Abuse Tolerance Improvement

E. Peter Roth
Sandia National Laboratories
Albuquerque, NM

DOE Vehicle Technologies Peer Review
Gaithersburg, MD
Feb. 26, 2008

This presentation does not contain any proprietary or confidential information

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.
Purpose of Work

Demonstrate Improvements In Inherent Thermal Abuse Tolerance

- Identify degradation mechanisms of gas and heat-producing reactions in lithium ion rechargeable cells.

- Identify and develop advanced materials or combination of materials that will minimize the sources of cell degradation during abuse events, thus enhancing safety.

- Build and test full size cells to demonstrate improved abuse tolerance.
Barriers: How Do We Improve Abuse Tolerance?

- **Intrinsic Properties:**
  - Reduced Enthalpy of Reaction
  - Reduced Reaction Kinetics
    - Reactions of new low energy materials need to be verified
      - Iron Phosphate cathodes
      - Lithium Titanate anodes
  - Reduced Gas Generation
  - Lower Flammability of Solvents
    (composition/additives)

- **Cell Level Mechanical Mechanisms:**
  - Separators (shutdown properties, integrity)
Approach: Main Areas of Thermal Abuse Response Research

I. Effect of materials on thermal runaway
   – New anode and cathode materials
   – Electrolytes and additives

II. Overcharge response
   – Effect of anode and cathode materials on heat and gas generation
   – Effect of separator properties above shutdown
   – Overcharge additives

III. Separators
   – Effect of loss of melt integrity
   – High voltage standoff
Summary of Accomplishments

- Demonstrate Improved Thermal Abuse Response in High Power Cells
  - Expanded quantitative measurements of thermal runaway over a broader range of materials (LiCoO₂, Spinels, LiFePO₄) demonstrating much reduced reactions
  - Characterized electrolyte composition and additives that reduce peak thermal runaway reactions

- Overcharge
  - Provided quantitative characterization of overcharge response
  - Overcharge shuttle (Air Products) demonstrating high voltage charge limiting effects
    - Identified sequence of gas generation during overcharge showing H₂ as first gas released

- Characterized Role of Commercial Separators in Cell Abuse Response
  - Showed improved high temperature melt integrity for new commercial separators
  - Showed comparable response to voltage breakdown both at material and cell level which can lead to internal hard shorts and thermal runaway
Effect of Materials on Abuse Tolerance and Cell Thermal Runaway

Thermal Ramp Response (100% SOC)

- Stage 1: Room Temperature to 150°C – Onset of thermal runaway - Anode
- Stage 2: 150°C - 180°C – Venting and accelerated heating – Anode/Onset Cathode
- Stage 3: 180°C and above – Explosive decomposition (flame) – Cathode/Anode

Ramp Temperatures

Differential Temperature Rate

<table>
<thead>
<tr>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (C)</td>
<td>Rate (°C/min)</td>
<td>Temperature (C)</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>50</td>
<td>5</td>
<td>150</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>150</td>
<td>15</td>
<td>250</td>
</tr>
<tr>
<td>200</td>
<td>20</td>
<td>300</td>
</tr>
</tbody>
</table>

Sandia National Laboratories
Analytical Techniques

• Material Characterization
  – Thermal Analysis
    • DSC, TGA
  – Gas Analysis
    • GCMS, MS, FTIR
  – Electrolyte Analysis
    • HPLC

• Thermal Runaway
  – Accelerating Rate Calorimetry (ARC)
    • Heat and Gas Generation Under Adiabatic Conditions
  – Thermal Ramp
    • Constant Heating Rate to Failure

• Overcharge
  – Quantitative Heat and Gas Generation
Cell Chemistries Evaluated in ATD Program

- **Cathode materials:**
  - LiCoO$_2$
  - LiNi$_{0.85}$Co$_{0.15}$O$_2$ (Gen1)
  - LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$ (Gen2)
  - LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$; Li$_{1.1}$(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)$_{0.9}$O$_2$ (Gen3)
  - LiMn$_2$O$_4$ (Spinel)
  - LiFePO$_4$

- **Anode materials:**
  - MCMB (Gen1 and 3)
  - MAG10 (Gen2)
  - GDR (Gen2)

- **Electrolytes/salts:**
  - EC:EMC (3:7) 1.2M LiPF$_6$
  - EC:PC:DMC (1:1:3) 1.2M LiPF$_6$
  - LiBOB, LiBETI

- **Additives:**
  - SEI enhancer – Vinyl ethylene carbonate (VEC); Vinylene carbonate (VC)
  - Flame retardants– e.g. Phosphazene-based “Phoslyte” from Bridgestone; phosphate TPP; ...
Improved Cathode Stability Results in Increased Thermal Runaway Temperature
And Reduced Peak Heating Rate for Full Cell

- **LiCoO$_2$**
- **Gen2: LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$**
- **Gen3: Li$_{1.1}$(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)$_{0.9}$O$_2$**
- **LiMn$_2$O$_4$**
- **LiFePO$_4$**

**Normalized Rate (C/min)**

**Temperature (C)**
Normalized Rate (C/min)

Thermal Runaway Cathode Comparisons (Expanded View)

Initial Onset Reactions Dominated by Anode
Cathode Reaction Onset 160°C-180°C

Gen2: LiNi_{0.8}Co_{0.15}Al_{0.05}O_2
Gen3: Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2
LiMn_2O_4
LiCoO_2
LiFePO_4
EC: PC: DMC
1.2M LiPF_6
ARC
100% SOC

Temperature (C)

Normalized Rate (C/min)
Solvent Composition Affects Peak Reaction Kinetics

EC:PC:DMC\LiPF_6 electrolyte has shown the greatest reduction in reaction rate

![Graph showing the effect of solvent composition on reaction rate.](image)
EC:PC:DMC\(\text{LiPF}_6\) electrolyte has shown reduction in reaction rate for the two main cathode chemistries studied.

\[
\text{Li}_{1.1}\left(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\right)_{0.9}\text{O}_2
\]

\[
\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2
\]
Reduction in Electrode\Electrolyte Reactions Seen for LiCoO$_2$ with EC:PC:DMC Solvents

Little Difference in Reaction Rate at Temperatures Below 200 °C Implies Difference in Reaction not at Cathode Surface Prior to Cathode Decomposition

Least Effect Of Solvent Composition On This The Most Reactive Of The Cathode Materials

![Graph showing rate (C/min) vs. temperature (°C) for different solvent compositions](image)

LiCoO$_2$
Gas Evolution is a Critical Property Affecting Safety

Peak Gas Generation Volume Similar for Different Cathodes with Same Electrolyte (EC:PC:DMC/LiPF₆)
Total Gas Generation up to 450°C Comparable for all Chemistries

Gas Generation at End of Peak Runaway (1 C/min).
Most Important for Safety

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Peak Gas Vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂</td>
<td>900-1000 ml</td>
</tr>
<tr>
<td>Gen2</td>
<td>600-900 ml</td>
</tr>
<tr>
<td>Gen3</td>
<td>900-1000 ml</td>
</tr>
<tr>
<td>LiMn₂O₄</td>
<td>700 ml</td>
</tr>
<tr>
<td>LiFePO₄ (Elec. ?)</td>
<td>500 ml</td>
</tr>
</tbody>
</table>

1.2 Ah MCMB/LiCoO₂ EC:PC:DMC/1.2M LiPF₆
Thermal Ramp Apparatus
Ramp to runaway in air with external ignition

- Similar to “hot box” test (6°C/min), complementary to ARC test.
- Spark Source provides ignition if flammable gas is present.
- More accurate measurement of electrolyte flammability.
- Analysis of differential temperature rate (cell vs. block) provides sensitive measurement of cell response.
Thermal Ramp Shows Improved Abuse Response For Gen3 Cells as Seen by ARC Measurements

Heating Block and Cell Temperatures

Cell Heating Rates

Sandia National Laboratories
Greater Abuse Tolerance Shown for New Chemistries with Reduced or No Cathode Oxygen Release

Anode Reactions Still Contribute to Runaway

LiFePO$_4$ olivine cathodes show the greatest reduction in heating rate and increased onset temperature for runaway.

LiFePO$_4$ Nanophosphate Cells
Provided by A123

Sandia National Laboratories
Movie Clips of Cell Thermal Runaway Showing Improved Response of LiFePO₄

50% Li/Ni/Co/Mn and 50% LiMn₂O₄ Cell

A123 LiFePO₄ Cell

Explosive Combustion of Vent Gases (mostly solvent vapors)

100% SOC

26650 Commercial Cells
II. Overcharge Response

- Overcharge is one of the most energetic abuse conditions
  - Highly reactive, unstable cathode
  - Highly lithiated anode

- High levels of heat generation
  - Separator shutdown and possible internal short
  - Initiation of thermal decomposition runaway

- Flammable gas generation
  - Hydrogen
  - Venting of solvent vapors
Overcharge Gas Generation

We have previously shown that explosive gases are generated during overcharge: Hydrogen and flammable solvent vapors.
**Sequence of Gas Generation During Overcharge**

- 18650 Gen2 Cell/ LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$/EC:PC:DMC/LiPF$_6$
- Helium background to keep temperature below separator shutdown
- **Cell can cut open to allow gas escape during run**
- Real-Time Mass Spectrometry Analysis

**Hydrogen Generation at Onset of Heat Generation**
Gas Species Detected

Hydrogen\CO \textsubscript{2} Generation Precedes Generation of Other Gas Species

![Graph showing gas species detection over time](image)
Abuse Response Improved with Electrolyte Additives

- Additives to improve:
  - SEI
    - VEC, VC
  - Electrolyte stability
    - LiBOB, LiBETI
  - Overcharge
    - Shuttle Additives
  - Flammability
    - Phosphazenes
    - Phosphates
Overcharge is One the Most Abusive Conditions for Li-ion Cells: Improved Response with Overcharge Additive

$0.4M \text{Li}_2\text{B}_{12}\text{F}_9\text{H}_3$ and $0.1M \text{LiPF}_6$ in EC/DEC (3:7)

Shuttle Mechanism Limits Cell Voltage and Peak Heating Rate During Overcharge

Material developed by Air Products and Chemicals, Inc.
III. Separator Failure
Results in High-Rate Cell Failure for Several Abuse Conditions

Sandia has developed a method for characterizing separator response and is correlating these properties to observed cell behavior.

- Separator Characterization
  - AC Impedance during thermal ramp
    - Onset temperature of shutdown
    - Upper integrity temperature
  - DC resistance under high potential
    - Upper integrity temperature
Schematic of Separator Characterization Apparatus

- Compressive Weight
- Top Heater
- Bottom Heater
- Top Platen
- Bottom Platen
- To Impedance Meter/Power Supply
- Upper TC
- Lower TC
- To Temperature Controller
- Separator Sample Assembly
- Bottom Ni Electrode
- Top Ni Electrode
- Kapton Tape (bottom only)
- Separator/ Electrolyte

Separator Sample Assembly (Top View)
Separator Impedance During Thermal Ramp

Polyethylene-based shutdown separators

Shutdown temperature is well defined.
Upper integrity temperature varies over broader temperature range, affected by pressure and surface irregularities.

3 runs of each

Z Total
1000Hz/50mV

Temperature (°C)

Entek
143C/(153C-158C)

Tonem
139C/(190C-204C)

Celgard
131C/(165C-167C)

Sandia National Laboratories
Separator Voltage Integrity

DC Resistance Above Shutdown

Local currents through pinhole defects above shutdown result in local heating and further separator failure leading to shorting of electrodes.

![Graph showing temperature vs. resistance for different materials (Celgard 2325 and Tonen) at various temperatures (155°C and 186°C).]
Separator Breakdown and Cell Thermal Runaway

Inadequate Shutdown Protection

Separator Maintains Integrity With 19V Applied For Two Minutes

Cell Continues to Heat After Shutdown With 6 W of Input Power

Gen2 Cell Chemistry Celgard 2325 Separator

1C/1.4 Amp Charge
Forced Internal Shorts

Cells with soft shorts taken above separator shutdown
Potential applied to accelerate breakdown at cell defect

Hard Short Leading to Thermal Runaway

Immediate Separator Failure With Potential
Cell Thermal Runaway (1 amp current limit)

Intermediate Short with Cell Heating but No Thermal Runaway

Delayed Separator Breakdown
With No Cell Runaway (1 amp current)

Sandia National Laboratories
Internal Short With Self-Healing

Separator Response is a Function Such Properties as Mechanical Puncture Strength, Melt Integrity, and Melt Shrinkage

MCMB/LiMn$_2$O$_4$ Spinel/EC:PC:DMC:1.2M LiPF$_6$
Two Identical Cells: 0.65 Ah

MCMB/LiMn$_2$O$_4$ Spinel/EC:PC:DMC:1.2M LiPF$_6$
Two Identical Cells: 0.65 Ah

ARC Sandia National Laboratories
Thermal Abuse Observations

• Steady Improvements in Abuse Tolerance Have Been Achieved.
• Flammable Electrolyte and Gas Generation Are Still an Issue.

- Increased thermal stability has been demonstrated with more stable cathodes ($\text{Li}_{1.1}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.9}\text{O}_2$; $\text{LiMn}_2\text{O}_4$ Spinel and $\text{LiFePO}_4$)
  - Improved stability results from decreased oxygen generation

- Anode reactions are still important to provide better abuse tolerance

- EC:PC:DMC-based electrolyte shows improved abuse tolerance with commonly used cathode chemistries

- Some additives have shown improvements in thermal and overcharge abuse response

- Separator integrity important to cell stability
  - New separators show increased stability range
Abuse Tolerance Studies
Future Work

- Determine relative contributions of anode and cathode on thermal abuse response for a wider range of chemistries (e.g. titanate anodes)
- Continue to develop quantitative understanding of relationship between anode/cathode decomposition and cell thermal runaway
- Determine response of new cell materials in 18650 cells
  - Effects of improved electrolytes/additives
  - Effects of anode/cathode cell balance on abuse response
  - Effects of new stable separators
- Model thermal response of full cell using measured cell thermophysical properties (continuation of earlier modeling work)
Publications and Presentations
FY07 - Present

- **Publications**
  - Abuse Response of 18650 Li-Ion Cells with Different Cathodes Using EC:EMC/LiPF6 and EC:PC:DMC/LiPF6 Electrolytes, E. P. Roth, accepted for publication in ECS Transactions - Washington, DC Volume 11, Battery Safety and Abuse Tolerance

- **Presentations**
  - Safety Issues for Li Ion Cells, E. P. Roth, D. H. Doughty, Li Mobile Power 2006, Dec. 4-5, 2006, Miami, FL
  - Li-Ion Safety: New Material and Cell Performance, E. P. Roth, Space Power Workshop, Apr. 24-26, 2007, Los Angeles, CA
  - Lithium-Ion Battery Abuse Tolerance Testing Against Key Design Parameters , E. P. Roth, 7th International ADVANCED AUTOMOTIVE BATTERY and Ultracapacitor CONFERENCE and SYMPOSIA, May 14-18, 2007, Long Beach, CA
  - Abuse Response of 18650 Li-Ion Cells with Different Cathodes Using EC:EMC/LiPF6 and EC:PC:DMC/LiPF6 Electrolytes, E. P. Roth, 212th ECS Meeting, Oct. 7-12, 2007, Washington D.C.,
Acknowledgements

Thanks to Dave Johnson, Craig Carmignani, Jill Langendorf, and Lori Davis at Sandia for their assistance in performing this work.

This work was performed under the auspices of DOE FreedomCAR & Vehicle Technologies Office through the Advanced Technology Development (ATD) High Power Battery Development Program.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.