondary Batteries for The Propulsion of Electric Road Vehicles").

- **ISO**[48] – The International Organization for Standardization is developing a new test standard for battery systems that will be used in vehicles (ISO/CD 12405-2 "Electrically Propelled Road Vehicles — Test Specification for Lithium-ion Traction Battery Packs and Systems").

- **EUCAR**[49] – European Council for Automotive R&D has established performance standards, particularly the EUCAR Severity Hazard Levels and Descriptions[50] that are widely used to characterize the response of test articles to abuse tests.

- **VDA**[51] – The Verband der Automobilindustrie e.V. is a German interest group supporting the German automobile industry. VDA published a series of standards and

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[43] SAE J2464. (2009). "EV & HEV Rechargeable Energy Storage System (RESS) Safety and Abuse Testing Procedure." Published 11/06/2009 by SAE International and available from www.sae.org

[44] Ashtiani, C. (2008). "Analysis of Battery Safety and Hazards' Risk Mitigation." *Electrochemical Society Transactions*, 11 (19), 1 (2008).

[45] "USCAR: USABC Manuals." USCAR. http://www.uscar.org/guest/article_view.php?articles_id=86. Last accessed March 2012.

[46] "Technical Manual for Batteries, Navy Lithium Safety Program Responsibilities and Procedures." NAVSEA S9310-AQ-SAF-010. http://www.everyspec.com/USN/NAVSEA/NAVSEA_S9310-AQ-SAF-010_4137/

[47] International Electrotechnical Commission (IEC)., http://www.iec.ch/.

[48] International Organization for Standardization (ISO). http://www.iso.com/.

[49] European Council for Automotive R&D (EUCAR). http://www.eucar.be/.

[50] Josefowitz, W., et al. (2005). "Assessment and Testing of Advanced Energy Storage Systems for Propulsion–European Testing Report." *21st Worldwide Battery, Hybrid and Fuel Cell Electric Vehicle Symposium & Exhibition Proceedings*. Monaco, EU. April 2–6, 2005.

[51] Verband der Automobilindustrie (VDA). http://www.vda.de/en/index.html.

recommendations. Among those is "Test Specification for Li-ion Battery Systems for Hybrid Electric Vehicles," March 2007.

- **JARI**[52] – The Japan Automobile Research Institute is developing battery safety and abuse test standards.

- **JIS**[53] – Japanese Industrial Standard JIS C 8714, "Safety Tests for Portable Li-Ion Secondary Cells and Batteries for Use in Portable Electronic Applications."

- **National Aeronautics and Space Administration (NASA)** – When a battery-powered system to be used in manned space flight is being designed, NASA recommends reference document JSC-20793, "Crewed Space Vehicle Battery Safety Requirements," issued by the NASA Engineering Directorate's Energy Systems Division.[54] Its purpose is to define hazard sources, discuss typical system safety measures, and identify issues inherent to battery chemistries. As a high-level best-practices design guideline, the document does not contain detailed information on test and qualification procedures. NASA requires a two-fault tolerance. The document takes this definition in a slightly different direction by defining categories of failure for critical equipment. It specifies ways in which critical equipment react to the first failure and then to the second failure. In this way, equipment can actually cease to function after the first failure as long as it does not affect the mission (no damage to equipment, no contingency or emergency procedures required). The second failure must be controlled, such that there is no injury to personnel and no loss of vehicle or ground facilities.

Another approach is to incorporate design guidance information in the test standard. An example of this is **IEEE 1625**, which is a 93-page standard that provides recommendations and guidelines for cell fabrication and assembly techniques. UL documents often contain a lesser degree of design guidance that supplements the test protocols.

Each standard anticipates use and abuse conditions and develops tests accordingly. Overview comparisons between these standards are given in Table 2 and Table 3. It is interesting to note that test parameters are sometimes very consistent (e.g., high-altitude simulation requires a reduced pressure that is equivalent to 50,000 ft altitude), but others are either completely absent or have quite different experimental test conditions.

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[52] Japan Automobile Research Institute (JARI). http://www.jari.or.jp/english/.
[53] Japanese Industrial Standards Committee, http://www.jisc.go.jp/eng/index.html.
[54] "Design Guidelines Safety Philosophies, Hazard Control, and Safety Verification." University of Colorado Engineering School course notes, http://www.colorado.edu/engineering/ASEN/asen5519/06design-guidelines.htm.

Table 2. Comparison of Standard Test Procedures from UN, UL, IEEE, and U.S. Navy
Simplified Comparison Omits Many Test Details.

Test Title	Shipping — Cell & Pack Testing		Usage						
			Cell Testing					Cell & Pack Testing	
			Portable Electronic Applications					Military Applications	
	SHIPPING UN Manual of Tests & Criteria	Canada Shipping Permit SH-6153	UL 1642 Lithium Batteries	UL 2054 Household and Commercial Batteries	IEEE 1625 Laptop Rech. Batteries	IEEE 1725 Cell Phone Rech. Batteries	Japan JIS C8714 "Safety tests for Portable Li Ion cells and batteries for use in portable electronics"	NAVSEA S9310-AQ-SAF-010	MIL-PRF-32052
Altitude	T1. 6 hr @ 0.11 atm		6 hr @ 0.11 atm		6 hr @ 0.11 atm				6 hr @ 0.11 atm
Hazardous Substance Monitoring									
Temperature Cycling (Thermal Shock)	T2. 10 cycles of 6 hr @ 75°C & -40°C	2 cycles of 6 hr @ 75°C & -40°C	10 cycles of 6 hr @ 70°C & -40°C	10 cycles of 6 hr @ 70°C & -40°C	5 cycles of 4 hr @ 75°C & -20°C				
Compromise of Thermal Insulation									
High Temperature			130°C for 10 min	130°C for 10 min	130°C for 10 min	130°C for 60 min	Ramp at 5°C/min to 130°C. Hold for 10 min. 5 each that were charged at the highest temperature and the lowest temperature.	500°C for 60 min	
Vibration	T3. 12 reps up to 8 g peak		10 to 55 Hz at 1 Hz/min	The frequency is to be varied at the rate of 1 hertz per minute between 10 and 55 hertz and return in not less than 90 nor more than 100 minutes. The battery is to be tested in three mutually perpendicular directions.	10 to 55 Hz at 1 Hz/min				10 to 55 Hz at 1 Hz/min
Mechanical Shock	T4. 3 ea 150g shocks for cells, 50g shocks for	3 ea 150g shocks	3 ea 125-175g shocks	3 each x 3 axes: 3 ms with the min. average acceleration is 75 g (peak acceleration shall	3 ea 125-175g shocks				3 ea 40g shocks

Test Title	Shipping		Usage							
	Cell & Pack Testing		Cell Testing					Cell & Pack Testing		
			Portable Electronic Applications						Military Applications	
	SHIPPING UN Manual of Tests & Criteria	Canada Shipping Permit SH-6153	UL 1642 Lithium Batteries	UL 2054 Household and Commercial Batteries	IEEE 1625 Laptop Rech. Batteries	IEEE 1725 Cell Phone Rech. Batteries	Japan JIS C8714 "Safety tests for Portable Li Ion cells and batteries for use in portable electronics"	NAVSEA S9310-AQ-SAF-010	MIL-PRF-32052
	modules and packs.			be between 125 and 175 g)					
External Short Circuit	T5. less than 100 mΩ at 55 C	less than 100 mΩ at 55 C	less than 100 mΩ at 20 C & 55 C	80 ±20 m ohm at both 20 ±5°C and at 55 ±2°C	less than 100 mΩ at 20 C & 55 C	less than 50 mΩ at 55°C	Circuit resistance = 80 +/- 20 mOhm at 55°C for 24 hr. 5 cells each that were charged at the highest temperature and the lowest temperature AND 5 packs each that were charged at the highest temperature and the lowest temperature. 100% SOC.	less than 20 mΩ at 20 C	at 20 C
External Short Circuit On Cycled Cells						less than 50 mΩ at 55°C		less than 20 mΩ at 20 C	
Partial Short Circuit									
Impact	T6. 9.1 kg from 61 cm.		9.1 kg from 61 cm.	A 9.10 ±0.46 kg (20 ±1 pound) weight is to be dropped from a height of 610 ±25 mm (24 ±1 inch) onto the sample.					
Overcharge	T7. Charge to 200% SOC		to 250% SOC	to 150% SOC at room temperature.	to 250% SOC			20 reps to 125% max voltage	to 400% SOC
Overcharge Protection Evaluation							One cell in a battery is forced discharge and current follow is measured between cells. 1 battery. 100% SOC.		
Forced Discharge (Over-discharge)	T8. Discharge to -100% SOC		to -100% SOC	Place one discharged cell in a string of charged cells, and discharge the pack (to -100% SOC).	to -150% SOC			20 reps to -25% SOC	to -100% SOC

Test Title	Shipping — Cell & Pack Testing		Usage — Cell Testing — Portable Electronic Applications					Usage — Cell & Pack Testing — Military Applications	
	SHIPPING UN Manual of Tests & Criteria	Canada Shipping Permit SH-6153	UL 1642 Lithium Batteries	UL 2054 Household and Commercial Batteries	IEEE 1625 Laptop Rech. Batteries	IEEE 1725 Cell Phone Rech. Batteries	Japan JIS C8714 "Safety tests for Portable Li Ion cells and batteries for use in portable electronics"	NAVSEA S9310-AQ-SAF-010	MIL-PRF-32052
Crush			3000 lbs. force		13 kN force		Use Force of 13 +/- 1 kN between flat surfaces or up to 10% deformation. 5 cells each that were charged at the highest temperature and the lowest temperature. 100% SOC.		
Open Flame Test (Fuel Fire or "Projectile")			A cell contained in a wire cage is heated from below by a burner flame - No Projectiles	A cell contained in a wire cage is heated from below by a burner flame - No Projectiles		A cell contained in a wire cage is heated from below by a burner flame - No Projectiles			
Float Charge					28 days at 20°C and 100% SOC (float charge)				
Cell Balance									within 5%
Cycle Life									Meet cell performance specs.
High Rate Discharge w/o Cooling									Meet cell performance specs.
Low Temperature									depends on application
Retention of Charge									94% retention - depends on application
Drop Test				from 1 meter in an orientation so it strikes a	from 1 meter		Height of drop specified by JIS C6950 or C6065. 5 cells each that were		

Test Title	Shipping		Usage						
	Cell & Pack Testing		**Cell Testing**					**Cell & Pack Testing**	
			Portable Electronic Applications					Military Applications	
	SHIPPING UN Manual of Tests & Criteria	Canada Shipping Permit SH-6153	UL 1642 Lithium Batteries	UL 2054 Household and Commercial Batteries	IEEE 1625 Laptop Rech. Batteries	IEEE 1725 Cell Phone Rech. Batteries	Japan JIS C8714 "Safety tests for Portable Li Ion cells and batteries for use in portable electronics"	NAVSEA S9310-AQ-SAF-010	MIL-PRF-32052
				concrete surface in the position that is most likely to produce the adverse results			charged at the highest temp. and the lowest temp. 100% SOC. 3 batteries. 100% SOC.		
Separator Shutdown						>100x resistance after shutdown			
Separator High Temperature Stability						150°C for 10 min			
High Temperature Storage									
Nail Penetration									
Internal short circuit							Foreign particle (L-shaped Ni 02.x0.1x1 mm^3) is inserted into charged cell in 2 places – a) between pos active and neg active and b) between Al foil and neg active material. Place cell into pressing jig and press at 0.1 mm/s until 50 mV drop or 800 N force is achieved. Height of drop specified by JIS C6950 or C6065. 5 cells each that were charged at the highest temperature and the lowest temperature. 100% SOC.		
Roll-Over									
Immersion									
Humidity Exposure									

Test Title	Shipping		Usage						
	Cell & Pack Testing		Cell Testing					Cell & Pack Testing	
			Portable Electronic Applications					Military Applications	
	SHIPPING UN Manual of Tests & Criteria	Canada Shipping Permit SH-6153	UL 1642 Lithium Batteries	UL 2054 Household and Commercial Batteries	IEEE 1625 Laptop Rech. Batteries	IEEE 1725 Cell Phone Rech. Batteries	Japan JIS C8714 "Safety tests for Portable Li Ion cells and batteries for use in portable electronics"	NAVSEA S9310-AQ-SAF-010	MIL-PRF-32052
(Dewing)									
Extreme Cold Temperature									
Propagation Resistance									
Fault Analysis							Recommended		
Elec. Safety Device								20 reps to 125% max voltage and -25% SOC with protection in place	
Abusive Overcharge				Charge at 2C -rate with protective devices in place.					
Overdischarge Protection Evaluation									
250 N Steady Force Test				External enclosures of the battery pack are to be subjected to a steady force of 250 ±10 N (56 ±2 pounds force) for a period of 5 seconds, to the top, bottom and sides of the battery pack.					
Mold Stress Relief Test				The samples (fully discharged) are to remain in the oven at 70°C (158°F) for 7 hours.					

Test Title	Shipping		Usage							
	Cell & Pack Testing		Cell Testing						Cell & Pack Testing	
			Portable Electronic Applications						Military Applications	
	SHIPPING UN Manual of Tests & Criteria	Canada Shipping Permit SH-6153	UL 1642 Lithium Batteries	UL 2054 Household and Commercial Batteries	IEEE 1625 Laptop Rech. Batteries	IEEE 1725 Cell Phone Rech. Batteries	Japan JIS C8714 "Safety tests for Portable Li Ion cells and batteries for use in portable electronics"		NAVSEA S9310-AQ-SAF-010	MIL-PRF-32052
Battery Pack Component Temperature Test				A battery pack temperature should be <75°C under charge and discharge.						
Battery Pack Surface Temperature Test				During Charge & discharge, accessible parts should be below 55°C (metal) or 75°C (plastic).						

Table 3. Comparison of Standard Test Procedures from SAE, USABC, IEC, and ISO

Simplified Comparison Omits Many Test Details.

Test Title	Usage							
	Cell & Pack Testing							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Altitude								
Hazardous Substance Monitoring	Analysis of electrolyte vapors and airborne volatiles and particulates released during abuse tests					Toxic emissions through openings other than exhaust openings during testing are not allowed or limited to ERPG-2 levels or OSHA TWAs.		
Temperature Cycling (Thermal Shock)	5 cycles between 70°C & -40°C - hold cells for 1 hour, hold modules and packs for 6 hours.	5 cycles between @ 80C & -40°C - hold cells for 1 hour, hold modules and packs for 6 hours.	J2464 or UN T2 testing are acceptable.	30 cycles between T(min) and T(max). Repeat series of cycles between 65 °C and -20 °C at various SOC for EV and HEV.	with all thermal controls disabled, thermally cycle the DUT between 85 °C or Tmax (as specified between supplier and customer) and -40 °C	A fully charged electrical energy storage assembly (MOSOC per 6.1) shall be subjected to the thermal shock test of SAE J2464, except that the temperature extremes are from 85 ±2°C to −40 ±2°C.		
Compromise of Thermal Insulation								

Test Title	Usage							
	Cell & Pack Testing							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	FreedomCAR EESS Abuse Test Manual (SAND2005-3123)	SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells	IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing	ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems	UL 2580 "Batteries for Use in Electric Vehicles"	Korea MVSS 18-3 "Driving Battery Safety Test"	India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"
High Temperature	Determine maximum temperature at which cell is stable indefinitely.	ARC test or thermal ramp to 200°C - determine self-heating rate		130°C for 30 min				
Vibration	See J2380	The r.m.s. acceleration value shall be 27,8 m/s².	UN Test Manual, Test T.3 (12 reps up to 8 g peak) or SAE J2380 for full system. Subsystem testing must be followed by vehicle vibration test.	Perform the test referring to IEC 60068-2-64 random vibration.	Perform the test according to IEC 60068-2-64 random vibration. Use test duration of 8 h for each plane of the DUT. The r.m.s. acceleration value shall be 27,8 m/s².	A sample is subjected to a vibration endurance test in accordance with the anticipated end application vehicle vibration profile. In the absence of this information, SAE J2380 shall be used.		The battery module shall be subjected to sinusoidal vibration for at an acceleration of 3 g in both the axis and a frequency of 30-150 Hz at a sweep rate of 1 octave per minute. Testing is to be carried out for 2 hours in each axis.
Mechanical Shock	18 ea. 25g shocks = XYZ negative & positive directions x 3 times.	Combined with Vibration	UN Test Manual, Test T4; or SAE J2464, Section 4.3.1 OR during crash vehicle tests simulating front, rear and side impacts, as defined in FMVSS 305, S6.1, 6.2, 6.3	500 m/s² (50g) 6 msec. 60 ea. = XYZ negative & positive directions x 10 times. HEV at 80% SOC and EV at 100% SOC	Perform the test according to ISO 16750-3 (500 m/s² (50g) 6 msec).	A fully charged sample is to be subjected to the Shock Test in accordance with SAE J2464, with the parameters as outlined in Table 24.1 (half sine wave, 25 g for 15 sec). 18 repeats.		The battery shall be subjected to the 10 shocks in each axis in half-sine wave, 30 g amplitude and 15 ms duration.

41

	Usage							
Test Title	**Cell & Pack Testing**							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
External Short Circuit	Perform 2 short circuit tests: a hard short (≤ 5 mOhm) and moderate short at a resistance comparable to the test article resistance at 25 °C ± 5 °C.	Apply a 'hard short' of ≤5 mΩ in less than one second; hold for 10 minutes at 20 C	UN Test Manual, Test T.5; or the pack hard short circuit condition defined in SAE J2464, Section 4.5.1. With flammable gas monitoring.	≤5 m ohm for 10 min. at 20 C. The sample rate for voltage and current recording shall be ≤ 10 ms	Use an appropriately sized conductor of ≤100 mΩ to apply a 'hard short' in less than one second for 10 minutes	Total circuit resistance less than or equal to 20 mOhm. Testing is repeated at a load that draws a maximum current no less than 15% below the operation of the short circuit protection	Resistance = 50mΩ for 1 hour or when current does not flow for 5 minutes. SOC 80%	less than or equal to 5 mOhm for 10 minutes, or for systems with less than 0.9 m/V system voltage ± 0.1m internal resistance, a conductor of equal or less than 1/10 of the minimum resistance of the cell/module shall be used.
External Short Circuit On Cycled Cells								
Partial Short Circuit	Incorporated into External Short Circuit.	Pack response to short in cell or string.						
Impact								

	Usage							
Test Title	**Cell & Pack Testing**							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Overcharge	Cells should be charged at two rates: a) 1 C-Rate constant current and b) at the maximum use current to 200% SOC	32 A to 200% SOC	"Single Point Overcharge Protection System Failure" to simulate single point failure of battery system charge control system when the battery system charge device is no longer being controlled. With flammable gas monitoring.	Charge until the cell voltage reaches 2X maximum voltage, or 200 % SOC	Continue charging until the DUT fails or until it reaches 200% SOC, depending on the agreement between the test team and the manufacturer. The recommended charge current is 32 A (but can be modified). The upper limit for the power-supply voltage determined by actual hardware.	Imbalanced Charging Test. One module at approximately 50% of its specified state of charge, while all other modules at o% SOC. Charge according to manufacturer's recommendations.	Charge to 1.5 times the nominal voltage with 32 A constant current. End charging when SOC 150% is reached.	To 200 % SOC by charging at a constant charging current of 0.1(C10) A value for a test duration of ten hours is reached.
Overcharge Protection Evaluation						Charge the test sample according to manufacturer instructions. Charge is terminated by the protective circuitry.		

43

	Usage							
Test Title	**Cell & Pack Testing**							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Forced Discharge (Over-discharge)	Cell test to -100% SOC and additional module test.	C/1 rate for 1.5 hours (Average SOC will be -50%), or until 50% of all subassemblies (for module- or pack-level tests) have achieved voltage reversal for 15 minutes.	"Single Point Over Discharge Protection System Failure" to simulate single point failure of battery system charge control system when the battery system discharge load is no longer being controlled. With flammable gas monitoring.	reverse charge at 1 C for 90 min. on a discharged cell resulting in -150% SOC	C/1 rate for 1.5 hours (Average SOC will be -50%) or until 25% of the nominal voltage level has achieved.		From 0% SOC, discharge the driving battery with 1C for 30 minutes = -150% SOC.	

44

	Usage							
Test Title	**Cell & Pack Testing**							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Crush	Crush to 85% of the initial dimension; hold for 5 min. & continue the crush to 50% .	to 85% of the initial dimension; hold for 5 min. & continue the crush to 50% .	Option 1: SAE 2464 except: Crush condition shall simulate the expected battery enclosure intrusion for each of the conditions defined in FMVSS 305, S6.1, 6.2 & 6.3. Option 2: SAE J2464 except: crush termination at a force of 100 kN. Option 3: during vehicle crash tests simulating front, rear and side impacts, as defined in FMVSS 305, S6.1, 6.2, 6.3	Crush to 85% of the initial dimension or the force of 1000 times the weight of cell applied or until voltage drop of 1/3 of the original cell voltage occurs. Use a sphere or hemisphere with a 150 mm dia. (for a prismatic cell) or the round bar 150 mm dia. (for crush a cylindrical cell). HEV at 80% SOC & EV at 100% SOC.		A sample shall be crushed between a fixed surface and a ribbed test platen in accordance with the test fixture described in SAE J2464. Crush all 3 axes. Exceptions: max force = 100 kN. The DUT may be installed in a protective framework representative of what is provided in the vehicle.		

Test Title	Usage							
	Cell & Pack Testing							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Open Flame Test (Fuel Fire or "Projectile")	10 min at 890°C - Simulate fuel fire	10 min at 890°C - Simulate fuel fire	The complete battery system is to be subjected to a high temperature heat and flame environment until the battery system is fully involved in the fire. Procedures described in SAE J2464 (Section 4.4.1), ECE R34 (Annex 5, Sections 5.3-5.8), SAE J2579 (Appendix C.8), or FMVSS 304 (S8.3) are allowed.			A fully charged DUT shall be subjected to a uniform fire source along the length of the assembly at its bottom surface. Within 5 min of ignition, at least one thermocouple shall indicate a minimum temperature of 590°C (1094°F). The test is concluded when this minimum temperature indication of 590°C (1094°F) has been maintained for 20 min.	Install the driving battery directly above flame. Apply heat between 890℃ and 900℃ for 2 minutes to the bottom of the driving battery. SOC 80%.	
Float Charge		60 days at 40°C, 60°C and 80C at 20% SOC, 50% SOC and 20% SOC, 50% SOC and 100% SOC (float charge)						

Test Title	Usage							
	Cell & Pack Testing							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Cell Balance								
Cycle Life								
High Rate Discharge w/o Cooling	With active thermal controls disabled, twenty (20) full charge/discharge cycles at maximum expected rate with no rest period	With active thermal controls disabled, twenty (20) full charge/discharge cycles at 3-kW constant power rate with no rest period	Tested in accordance with SAE J2464 with min/maximum SOC defined by operational cycles. With flammable gas monitoring.			Active thermal controls (primary and secondary) disabled. One full charge/discharge cycles should be performed as followed by a rest period of 7 hours between charge and discharge.		
Low Temperature								
Retention of Charge								

	Usage							
Test Title	**Cell & Pack Testing**							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Drop Test	Drop from 2 meters on the most vulnerable location.	from 10 meters	Minimum of 1 meter on most likely impact orientation at "operational" SOC.			Sample is to be dropped in the position most likely to produce the adverse results and in a manner and height (minimum height of 1.0 m) most representative of what would occur during maintenance and handling.	free fall from a height of 4.9 m to a concrete floor	
Separator Shutdown	Apply 20+ volts at 5 °C above the measured shutdown temperature							
Separator High Temperature Stability								
High Temperature Storage		See Float Charge					Place the driving battery at 80℃ for 4 hours. SOC 80%.	

	Usage							
Test Title	**Cell & Pack Testing**							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Nail Penetration	8 cm/s or greater and rod diameter shall be 3 mm rod (for cells) and 20 mm rod (for modules and packs) .	8 cm/s and the diameter of the rod shall be 3 mm rod (for cells) and 20 mm rod (for modules and packs) .						8 cm/s nominal and rod diameter shall be 3 mm rod (for cells) and 20 mm rod (for modules and packs) .
Internal short circuit								
Roll-Over	Complete revolution in 1 minute. Then rotate the RESS in 90 degree increments for one full revolution.	One complete revolution for one minute in a continuous, slow-roll fashion. Then rotate the EESS in 90° increments for one full revolution				At full SOC, the sample shall be rotated at a continuous rate of 90°/15 s. Testing shall subject the sample to a 360° rotation in 3 mutually perpendicular different directions.		Rotate the battery module one complete revolution in one direction, for one minute in a continuous, slow-roll fashion, and observe leakage. Rotate the battery module in 90° increments in same direction for one full rev. Hold the battery module for one hour at each position.

	Usage							
Test Title	**Cell & Pack Testing**							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Immersion	In salt water for a minimum of 2 hour.	In salt water for a minimum of 2 hour.	Tested in accordance with SAE J2464.			With the DUT in its normal operating orientation and with switches/contactors in closed position, it shall be subjected to the Immersion test of SAE J2464.	completely submerse the driving battery with 0.6M of salt water and stabilize it at 25±5℃ for 1 hour. SOC 80%	
Humidity Exposure (Dewing)			Tested in accordance with IEC 60068-2-30 with a severity of 55°C with 6 cycles, utilizing Variant 1 during the temperature lowering period.		Perform the test in reference to IEC 60068-2-30, with a severity of 80°C with 5 cycles			
Extreme Cold Temperature								

Test Title	Usage							
	Cell & Pack Testing							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Propagation Resistance	Does cell failure propagate in battery pack? Cause one cell to enter thermal runaway and observe the pack. Repeat for different geometric locations.	Does cell failure propagate in battery pack? Cause one cell to enter thermal runaway and observe the pack. Repeat for different geometric locations.				Use J2464 Propagation Test. A representative subassembly consisting of one or more modules and surrounding representative environment is allowed, if it can be demonstrated that there is no propagation beyond the subassembly.		
Fault Analysis			Perform fault analysis of the system design that single point faults will not result in fire, explosion or battery enclosure rupture.			Required. References IEC 60812, SAE J1739, MIL-STD-1629A for FMEA; IEC 61025 for FTA; SAE ARP4761 for SAP; IEC 61508-1 for Functional Safety.		
Elec. Safety Device								
Abusive Overcharge								

Test Title	Usage							
	Cell & Pack Testing							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Overdischarge Protection Evaluation						The DUT is to be subjected to a constant discharging current that will discharge a battery at 95% of the passive protection device ratings for the pack, or individual modules. The test will continue until the passive protection device(s, or the minimum cell voltage/maximum temperature protection device(s) are activated.		
250 N Steady Force Test								
Mold Stress Relief Test								
Battery Pack Component Temperature Test								

Test Title	Usage							
	Cell & Pack Testing							
	Automotive Applications							
	SAE J2464 2009 HEV and EV Battery Abuse Tests	**FreedomCAR EESS Abuse Test Manual (SAND2005-3123)**	**SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Li-based Rechargeable Cells**	**IEC 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing**	**ISO/CD 12405 Electrically propelled road vehicles — Test specification for lithium-ion traction battery packs and systems**	**UL 2580 "Batteries for Use in Electric Vehicles"**	**Korea MVSS 18-3 "Driving Battery Safety Test"**	**India AIS-048 "Battery Operated Vehicles - Safety Requirements of Traction Batteries"**
Battery Pack Surface Temperature Test								

Because of the importance of SAE standards, a more detailed comparison of SAE J2464 and J2929 is presented in Table 4.

Table 4. Comparison of SAE Standards J2464 and J2929

Test Title	Shipping UN Manual of Tests & Criteria	Automotive Applications	
		SAE J2464 2009 EV and HEV Rechargeable Energy Storage System (RESS) Safety and Abuse Testing	SAE J2929 Electric and Hybrid Vehicle Propulsion Battery System Safety Standard – Lithium-based Rechargeable Cells
Hazardous Substance Monitoring		Analysis of electrolyte vapors and airborne volatiles and particulates released during abuse tests	
Temperature Cycling	10 cycles of 6 hr @ 75C & -40C	5 cycles between +70C & -40C - hold cells for 1 hour, hold modules and packs for 6 hours.	J2464 or UN T2 testing are acceptable.
High Temperature Stability		Determine maximum temperature at which cell is stable indefinitely.	
Vibration	12 reps up to 8 g peak		UN Test Manual, Test T.3 (12 reps up to 8 g peak) or SAE 2380 for full system. Subsystem testing must be followed by vehicle vibration test.
Mechanical Shock	3 ea 150g shocks	18 ea. 15 msec 25g shocks = XYZ negative & positive directions x 3 times.	UN Test Manual, Test T.4; or SAE J2464, Section 4.3.1 OR during crash vehicle tests simulating front, rear and side impacts, as defined in FMVSS 305, S6.1, 6.2, 6.3
External Short Circuit	less than 100 mΩ at 55 C	Perform 2 short circuit tests: a hard short (≤ 5 mOhm) and moderate short at a resistance comparable to the test article resistance at 25 °C ± 5 °C.	UN Test Manual, Test T.5; or the pack hard short circuit condition defined in SAE J2464, Section 4.5.1. With flammable gas monitoring.
Overcharge	to 200% SOC	Cells should be charged at two rates: a) 1 C-Rate constant current and b) at the maximum use current to 200% SOC	"Single Point Overcharge Protection System Failure" to simulate single point failure of battery system charge control system when the battery system charge device is no longer being controlled. With flammable gas monitoring.
Forced Discharge (Overdischarge)	to -100% SOC	Cell test to -100% SOC and additional module test.	"Single Point Over Discharge Protection System Failure" to simulate single point failure of battery system charge control system when the battery system discharge load is no longer being controlled. With flammable gas monitoring.
Crush		to 85% of the initial dimension; hold for 5 min. & continue the crush to 50%, with a force maximum to a maximum of 1000 times the weight	Option 1: SAE 2464 except: Crush condition shall simulate the expected battery enclosure intrusion for each of the conditions defined in FMVSS 305, S6.1, 6.2 & 6.3. Option 2: SAE J2464 except: crush termination at a force of 100 kN. Option 3: during vehicle crash tests simulating front, rear and side impacts, as defined in FMVSS 305, S6.1, 6.2, 6.3
Open Flame Test (Fuel Fire)		10 min at 890C - Simulated fuel fire	The complete battery system is to be subjected to a high temperature heat and flame environment until the battery system is fully involved in the fire. Procedures described in SAE J2464 (Section 4.4.1), ECE R34 (Annex 5, Sections 5.3-5.8), SAE J2579 (Appendix C.8), or FMVSS 304 (S8.3) are allowed.
High Rate Discharge w/o Thermal Management		With active thermal controls disabled, twenty (20) full charge/discharge cycles at maximum expected rate with no rest period	Tested in accordance with SAE J2464 with min/maximum SOC defined by operational cycles. With flammable gas monitoring.
Drop Test		from 2 meters at full SOC.	from 1 meter on most likely impact orientation at "operational" SOC.
Separator High Temperature Stability		Apply 20+ volts at 5 °C above the measured shutdown temperature	
Nail Penetration		8 cm/s or greater and rod diameter shall be 3 mm rod (for cells) and 20 mm rod (for modules and packs) .	
Roll-Over		Complete revolution in 1 minute. Then rotate the RESS in 90 degree increments for one full revolution.	
Immersion		In salt water for a minimum of 2 hour.	Tested in accordance with SAE J2464.
Humidity Exposure (Dewing)			Tested in accordance with IEC 60068-2-30 with a severity of 55°C with 6 cycles, utilizing Variant 1 during the temperature lowering period.
Passive Propagation Resistance		Does cell failure propagate in battery pack?	
Fault Analysis			Perform fault analysis of the system design that single point faults will not result in fire, explosion or battery enclosure rupture.

5 Safety Devices

Safety devices are incorporated into cells, modules, and battery packs to protect against off-normal conditions. These safety devices mostly work very well, which accounts for the relative safety of cells and battery packs in the field.

To manage the consequences of heat and gas generation, many batteries have the following safety features:

- **Battery Management System (BMS)** controls electrical distribution within a battery pack and protects against over- or under-voltage conditions as well as excessive current. Moreover, it may have temperature sensors that shut down the pack if the upper or lower temperature limits are exceeded.

- **Cell Vent or Tear Away Tab** allows the safe release of gas if excessive pressure builds up within cells. Vents allow predictable pressure relief and are usually activated if the internal cell pressure exceeds 10 bar (~150 psid). These features are incorporated to prevent injury that could be caused by uncontrolled bursting of a battery container.

- **Current Interrupt Device** protects against over-current that breaks the internal electrical connection when the internal pressure reaches a set value. This pressure rise results from internal gas generation caused by thermal or electrical abuse conditions exceeding design limits. This safety mechanism is a one-time device that permanently disables the cell.

- **Current Limiting Fuses** may be used in place of positive temperature coefficient (of expansion) devices when a sustained discharge is not preferred. Fusing of this type may utilize slow-blow time fuses or fast-acting fuses with little current-time latency. Time-delay and especially fast-acting fuses are external to a cell. However, fusible links may be installed in the cell.

- **Diodes** may be used for primary batteries to prevent inadvertent charging (blocking diode) or to steer the discharge current around a weak cell as in a discharge (bypass) diode.

These safety devices work very well, accounting for the relative safety of cells and battery packs in the field. (An estimate of failure rates of Li-ion rechargeable battery cells is less than 1 in 10^6.)

6   Typical Failure Modes – Mechanism of Failure

Different battery chemistries have varying failure modes, but several events are common among all types of batteries. A typical response of a cell to abusive conditions is the generation of heat and gas.[55,56] While they may be linked (i.e., gas and heat are produced by the same chemical reactions), there are examples where heat and gas are produced independently.

6.1   Thermal Abuse

Heat generation within batteries in response to abusive tests can make failures more hazardous. For example, a short circuit will heat up the cell because of Joule heating (I^2R) until the cell begins to produce heat by internal chemical reactions (i.e., above the temperature where onset of self-heating reactions begin). Overcharge can also generate heat within the cell due to other oxidative chemical reactions that can trigger thermal runaway. In both these cases, thermal management of the battery pack is critical.

To characterize heat and gas generation that might occur during off-normal conditions, cells and packs are exposed to elevated-temperature abuse conditions[57] that resemble conditions that might be (rarely) seen in the field. In these tests, the response of cells can be characterized as falling into three major temperature regimes.[58] These regimes are illustrated in Figure 9, which shows the temperature rise during thermal ramp of a fully charged Li-ion cell. ARC and thermal ramp tests are commonly used.

Onset of reactions can be interpreted differently depending on the test protocol. Reactivity of the anode with the electrolyte can be observed in ARC at temperatures as low as 80°C, but at a very low rate. Reactivity is a consequence of SEI decomposition, exposing the reactive anode to the self-heating reactions involving the electrolyte.[59]

In Figure 9, an external source of heat (that simulates an abuse event) is used to raise the temperature of the cell to the **Onset Temperat**ure, T(onset). A practical definition of T(onset) is typically a self-heating rate of 0.2°C/min. This low heat generation can be accommodated and dissipated in the battery packs. However, if this heat is not dissipated, the temperature will continue to rise due to sustained exothermic reactions above the onset temperature when the cell enters Stage 2 (**Acceleration**), which is characterized by more rapid and accelerating heat release.

Stage 2 results from increased electrolyte reduction at the anode due to continuing loss of the SEI and to onset of electrolyte oxidation at the active cathode surface. These reactions depend highly on the active material chemistries and SOC. Venting and release of smoke may occur during

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[55] Levy, S. C.; Bro, P. (1994). *Battery Hazards and Accident Prevention*. Plenum Press, New York, NY; p 113.

[56] Levy, S. C.; Bro, P. (1994). p 43.

[57] Roth, E. P.; Doughty, D. H. (2004). "Thermal abuse performance of high-power 18650 Li-ion cells," *Journal of Power Sources*, Vol. 128, April 2004. pp 308-318.

[58] Roth, E. P. (2008). "Abuse Response of 18650 Li-Ion Cells with Different Cathodes Using EC:EMC/LiPF$_6$ and EC:PC:DMC/LiPF$_6$ Electrolytes." *ECS Transactions*, Vol. 11 (19); pp 19-41.

[59] MacNeil, D. D.; Larcher, D.; Dahn, J. R. (1999). "Comparison of the Reactivity of Various Carbon Electrode Materials with Electrolyte at Elevated Temperature." *Journal of The Electrochemical Society*, 146 (10); pp 3596–3602.

Stage 2. Additional heating causes the cell to enter Stage 3 (Runaway), in which the high-rate cathode and/or anode reactions cause the temperature to rise rapidly (thermal runaway) and flame or explosion may follow. Thermal runaway is characterized by a self-heating rate of 10°C/min or greater. At this self-heating rate, it is highly unlikely that any intervention or external cooling mechanism could quench the ensuing thermal runaway.

Runaway temperature, T(runaway), is a strong function of cell size, cell design, and materials in the cell. T(runaway) can vary from 130°C to well over 200°C in Li-ion cells. Cathode materials that decompose to release oxygen at high temperatures have especially high reaction rates and reaction enthalpies.
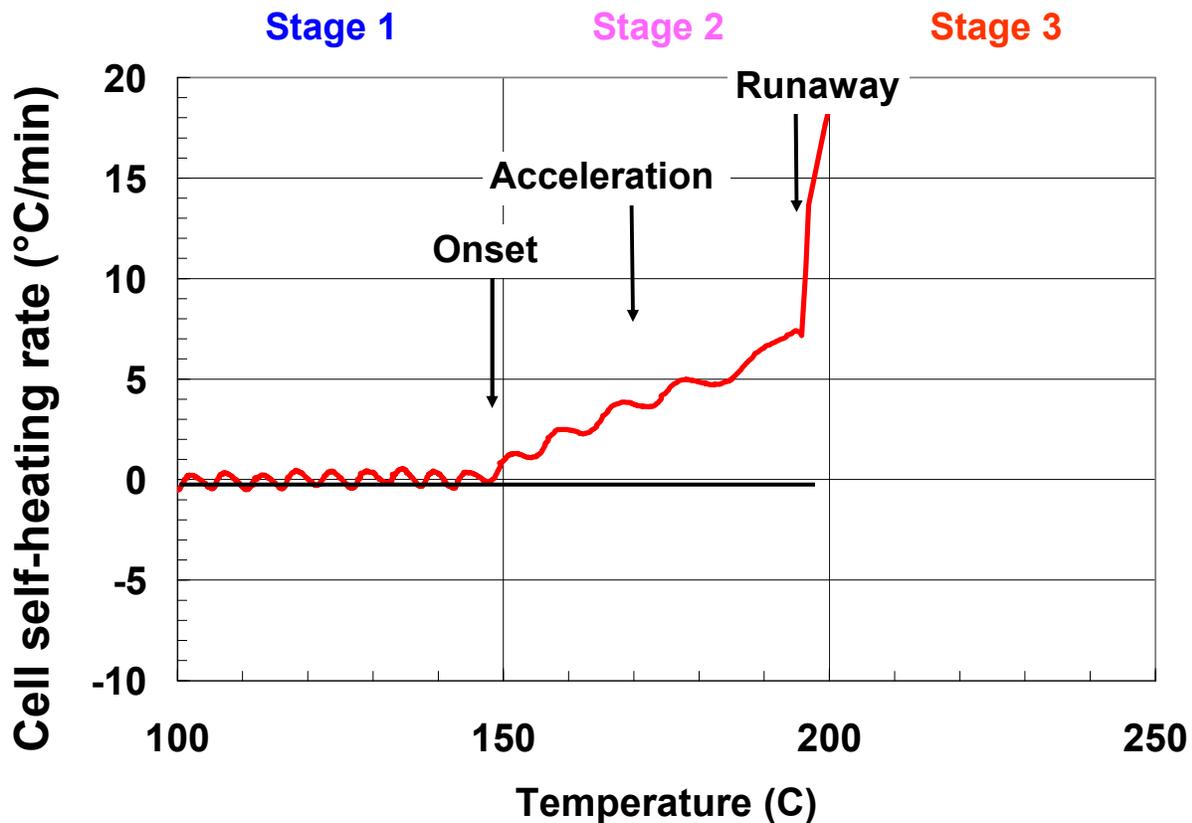
Figure 9. Cell self-heating rate during forced thermal ramp test of Li-Ion Gen 2 chemistry: anode = MCMB | electrolyte = 1.2 M LiPF$_6$ in EC:PC:DMC | cathode = LiNi$_{0.8}$Co$_{0.05}$Al$_{0.05}$O$_2$ | separator = Celgard 2325 trilayer.[60]

Some have argued that adiabatic tests, such as ARC, are not representative of battery failures. However, battery packs for EVs are large. For example, the Nissan Leaf battery pack is air-cooled and contains 192 stacked laminar battery cells (approximately 34 Ah each) with LiMn$_2$O$_4$ cathodes. The battery and control module together weigh 300 kg (660 lb.). The Tesla Roadster contains 6,831 water-cooled 18650-size Li-ion cells. It is not unreasonable to assume that an environment that is nearly adiabatic may be created in a large pack in which the cells in the

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[60] Doughty, D. H. (2005). "Li-ion Battery Abuse Tolerance Testing - An Overview." *AABC 2005 Proceedings*, Honolulu, HI, June 2005.

central portion are surrounded by other cells at the same temperature. The problem develops if there is inadequate thermal transfer to the external environment, either by design or by malfunction of the cooling system. If any condition allowed a cell or group of cells to reach T(onset) and the heat generated within the pack was not dissipated, the cells would continue to heat up due to chemical reactions within the cell. In this case, thermal runaway will ensue. The timing of thermal runaway can be delayed by minutes or several hours, since it depends on the particulars of construction of the battery pack and the operating environment. Incubation times of hours have been observed in accidents investigated by the U.S. Department of Transportation.[61] Events such as these have resulted in the Department of Transportation banning shipment of lithium batteries on passenger aircraft.[62] Accurate and easy-to-use thermal models of modules and packs would be a tremendous benefit in understanding the thermal environment of cells and packs under off-normal conditions.

6.2   Physical Damage

Physical damage (puncture, crush, vibration, or shock) has the possibility of creating an internal short circuit within the cell or creating a short circuit within a battery pack to cause current flow in an unintended and unanticipated manner. Internal short circuits are one of the most difficult failures to defend against. The potential for current flow in unintended manner should be evaluated by experimental tests on all battery packs.

In general, cells and batteries with higher specific energy (Wh/kg) and energy density (Wh/L) will produce a more energetic response when abused by puncture, crush, or shock. Additionally, cells with a flammable electrolyte or other flammable materials that could escape when the containment is compromised during physical damage have the potential to produce secondary fires.

6.3   Charge and Discharge Failures

Overcharge and overdischarge (voltage reversal) of rechargeable batteries can occur if the control electronics of the charging station or the battery pack control electronics in the BMS malfunction or if severe cell imbalance occurs in a battery pack.

Overcharge and overdischarge of rechargeable cells and batteries can occur due to charger failure or cell imbalance within a series/parallel connected battery. During charge, if several cells are connected in series and one has a higher SOC than the others do, it will reach full charge before the others. If the charger is designed to charge series strings (rather than individual cells), as the string reaches full charge, the cell will be overcharged. If overcharge occurs, a cell becomes more unstable and creates additional safety problems because it will have poorer thermal stability compared to un-abused cells (see Figure 28). Modern sophisticated BMS instrumentation can be programmed to detect and avoid this condition.

Likewise, during discharge of a battery pack, if one cell has a slightly lower beginning voltage or lower capacity than the others do, it will reach full discharge before the others. If the string is

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[61] Farrington, M. D. (2001). "Safety of lithium batteries in transportation." *Journal of Power Sources,* Vol. 96, Issue 1, 1 June 2001, pp 260–265.

[62] "Batteries can pose fire risk to planes." *USA Today*, 07 March 2007. http://www.usatoday.com/tech/news/techpolicy/2007-03-05-batteries-planes_N.htm.

then forced to continue discharging—a situation that can occur if system electronics are not sufficiently smart to identify the condition—it will discharge below 0.0 V into a state of "overdischarge" or "voltage reversal."[63] This will usually highly degrade the battery's ability to be recharged. Prolonged exposure to this condition (depth of reversal) can lead to safety problems, such as evolution of hydrogen and oxygen gases in large amounts sufficient to cause cell venting or metal plating on the cathode. In systems where multiple cells are used, a common quality-control standard condition is to use cells that have been matched to within ±5% cell capacity.

The ability to withstand overcharge depends strongly on the current level (low charging current is more likely to result in benign failure) as well as the chemistry of the battery. Aqueous electrolyte systems (e.g., lead-acid, nickel/cadmium, and NiMH) are relatively insensitive to overcharge because after 100% SOC is reached, additional current drives the electrolysis of water (which produces hydrogen and oxygen) and limits the maximum voltage that the cell experiences. Cells with an aqueous electrolyte may contain catalysts to recombine the H_2 and O_2 evolved during overcharge to reform water, which will minimize the accumulation of potentially explosive gas mixtures. However, this feature is not widely used in commercial lead-acid batteries and the prevalence of lead-acid battery explosions during charging is the major contributor to more serious injuries attributable to batteries.[64]

Li-ion and Li-polymer cells have poor response to overcharge abuse when compared with aqueous electrolyte cells because they do not have the protection of water electrolysis as an energy sink. In part, this poor response results from the higher energy content, more reactive electrode materials, and flammable electrolytes that create the potential for thermal runaway during the overcharge event.

The response of cells and battery packs during overcharge depends on overcharge parameters (current, maximum voltage), thermal environment, and cell materials and is a complex function of several failure mechanisms.[65] Extended overcharge can result in cell heating that initiates internal decomposition reactions of the electrodes and electrolyte that lead to thermal runaway. In addition, increased cell temperatures can result in melting of the separator material and subsequent internal shorting of the cell. This behavior is particularly problematic for shutdown separators that result in high-cell impedance at shutdown. For a single cell or a series configuration of cells, the charging power supply will apply the full compliance voltage across the single cell after separator shutdown occurs. Many separator materials have been observed to fail immediately or within a short time after shutdown in this condition, as shown in Figure 10.[66]

[63] Jeevarajan, J. A. Meeting abstract. - Electrochem. Soc. 1002 321 (2010). Also, "Hazards Associated with High Voltage High Capacity Lithium-ion Batteries." *ECS Transactions* (2011) 33(22): 1–6; doi:10.1149/1.3557704.
[64] Levy and Bro, pp 36-38.
[65] Belov, D.; Yang, M. H. (2008). *J Solid State Electrochem* (2008) 12: 885–894.
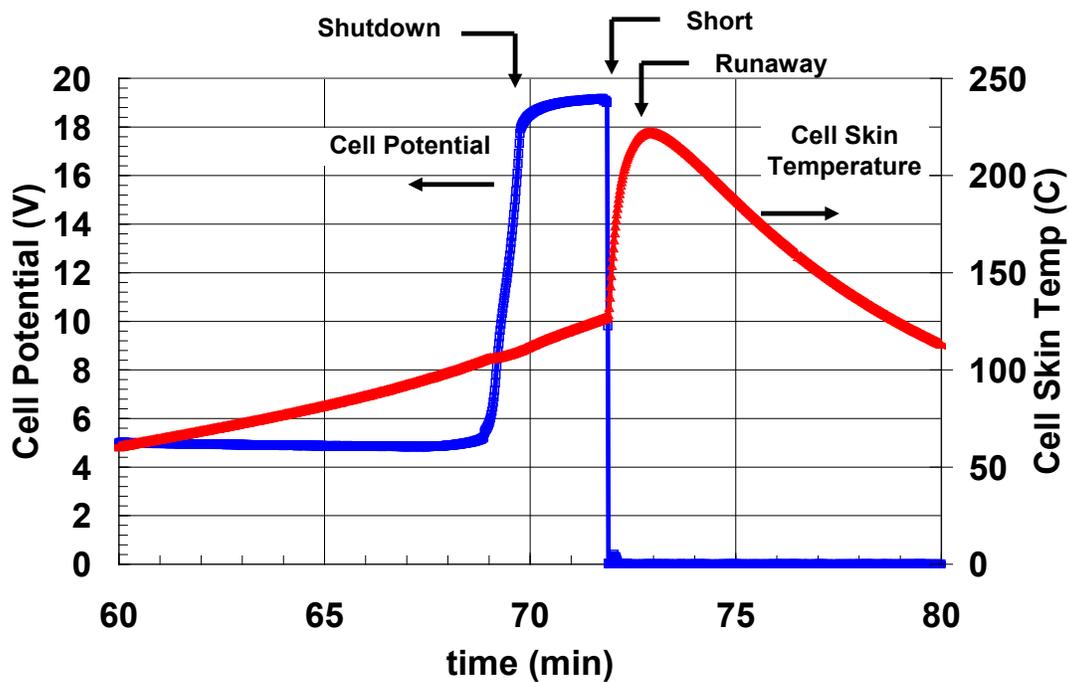[66] Roth, E. P.; Doughty, D. H. *AABC Proceedings*, 15–19 May 2006, Baltimore, MD.

Figure 10. Thermal runaway during overcharge due to separator failure following separator shutdown.[67]

The thermal response of Li-ion cells during overcharge is largely determined by the cathode chemistry. During the charge cycle, lithium is removed from the cathode oxide material. Different cathode oxide chemistries have different levels of lithium when fully charged, varying from $Li_{0.5}CoO_2$ to $Li_{0.0}FePO_4$ at 100% SOC. Overcharging continues to remove lithium from the structure, resulting in permanent crystallographic changes and increased oxidation potentials. Measurements of heat flow from the cells and cell skin temperature during overcharging has shown that there is a rapid increase in heat generation when all of the lithium has been removed from the cathode.[67] Figure 11 shows the cell temperature profiles during 1 C-rate overcharge for several common cathode materials where it is seen that lower lithium content at 100% SOC results in a reduced range of overcharge before increased heat output. Some of the most thermally stable cells have the lowest tolerance range for overcharge.

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[67] Roth, E. P.; Orendorff, C. (2009). Presentation to *Advanced Automotive Battery and EC Capacitor Conference* 2009, June 8–12, 2009, Long Beach, California.
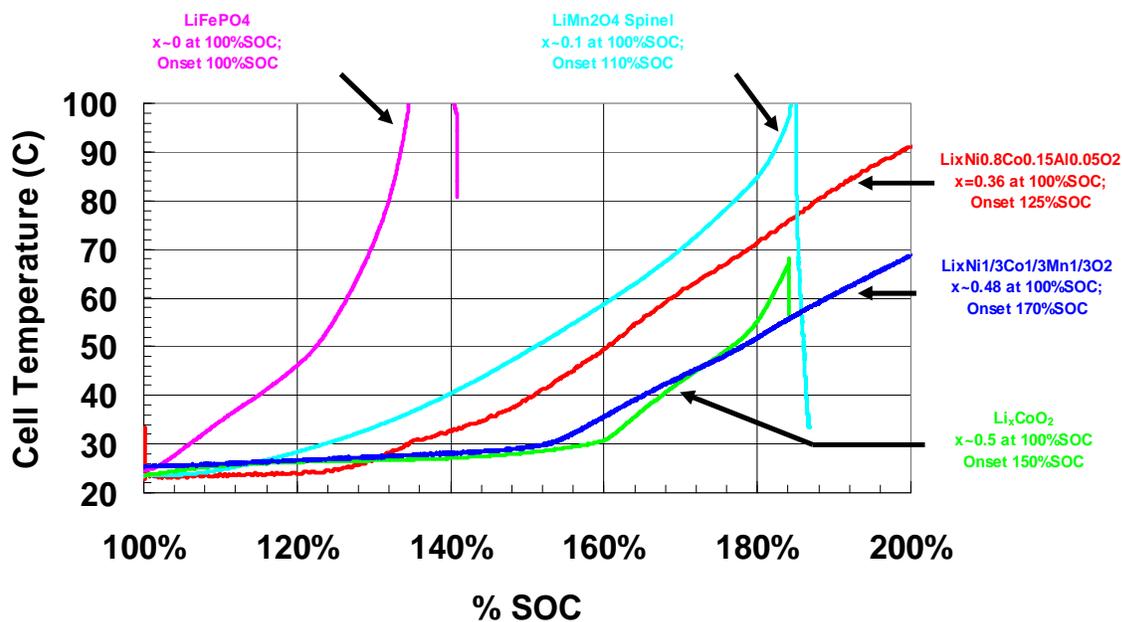
Figure 11. Heat output during overcharge for different cathode oxide chemistries, showing a marked increase in heat output when final lithium is removed from cathode.[68]

However, an important caution must be added regarding the above overcharge discussion. If the stability of the cathode becomes sufficiently good, other problems can become the determining factor in cell stability. For example, cells made with lithium iron phosphate (LiFePO$_4$, or LFP) cathode materials have the best thermal stability and overcharge stability. LiFePO$_4$ is thermally stable up to 250°C and does not evolve oxygen. The lithiated anode is still a significant source of energy. At high temperature, the SEI protective layer decomposes, exposing the lithiated carbon to the electrolyte. Reduction of the electrolyte can generate sufficient heat to cause a thermal runaway reaction with associated gas generation, venting, and possible fire. The electrolyte itself breaks down above 160°C, generating sufficient gas volume to cause cell venting.[68]

Yamaki and coworkers demonstrated that overcharge response of a lithiated graphite (LiC$_6$)/LiMn$_2$O$_4$ cell depended on charge current; at low current, overcharge test results were benign, but at high current levels, the cells entered thermal runaway.[39] Lithium plating on the anode is a possible failure mode during fast charge at low temperature. Lithium plating has the potential to create a finely divided lithium powder within the cell that may become electronically isolated from the anode. In addition, dendrites of lithium may grow from the anode through the separator, possibly resulting in an internal short circuit. This situation, if it arises, creates a safety vulnerability that could persist after the overcharge event terminated.

6.4   Short Circuit

An external short circuit is the most common type of battery abuse condition. All test protocols (for shipping approval as well as use environments) include short circuit tests. A cell is connected to a test circuit in which the external resistance either is matched to the unit impedance or is set as low as 1 mOhm. The current and cell temperature are monitored as well as

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[68] Roth, E.P. (2008). *ECS Transactions*, 11 (19) 19-41 (2008).

the cell response, such as venting and possible self-ignition. An example profile for a Li-ion cell is shown in Figure 12.
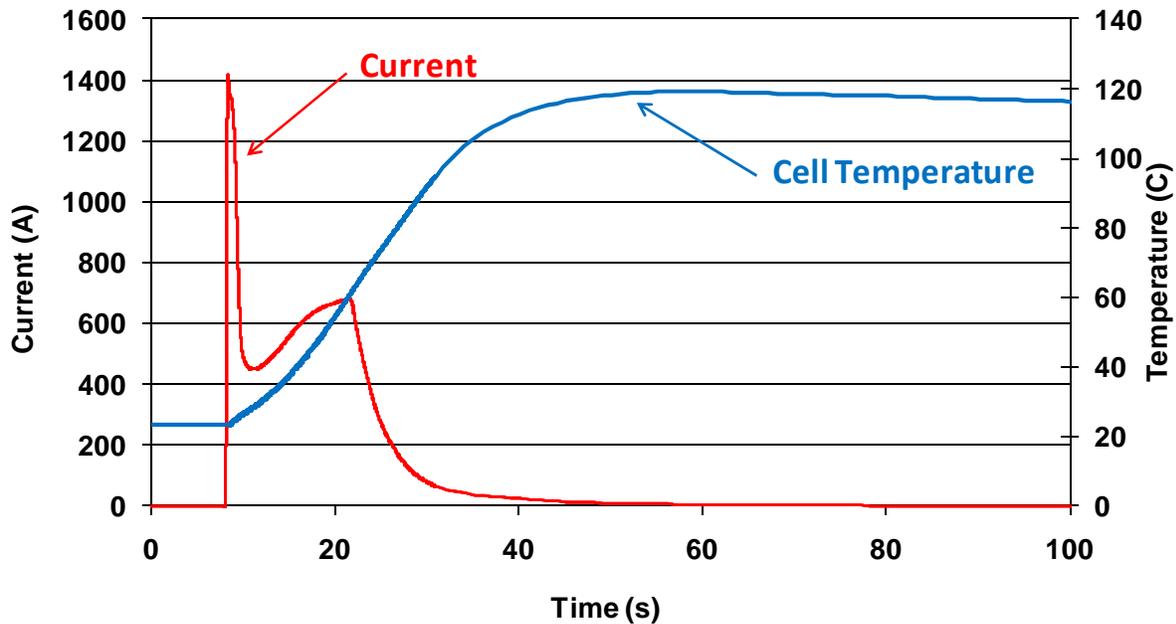
Figure 12. A 1-mOhm short circuit at room temperature of a Li-ion cell at 100% SOC.[69]

The plot shows the response of cells to a short circuit where the external circuit resistance was set to 1 mOhm. The cell current shows an initial peak determined by the cell resistance and the load. A secondary peak is often observed resulting from a drop in internal resistance with increasing temperature. Cells typically can withstand an external short circuit because thermal output is small and the cell is in contact with the test fixture. Thermal management will dictate if the response of the cells will be benign, as in this test, or exhibit thermal runaway. Large cells (i.e., over 10 Ah), cells that can sustain very large short circuit currents, cells that have higher internal resistance, and cells with low inherent thermal stability are more prone to exhibiting thermal runaway.

Internal short circuit is a failure mode where a current path develops within the cell. It can be caused by several factors, including a foreign object, poor cell design (e.g., lack of sufficient separation or insulation of electrodes in the cell), poor manufacturing processes (e.g., burrs on cut edge of current collector), or external pressure on the cell walls.

Internal shorts also may develop because of other abuse conditions that lead to internal gas generation and displacement of the internal electrodes so that they can contact each other, especially in pouch cells. This deformation mechanism can completely bypass "safe" separators designed to resist internal shorting.

Battery packs and modules have additional failure modes that cannot be examined by cell testing. New failure modes arise when the energy in cells is released to adjacent cells. Short

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[69] Typical response profile from SNL abuse laboratory. Source: SNL

circuit tests can reveal some of these failure modes. For example, a failure was observed in a short circuit test of a 12-cell series-connected string of 5-Ah Li-ion rechargeable batteries.[70] The pack was tested at room temperature in a standard short circuit test. The short circuit current was high, over 1,000 A, and as the cells in the series string increased in temperature due to Joule heating, the shutdown separator in one cell reached its critical temperature of ~130°C and the cell became resistive. It was quickly driven into voltage reversal (forced discharge). The voltage across this cell was about -38 V, the potential resulting from the other cells in the 12-cell string. Within ½ minute, the cell burst into flames. Had the cell not become resistive (i.e., fabricated without a shutdown separator) or had the current path been interrupted in some other way, the failure would not have happened. This failure is an example of combined failure modes—a short circuit triggering an overdischarge failure.

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[70] Doughty, D. H. (2005). "Li-ion Battery Abuse Tolerance Testing - An Overview." *Advanced Automotive Battery Conferenc*e *Proceedings*, June 13–16, 2005, Honolulu, HI.

7 Discussion of Safety and Abuse Response for Li-ion Rechargeable Battery Chemistries

Li-ion cells contain more energy because they have more reactive electrode materials. For example, the common cathode in today's Li-ion rechargeable batteries [lithium cobalt oxide ($LiCoO_2$, or LCO)] decomposes at elevated temperature to produce oxygen that exothermically reacts with organic materials within the cell.[71] The safety of a particular battery chemistry is directly related to the material choices for the anode, cathode, electrolyte, and separator. The performance of Li-ion batteries is most strongly dependent on the selection of the cathode material,[58] so the major classes of cathodes will be briefly discussed.

Several representative battery chemistries are discussed below. Each topic covers commercially important cell chemistry, briefly describing the relevant aspects of the materials used and the safety response.

The next sections discuss two classes of Li-ion rechargeable batteries—those with carbon anodes and liquid electrolytes (Li-ion cells) and those with carbon anodes and polymer electrolytes (Li-polymer cells). Each class has several variations, reflecting the tradeoff of materials choices that the manufacturer has made. The choice of cathode materials is probably the most important choice that determines the safety, energy density, power, and life of a particular lithium rechargeable chemistry.

Most commercially available Li-ion batteries utilize cathodes made of transition metal oxide, such as $LiCoO_2$ anodes made of graphitic carbon (which reversibly binds lithium to form an intercalation compound LiC_6 during charge) and a non-aqueous electrolyte. A wide range of carbonaceous compounds is suitable for use as the anode material, including coke, pure graphite and tailored carbon spherical particles, such as meso-carbon micro beads (MCMB).

All Li-ion cells employ non-aqueous electrolytes with a lithium-containing salts ($LiPF_6$ or other salts) dissolved in solvent mixtures of organic liquids, such as EC, PC, diethyl carbonate (DEC), or ethyl methyl carbonate (EMC). Numerous options for the choice of salts and/or solvents in such batteries are known to exist in the marketplace. Additionally, additives are used to modify the reactivity of the anode as well as to reduce the flammability of the electrolyte.

7.1 Cathodes in Li-Ion Batteries

The choice of cathode has the strongest influence on cell safety.[72] Many cathodes are in commercial cells or in development. Table 5 summarizes performance information on the most common cathodes in use today.

$LiCoO_2$ has been the cathode of choice for the majority of consumer-level Li-ion cells produced today. Although it delivers good capacity, it is the most reactive and has poorer thermal stability than the other cathodes. A calorimetric measurement of cells with different cathodes

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[71] Arai, H.; Tsuda, M.; Saito, K.; Hayashi, M.; Sakurai, Y. (2002). *Journal of The Electrochemical Society*, 149, A401–A406.

[72] Maleki, H.; Deng, G.; Anani, A.; Howard, J. (1999). "Thermal Stability Studies of Li-Ion Cells and Components." *Journal of The Electrochemical Society*, Vol. 146(9), pp. 3224–3229.

demonstrates this point. ARC is a common technique used to measure reactivity of battery materials and full cells and is particularly suited to characterize batteries. Self-heating of a cell or cell materials at elevated temperature is evidence of chemical instability. The plot of self-heating rate versus cell temperature provides a good characterization of chemical instability. A plot of self-heating rate versus cell temperature for full Li-ion 18650 cells fabricated with different cathodes is shown in Figure 13. Key parameters measured from ARC are onset temperature, maximum self-heating rate, and temperature width of the peak thermal runaway.

Table 5. Characteristics of Some Positive Electrode Materials[73]

Material	Specific capacity mAh/g	Midpoint V vs. Li at C/20	Comments
$LiCoO_2$	155	3.9	Still the most common. Co is expensive
$LiNi_{1-x-y}Mn_xCo_yO_2$ (NMC)	140-180	~3.8	Capacity depends on upper voltage cutoff. Safer and less expensive than $LiCoO_2$
$LiNi_{0.8}Co_{0.15}Al_{x0.05}O_2$ (NCA)	200	3.73	High capacity. About as safe as $LiCoO_2$
$LiMn_2O_4$ (Spinel)	100-120	4.05	Poor high temperature stability (but improving with R&D). Safer and less expensive than $LiCoO_2$
$LiFePO_4$ (LFP)	160	3.45	Synthesis in inert gas leads to process cost. Very safe. Low volumetric energy.
$Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O_2$	275	3.8	High specific capacity, R&D scale, low rate capability.
$LiNi_{0.5}Mn_{1.5}O_2$	130	4.6	Requires an electrolyte that is stable at high voltage.

$LiCoO_2$ cells are clearly less stable than cells with any of the other mixed-metal oxides shown in Figure 13 because their onset temperatures are higher and the maximum self-heating rates are lower. However, all these materials are unstable at elevated temperature. Work by Dahn and coworkers demonstrated that most cathode chemistries decompose and evolve oxygen.[74] Data on oxygen evolution at elevated temperature have been published for $LiCoO_2$,[75] $LiNiO_2$,[76] and $LiMn_2O_4$.[77] Oxygen production during high-temperature cathode decomposition is correlated with exotherms observed in ARC experiments. However, the $LiFePO_4$ cathode material does not generate oxygen even when fully decomposed at high temperatures, thus showing the lowest heating rate during thermal runaway. Figure 14 shows an expanded view of the thermal runaway peaks where it is clearly seen that the lowest heating rates occur for the $LiMn_2O_4$ cell (little oxygen generation) and the $LiFePO_4$ cell (no oxygen generation). Thermal runaway in these cells is dominated by anode/electrolyte reactions resulting from final breakdown of the protective SEI layer.

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[73] Dahn, J.; Erlich, G. M. (2011). "Lithium Ion Batteries" Reddy, T. B., ed. *Linden's Handbook of Batteries*, 4th ed. McGraw Hill, ISBN 978-0-07-162421-3; pp 26-8, copy of Table 26.3.

[74] Dahn, J. R., et al. (1994). *Solid State Ionics*, 69(3-4), p. 265-270.

[75] MacNeil, D. D.; Dahn, J. R. (2001). *Journal of The Electrochemical Society*, 148, A1205.

[76] Arai, H.; Tsuda, M.; Saito, K.; Hayashi, M.; Sakurai, Y. (2002). *Journal of The Electrochemical Society,* 149, A401.

[77] MacNeil, D. D.; Dahn, J. R. (2001). *Journal of The Electrochemical Society,* 148, A1211.
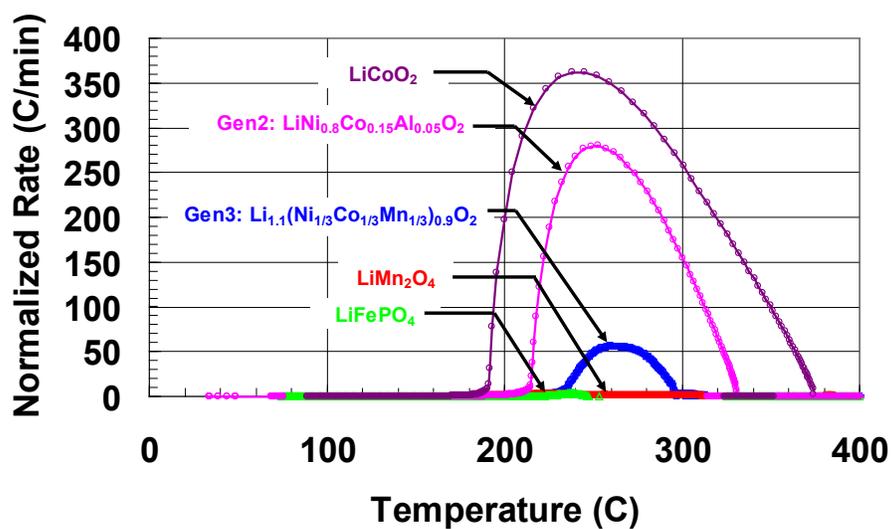
**Figure 13. Self-heating rate of 18650 full cell measured by ARC.
Improved cathode stability results in higher thermal runaway temperature (increased stability) and reduced peak heating rate.69**
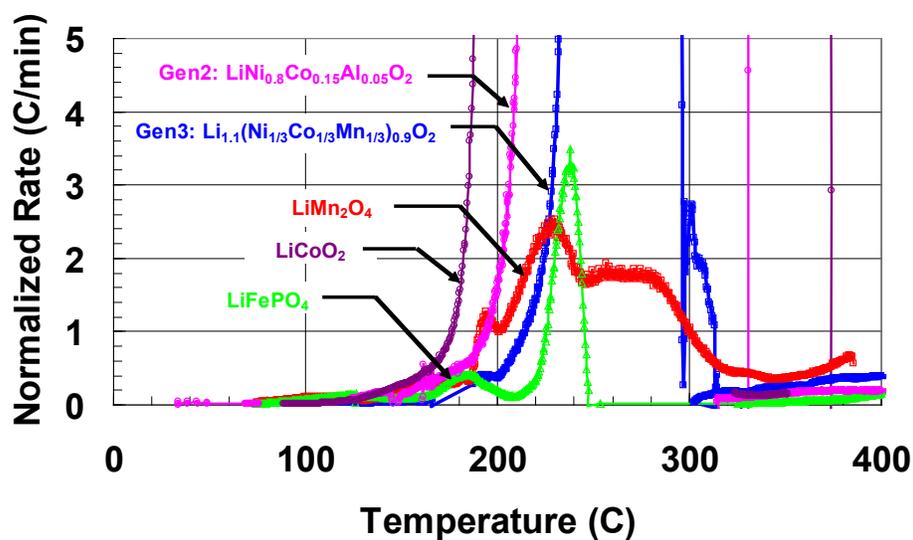

Figure 14. Expanded view of ARC profiles showing low rate thermal runaway of $LiFePO_4$ and $LiMn_2O_4$ cells. [69]

Figure 15 shows the thermal ramp results for the same cell chemistries discussed above. Although not as sensitive or as quantitative as ARC, the thermal ramp profiles show the same ordering of cell response with reduced oxygen generation. Cathode decomposition onset starts at 150°C to 250°C. The higher onset temperature of $LiMn_2O_4$ and $LiFePO_4$ cells again shows that they are more resistant to thermal abuse. Moreover, the reduced peak of self-heating rate of $LiFePO_4$-based cells makes them the safest cells Li-ion batteries on the market today.
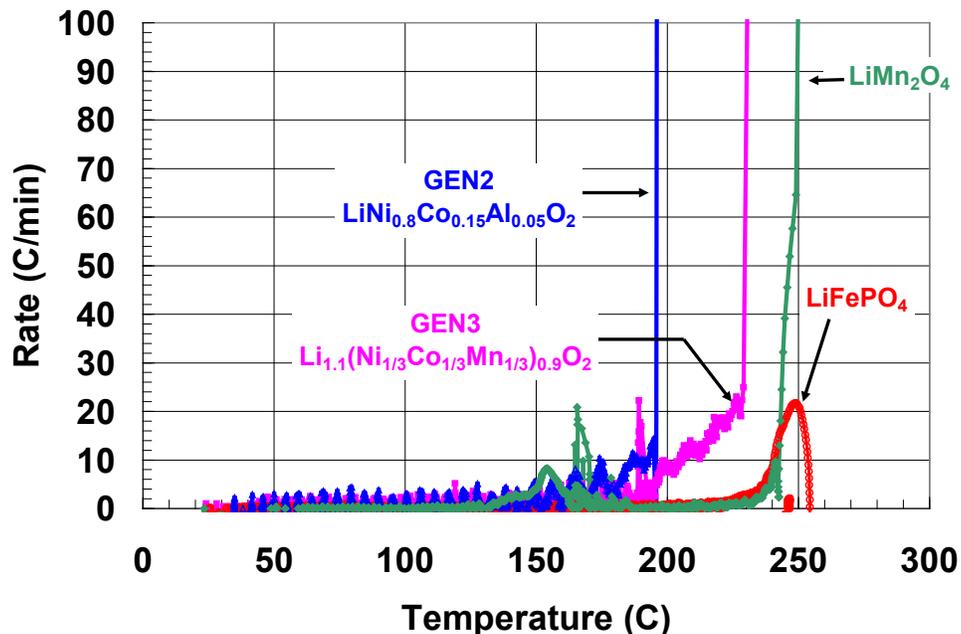
Figure 15. Onset of self-heating in thermal ramp experiment on Li-ion cells.
$LiFePO_4$ olivine cathodes show the greatest reduction in self-heating rate and increased onset temperature for runaway.37

7.2 Anodes in Li-Ion Batteries

Anode materials are chosen to have high capacity, high rate capability, low irreversible loss on formation cycling, and stability with respect to cycling and high-temperature exposure. Carbon anodes can be based on either natural or synthetic graphite, can have high or low surface area, and can have morphologies ranging from amorphous, spherical, or flaky grain structure. All of these material properties affect the thermal response of the anode under abuse conditions. As an example, DSC curves for three anode materials (100% SOC in electrolyte) are shown in Figure 16 for anode materials of different morphologies. The anodes are Sony hard carbon, MCMB (GEN1), and MAG10 flaky graphite (GEN2). All of the anodes showed a breakdown in the SEI layer starting around 120°C but with different rates of reaction at increasing temperature. The MAG10 anode material showed the highest level of reaction due to the poor SEI layer that formed on the particle edges.

The relative contribution of the anode and cathode material to the full cell response depends on the specific reactivity of the active materials and the mass loadings of each. As an example, Figure 17 shows a DSC comparison of the anode, cathode, and electrolyte for a GEN2 (MCMB/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) cell. The anode may have as large (or larger) specific enthalpy of reaction, but the reaction is spread out over a wide temperature range. The cathode reactions

occur at higher temperatures and over a much smaller temperature range. This often is the result of the high-rate Stage 3 thermal runaway.
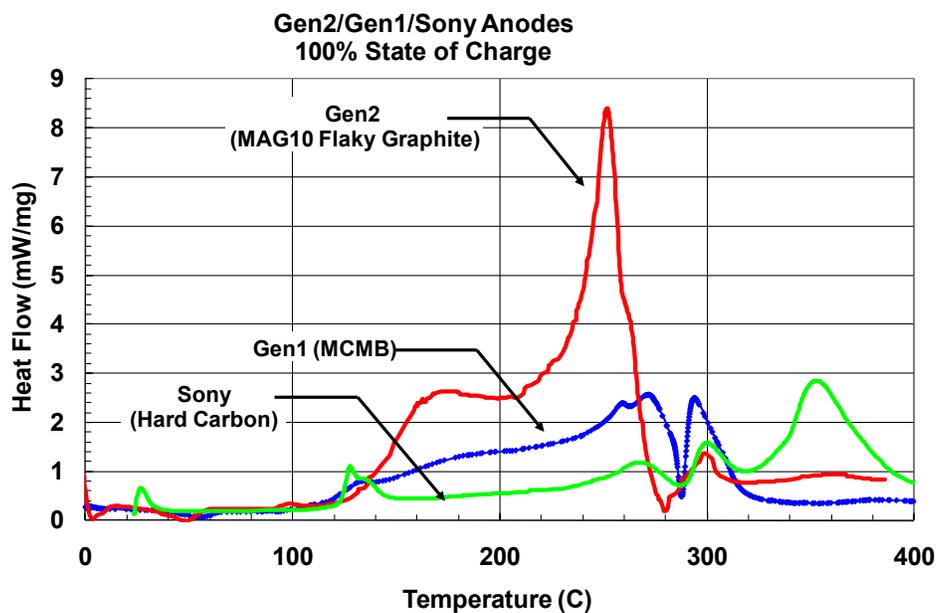
Gen2/Gen1/Sony Anodes
100% State of Charge

Figure 16. DSC profiles of anode carbon materials with different morphologies.[58]
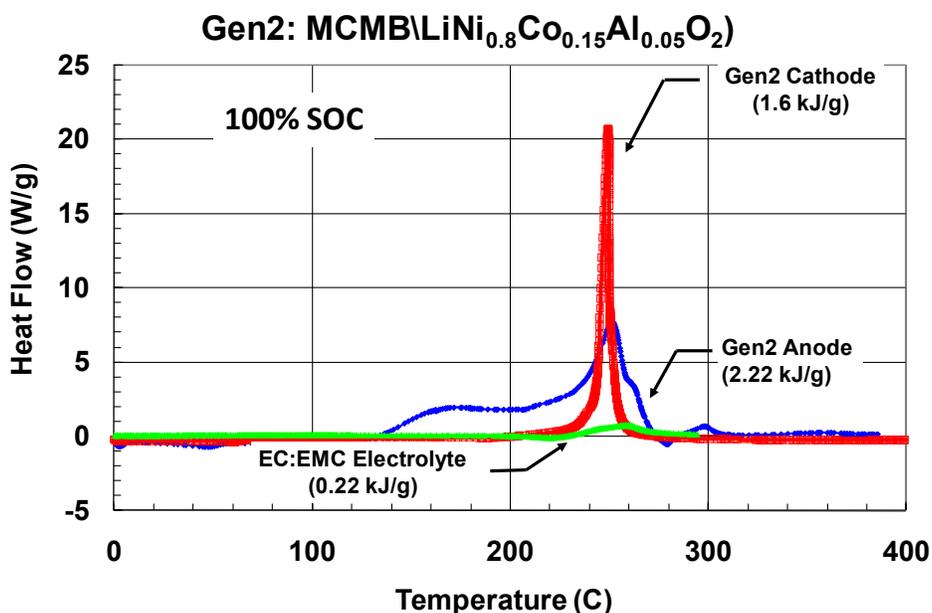
Gen2: MCMB\LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$)

Figure 17. DSC profiles showing contribution of anode, cathode and electrolyte to cell thermal reactions.[57]

The graphitic anodes used in common technology are only 50 mV or so above the potential of lithium. The low potential gives concern about plating of lithium under many aggressive charging scenarios or when the local current density is non-uniform.

The loss of lithium due to side reactions, such as SEI formation, may eventually lead to imbalance in the cathode lithiation. The failure mode for Li-ion cells under thermal runaway usually initiates with the dissolution of the protective SEI layer at the anode, allowing rapid heating and potential thermal runaway.

7.3 Separator Stability

An ideal shutdown separator will have a sharp transition to a very high resistance at a relatively low temperature, robust high-voltage standoff, and a wide temperature window of stability, as shown in Figure 18 below. Cell safety is critically dependent on the stability of the separator under extreme conditions of temperature and mechanical stress. Separators generally are classified into three groups: (1) microporous polymer membranes, (2) non-woven fabric mats, and (3) inorganic composite membranes.[78] The separators enhance cell safety by having properties of high mechanical strength (puncture resistance), high thermal stability, and shutdown properties. As discussed earlier, shutdown results when a component of separator material (usually polyethylene) melts and restricts ionic conduction through the cell. This feature may prevent further heating of the cell at a temperature well below thermal runaway. The effectiveness of the shutdown depends on whether the cell temperature does indeed immediately begin to decrease. If the temperature continues to drift upwards because of partial electrical conduction (partial shutdown), continued exothermic chemical reactions, or outside heating sources, thermal effects may diffuse to other parts of the cell or module, triggering a domino effect.

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[78] Sheng, S.; Zhang, J. (2007). *Journal of Power Sources* 164 pp. 351–364.
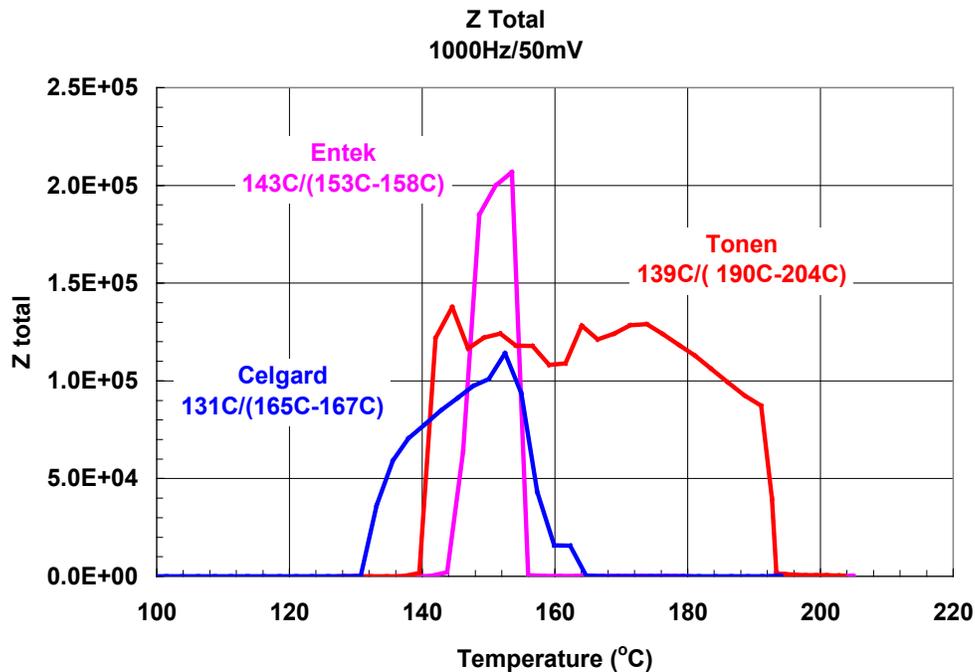
Figure 18. Impedance of electrolyte soaked separator materials showing shutdown and the temperature window of stability.[58]

7.4 Electrolytes

Li-ion batteries have the unique characteristic of using organic-based electrolytes compared to other electrochemical storage systems. These electrolytes are almost universally based on combinations of linear and cyclic alkyl carbonates. These electrolytes are sufficiently stable (kinetic stability results from protective SEI, which limits reactivity with the anode surface) to allow the use of lithium and LiC_6 as the anodic active component. Liquid electrolytes have good conductivity, which results in the high-power cell designs. However, these organic electrolytes have high volatility and flammability that pose a serious safety issue for their use in the consumer and transportation markets. Under extreme conditions of voltage and temperature, these electrolytes can react with the active materials of both anode and cathode to release significant heat and gas, as shown in the previous sections.

The choice of electrolytes is often based on performance criteria such as conductivity, temperature range (high and low), and voltage range stability. There are many combinations of solvent species, solvent ratios, electrolyte salts, and additives. The choice of electrolyte can also have a significant impact on the safety, thermal stability, and abuse tolerance of the cell. Some materials that have superior performance properties, such as $LiAsF_6$, cannot be used because of its high toxicity.[79] Some solvent species, such as PC, are limited in concentration because they cause disruption of the anode graphite grains. The choice of electrolyte often is not given full consideration to the effect on cell response during an abuse event. For example, the effect of electrolytes on the peak thermal runaway reaction in a nickel-cobalt-aluminum $(LiNi_{0.8}Co_{0.15}Al_{0.05}O_2)$ (GEN2) cell is shown in Figure 19.[68] The EC:PC:DMC(1:1:3)/1.2M

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[79] Reddy, T. B., ed. *Linden's Handbook of Batteries*. 4th edition. McGraw Hill, 2011, ISBN 978-0-07-162421-3, Ch. 7.3.1.

LiPF$_6$ electrolyte has significantly reduced the kinetics of the peak runaway reaction while not affecting the total enthalpy of the reaction as given by the width of the reaction peak. This effect is seen to be even more pronounced for the more stable GEN3 cathode chemistry [Li$_{1.1}$(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)$_{0.9}$O$_2$] as shown in Figure 20.
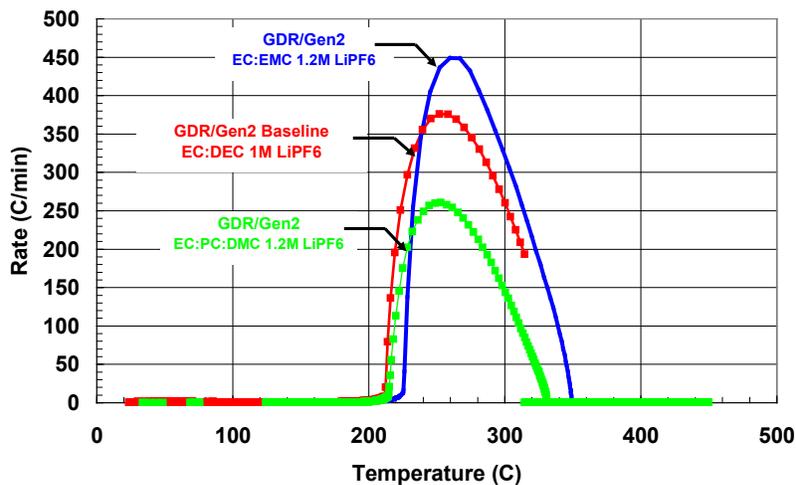

Figure 19. ARC profiles of GEN2 18650 cells with different solvent electrolyte species.[58]
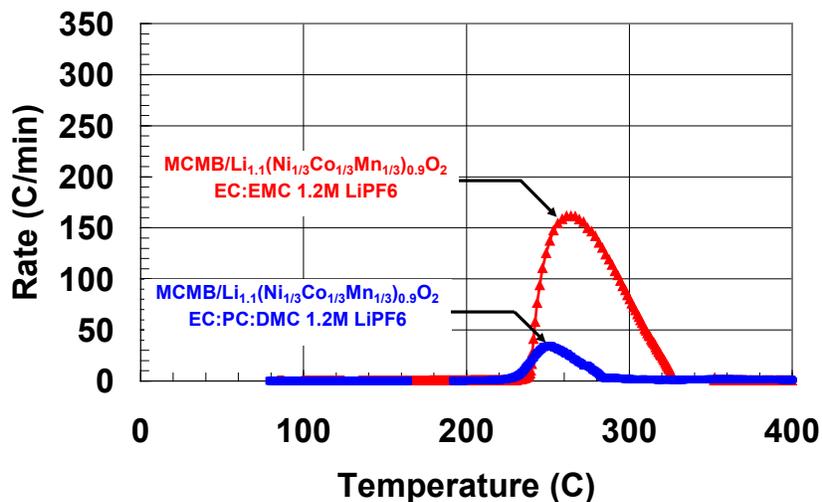

Figure 20. ARC profiles for GEN3 18650 cells with EC:EMC (3:7) and EC:PC:DMC (1:1:3) electrolyte solvents.[58]

The energy released by electrolyte reaction with the active materials is strongly dependent on the cell chemistry and SOC (see Section 7.6). The most energetic runaway reactions result from oxygen released during decomposition of the cathode and subsequent oxidation of the electrolyte. As an example, the contributions of the individual cell electrodes to the full cell thermal response are shown in Figure 21 for a GEN3 cell. Fully charged electrodes had been removed from a cell and resealed in an 18650 can with the electrolyte. For this chemistry, the reactions with the electrolyte are comparable over the whole temperature range for both the anode and cathode. Cell chemistries with little or no oxygen release (e.g., $LiMn_2O_4$ and $LiFePO_4$) will have thermal responses determined almost entirely by anode/electrolyte reactions.
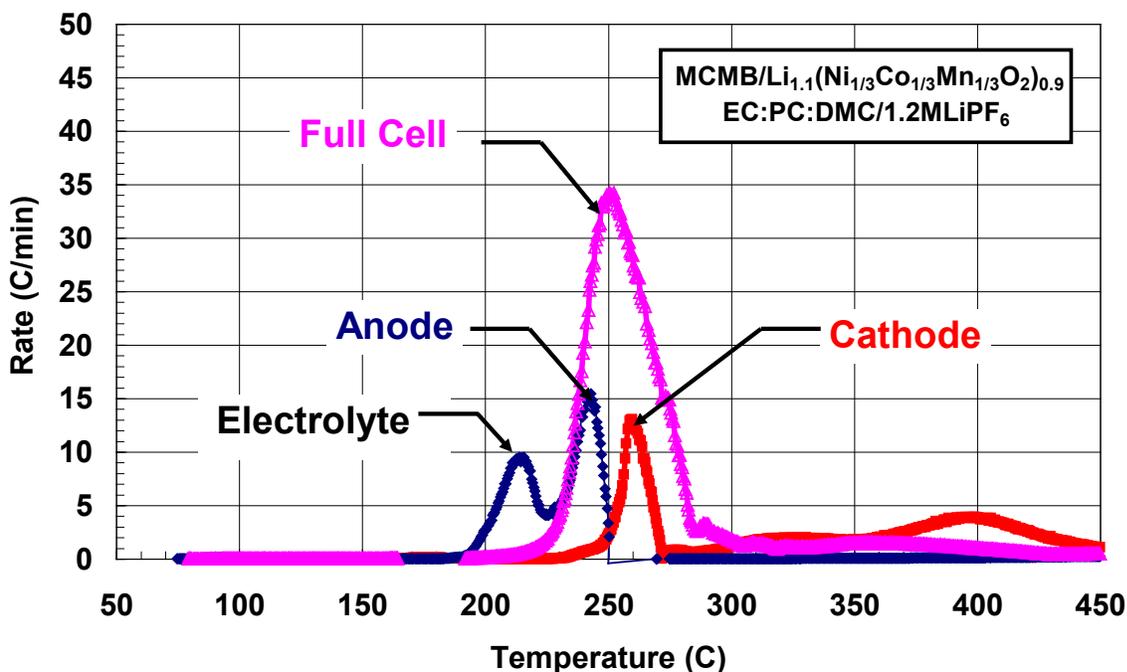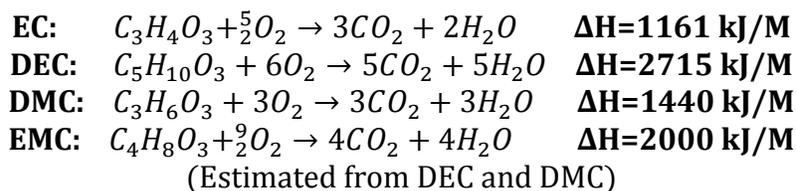

**Figure 21. ARC profiles of anode and cathode electrodes in electrolyte compared to full cell response.**[58]

The combustion enthalpies for some common solvents are shown below.[80,81]

EC: $\quad C_3H_4O_3 + \frac{5}{2}O_2 \rightarrow 3CO_2 + 2H_2O \quad$ **ΔH=1161 kJ/M**
DEC: $\quad C_5H_{10}O_3 + 6O_2 \rightarrow 5CO_2 + 5H_2O \quad$ **ΔH=2715 kJ/M**
DMC: $\quad C_3H_6O_3 + 3O_2 \rightarrow 3CO_2 + 3H_2O \quad$ **ΔH=1440 kJ/M**
EMC: $\quad C_4H_8O_3 + \frac{9}{2}O_2 \rightarrow 4CO_2 + 4H_2O \quad$ **ΔH=2000 kJ/M**
(Estimated from DEC and DMC)

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[80] *CRC Handbook of Chemistry and Physics.*
[81] http://webbook.nist.gov/chemistry/name-ser.html

The calculated combustion enthalpies based on moles of oxygen are quite similar for all solvents, with an average of 460 kJ/mole of O_2. However, the amount of oxygen released by even some of the most reactive cathodes is not nearly sufficient to cause complete combustion of the electrolyte. For example, GEN3 $LiNi_{1-x-y}Mn_xCo_yO_2$ only gives enough oxygen to react with 5%–15% of the electrolyte. Thus, the largest source of un-reacted material is the vented electrolyte, which can combust externally in air with an energy release several times that of the internal reaction enthalpies (as shown in Figure 22).
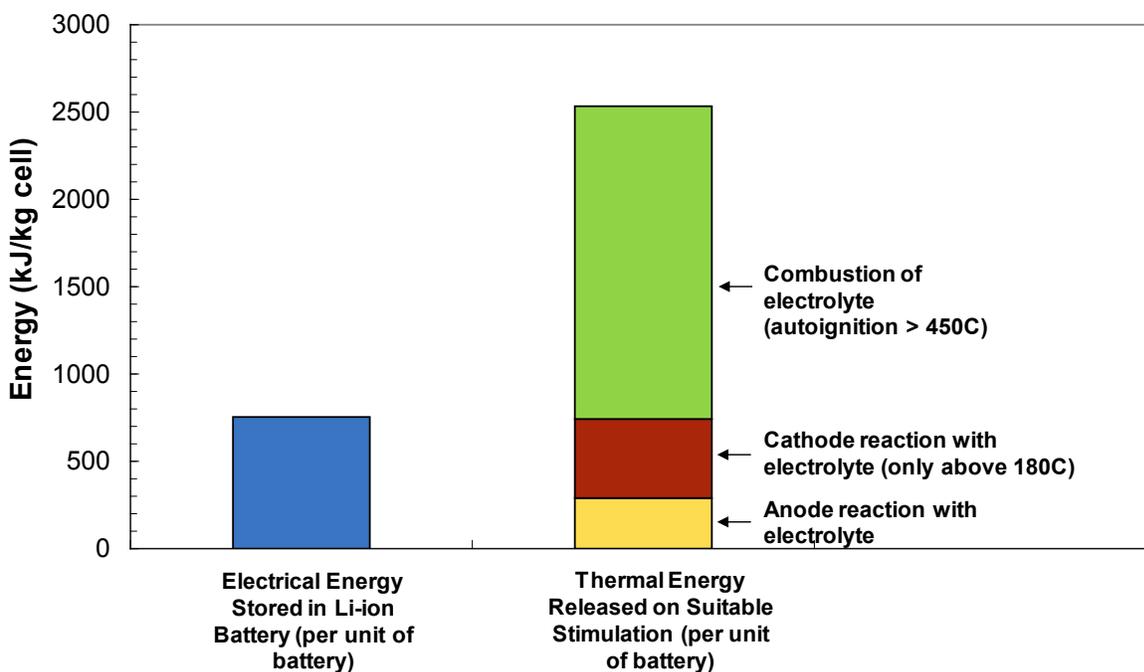
Figure 22. Comparison of stored electrical energy and energy released from decomposition reactions.[7]

The flammability of the vented electrolyte is a significant unresolved safety issue for Li-ion batteries. Accident scenarios involving burning electrolyte have some of the most serious consequences, resulting in cascading failure of other cells in the battery pack and involvement of adjacent materials and structures.

7.5   Gas Generation

Almost all electrochemical couples produce or have the possibility of producing gas. The toxicity and flammability of the evolved gas should be studied. Almost all aqueous systems will generate hydrogen gas by the decomposition (electrolysis) of water. For non-aqueous systems, the gas evolution over time must be addressed by incorporation of adequately designed safety vents on the cell to preclude a violent container failure.

Gas generation will result whenever the cell reaches the solvent decomposition temperature, whether from internal or external sources. Mixture of the solvent vapors with the surrounding air can result in a highly flammable or explosive composition that only requires an ignition source,

such as a simple spark, to ignite. Even the safest cathode and anode chemistries will not prevent this release of flammable vapors.[82]

Gas generation in Li-ion cells under abuse conditions has an indirect effect on safety by producing sufficient pressure and gas volume to aerosolize the flammable solvents into the surrounding environment during cell venting. Figure 23 shows the ARC thermal runaway profile of an 18650 cell showing the heat and gas volume generation. The alkyl carbonate-based electrolytes, which make up almost all of the Li-ion electrolytes, have been shown to break down at temperatures starting around 150°–200°C. Figure 24 shows ARC bomb data for the electrolyte only. Venting may occur at lower temperatures strictly due to increased vapor pressure, as seen in Figure 23 for a full cell. A high rate of gas generation usually accompanies (or immediately follows) the thermal runaway peak. Decomposition of organic solvents may form several gas species, some of which are flammable (H_2, CO_2, CO, and several low molecular weight hydrocarbon gases, such as CH_4 and C_2H_6 as shown in Figure 25).
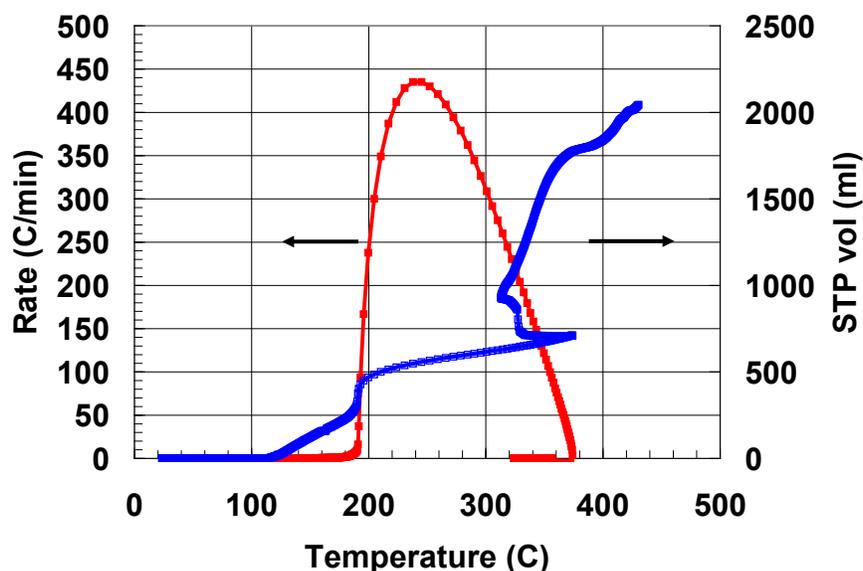

Figure 23. ARC thermal runaway profile of an 18650 cell (5 mL electrolyte) showing heat and gas generation.

(Unpublished SNL data)

[82] Harrisa, S. J.; Timmons, A.; Pitz, W.J. (2009). *Journal of Power Sources* 193 (2009) 855–858.
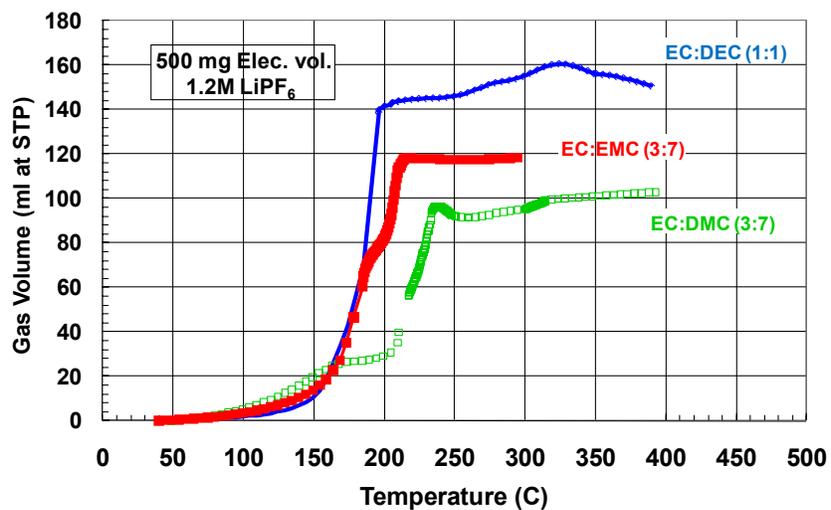
Figure 24. Gas generation of representative electrolyte solutions.

(Unpublished SNL data)

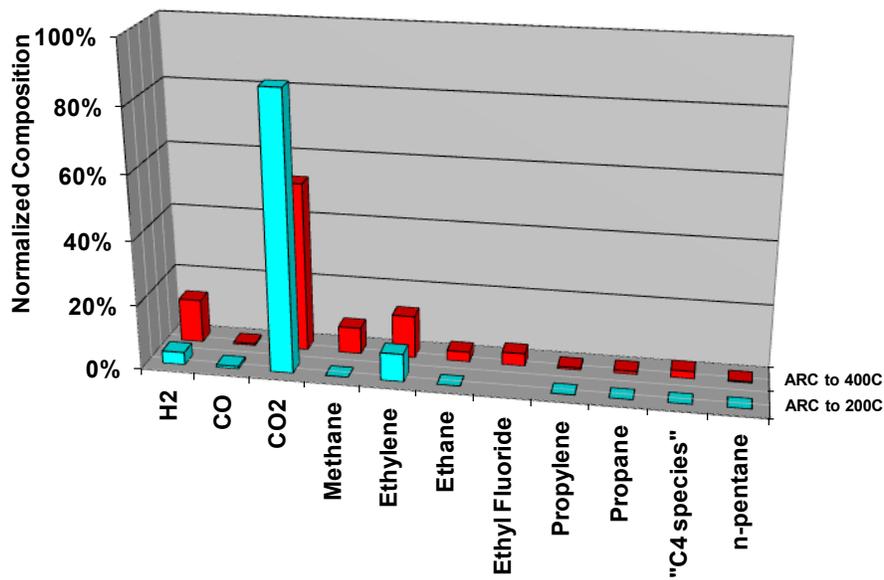**Temperature Effect for EC:EMC/1.2M LiPF$_6$**

Figure 25. Gas generation species for EC:EMC 1.2 M LiPF$_6$ electrolyte at 200°C and 400°C.

(Unpublished SNL data)

7.6 Effect of SOC on Thermal Stability

SOC is one of the most important factors in determining the response of a cell or pack to abusive events, which is why shipping regulations require that Li-ion rechargeable batteries be at a low SOC during shipment. While not many careful studies have been published on the effect of SOC and age, an SNL publication[37] provides quantitative comparison for two Li-ion battery chemistries ($LiCoO_2$ and $LiNi_{0.8}Co_{0.2}O_2$). While this summary report relies heavily on information published in that reference, information gleaned from other sources shows that most Li-ion battery chemistries would follow similar trends.

Figure 26 shows ARC results for commercial 18650 Sony cells (coke-based anode and $LiCoO_2$ cathodes) from 0% to 100% SOC. The onset of self-generated heating decreased to lower temperatures with increasing SOC, and the magnitude of the heating rate increased more rapidly with increasing temperature. Self-generated heating occurred as low as 50°C, but an accelerating heating rate was not observed until above 100°C. These thermal reactions are well below the cathode/electrolyte reaction range and are believed to result primarily from breakdown of the anode SEI layer and subsequent reduction reactions of the lithiated carbon with the electrolyte. The higher SOCs result in increased levels of lithiation of the anode that increases these reactions. These onset reactions exhibit a much lower heating rate than is seen during full thermal runaway, as shown in Figure 13.

The other cell chemistry examined in this study had an MCMB anode and a $LiNi_{0.8}Co_{0.2}O_2$ cathode (referred to as a GEN1 cell). Figure 27 shows the ARC profiles with increasing SOC showing lower SOCs were more stable. The MCMB carbon anode reactivity shows a weaker dependence on SOC compared to the coke-based anodes. Differences in morphology and structure of carbon anode material can greatly affect the stability of the SEI and Li intercalation kinetics.

The peak thermal response of a cell also increases rapidly with the degree of charge. Figure 28 shows the ARC profiles for Sanyo ($LiCoO_2$) cells with increasing SOCs from 3.8V to 4.3V. The onset of the high-rate (Stage 3) reactions did not change significantly with SOC, but the peak heating rates and the enthalpy of the high rate reactions increased markedly. This peak response depends strongly on the type of cathode material used. (Figure 11 showed how heat generation increased sharply during overcharge for cathodes at the point of complete lithium removal.) In addition, the anode/cathode capacity balance is important for maintaining stability at high SOC. Insufficient anode capacity compared to the cathode can result in lithium plating at high SOC and subsequently can cause high-rate thermal runaway.

During overcharge, excessive lithium is extracted from the cathode, and a corresponding excessive insertion and/or plating of lithium may occur at the anode. These conditions make both electrodes less thermally stable. Figure 28 shows the ARC profiles for Sony cells with increasing states of overcharge from 4.1V to 4.5V. There was a marked increase in reaction around 120°C with some increase in reaction as low as 70°C. Overcharge resulted in an increase in the lithiated anode reaction and apparent reduction in the effectiveness of the SEI layer.
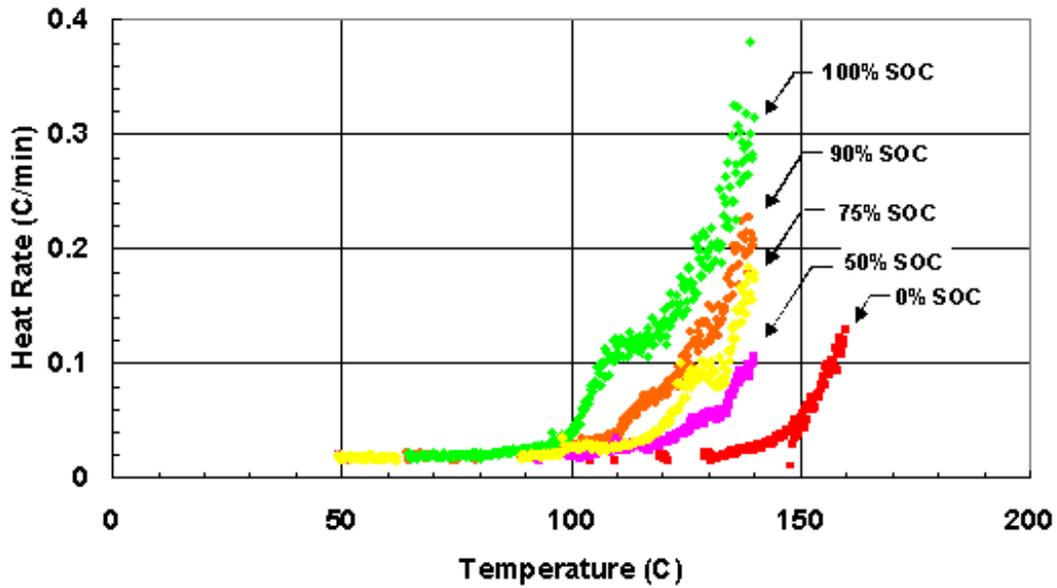
Figure 26. ARC runs for Sony 18650 cells versus SOC.[58]
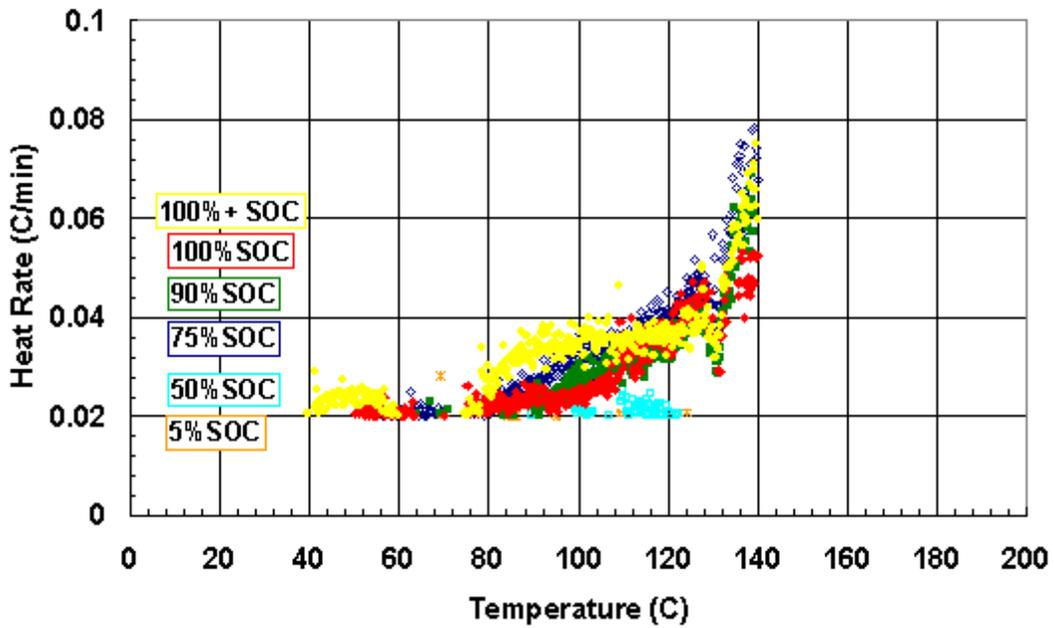
Figure 27. ARC runs for GEN1 cells vs. SOC.[37]
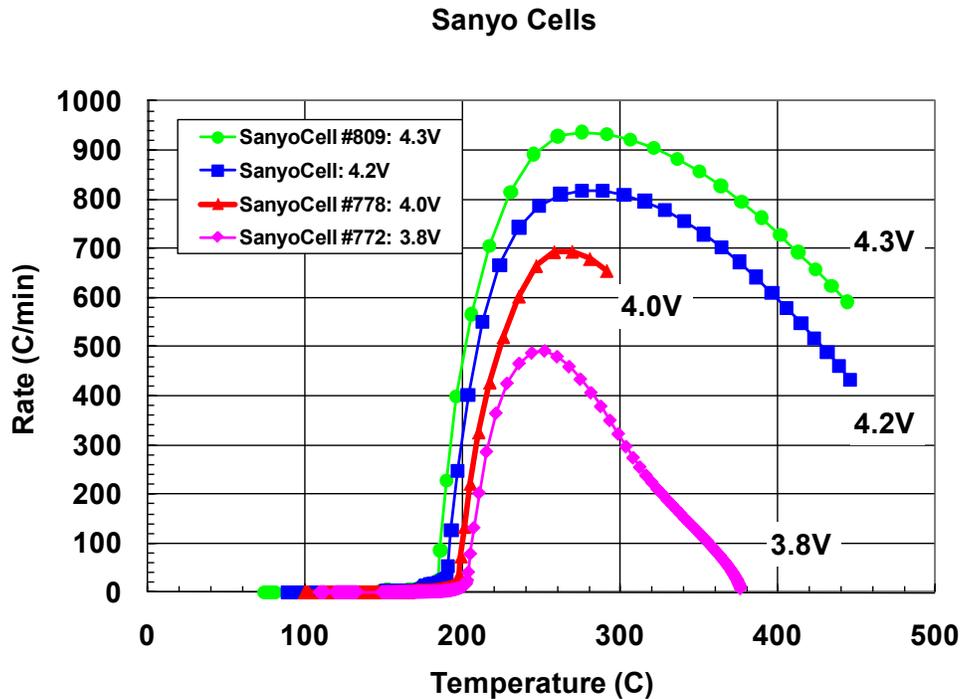
Sanyo Cells

Figure 28. ARC profiles of Sanyo 18650 cells at increasing SOCs.

(Unpublished SNL data)

Finally, the magnitude of response of a cell to an internal short circuit will be influenced by the SOC. When a cell is at 100% SOC, an internal short circuit often results in thermal runaway of the cell. However, when the cell is at 80% SOC, the maximum temperature will be reduced to 200°C. At 70% SOC, an internal short circuit can be well tolerated.[83]

7.7 Effect of Age and Cycling On Thermal Stability

As Li-ion batteries age, they slowly lose capacity by several mechanisms.[84] The most important mechanism is the buildup of resistive decomposition products in the surfaces of the electrodes. The decomposition products have the result of increasing cell impedance, which reduces the maximum discharge rate that the cell can sustain and increases the Joule heating during a high rate of discharge. Although much study has gone into understanding and modeling the lifetime of cells with aging, little work has been done on the effects of aging on thermal stability and abuse tolerance.

USABC goals, in line with the DOE research program for HEVs, are a calendar life of 15 years for HEVs and 10 years for EVs.[85] A cycle lifetime of up to 1,000 cycles at 80% depth of discharge is also required. Little or no safety testing has been performed on cells approaching

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[83] Zhang, Z. "Perspectives on Safety and Life for Li-Ion Application in Electric Drive Vehicles (EDV)." Presented at Pacific Power Source Symposium 2011, Hilton Waikoloa Village, Hawaii, January 10-15, 2011.
[84] Vetter, J.; Novák, P.; Wagner, M. R.; Veit, C.; Möller, K.-C.; Besenhard, J. O.; Winter, M.; Wohlfahrt-Mehrens, M.; Vogler, C.; Hammouche, A. (2005). *Journal of Power Sources* 147 (2005) pp 269–281
[85] http://www.uscar.org/guest/teams/11/Electrochemical-Energy-Storage-Tech-Team

these lifetime limits. There are valid concerns about the stability of the active materials, separators, and possible reactions involving new degradation or contamination products. Further testing of these aged cells is planned as part of the ABR program.

This topic was investigated at SNL during the early part of the Advanced Technology Development program.[37, 86] Decomposition products can passivate the electrode surfaces, making them more stable at elevated temperature. These effects of aging on the onset of thermal runaway were measured by performing ARC runs of thermally aged cells.

Figure 29 shows the results for Sony cells that had been aged for 6 months at 25°C, 11 days at 60°C, and 6 weeks at 70°C. All cells were measured at 100% SOC. The cells showed a loss of low-temperature reactivity with increased aging. The data show that aging resulted in loss of the low-temperature heat output with increasing time and temperature. The onset temperature of sustained heat output increased with increased time/temperature aging. These measurements suggest that the anode protection layer is undergoing partial conversion from the metastable species to the stable inorganic species even at these low temperatures. The majority of this conversion takes place relatively quickly (less than two weeks) even at 60°C, as little further change was noticed for the 70°C/6-week cell. After decomposition of the SEI anode protection layers (>120°C), the exothermic heating rates are similar regardless of the previous aging history. Notably though, the reaction rate immediately following onset was more abrupt with increased aging, showing further evidence of a breakdown of a growing SEI layer exposing the previously protected lithiated anode particles. Higher temperature measurements were not performed during this early phase of the ABR program.

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[86] Roth, E. P. (2000). "Thermal Characterization of Li-ion Cells Using Calorimetric Techniques." *39th Power Sources Conference Proceedings*, June 12–15, 2000, Cherry Hill, New Jersey.
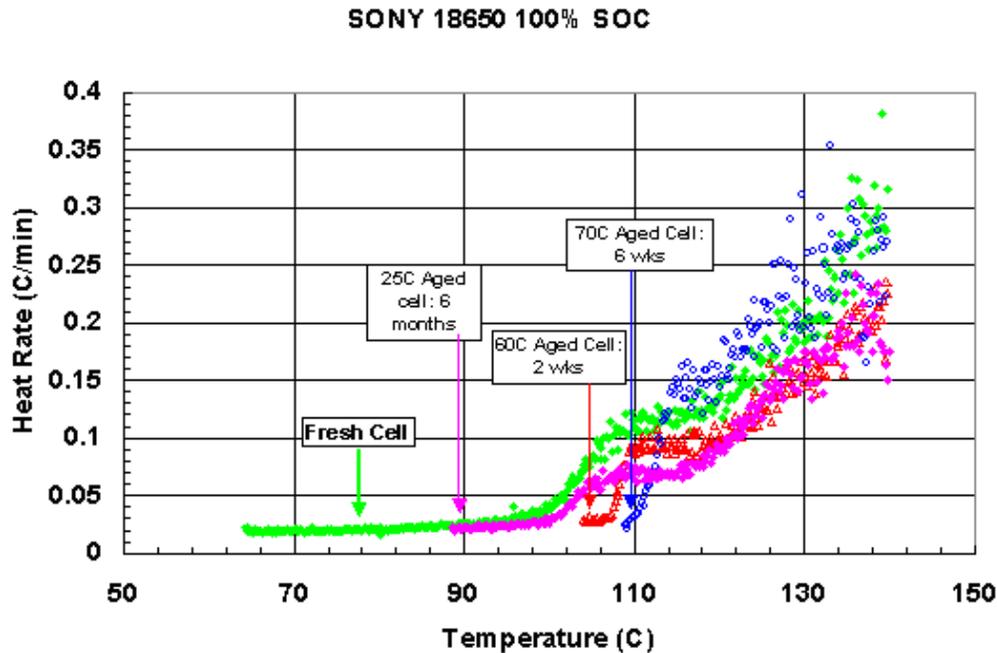
Figure 29. ARC runs of fresh and aged Sony cells at 100% SOC[37]

ARC measurements were also performed on GEN1 cells that underwent accelerated cycle aging at elevated temperatures of 40°C, 50°C, and 60°C. The cycle consisted of a discharge/charge profile resulting in a decrease in SOC of 3%, 6%, or 9% from a baseline of 80% SOC. All cells were placed at 100% SOC for ARC measurements up to 160°C.

The ARC profiles for the cells cycled at 50°C with 3%, 6%, and 9% delta SOC are shown along with the unaged baseline cell data shown in Figure 30. The cells aged at 50°C showed increased stability as measured by increasing T(onset) temperature, which means that self-sustained heating did not occur until above 80°C for the cycled cells. Above 80°C, the heating rates were very similar to those for the unaged cell. The dip in the heating rate at 130°C resulted from the melting of the separator material.
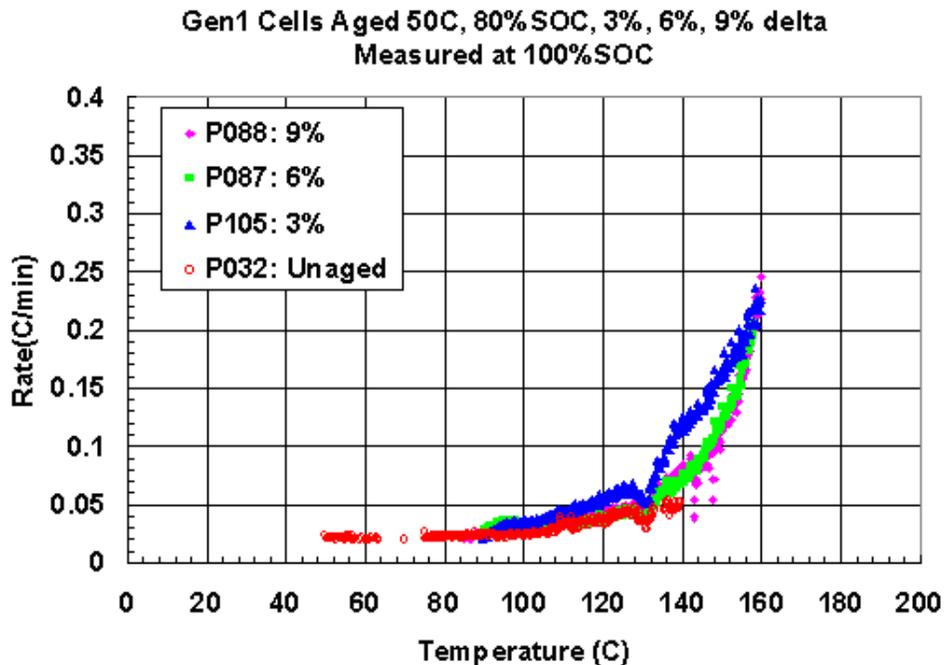
Figure 30. ARC runs of GEN1 cells (100% SOC) aged at 50°C, 8% SOC, at 2%, 6% and 9% delta SOC.[37]

7.8 Effect of Cell Energy on Thermal Stability

As mentioned previously, higher energy cells have a stronger response to abuse events and usually have poorer safety performance. A study by Exponent Failure Analysis Associates[87] investigated the thermal stability of cells that contained the same energy but were manufactured with four different cathodes. The cathodes studied and the cells that were prepared are summarized in Table 6.

Power and energy characteristics of the tested cells were consistent with expectations for cell design and electrode chemistry.

Cells were charged to predetermined levels prior to ARC testing with the goal of comparing cells with identical capacity. All four cells were tested after being charged to a capacity of 1.1 Ah. Three cells were tested at 1.5 Ah, two at 2.2 Ah, and one at 2.5 Ah. The cell test matrix is shown in Table 7.

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[87] White, K.; Horn, Q.; Singh, S.; Spray, R.; Budiansky, N. (2010). "Thermal Stability of Lithium-ion Cells as Functions of Chemistry, Design and Energy." Presented at *Lithium Mobile Power 2010*, Boston MA, November 4-5, 2010.

Table 6. Characteristics of Exponent Test Cells Made with Four Different Cathodes[87]

Sample	Capacity	Energy
LiNi $_{1/3}$ Co $_{1/3}$ Mn$_{1/3}$O$_2$ NCM	1.5 Ah	5.5 Wh
LiCoO$_2$ LCO	2.2 Ah	8.2 Wh
LiCoO$_2$ LCO	2.6 Ah	9.5 Wh
LiFePO$_4$ LFP	1.1 Ah	3.5 Wh

Table 7. ARC Test Sample Charge Energy[87]

Cell ID	1100 mAh	1500 mAh	2200 mAh	2500 mAh
LFP	X			
NCM + LMO	X	X		
LCO	X	X	X	
LCO	X	X	X	X

The ARC was used to evaluate thermal stability. The experimental measurements used were self-heating onset temperature and self-heating rate at 180°C, important measures of thermal stability and cell safety.

The ARC results are shown in Figure 31 and Figure 32. The self-heating onset temperature is a strong function of cell charge energy (i.e., SOC). The onset temperature of high-energy LiCoO$_2$ at 82% SOC is comparable to LiFePO$_4$ but LiCoO$_2$ has 50% more capacity. The self-heating rate at 180°C appears to be dependent on cell energy rather than cell chemistry or cell design. These data also suggest an exponential relationship between energy and self-heating rate.
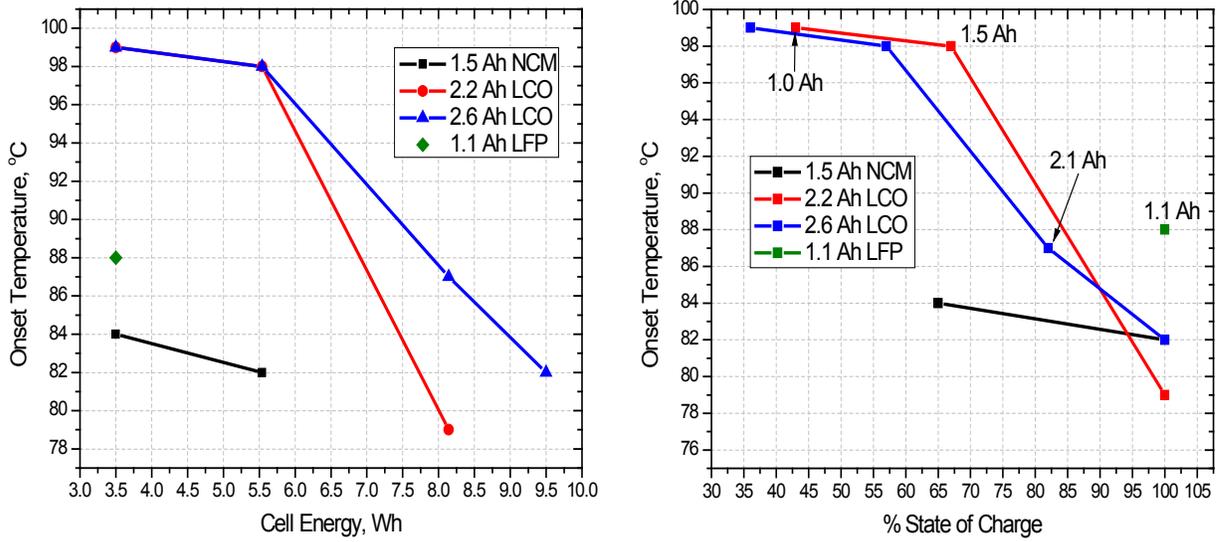
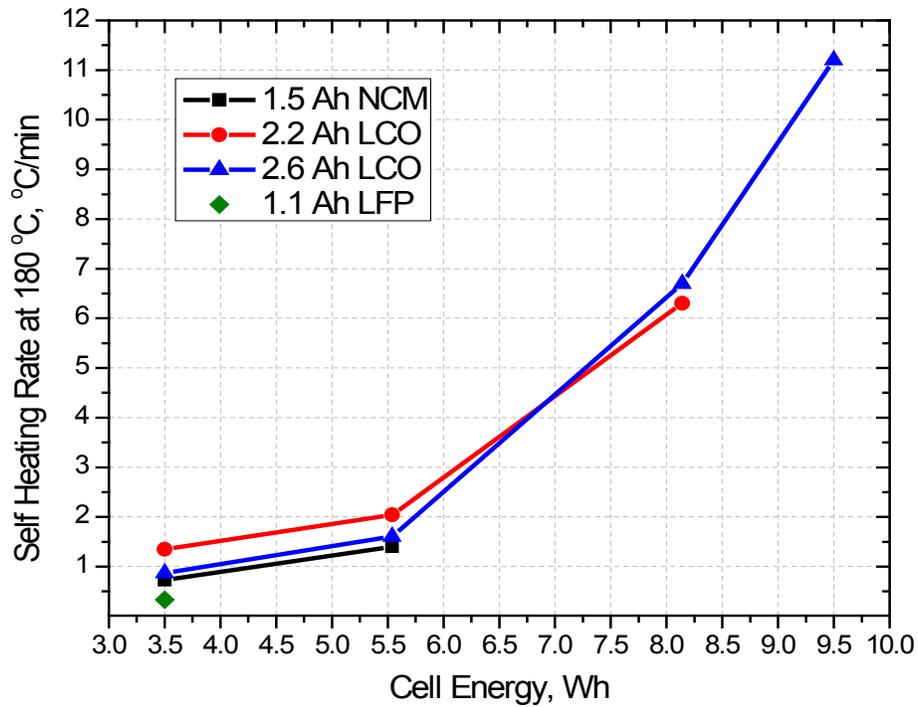**Figure 31. Self-heating onset temperature as a function of cell energy and SOC.**[87]

Figure 32. Self-heating rate at 180°C.[87]

The authors at Exponent Failure Analysis Associates raise questions about the validity of improved safety claims attributed to cathode substitution that may, in fact, be a result of the low energy design. This work poses the question of whether cell energy content determines the safety and abuse tolerance response of a cell rather than the current thinking that the materials determine the safety and abuse tolerance response.

This conclusion is controversial, but supports informal discussion with Prof. Gerd Ceder,[88] who states, "The stability of phosphate cathodes is a result of the lower voltage, not inherent chemical stability." The roadmap recommends that a comprehensive investigation that separates the effect of materials and cell capacity and identifies the role(s) of active materials be funded. Further, a validated cell abuse model should be developed to help elucidate and understand these effects.

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[88] Private communication, Gerd Ceder, January, 12, 2011.

8 Review of Approaches to Improve Safety and Recommendations

8.1 Issues that Control Abuse Response

The issues that drive materials developers, cell designers, and battery pack manufactures can be summarized by the following topics:

- Oxidative capacity of cathode (O_2 generation and surface oxidation potential)
- Stability of anode SEI
- Stability of separator
- Is separator shutdown a good thing in EVs and HEVs?
- Electrolyte flammability and reactivity with electrode materials
- Likelihood of internal short circuit occurring
- Likelihood of single cell failure propagating to adjacent cells.

The following sections discuss research efforts that are addressing these concerns.

8.2 Cathodes

The first of the two cathode issues is the oxidative capability of the cathode. The cathode's active material surface is a source of high-oxidation potential at high SOC and overcharge. The contact between the cathode surface and the common organic electrolytes used in Li-ion cells can result in increased surface impedance due to:

- The formation of reaction products
- Dissolution of the transition metal active species from the cathode particles
- Irreversible structural changes in the cathode materials.

These reactions are deleterious and can reduce the rate capability, capacity, and stability of the cathode material. These reactions also produce heat at a significant rate, which can lead to thermal runaway in the cell.

The $LiFePO_4$ cathode family has higher oxidative stability than do layered oxides such as $LiCoO_2$. However, safety is achieved in cells with significantly reduced energy. $LiFePO_4$ materials are sufficiently well studied in the commercial and academic sectors. Moreover, the low specific energy will limit their usefulness in many traction applications that require high energy. Therefore, the author of this roadmap recommends that DOE investments be targeted elsewhere for the development of new, high-energy cathode materials.

High-voltage cathodes are being explored by groups because of the attraction of high energy. However, high-potential cathodes in lithium systems have shown evidence of oxidative potential and oxygen evolution, which can lead to thermal runaway problems. It has been shown that for several cathode systems, there is a linear relation between the logarithm of the equilibrium oxygen pressure and the potential, independent of both the chemical compositions and the crystal

structures of the phases involved.[89] Thus, the worry about oxygen generation at high potential can be exacerbated by using high-voltage cathodes. In his publication, Huggins cautions about using high-voltage cathodes because of their enhanced oxidative tendency that portends safety problems.

TIAX has developed CAM-7, a stabilized, doped $LiNiO_2$-class cathode material with a unique combination of high energy density and high power density that enables significantly longer run times in both high-energy and high-power Li-ion applications.[90] CAM-7 supports discharge capacities exceeding 200 mAh/g without requiring charging beyond the normal Li-ion charge voltage of 4.2 V. In addition, CAM-7 supports excellent high-power discharge capacities as illustrated by delivery of >130 mAh/g discharge capacity at a rate of 100°C. It has the highest capacity at high rates of discharge as any cathode that has been announced recently.[91] The reported safety of this cathode material looks promising,[92] but the impact on industry is still to be determined. The TIAX approach, typical of many groups in the United States and elsewhere, is to make incremental improvements on today's mixed oxide cathode materials. Success is to be expected, and Li-ion rechargeable battery technology for vehicles will benefit from incremental improvement in performance and safety. However, it will not produce a new generation of cathodes. A different approach is needed.

First principles calculation can be a good guide to understanding safety aspects, such as oxygen generation at high SOC. Ceder's group at MIT has developed a methodology that, combined with large computing resources and their analysis software, allows the same analysis on a much larger scale for intercalation compounds.[93] The goal is to identify candidate materials that have high-capacity, low-oxidative potential, and are not currently being studied as cathode materials. The ability to perform these calculations rapidly on many potential material stoichiometries provides a powerful tool. Figure 33 shows a plot of chemical potential of oxygen (which is related to oxidative reaction potential and O_2 evolution) versus voltage for an extremely wide range of hypothetical materials and structures. Early results support the conclusion that, in general, the higher voltage cathode creates worse thermal stability. However, new polyanion structures potentially achieve a better tradeoff between voltage and thermal stability. Borates and silicates seem to offer the best voltage to thermal stability performance. Calculations such as these can provide guidance to synthetic programs to discover new cathode materials that can have high capacity and improved safety.

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[89] Huggins, R. A. (2009). *ECS Transactions*, 16 (29) 37–47.

[90] Pullen, A.; Ofer, D.; Clatterbuck, D.; Rempel, J.; Oh, B.; Dalton-Castor, S.; Barnett, B.; Sriramulu, S. (2010). "A Lithium Nickelate-Based Cathode Material for High-Energy, High-Power Lithium-Ion Batteries" Abstract #1004, *218th ECS Meeting*, Las Vegas, NV, Oct. 10–15, 2010.

[91] Whittingham, M. S. (2011). "Energy Storage Materials: The Past and the Future." *Pacific Power Source Symposium 2011,* January 10–14, 2011. Waikoloa, HI.

[92] Barnett, B. (2010). "TIAX CAM-7 High-Capacity, High-Power Cathode." Knowledge Foundation *Battery Safety 2010 Proceedings*, Boston, November 3, 2010.

[93] Ong, S. P.; Jain, A.; Hautier, G.; Kang, B.; Ceder, G. (2010). *Electrochem. Comm.* 12 (2010) 427–430.
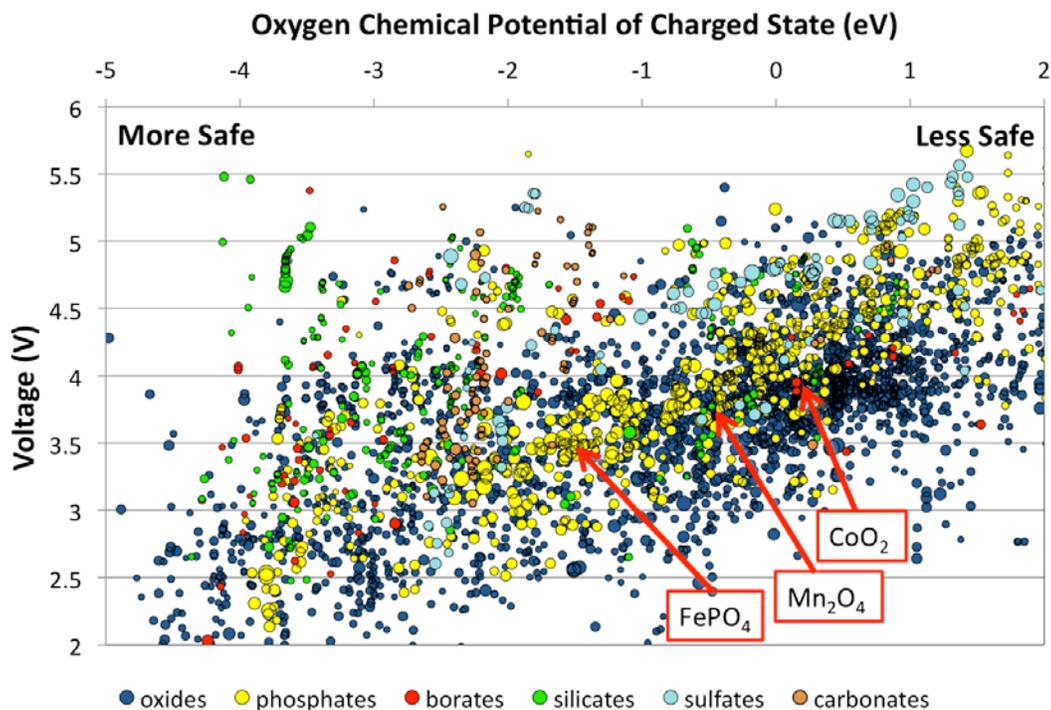
Figure 33. Calculated relationship between oxygen chemical potential at full charge and voltage for many cathodes.

Source: A. Jain, G. Hautier, S. P. Ong, et al. Physical Review B 2011, 84, 045115

Cathode conversion reactions are another fertile field for development of high capacity, safe cathodes. Several material compositions are potentially available for study, but this discussion will highlight only one system being explored by Prof. Glenn Amatucci – nanostructured FeF_3.[94,95] FeF_3 has a theoretical specific capacity of 820 mAh/g and a theoretical specific energy of 1,783 mWh/g. These values are several times higher than those of typical lithium battery cathode materials. The cathode can be paired with traditional Li-ion anodes as well, but only achieves limited cycle life (less than 50 cycles). Materials were cycled in cells that gave 550 mAh/g (cathode) and over 400 Wh/kg (cell level). Preliminary safety tests of FeF_3 are encouraging. The thermal stability of FeF_3 has also been studied.[96] DSC was run on charged and discharged FeF_3 cathodes, with and without an electrolyte. The DSC results indicated that FeF_3 was stable in the electrolyte after lithiation and delithiation. The only exotherms observed were attributed to electrolyte decomposition. Thus, proof-of-principle has been established showing a cathode can deliver very high energy without adding to the thermal instability of a cell. This type of work should be expanded in future DOE programs.

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[94] Cordova, S.; Johnson, Z.; Pereira, N.; Badway, F.; Amatucci, G. G.; Abraham, K.M. (2008). "A Very High Specific Energy Rechargeable Lithium Battery Chemistry." *43rd Power Sources Conference Proceedings*, July 7–10, 2008, p. 569.

[95] Amatucci, G. G. (2010). "Metal Fluoride Conversion Nanocomposites: An Alternative Road for Lithium-Based Energy Storage." *Li Mobile Power*, Boston, MA, November 4–5, 2010.

[96] Zhou, M.; Zhao, L.; Doi, T.; Okada, S.; Yamaki, J.-I. (2010). "Thermal stability of FeF_3 as Positive Electrode for Lithium Ion Batteries." Abstract 3A06, *51st Battery Symposium in Japan Proceedings*, November 9–11, 2010, Nagoya, Japan.

Significant research has been directed at investigating different coatings for the various cathode particles with the goal of reducing oxidative surface reactions.[97] It was observed that "when the surface of cathode materials, including $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, and $LiMnO_2$ are coated with oxides, such as MgO, Al_2O_3, SiO_2, TiO_2, ZnO, SnO_2, ZrO_2, $Li_2O \cdot 2B_2O_3$-glass, and other materials, the coatings prevent the direct contact with the electrolyte solution, suppress phase transition, improve the structural stability, and decrease the disorder of cations in crystal sites."

Another proposed advantage of including these oxides is that they can act as scavengers for hydrogen fluoride (which results from reactions of the $LiPF_6$ and trace water in the electrolyte and can cause corrosive attack of the cathode particles).[98] The advantages of these coatings depend on several properties such surface coverage, coating thickness, Li-ion diffusivity, and long-term mechanical stability after cycling. All of these properties affect the performance of the cell but also affect the thermal abuse response. In order to improve the thermal abuse response of a cell, these coatings must be stable and maintain their protective properties at high temperatures where the kinetics of the cathode/electrolyte reaction greatly increase the exothermic output and where the structural stability of many cathode materials begins to degrade.

Cathode coatings are believed to delay or mitigate these reactions that lead to thermal runaway.[99] DSC results have shown significant heat reduction with application of some of these coatings, indicating that, when the surface reactions are minimized by the coating, the oxygen generation inside the powders can be reduced. Some of these coatings can also possibly mitigate the cell response during overcharge, e.g., $AlPO_4$-coated $LiCoO_2$[100] and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$.[101] Recent work has investigated coatings for the more recently used NMC "333" [$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$] cathode. Coatings such as ZrO_2,[102] ZrF_x,[103] and AlF_3[98] have shown improved cycling performance and lower thermal reactivity. For example, ARC tests were performed at SNL on several 18650 cells using AlF_3-coated NMC cathodes provided by Argonne National Laboratory.[104] Figure 34 shows the ARC thermal response profiles for uncoated and AlF_3-coated cathodes in 18650 cells. All of the coated electrodes showed reduced heating rates and had about 20°C higher thermal runaway onset temperatures (~260°C). Variations in the peak heating rates are believed to result from variations in coating thickness and coverage on the cathode particles at these temperatures.

[97] Li, C.; Zhang, H.P.; Fu, L.J.; Liu, H.; Wu, Y.P.; Rahm, E.; Holze, R.; Wu., H.Q. (2006). *Electrochimica Acta* 51 3872–3883.

[98] Chen, Z.; Qin, Y.; Amine, K.; Sun, Y.-K. (2007). *J. Electrochem. Soc.*, 154 _3, A168-A172.

[99] Cho, J.; Lee, J-G; Kim, B.; Park, B. (2003). *Chem. Mater.* 15, 3190–3193.

[100] Cho, J. (2004). *Journal of Power Sources* 126, 186–189 (2004).

[101] Cho, J.; Kim, H.; Park, B. (2004). *J. Electrochem. Soc.*, 151, 10, A1707–A1711.

[102] Li, J.; Zhang, Q.; Liu, C.; He. X. (2009). *Ionics* 15, 493–496.

[103] Yun, S.H.; Park, K-S.; Park, Y.J. (2010). *Journal of Power Sources* 195, 6108–6115.

[104] Orendorff, C. (2011). *Advanced Automotive Battery Conference Proceedings*, Pasadena, CA, January 25, 2011.
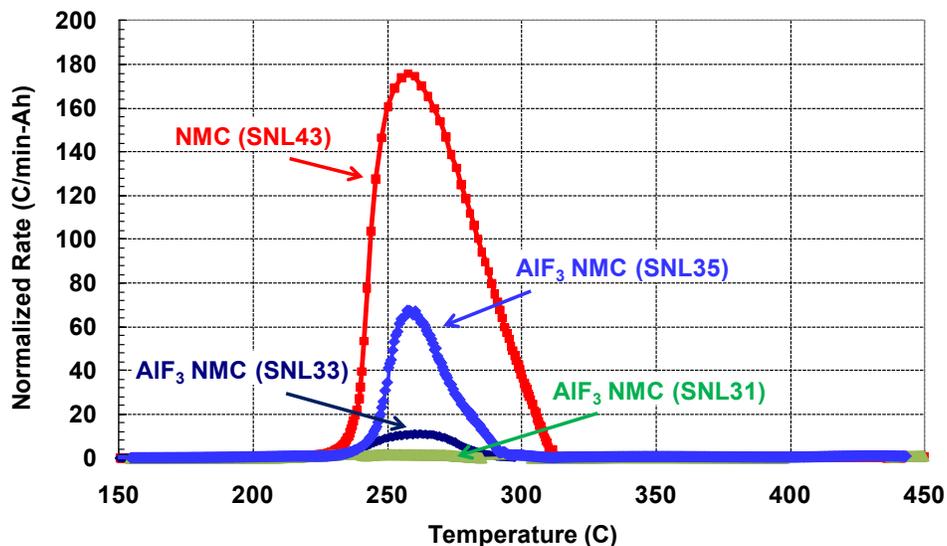
Figure 34. ARC profiles of 18650 cells with AlF$_3$-coated and uncoated NMC cathodes.

(Unpublished SNL data)

Direct measurements of the thermal properties of the coated cathode materials also confirm and clarify the role of the cathode in the full cell thermal response. Figure 35 shows DSC measurements on coated and uncoated cathode materials; it can be seen that the coating delayed the onset of thermal decomposition by at least 20°C as seen in the ARC measurements of the full cell.[105]

Figure 36 shows ARC measurements of the individual 18650 electrodes compared to one of the most passivated full cells using the AlF$_3$-coated NMC electrodes. The contributions of the anode and cathode to the full cell response can be clearly seen where initial reactions arise at the anode followed by the higher-temperature cathode reactions. The coated cathode thermal response has now been reduced to a level comparable to that of the anode material.

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[105] Data from Argonne National Laboratory obtained as part of the DOE ABR Program.
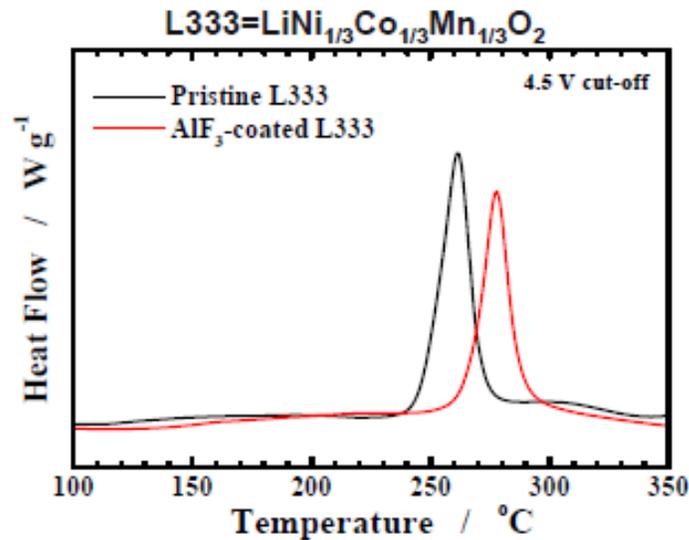
Figure 35. DSC measurements of AlF$_3$-coated and uncoated NMC cathodes.[105]
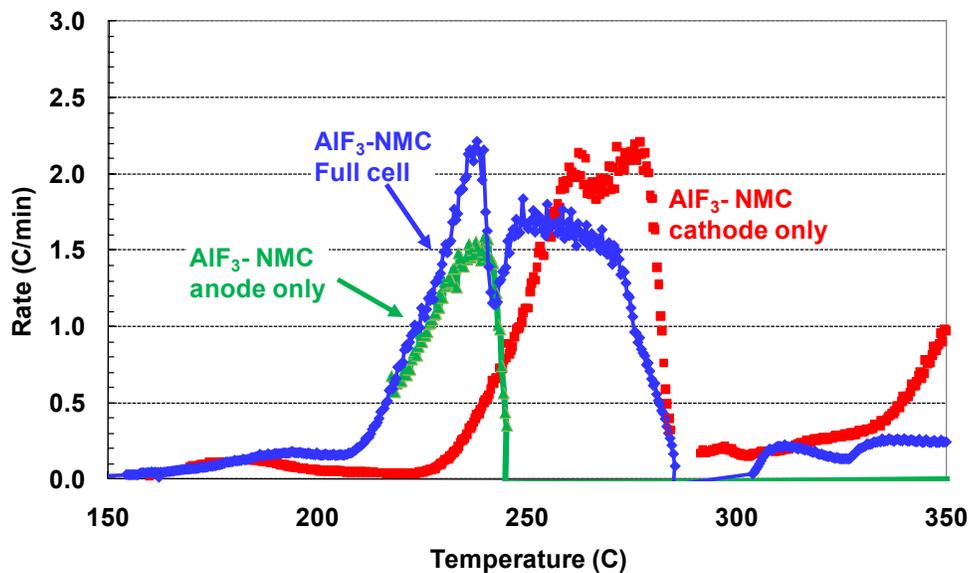
Figure 36. ARC measurements of full cell and individual 18650 electrodes with AlF$_3$-coated NMC cathodes.

(Unpublished SNL data)

Cathode coatings show good potential to improve cell abuse tolerance and are considered by Mike Thackeray as the highest priority in cathode safety topics.[106] However, the mechanism-of-action as well as durability issues have not been solved.[107] The potential of cathode surface modification techniques is very promising and should be included in the funding priorities of future DOE safety and abuse tolerance programs.

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[106] Private communication, Mike Thackeray, January 10, 2011.
[107] Private communication, Ratnakumar Bugga, January 10, 2011.

8.3 Anodes

The use of alternate anode materials may also affect cell safety. Materials that operate at higher voltage with respect to lithium potential include lithium alloys and various intercalation materials of which lithium titanate ($Li_4Ti_5O_{12}$, or LTO) is one example[108] and Li-metal alloys are another.[109] The benefits of these anodes are improved thermal stability and the potential for competitive performance in high-rate cell designs.[110]

8.3.1 LTO Anodes

$Li_4Ti_5O_{12}$ anode has been proposed as a "safe alternative" to graphite electrodes. Manev[111] outlined the advantages of using $Li_4Ti_5O_{12}$ anodes:

- No lithium plating.

- Lower self-heating with respect to graphite.

- Heat generation at elevated temperature is less than graphite.

- $Li_4Ti_5O_{12}$ can absorb O_2 from the cathode, thus increasing the stability of the cell.

- Calendar life is estimated to be 20+ years.

However, from Manev's Knowledge Foundation presentation in November 2010, we learned that the cell-level specific energy is 75 Wh/kg. $LiFePO_4/Li_4Ti_5O_{12}$ cells have even lower specific energy—only 50–60 Wh/kg, as estimated by Hydro Quebec.[112] This energy level is only slightly more than improved NiMH, a proven technology for vehicle applications. NiMH started at 45 Wh/kg and is now projected to be 80 Wh/kg within five years.[113] The author of this roadmap therefore concludes that $Li_4Ti_5O_{12}$-based cells will have insufficient energy to have a substantial presence in EVs and HEVs. The roadmap does not recommend that additional resources should be spent developing this electrochemical couple for traction applications.

8.3.2 Lithium Alloy Anodes

It is generally recognized that, while they deliver high capacity, Li-metal anodes paired with Li-ion cathodes will not have sufficient safety for EV and HEV traction applications. Therefore, lithium alloys are gaining commercial and academic interest because of the high-energy content.[91] Many lithium alloys are being developed that produce Li-ion cells with much higher energy than carbon-based anodes.

Silicon is an attractive anode material for Li-ion batteries because it has a low discharge potential and the highest known theoretical charge capacity (4,200 mAh/g).[114] Although this is more than

[108] Ohzuku, T.; Ueda, A.; Yamamoto, N. (1995). *J. Electrochem. Soc*. 142 1431.

[109] Todd, A. D. W.; Mar, R. E.; Dahn, J. R. (2007). *J. Electrochem. Soc.* 154 A597.

[110] Christensen, J.; Srinivasan, V.; Newman, J. (2006). *J. Electrochem. Soc*. 153 A560.

[111] Manev, V. (2010). "Large Format $Li_4Ti_5O_{12}$ Li-ion Batteries – Performance and Applications." *Li Mobile Power,* Boston, MA, Nov. 4–5, 2010.

[112] Zaghib, K. (2011). "Olivine-Polymer Ionic Liquid-Lithium for High Energy Batteries for Green Transportation." *Pacific Power Source Symposium 2011*, Jan. 10–14, 2011. Waikoloa, HI.

[113] Fetcenko, M. (2011). "NiMH Advanced Materials for Consumer, Vehicle and Stationary Applications." *Pacific Power Source Symposium 2011*, Jan. 10–14, 2011. Waikoloa, HI.

[114] Boukamp, B. A.; Lesh, G. C.; Huggins, R. A. (1981). "All-solid lithium electrodes with mixed-conductor matrix." *J. Electrochem. Soc*. 128, 725–729.

ten times higher than existing graphite anodes and much larger than various nitride and oxide materials, macro-scale silicon-based anodes have limited applications due to silicon's large volume changes (400%) upon insertion and extraction of lithium, which results in pulverization and rapid capacity fading.

Recently, it has been demonstrated that anodes based on silicon nanowires circumvent these issues as they can accommodate large strain without pulverization, provide good electronic contact and conduction, and display short lithium insertion distances.[115] However, silicon nanowire-only anodes possess the following potential drawbacks:

- Reduced Electrical Conductivity: Crystalline silicon nanowires are less conductive than carbonaceous materials due to their semiconducting natural properties. Silicon nanowires become amorphous with lithium insertion and stay in an amorphous state after the first cycle.

- Structural Changes: The electrical conductivity of the silicon nanowires is further reduced after lithiation due to dramatic structural changes. The increased resistivity will also generate Joule heat, leading to potential safety problems. It will also reduce battery capacity at a rapid discharge/charge rate, which is required for high-power applications.

- Less Structure Integrity: The structural change from pristine crystalline silicon nanowires to porous amorphous nanostructures could degrade its mechanical robustness, yielding potential nanowire fracture and reduced battery capacity.

- Less Area Capacity: Newly grown silicon nanowires have less density compared to conventional carbonaceous anodes.

Groups are working to overcome these and other technical problems, and a recent report from Stanford University shows an improved cycle life for an anode that has a three-fold higher capacity than graphite.[116] However, there is no published work that we could find on the safety of batteries made with silicon or other alloys. Because these batteries could be proposed for use in traction applications, the DOE should have a program to investigate the safety issues with batteries made with high-capacity Li-alloy anodes.

8.3.3 Additives to Stabilize Anode Surface

The SEI is a protective film that develops on the anode during the initial formation step of cell processing. This film develops from interaction of the electrolyte with the anode surface during initial lithiation and occurs at a potential higher than the intercalation potential for the solvated lithium ions. This prevents the destructive exfoliation of the graphite that can occur if intercalated solvent molecules are reduced within the graphite planes. The composition of this SEI layer is quite complex and has been studied for many years.[117,118,119,120, 121] The film has been

[115] Chan, C. K.; Peng, H.; Liu, G.; Mcilwrath, K.; Zhang, X. F.; Huggins, R. A.; Cui, Y. (2008). "High performance lithium battery anodes using silicon nanowires." *Nature Nanotechnology 3*, 31–35.

[116] Cui, Y. (2010). "3X Capacity from Silicon-Nanowire-based Li-ion Batteries." Presented at *Lithium Mobile Power 2010*, Boston MA, November 3, 2010.

[117] Peled, E. (1979). *J. Electrochem. Soc.*, 126 12 2047-2051.

[118] Aurbach, D.; Markovsky, B.; Shechter, A.; Ein-E1i, Y.; Cohen, H. (1996). *J. Electrochem. Soc.*, 143 12 3809–3820.

[119] Peled, E.; Golodnitsky, 0.; Ardel, G. (1997). *J. Electrochem. Soc.*, Vol. 144, 8.

seen to be multi-layered and non-uniform and consists of several inorganic and organic decomposition products. The composition of these products depends strongly on the composition of the electrolyte solvents and salt. Ideally, these films should be relatively thin, have low-porosity to prevent electrolyte contact with the graphite, and have high Li-ion conductivity. They should also be mechanically flexible to accommodate expansion of the anode layer during intercalation, free of micro cracks, and stable at elevated temperatures.[122]

The formation of this layer results in irreversible capacity loss due to the loss of lithium from the cathode material. This must be an acceptable loss because this film prevents further reaction between the electrolyte and the lithiated anode, which otherwise would continue to consume the lithium ions. The SEI forms quickly but continues to develop with time. The layer thickness has been shown both experimentally and theoretically to increase with the square root of time.[122, 123] The increasing thickness of the SEI layer can result in increased impedance at the anode and reduced rate capability, but it also increases the thermal stability of the protective layer, as shown in Figure 29.

Several electrolyte additives have been proposed and tested to improve the stability of the SEI layer, thus reducing irreversible losses, increase lifetime, and improve thermal stability. Two of the most common SEI film-forming additives being used in cells today are vinylene carbonate (VC) and vinyl ethylene carbonate (VEC). Extensive work has gone into characterizing and modeling the effects of these additives. [124, 125, 126, 127, 128]

Work by Aurbach et al.[129] showed that VC polymerizes on the lithiated graphite surfaces, forming poly alkyl Li-carbonate species that suppress both solvent and salt anion reduction. Shima et al.[130] have shown increased thermal stability of electrolytes with this additive while Ota et al.[121] showed enhanced thermal stability of the VC-derived SEI coating on the exposed anode surfaces. It has also been shown that adding a few weight-percent of VEC to PC-based electrolytes significantly improves their performance.[125] Calculations in this work showed VEC underwent direct two-electron reduction more readily than EC and PC and thus should react more readily to form the passivating Li_2CO_3. Lucht et al.[126] have investigated electrolyte stabilizing additives that reduce species known to attack the SEI layer, namely dimethyl acetamide and N-methyl-2-pyrrolidone (NMP). These Lewis-based stabilizing agents have been

[120] Aurbach, D.; Markovsky, B.; Levi, M.D.; Levi, E.; Schechter, A.; Moshkovich, M.; Cohen, Y. (1999). *J. Power Sources* 81–82 95–111.

[121] Aurbach, D.(2000). *J. Power Sources* 89 _206–218.

[122] Ploehn, H. J.; Ramadass, P.; White, R. E. (2004). *J. Electrochem. Soc.*, 151, A456-A462.

[123] Yoshida, T.; Takahashi, M.; Morikawa, S.; Ihara, C.; Katsukawa, H.; Shiratsuchi, T.; Yamaki, J-I. (2006). *J. Electrochem. Soc.*, 153 _3_ A576-A582.

[124] Ota, H.; Sakata, Y.; Inoue, A.; Yamaguchi, S. (2004). *J. Electrochem. Soc.*, 151 10 A1659-A1669.

[125] Vollmer, J. M.; Curtiss, L. A.; Vissers, D. R.; Amine, K. (2004). *J. Electrochem. Soc.* 151 1 A178-A183.

[126] M. C. Smart, B. L. Lucht and B. V. Ratnakumar. *J. Electrochem. Soc.*, 155 _8_ A557-A568 (2008)

[127] W. Li, A. Xiao, B. L. Lucht, M. C. Smart, B. V. Ratnakumar. *J. Electrochem. Soc.*, 155 _9_ A648-A657 (2008)

[128] C. Jehoulet, P. Biensan, J. M. Bodet, M. Broussely, C. Moteau, and C. Tessier-Lescourret. "Batteries for Portable Applications and Electric Vehicles," A. R. Landgrebe and C. F. Holmes, eds, pp. 97–18, p. 974, *The Electrochemical Society Proceedings Series*, Pennington, NJ (1997).

[129] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider. *Electrochimica Acta* 47 1423–1439 (2002)

[130] E.-G. Shima, T.-H. Nama, J.-G. Kima, H.-S. Kim, S.-I. Moon. *J. Power Sources* 172 901–907 (2007).

found to reversibly bind with phosphorus pentafluoride (PF_5), preventing $LiPF_6$ and carbonate solvents from decomposition at high temperatures.

Although these additives have been investigated as to their ability to improve SEI stability for improved performance and for moderately elevated temperature stability, little work has been performed on their effect on high temperature thermal runaway response in full cells. Although SNL and Argonne National Laboratory have produced and measured a number of cells with VC and VEC additives, a systematic study with a sufficient number of cells to determine a definitive response has not been performed. Continued work on these promising materials is justified because they can effectively and economically enable the use of otherwise unstable and reactive materials being designed for ever higher potentials and energy.

8.4 Separators
8.4.1 Ceramic Composite Separators
The concern about internal short circuits has resulted in a search for new separators, as well as modifications of existing electrode materials. Improvements in safety response have been achieved by introducing ceramic particles as either coatings or inclusions in the separator to prevent electrical shorting even at temperatures well above the melt temperature. There are two basic approaches:

1. Composite separator (polymer and ceramic particles dispersed in the bulk of the polymer)

2. Coating of polymer/ceramic composite on the separator or on one (or both) of the electrodes.

Use of ceramic coatings seems to be widespread. The heat resistant layer plays a key role in managing safety by preventing contact between the anode layer and the cathode layer at the cell level.

Information on which company is using these approaches is hard to verify because of the proprietary nature of development efforts. Information from personal contacts seems to highlight the importance of this approach. For example, Dr. Jeon Oh said that, "SK Energy uses Al_2O_3-coated separators (both sides) because it allows the cells to pass blunt rod simulated internal short circuit test."[131] *[It is important to note that SK Energy is the manufacturer of 25-Ah and 50-Ah cells designed for EV and HEV applications. Dr. Oh claims that their customers require ceramic-coated separators for safety.]*

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[131] Private communication, Jeon Oh, November 10, 2010.

Companies that manufacture cells containing heat-resistant separators are believed to be:

- **Panasonic** – We received information that Panasonic has announced a coating on one side of a separator or on a cathode before winding cell. We believe that they are using Al_2O_3.

- **LG Chem** – LG Chem is using a coated separator (likely both sides). The guess is that they are using Al_2O_3.

Separator manufacturers who are developing heat-resistant separators are:

- **Entek** – Entek has a DOE program to produce ceramic-filled ultra-high molecular-weight poly(ethylene) porous separator membranes. The studies include Al_2O_3 and SiO_2.[132] [Notes: Rick Pekala thinks that Al_2O_3 is too expensive. Most manufacturers use fumed Al_2O_3, which at \$20/kg is too expensive for large-scale battery use. SiO_2 has potential weakness due to hydrogen fluoride attack. Additionally, it carries a lot of water, and the separator needs to have extra drying step to avoid introducing water into the battery. Entek is making 12-µm ceramic-filled separators.]

- **Asahi** – Indications are that Asahi is incorporating ceramic-filler in the bulk polyolefin shutdown separator. This information is sketchy, and there is no information on the type of ceramic. Asahi appears to be the only Japanese manufacturer working on ceramics in the polymer bulk. Other companies are coating an inorganic-filled polymer on the surface of the separator or cathode.

- **Sony** – Sony has described the development of a two-sided, coated ceramic separator that can reduce the risk of failing a high-current internal short circuit test.[133]

- **Degussa** – Degussa has a polyethylene terephthalate-based composite separator marketed as Separion. Whether this is a ceramic filler is not certain, but likely Al_2O_3 or SiO_2, or some mixture of these (although their patents claim eight different ceramic materials). A study was done at ZSW, a German R&D laboratory, on 8-Ah cells with $LiMn_2O_4$ cathodes that contained a normal polyolefin shutdown separator and the Degussa new ceramic separator without shutdown properties.[134] They demonstrated that the thermal runaway produced by overcharge could be avoided with the more stable (ceramic) separator.

- **Celgard** – John Zhang[135] said that, "Ceramic-coated shutdown separators are being developed by Celgard, but the experienced manufacturers are staying with traditional separators."

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[132] R. Waterhouse, R. Pekala, Y. Patil, S. Peddini, J. Emanuel, J. Frenzel, D. Lee, D. Spitz, G. Fraser-Bell. "Development of Separators with Inorganic Fillers for Advanced Lithium Ion Batteries." Presented at *Lithium Mobile Power 2010,* Boston MA, November 3, 2010.

[133] A. Kajita et al. "A Novel Separator with Ceramic Layers for Li-ion Batteries." Abstract 1B26, *51st Battery Symposium*, Nov. 9–11, 2010, Nagoya, Japan.

[134] H. Döring, B. Schmid, H. Brazel. *Overcharge at 3 C rate and 12 V limit for fresh and cycled Li-Cells with Polyolefin and Separion Separators*. Center for Solar Energy and Hydrogen Research, Baden-Württemberg, Germany. Report No. RP-ZSW-05_2005, May 2005.

[135] Private communication, John Zhang, January 10, 2011.

There are several fundamental questions that need to answered, such as will a ceramic-coated "shutdown separator" actually shut down? Will ceramic coating prevent shrinkage and shutdown? Rick Pekala[136] says that, with the proper processing, the shutdown can still be observed with ceramic-coated polyolefin shutdown separators. It seems that the microstructure at the interface and the degree of entanglement between the two polymer structures plays an important role. Additional investments from DOE would be valuable in understanding the fundamental material interactions and benefits of ceramic coatings in lithium-ion rechargeable batteries.

8.4.2 Electroactive Separators for Overcharge Protection

Much research has been focused in recent years on development of internal and self-actuating overcharge protection mechanisms for Li-ion batteries. Electroactive polymers have the ability to switch rapidly between conductive and insulating states and sustain high-current densities. Electroactive polymers can provide overcharge protection for rechargeable lithium batteries when impregnated into a porous membrane separator. A small amount of the polymer can provide self-actuated, reversible protection for cells for a variety of chemistries by providing an electrically conductive pathway for the excess electrical charge during overcharge.

As an electroactive material, the polymer should have an oxidation potential slightly lower than the terminating potential of the cathode and considerably lower than the decomposition potential of the electrolyte. Electroactive polymers are influenced by factors, such as the loading of the polymer, the morphology of the deposited polymer, the porosity of the composite, and the availability of doping anions from the electrolyte.

The most investigated electroactive polymers are thiophene-based polymers[137,138,139] and phenylamine-based polymers.[140,141] Solutions of these polymers are used to impregnate standard commercial separators and then dried. Bilayer separators have also been used where different electroactive polymers are used for contact with either cathode or anode (see Figure 37).[134] The layers work in parallel with the active electrodes so as not to introduce excess resistance, especially at low temperatures. This configuration allows significantly high current densities while maintaining low cell potential during the overcharge (Figure 38). This modified configuration may be implemented in larger battery cells, which have uncoated current collector areas that are designated for tabs. Improvements still need to be made in current density, stability against different electrode materials, and low-temperature performance.

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[136] Private communication, Rick Pekala, November 4, 2010.

[137] G. Chen, T. J. Richardson. *J. Electrochem. Soc.*, 157, 6, A735-A740 (2010).

[138] G. Chen, T. J. Richardson. *Electrochemical and Solid-State Letters*, 7, 2 A23–A26 (2004).

[139] S. L. Li, L. Xia, H. Y. Zhang, X. P. Ai, H. X. Yang, Y. L. Cao. *J. Power Sources* (2010), doi:10.1016/j.jpowsour.2010.09.111

[140] S.L. Li, X.P. Ai, H.X. Yang, Y.L. Cao. *J. Power Sources* 189 771–774 (2009).

[141] J.K. Feng, X.P. Ai, Y.L. Cao, H.X. Yang. *J. Power Sources* 161 545–549 (2006).

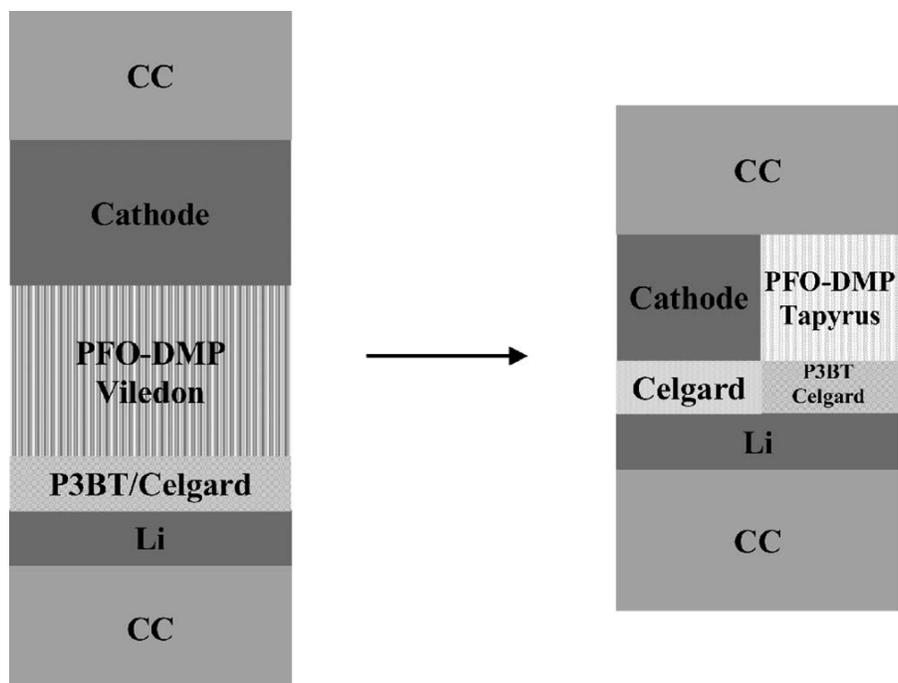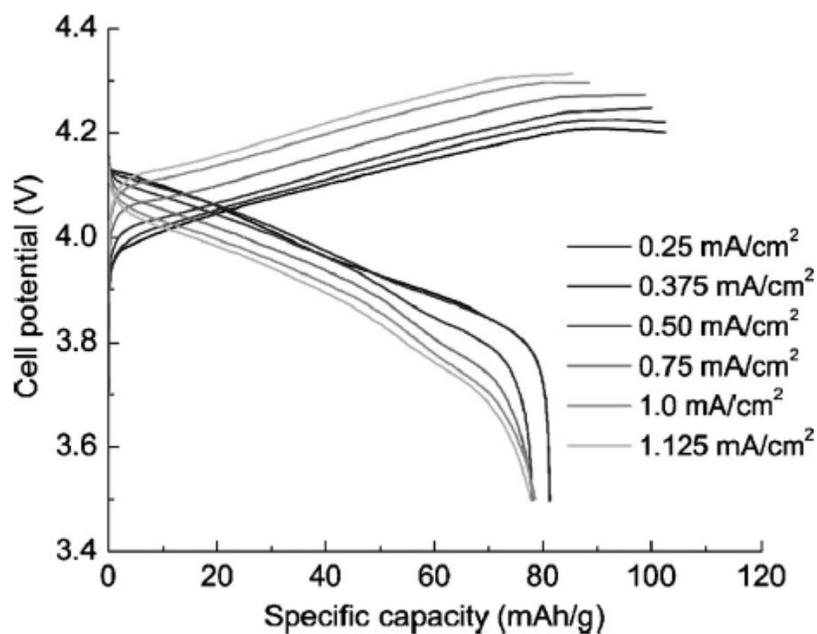**Figure 37. Schematic of alternative designs using electroactive separator for overcharge protection.**[139]

Figure 38. Rate performance of a protected Li$_{1.05}$Mn$_{1.95}$O$_4$–Li cell with the bilayer, parallel cell configuration.[139]

8.5 Electrolytes

As discussed earlier, flammability of the vented electrolyte is a significant unresolved safety issue for Li-ion batteries. The energy released by a burning electrolyte is several times larger than the energy stored in a battery. Accident scenarios involving burning electrolyte have some of the most serious consequences, resulting in cascading failure of other cells in the battery pack and involvement of adjacent materials and structures.

8.5.1 Non-flammable Electrolytes

Two mechanisms have been suggested to explain the flame retardation:

- A physical char-forming process, which builds up an isolating layer between the condensed and gas phases to retard the combustion process

- A chemical radical-scavenging process, which terminates the radical chain reactions responsible for the combustion reaction in the gas phase.

Most flame-retarding additives used in liquid electrolytes are based on organic phosphorus compounds and their halogenated derivatives, and the radical-scavenging mechanism appears to explain experimental results.

The four main categories of flame retardant additives that have been investigated are phosphates, phosphazenes, phosphides, and ethers. The additives that have been evaluated in the literature generally fall within one of two main categories, phosphorous-containing compounds, and halogen-containing compounds. In the vapor phase, the common mechanism is that phosphorous or fluorine radicals, which are provided by the decomposition of the additive, react with hydrogen radicals that are part of the flame's chain-reaction mechanism. Numerous flame-retardant additives have been tested in most of the standard Li-ion electrolytes with mixed results.[142,143,144,145] Often, the amount of additive required to achieve non-flammability significantly reduces cell performance. Furthermore, some of the additives are not stable with the active electrode materials, especially against reduction at the anode. Non-flammable electrolyte additives, such as triphenyl phosphate and dimethyl methyl phosphonate, participate in SEI formation and concentration may decrease as cells age.[146] Use of flame-retardant additives then requires additional additives to stabilize the anode. The long-term effect of these additives on cell lifetime and performance is not known.

One of the major difficulties in evaluating the effectiveness of a flame retardant is a meaningful test that is relevant to the case of a venting Li-ion cell. Most tests are based on open flame or burning wick-type configurations. These tests are useful for evaluating the relative performance of different additives, but do not adequately recreate the conditions of a vented cell that produces a fine mist of aerosolized electrolyte and vapors. Flammability needs to be determined with full

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[142] K. A. Smith, M. C. Smart, G. K. S. Prakash, B. V. Ratnakumar. *ECS Transactions*, 16 (35) 33–41 (2009).

[143] K. Xu, M. S. Ding, S. Zhang, J. L. Allen, T. R. Jow. *J. Electrochem. Soc.*, 149 (5) A622–A626 (2002).

[144] X. Wang, C. Yamada, H. Naito, G. Segami, K. Kibe. *J. Electrochem. Soc.*, 153 (1) A135–A139 (2006).

[145] Y. Shigematsu, M. U., and J. Yamaki. *J. Electrochem. Soc.*, 156 (3) A176–A180 (2009).

[146] R. Bugga, "Advanced Lithium-Ion Batteries For NASA Lunar Missions." *Pacific Power Source Symposium 2011,* Jan. 10-14, 2011. Waikoloa, HI.

cells under controlled thermal conditions with multiple ignition sources to test for different fuel/air ratios.[79]

8.5.2 Ionic Liquids

Ionic liquids (ILs) are being investigated because they have the potential to improve abuse response, particularly with respect to the flammability of an electrolyte.[147] ILs are non-volatile, non-flammable, highly conductive, environmentally compatible, and can safely operate in a wide temperature range. This unique combination of favorable properties makes ILs very appealing materials as stable and safe electrolytes in lithium batteries.

Batteries filled with such a type of electrolytes do not contain any volatile components; therefore, they are not flammable. Room temperature ILs are characterized by negligible vapor pressure, which makes them inflammable. In addition, they show a broad electrochemical stability window, generally >4 V, which is necessary for the application in Li-ion batteries with high-energy cathodes.

ILs are formed by the combination of a weakly-interacting large cation, such as the imidazole type, and a flexible anion, such as N,N-bis(trifluoromethanesulfonyl) imide. A recent review article describes substantial progress in the application of ILs to Li-ion rechargeable batteries.[148] The review article includes references to over 70 combinations of ILs and standard Li-ion electrolyte and electrode combinations. This area of research is very active, as demonstrated by the fact that 78 presentations were on the program at the 218th ECS Meeting in Las Vegas, Nevada, in October 2010.

The stability range of the Li^+ conducting electrolyte of above 4 V is necessary in practical applications to Li-ion batteries. The electrochemical stability of liquid aprotic quaternary ammonium salts, determined usually at glassy carbon or platinum electrodes, is within a wide range of 4–6 V. Popular imidazolium salts show stability of ~4 V, while piperidinium and pyrrolidinium salts, especially based on imide anions, show stability of ~6 V. Symmetrical tetraalkylammonium cations (e.g., tetraethylammonium tetrafluoroborate) have been used for a long time as supporting electrolytes in organic solvents due to their good stability.

Thermal stability of different room temperature ILs may be estimated from DSC experiments. Classical solutions in molecular solvents (cyclic carbonates) show a decrease in weight due to solvent evaporation at increased temperatures. For example, the solution of $LiBF_4$ in gamma-butyrolactone (GBL) + EC shows a decrease in weight at around 90°C to 200°C. The weight loss reached 88% at 200°C with the decomposition of the residual of 12% between 200°C and 250°C (decomposition of the salt).[149]

The substantive issues that must be resolved with ILs are:

- High viscosity

- Lack of anode passivation

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[147] B. Scrosati , J. Garche. *Journal of Power Sources* 195 (2010) 2419–2430.

[148] A. Lewandowski, A. Swiderska-Mocek. *Journal of Power Sources* 194 (2009) 601–609.

[149] H. Nakagawa, S. Izuchi, K. Kuwana, T. Nukuda, Y. Aihara. *J. Electrochem. Soc*. 150 (2003) A695.

- Low ionic conductivity (leading to low current densities)

- Poor wettability of electrodes and separators.

The viscosity of ILs is much higher than that of water (H_2O = 0.89 cP at 25°C). Typically ionic conductivity is at the level of 30 – 50 cP, but in some cases it is much higher, even several hundred centipoise.

The approach being developed at Hydro Quebec is to use aprotic polymer electrolytes, such as polyether, that are compatible with ILs.[150] To overcome the viscosity problem, they use vacuum impregnation at 60°C to achieve good wetting and good capacity.

The payoff of developing an IL that would give good performance in a Li-ion rechargeable battery is huge. It could largely eliminate the flammable electrolyte issue.

8.5.3 Overcharge Protection Additives

Overcharge protection can be achieved by mechanical, electrical, or electrochemical means.[151] One method that has been actively pursued is through the use of additives to the electrolyte that are activated at the high-overcharge potentials.[152] Overcharge protection additives can generally be classified as redox shuttle additives or shutdown additives. The former protects the cell from overcharge reversibly, while the latter terminates cell operation permanently. Shutdown additives are polymerizable compounds that can be electrochemically polymerized at an overcharged cathode. The polymerized coating can reduce the charging current and thus protect the batteries from the hazardous overcharge condition.

For most commercial Li-ion batteries, the upper cut-off potential can be as high as 4.2 V. The oxidative decomposition of the electrolyte can occur at about 5 V, which is often seen as a voltage plateau during overcharge. To avoid the decomposition of electrolyte, the polymerization reaction should take place in the region of 4.2 V – 5.0 V. Biphenyl, cyclohexyl benzene, and other substituted aromatic compounds constitute the polymerizable class of shutdown additives.[153,154] Although these compounds may be useful in consumer-level batteries with few cells, they may not provide protection in vehicle-level batteries, which can have more than a hundred cells in series. Because a single high-impedance cell would see a significant over-potential from the other cells or the charging system, breakdown of the polymerized film could readily occur.

Redox shuttles involve electrochemical oxidation of a compound at the positive electrode, resulting in a radial cation, which diffuses to the negative electrode and gets reduced. The shuttle molecules then diffuse back to the positive electrode to restart the process. Thus, redox shuttles shunt the excess charge during overcharge and act as a controlled internal "short." This can indefinitely limit the cathode potential near the oxidation potential of the shuttle additive. During

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[150] K. Zaghib. "Olivine-Polymer Ionic Liquid-Lithium For High Energy Batteries For Green Transportation." *Pacific Power Source Symposium,* Jan. 10-14, 2011. Waikoloa, HI.

[151] P.G. Balakrishnan, R. Ramesh, T. P. Kumar. *Journal of Power Sources* 155 401–414 (2006)

[152] S. S. Zhang. *Journal of Power Sources* 162 1379–1394 (2006)

[153] M.Q. Xu, L.D. Xing, W.S. Li, X.X. Zuo, D. Shu, G.L. Li. *Journal of Power Sources* 184 427–431(2008)

[154] K. Shima, K. Shizuka, M. Ueb, H. Ota, T. Hatozaki, J.-I. Yamaki. *Journal of Power Sources* 161 1264–1274 (2006)

normal operation, the oxidation potential of the shuttle additives is not reached and the molecules remain inert.

The maximum current that the shuttle additive can carry depends on several factors, including the concentration of the shuttle molecules in the electrolyte, the diffusion constant of the shuttle molecules, and the number of charges carried by the shuttle molecules.[149]

There have been hundreds of compounds investigated for this purpose[155,156] and are often aimed either at high-voltage cathodes[157,158] (e.g., $LiCoO_2$, Mn-spinel, $LiNi_{1-x-y}Mn_xCo_yO_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) or lower voltage materials (e.g., $LiFePO_4$).[153,159] The limitations on the use of shuttle additives often are due to limited charge rate, stability at high potentials, reduction of cell performance, and heat generation during shuttle activation.[156] One promising shuttle is based on electrolyte solutions containing the StabiLife electrolyte salt $Li_2B_{12}F_{12}$.[155] The dodecaborane molecular structure is shown in Figure 39. This shuttle has been shown to be effective at 1C charging rates for the high-voltage class of cathodes (Figure 40). Effective overcharge shuttles may require tailor-made compositions for each type of cell chemistry.

The roadmap recommends that enough work is being done in industry and in academic laboratories in this area. Moreover, because the chemistry may not have broad applicability to all types of cathodes and anodes, a "generic overcharge shuttle" may not be achievable.

[155] Z. Chen, Q. Wang, and K. Amine. *J. Electrochem. Soc.*, 153, 12, A2215-A2219 (2006)

[156] C. Buhrmester, J. Chen Lee, M. Junwei, J. Richard, L. Wang, J. R. Dahn. *J. Electrochem. Soc.,* 152 _12_ A2390–A2399 (2005)

[157] L. M. Moshurchak, W. M. Lamanna, M. Bulinski, R. L. Wang, R. R. Garsuch, J. Jiang, D. Magnuson, M. Triemert, J. R. Dahn. *J. Electrochem. Soc.*, 156, 4, A309–A312 _(2009)

[158] G. GirishKumar, W. H. Bailey III, B. K. Peterson, W. J. Casteel, Jr. *J. Electrochem. Soc.*, 158, 2, A146–A153 (2011)

[159] J. R. Dahn, Junwei Jiang L. M. Moshurchak, M. D. Fleischauer, C. Buhrmester, L. J. Krausec., *J. Electrochem. Soc.*, 152 6 A1283–A1289 (2005)
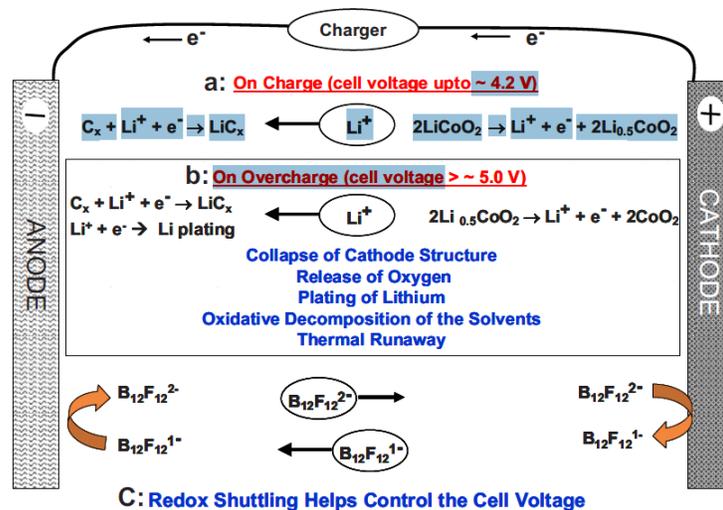
Figure 39. StabiLife Salt used as redox shuttle from Air Products[158]
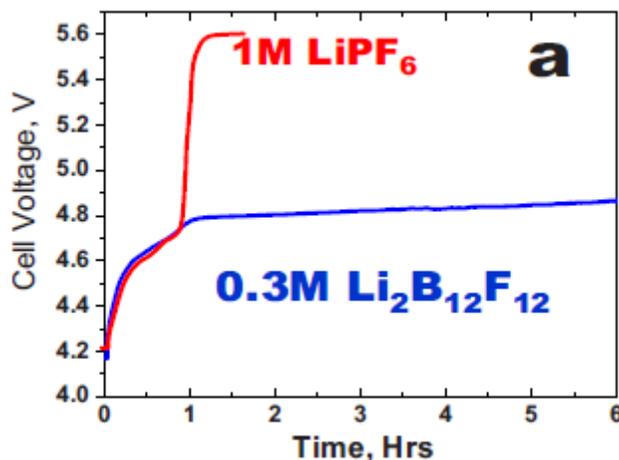
Figure 40. Effect of overcharge shuttle compared to normal cell during overcharge. The cell (MCMB anode and LiCoO2 cathode) was charged at 1C overcharge rate.158

8.6   Improved Diagnostic Tests

8.6.1   Internal Short Circuit

Internal short hazards have been looked into extensively in the past few years due to the inadvertent fires that occurred during transportation, as well as the recalls by major Li-ion cell manufacturing companies. Internal shorts arise from two sources:

- Those created by separator flaws or native contamination or foreign object debris introduced during manufacturing that manifest themselves during transportation or use.

Commercial 18650 Li-ion cells are manufactured in the millions every month. If the quality control is not stringent, there is a higher probability of getting internal cell shorts due to the presence of impurities such as metal particles and burrs. Even the best-quality manufacturers have had problems.

- Those created due to misuse of the batteries. The proposed origin is the creation of dendrites when the cells are subjected to voltages, currents, and temperatures beyond the manufacturer's recommendation (current and voltage anomalies can be caused by fast charge or poor cell balance in packs) or due to localized heating or large thermal gradients within a battery module. Another factor that could cause this is inadequate cell design that causes dry-out of the electrode in certain areas of the cell.

An internal short hazard is one of the most difficult to reproduce, yet it is the most important to solve to improve safety. No one test has gained acceptance by industry or test organizations.

- UL Blunt Nail Crush. This procedure calls for crushing the cell with a blunt nail until detection of a 100-mV open circuit voltage drop.
  - o PRO: Method does not require a lot of special sample preparation.
  - o CON: Short mechanism depends on how the blunt nail interacts with internal construction.
- NASA blunt nail method. This method has some similarities to the UL blunt nail crush test.
  - o Pass/fail depends on vibration tests after blunt nail crush.
- Battery Association of Japan Forced Internal Short-Circuit Test. This procedure requires disassembly of a charged cell, insertion of an L-shaped nickel metal particle, cell reassembly, and test.
  - o PRO: Can control location of internal short circuit
  - o CON: Safety concerns. Requires special equipment and cell preparation facilities. Difficult to perform.
- Saft – Internal Heater Wire. A heater wire inserted into cell. Application of current (external power supply) will melt the separator, and a short circuit ensues.
  - o PRO: Can control location of internal short circuit.
  - o CON: Heating too diffuse – behaves like internal thermal ramp test.
- SNL – Thermal trigger w/low temperature melting alloy. During winding of cells, low melting temperature (~65°C) alloy particles are incorporated.
  - o PRO: Can produce internal short circuit in 18650 cells.
  - o CON: Elevated temperature is required, and result depends on cell geometry (cylindrical versus prismatic).

It is clear that these tests can cause irreproducible results and are difficult to control. These challenges need to be overcome so that the test is tolerant of cell construction variables (i.e.,

spiral versus planar geometry). An additional problem is that results can be convoluted with other factors that influence thermal stability.

The core difficulty in simulating an internal short circuit is that there are different shorting paths within the cell that can cause different short circuit responses. Different current paths are demonstrated in Figure 41.
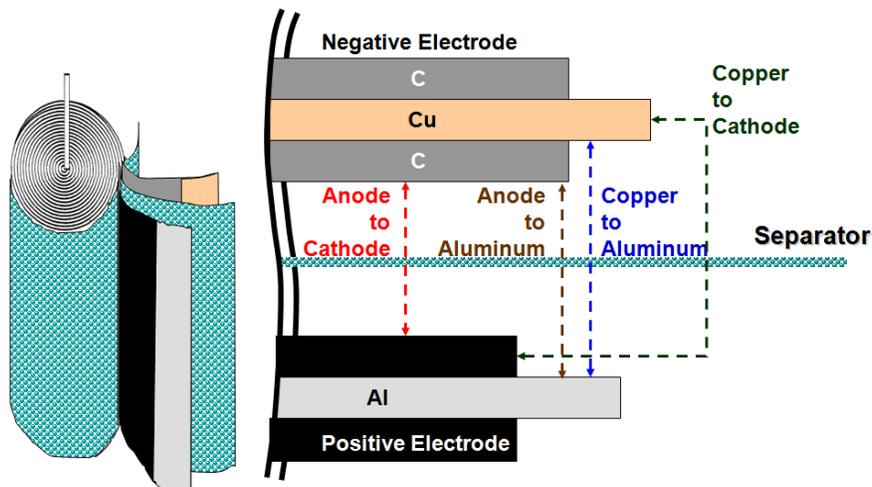
Figure 41. Sources of variability in internal short circuit test arise because there are four kinds of internal short circuit conditions.[85]

The four types of internal short circuit are:

1. Anode to cathode

2. Anode to aluminum

3. Copper to aluminum

4. Copper to cathode.

The current that flows through each path depends on the resistance of each element. Moreover, the elements in the current path are heated rapidly and the thermal stability of the two electrodes varies widely. Current understanding [83] of internal short circuit electrode reactivity comes from Saft (France) testing of propagation of each electrode. Thermal conductivity of the carbon anode is ~10 W/mK, but the thermal conductivity of the cathode is ~0.5 W/mK. Firing a laser at each of the two electrodes in an inert atmosphere glove box shows that the charged anode will burn rapidly and consume the entire electrode, but the charged cathode will not propagate the thermal runaway. Consequently, shorting to the cathode material will most likely not create a thermal runaway event from an internal short circuit failure. Thus, types 1 and 4 have minimal potential to cause thermal runaway, whereas types 2 and 3 will cause thermal runaway. This analysis and thermal reactivity data led to the application of inorganic barrier coatings on separators and anodes (unfortunately termed heat resistant layers [HRL] in the literature).

A second element of susceptibility of a cell to thermal runaway from an internal short circuit lies in the ability of a cell to dissipate heat. The first-order characteristic is surface-to-volume ratio (i.e., high-surface-to-volume ratio will dissipate heat the fastest). Therefore, cell size is an important factor. Cell models need to be incorporated into module and battery pack models to adequately capture the dynamics of heat dissipation. These models are being developed,[160] but the pace needs to increase.

The take-away message from this analysis is that our understanding of the internal short circuit event is superficial and the tests meant to simulate the event are not well developed. A systematic R&D program that elucidates the details of internal short circuits as well as heat dissipation would support a model of the internal short circuit event that would have substantial potential for safety improvement.

8.7 Modeling

Battery modeling is well developed, with academic and national laboratory groups very active in the area of investigation.[161] However, not much attention has been directed at modeling safety and abuse tolerance issues. Some of the earliest work developed a thermal model of an 18650 cylindrical cell.[162] Since then, thermal models have been used to analyze temperature gradients in cells and battery packs.[163] Recently, however, groups at NREL, SNL, TIAX, Battery Design LLC and universities have increased their efforts.

Modeling of internal short circuit events is being developed by Celgard,[157] TIAX,[7] and NREL.[164,165] However, the results do not sufficiently capture the complexity of the internal short circuit event. The location of the internal short circuit—not only between which layers within the cell as described above, but also the proximity to a tab or other heat-sink—shows important effects in the models being developed. Another interesting factor that needs to be captured in any model is the effect of cell size on the internal short circuit and abuse tolerance in general. Intuitively, small cells seem to be more forgiving and safer in most abusive situations (e.g., button cells versus laptop cells). But the tradeoffs are not so clear when different cell geometries are considered (i.e., different heat management strategies).

Validation of these internal short circuit models results poses significant challenges since experiments cannot readily control the location of an induced short circuit and often lead to results that are not adequately reproducible or that have a satisfactory conclusion. Recent efforts

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[160] S. Santhanagopalan, P. Ramadass, J. (Z.) Zhang. *Journal of Power Sour*ces 194 (2009) 550–557.

[161] R. Spotnitz. The Electrochemical Society Interface, Winter 2005, p. 39-42.

[162] T. D. Hatchard, D. D. MacNeil, A. Basu, J. R. Dahn. *Journal of The Electrochemical Society*, 148, A755-A761 (2001).

[163] A. Pesaran, A. Vlahinos, D. Bharathan, G.-H. Kim, and T. Duong. Presented at *21st Electric Vehicle Symposium,* Monaco, April 4–7, 2005.

[164] G. H. Kim, A. Pesaran, R. Spotnitz. "A Three Dimensional Thermal Abuse Model for Lithium Ion Cells." *J. Power Sources*, 170(2), pp. 476-489, 2007 and Gi-Heon Kim., "Li-ion Abuse Model Development," 2009 Energy Storage Annual Progress Report.

[165] S. Santhanagopalan, P. Ramadass, Z. Zhang, "Numerical Experiments on Internal Short Circuit," Presented at the *15th International Meeting on Lithium Batteries*, Montréal, Canada, June 2010.

by several national laboratories and the industry have tried to address these concerns,[166] but significantly more work needs to be done.

Modeling overcharge, electrolyte decomposition, gas evolution, and lithium deposition are all areas that need the development of better models, as well as validation of models that are currently used. This effort should be a priority in future DOE R&D programs.

The other area where models are finding utility is at the battery pack level. The primary need is for accurate, validated, easy-to-use thermal models. NREL is well established in developing battery thermal models. NREL researchers are applying these techniques to characterize battery pack response to abusive environments.[167] It is the opinion of the roadmap author that these efforts are well funded and should continue to be supported. The only area that might deserve attention is if new approaches arise that look promising for solving the problems and are not included in the current battery modeling program.

8.8   State of Health Monitoring and Failure Prediction

Failures often have a long incubation period, but when a "tipping point" is reached, the failure happens very fast. The "tipping point" is usually governed by heat generation and heat dissipation from the cell and battery pack to the environment. The internal temperature of a cell is difficult to measure, but it is the most crucial measure of whether a cell or module is entering the danger zone. By the time the temperature sensor (typically located on the external surface of a cell) begins to show a "statistically significant temperature rise," the rate of temperature rise is too large and thermal runaway will ensue.

Diagnostic methods that could alert the BMS to incipient failures would pay big dividends in preventing major incidents.[168] The goal is to develop diagnostic techniques that can identify an incipient failure and take action early enough to prevent thermal runaway. Diagnostics, artificial intelligence, or other data analysis techniques need to be developed to predict failure.

Quallion is developing a safety prediction technology that employs an embedded micro-reference electrode with using $Li_4Ti_5O_{12}$-coated microelectrode.[169] Quallion's goal is to predict failure within a cell before it becomes an issue for the battery pack. The use of a $Li_4Ti_5O_{12}$ coating provides a very stable voltage that can be used to compare actual voltages of both electrodes. The Quallion approach is one of many that might be used to give an "early warning" alert to the BMS that a failure is about to occur. The cell should be taken "off line" when its temperature exceeds 100°C – 130°C. The added time may be important to avoid propagation of failure within a module or pack. Dendrite formation should be able to be detected by electrochemical impedance spectroscopy.

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[166] C. J. Orendorff, E. P. Roth, and T. Lambert. "Lithium-Ion Cell Safety Issues of Separators and Internal Short Circuits." Meeting abstract, *Electrochem. Soc.* 1002, 333 (2010).

[167] G-H. Kim, K-J. Lee, L. Chaney, K. Smith, E. Darcy, A. Pesaran. "Numerical Analysis on Multi-physics Behaviors of Lithium-ion Batteries for Internal and External Short." Meeting abstract, *Electrochem. Soc*. 1002 331 (2010); G-H. Kim. "Li ion Abuse Model Development," 2009 DOE Energy Storage Annual Progress Report; G.H. Kim, A. Pesaran, R. Spotnitz, "A Three Dimensional Thermal Abuse Model for Lithium Ion Cells," *J. Power Sources,* 170(2), pp. 476-489, 2007.

[168] Private communication, Brian Barnett, May 12, 2010.

[169] Private communication, Hisashi Tsukamoto, January 11, 2011.

Some investigators believe that an internal short circuit is most likely due to dendrite growth (from iron or copper dissolution).[170] They report data from synchrotron X-ray studies on the electrode structural changes of the Li-ion ($LiFePO_4$) cell during cycling. They also used X-ray diffraction, transmission electron microscopy, and scanning electron microscopy to investigate failures of Li-ion cells. Their early observations are:

- The failure mechanism of $LiFePO_4$ under overdischarge is caused by copper dendrite formation.

- The failure mechanism under overcharge is caused by steel can dissolution and iron dendrite formation.

- Lithium plating is also observed during overcharge.

These results are consistent with observations made at Exponent during failure investigations.[171]

Entropy measurement as diagnostic tool for cell state of health is being developed by Rachid Yazami and Sanyo.[172] Entropy is sensitive to phase and structural changes and may be useful in predicting degradation and perhaps even incipient failure. The technique requires open circuit voltage measurement at range of temperatures, approximately 25°C-40°C. Typically, the cells are cooled to get information and avoid self-discharge at higher temperatures. The goal of their efforts is to develop a technique in which cells could be tested in situ. Yazami has started a company in Singapore to commercialize the idea.

Other examples of advanced diagnostic procedures being developed for batteries include a collaboration between Hydro Quebec and Hitachi High Energy in Tokyo.[150] K. Zaghib reported the use in-situ scanning electron microscopy to evaluation the effect of cycling of Li-metal batteries.

The techniques mentioned above are only examples of creative approaches being used to understand battery aging and failures. Our point is not to necessarily endorse these approaches, but to highlight innovative work in this area. Development of improved diagnostic tests should be a priority in future DOE R&D programs to allow investigation of cell and battery failures with the goal of predicting failure modes, allowing time for intervention, and preventing accidents.

If electric-powered transportation is to become universally available in all automotive lines, cell and pack manufacturing processes and procedures need to be improved. Six-sigma (6σ) process control still allows a 3.47 part-per-million failure rate, which is about what the Li-ion rechargeable battery failure rate is today. This is not good enough. The approach being pursued by Kentucky-Argonne Battery R&D Center is to "build in safety" by better control of manufacturing processes. Safety will be accomplished by having a "defect free" manufacturing process and "defect free" material used in the cell.[173] This roadmap proposes that these efforts

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[170] Private communication, Jian Xie, October 13, 2010.

[171] Private communication, Brian Barnett, November 4, 2010.

[172] R. Yazami et al. "Cathode Materials Degradation Mechanism from Thermodynamics and Crystal Structure Studies." Presented at *Lithium Mobile Power 2010*, Boston MA, November 3, 2010.

[173] R. Brodd, Kentucky-Argonne Battery Manufacturing R&D Center Activities." *Pacific Power Source Symposium 2011*, January 10–14, 2011. Waikoloa, HI.

are sufficient for now, but DOE should continue to monitor them and look for ways to support their effort.

8.9 Battery Pack and Module Safety

Information on in-vehicle safety is more difficult to obtain because it is often proprietary and closely guarded by module and battery pack manufacturers. The following summaries were obtained during interviews for this roadmap:

- The best companies have several "layers" of safety. Toyota ("Best HEV Company") has six to seven "defensive lines," and other companies have one to two defensive lines.

- Researchers in Japan are working on $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $LiCoO_2$. They must believe that these systems have suitable safety. In our experience, the cells with the best thermal stability system do not always result in the safest system:

  - Safety also depends on interaction of cells, thermal management, etc.

  - Integrators need to know why and how their cells fail and have design mitigation strategies.

- There may be an over-reliance on coated separators or coated electrodes to improve safety. Inexperienced companies often have "ridiculous expectations" of separators. Some believe that the heat resistant layer will not prevent internal short circuits.[174]

- Small versus large format cells: which is better? Which is safer? There is a divergence of opinion on the topic. The decision needs to be evaluated with respect to module and pack design. Electrical interactions and current flow need to be studied, tested, and modeled. However, most opinions favor small cells for safety.

  - Toyota is taking a small cell approach to its HEVs. Simple calculation of heat released due to an internal short circuit shows a 20-Ah cell cannot avoid runaway because local temperatures will exceed 180°C.[174]

  - For example, if during a short circuit a single cell failure occurs in a five-cell series of 5-Ah cells, the failed cell will have to dissipate 25 Ah of energy. Overcharge will have same effect. Few cells can survive that condition.

- The "tipping points" to thermal runaway are:

  - 130°C – 140°C – Anode SEI decomposition and rapid anode/electrolyte reactions commence.

  - 180°C – O_2 generation commences from cobalt- or nickel-containing cathodes with subsequent oxidation of the electrolyte. By then, it is too late.

The wiring design can affect abuse response. Quallion presented a "Matrix" wiring strategy in which each parallel string was connected between cells.[175] This "balancing line" approach has been used by others. It provides additional safety because it avoids high transient voltages that could occur in a single string of cells after individual cell failure. Hisashi Tsukamoto showed that

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[174] Private communication, John Z. Zhang, January 11, 2011.

[175] H. Tsukamoto. "Quallion Wide Temperature Technology and Hybrid Matrix Battery," *Pacific Power Source Symposium 2011*, Jan. 10–14, 2011. Waikoloa, HI.

the "Matrix" design in Figure 42 prevented cascade of failure after thermal runaway was induced in one cell.
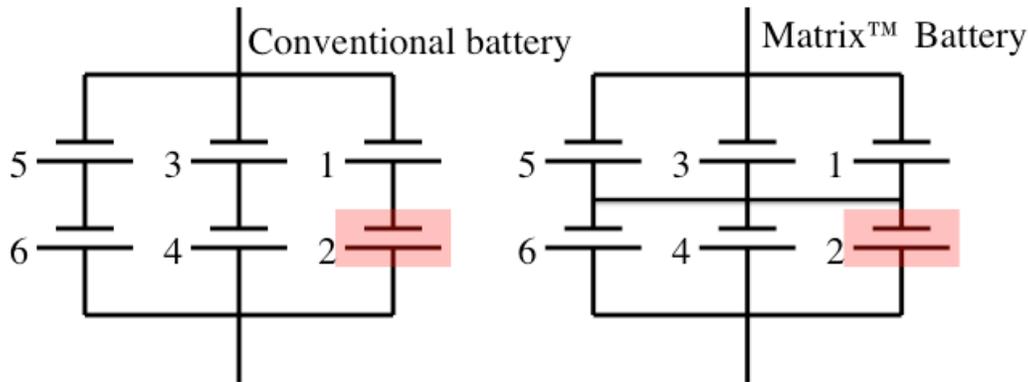
Apply local heating (>250°C) to Cell No.2

Figure 42. Wiring diagram of conventional and "Matrix" design in two battery packs. Cell No. 2 was driven into thermal runaway. The failure propagates to the entire battery in the conventional pack, but propagation DID NOT proceed in the "Matrix" pack.176

- Heat conduction between cells is a crucial parameter to control because it strongly influences failure propagation. This effect has been modeled,[176] but much more work is needed.

  o An example was given of a 3S4P arrangement of 18650 cells. With a 0.5-mm gap, if one cell goes into thermal runaway, all cells will go. This is not safe under any circumstance. If the separation is increased to 5 mm, propagation does not occur.

  Heat-absorbent materials such as low-molecular-weight polyethylene[172] or paraffin,[177] called phase change materials, can be designed to absorb energy by melting at a desired temperature, such as 120°C – 140°C. Battery packs equipped with these materials as spacers or liners between cells are more abuse tolerant because the phase change material limits temperature rise and increases the uniformity of temperature distribution.

- A difficult question to answer is whether or not there is an advantage to using shutdown separators in large format cells or packs for HEVs and EVs. The information obtained for this report did not lead to a firm conclusion.

The roadmap recommendations for module and battery pack safety efforts will focus on modeling and design tools. These should be generally applicable (i.e., not specific to a certain design or cell size), validated, and easy to use. The benefit would be for large original equipment

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[176] R. Spotnitz, D. H. Doughty et al. *Journal of Power Sources* 163 (2007) 1080–1086.

[177] R. Sabbah, R. Kizilel, J.R. Selman, S. Al-Hallaj. *Journal of Power Sources* 182 (2008) 630–638.

manufacturers to check their results and for small original equipment manufacturers to receive guidance to solve problems that they may not be able to solve in-house.

9 Conclusions and Recommendations

Batteries must have sufficient safety for their targeted application. The safety and abuse tolerance of electrochemical cells depends on materials, chemical interactions, the nature of the abusive event, as well as battery pack and BMS control engineering. Improved abuse tolerance and engineering leading to "graceful failure" is a challenge that encompasses many areas of study and specialization.

It is clear that the safety of Li-ion rechargeable batteries needs to be improved. While the activities mentioned in this roadmap are making progress in improving the safety of the traction batteries proposed for use in EVs and HEVs, more needs to be done. Past efforts have traded increased battery safety for lower energy.

The goal of this roadmap is to identify opportunities where high energy and safety can be met simultaneously. For example, R&D priorities that, if achieved, will enable development of cells and batteries that can support long driving range and have sufficient safety to be used in EVs and HEVs.

The following topics are identified as needs that are not being met and on which additional funding would have the greatest impact to enable safe, high-energy vehicle batteries. The recommendation of the roadmap is that these topics be a priority in future DOE R&D programs. *[Note: Topics that are not recommended for future investments are not listed here. The individual sections in this roadmap provide discussion and reasoning for these decisions.]*

This roadmap provides recommendations in the following three areas:

1. Improve our understanding of failure modes.

    A. Failure modes such as internal short circuits have substantial negative consequences and are difficult to characterize. Our understanding of the internal short circuit event is superficial, and the tests meant to simulate the event are not well developed. We recommend a systematic R&D program that would:

        i. Elucidate the details and provide a better understanding of initiation and propagation of internal short circuit.

        ii. Develop a standardized test method that would determine cell susceptibility to this failure mode and provide validation tests to support development of models for the internal short circuit event.

    B. Propagation of a failure from cell to cell, leading to catastrophic failure cannot be tolerated. Building an easy-to-use, validated cell and battery pack abuse model that realistically captures propagation is essential. Standardized test method for propagation should be a priority. A propagation model would have a great benefit if it could serve as a trusted guide for battery pack manufacturers to avoid propagation of failures in all battery packs.

2. Develop better characterization tools.

A. Failures often have an incubation period of several hours, but when a "tipping point" is reached, the failure happens very fast. Diagnostic methods that could alert the BMS to an incipient failure and trigger early intervention would pay big dividends in preventing major incidents. Examples are development of diagnostic techniques to:

   i. Detect lithium plating on the anode

   ii. Identify and predict aging-related failures

   iii. Detect the presence of debris or imperfections within the cell that could lead to an internal short circuit.

B. Models for cell, module, and battery pack safety should be a priority because they will drive understanding and improvements in the safety of large battery packs. Large original equipment manufacturers will benefit by having an independent check of their results, and small original equipment manufacturers will benefit by receiving guidance to solve problems that they may not be able to solve in-house.

   i. Models should be generally applicable (i.e., not specific to a certain design or cell size), validated, and easy to use.

   ii. Internal short circuit, overcharge, electrolyte decomposition, gas evolution, and lithium deposition are areas that need the development of better models and validation

   iii. Failure propagation model mentioned above.

3. Improve the safety of energy storage technologies.

A. Cathodes continue to be a source of failure in Li-ion rechargeable batteries. New cathode materials, which are being designed to achieve high-energy targets, can be unstable and reactive. Three areas are recommended for R&D investment:

   i. Coated cathodes. The potential of cathode surface modification techniques is very promising because it will allow use of high-energy materials and avoid electrolyte oxidation.

   ii. Novel discovery methods. Calculations of the oxidative stability of layered cathodes can provide synthetic R&D programs with guidance to discover new cathode materials that can achieve high capacity and improved safety.

   iii. Cathode conversion reactions are a fertile area for research, and a systematic investigation to develop high-capacity and safe cathodes should be a priority.

B. Non-flammable electrolyte development. The flammability of the vented electrolyte is one of the most significant unresolved safety issues for Li-ion batteries. From the roadmap author's viewpoint, non-flammable electrolyte additives are unlikely to be a permanent solution to the electrolyte flammability problem. Therefore, the author recommends a concerted effort in IL electrolytes that could permanently solve the electrolyte flammability issue.

C. Develop methods to prepare a "Permanent SEI." The breakdown of SEI at temperatures ~130°C – 140°C is an important trigger to thermal runaway that needs

to be eliminated, or at least stabilized to temperatures greater than 200°C. Additives to stabilize the anode surface have made improvements, but do not last the life of the cell and are compromised at elevated temperatures.

D. New separators (and/or ceramic coatings applied to a separator or electrode) can provide protection from internal short circuits and other abusive events. Many questions remain to be answered:

   i.   What method of application of a ceramic heat resistant layer provides the best safety result?

   ii. What is the mechanism of the heat-resistant layer that provides abuse tolerance?

   iii. Are there preferred ceramic particles (chemical composition or morphology) for the ceramic composite layer?

   iv. Is the durability sufficient? Will the separator layer perform for life of the cell?

E. Understand the safety performance of batteries containing anodes made with silicon or other alloys. Because batteries with alloy anodes could be proposed for use in traction applications, the DOE should have a program to investigate the safety issues with batteries made with high-capacity Li-alloy anodes.

Glossary

cell	An assembly of at least one positive electrode, one negative electrode, and other necessary electrochemical and structural components. A cell is a self-contained energy storage device whose function is to deliver electrical energy to an external circuit.
explosion	A very fast release of energy sufficient to cause pressure waves and/or projectiles that may cause considerable structural and/or bodily damage, depending on the size of the test article. The kinetic energy of flying debris from the test article may be sufficient to cause damage as well.
fire or flame	Ignition and sustained combustion of flammable gas or liquid (approximately more than one second). Sparks are not flames.
GBL	Gamma-butyrolactone ($C_4H_6O_2$) is a solvent used in electrode manufacturing processes. It has a boiling point of 206°C.
$I^2 R$	I is the current flowing in the conductor, and R the resistance of the conductor. With I specified in amperes and R in ohms, $I^2 R$ represents the Joule heating as current flows through an object.
module	A grouping of interconnected cells in series and/or parallel arrangement into a single mechanical and electrical unit.
NMP	N-methyl-2-pyrrolidone is a high-boiling (202°C – 204°C) solvent.
pack	Interconnected modules, including all ancillary subsystems for mechanical support, thermal management, and electronic control.
PHEV	A plug-in hybrid vehicle is a hybrid electric vehicle designed to be charged from an electrical grid while stationary.
redox	Reduction-oxidation.
rupture	The loss of mechanical integrity of the test article container, resulting in release of its contents. The kinetic energy of the released material is not sufficient to cause physical damage external to the device under test.
SEI	A solid electrolyte interphase or the passivation layer that forms on Li-ion rechargeable battery anode materials.
SOC	The state of charge is the relative capacity expressed as a percentage of the fully charged capacity.
Thermal runaway	The uncontrolled increase in the temperature of the device under test driven by exothermic processes, such that heat is generated at a rate that exceeds the heat dissipation rate.
Thermal stability limit	The maximum temperature at which battery is stable indefinitely.

Appendix A. Invitation Letter

The following letter was sent to the people listed in Table 1.

You are invited to participate in the development of a "Roadmap for Safety and Abuse Testing of Lithium-Ion Batteries for HEVs, PHEVs and EVs."

One of the goals of the DOE Energy Storage R&D Program at the Office of Vehicle Technologies is to foster the development lithium-ion batteries that are safe and abuse tolerant in electric drive vehicles. As lithium-ion technology matures, high-energy batteries will be produced and more car companies will deliver to consumers electric drive vehicles containing lithium-ion batteries. In this environment, the safety issue will become paramount.

To address this concern, the DOE Office of Vehicle Technologies has initiated the development of a roadmap to identify approaches to improve traction battery safety in electric drive vehicles. The starting point is to understand the current state of lithium-ion rechargeable battery safety technology and highlight industry efforts that will improve safety of lithium-ion batteries in vehicular applications. The effort will identify gaps and opportunities as well as highlight research topics that should be pursued to achieve the goals.

Dan Doughty, Battery Safety Consulting Inc., will lead the roadmap effort. The participation of your organization is very important to the success of this effort. If you are not able to participate, please identify someone in your organization who could participate or serve as a point of contact.

Questions:

- What are the key problems in lithium-ion rechargeable battery safety and abuse tolerance?

- What are the key developments in lithium-ion rechargeable battery safety and abuse tolerance?

- What are research directions in safety and abuse tolerance that your lab is taking?

- What are research directions in safety and abuse tolerance you see in the battery suppliers and automotive OEMs?

- What are modeling needs?

- What actions should DOE Office of Vehicle Technologies take to improve safety and abuse tolerance of lithium-ion rechargeable batteries in automotive applications?