Abuse Tolerance Improvement

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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.

Overview

Timeline

- Start Date: Oct. 2007
- End date: Oct. 2014
- Percent complete: <10%

Budget

- Total project funding
  - $700K
- FY08 Funding: $700K
- FY09 Funding: $700K
- Funding for FY10: TBD

Barriers

- Barriers addressed
  - Develop intrinsically abuse tolerant Li-ion cells and batteries
  - Obtain access to latest promising materials from developers
  - Funding to develop needed expansion and test development

Partners

- ANL, LBNL, BNL, INL

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Objectives/Milestones

OBJECTIVES

- 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.

MILESTONES

- Demonstrate improved abuse tolerant cells and report to DOE and the battery community.

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Approach

Use Cell Level Abuse Testing to Characterize and Develop Abuse Tolerant Cells

- **Effect of materials on thermal runaway**
  - Use Sandia cell building capabilities to test new anode and cathode materials
  - Electrolytes and additives
- **Overcharge response**
  - Effect of anode and cathode materials on heat and gas generation
- **Separators**
  - Effect of loss of melt integrity
  - High voltage standoff
  - Effect of internal shorts from artificial stimulation

Technical Accomplishments/ Progress/Results

- Quantitatively shown the individual thermal effects of $LiMn_2O_4$ and $LiFePO_4$ cell cathode\anode materials in 18650 cells and shown that anode reactions dominate thermal runaway
- Shown by comparative characterization of commercial and research cells with $LiFePO_4$ cathodes that abuse response normalized by cell capacity is very similar for all cells of this chemistry regardless of manufacturing source or cell design
- Shown gas generation and flammability to be some of the most critical issues for cell level abuse response
- Gas generation during peak runaway normalized by cell capacity has been shown to be independent of cell chemistry and determined primarily by electrolyte quantity

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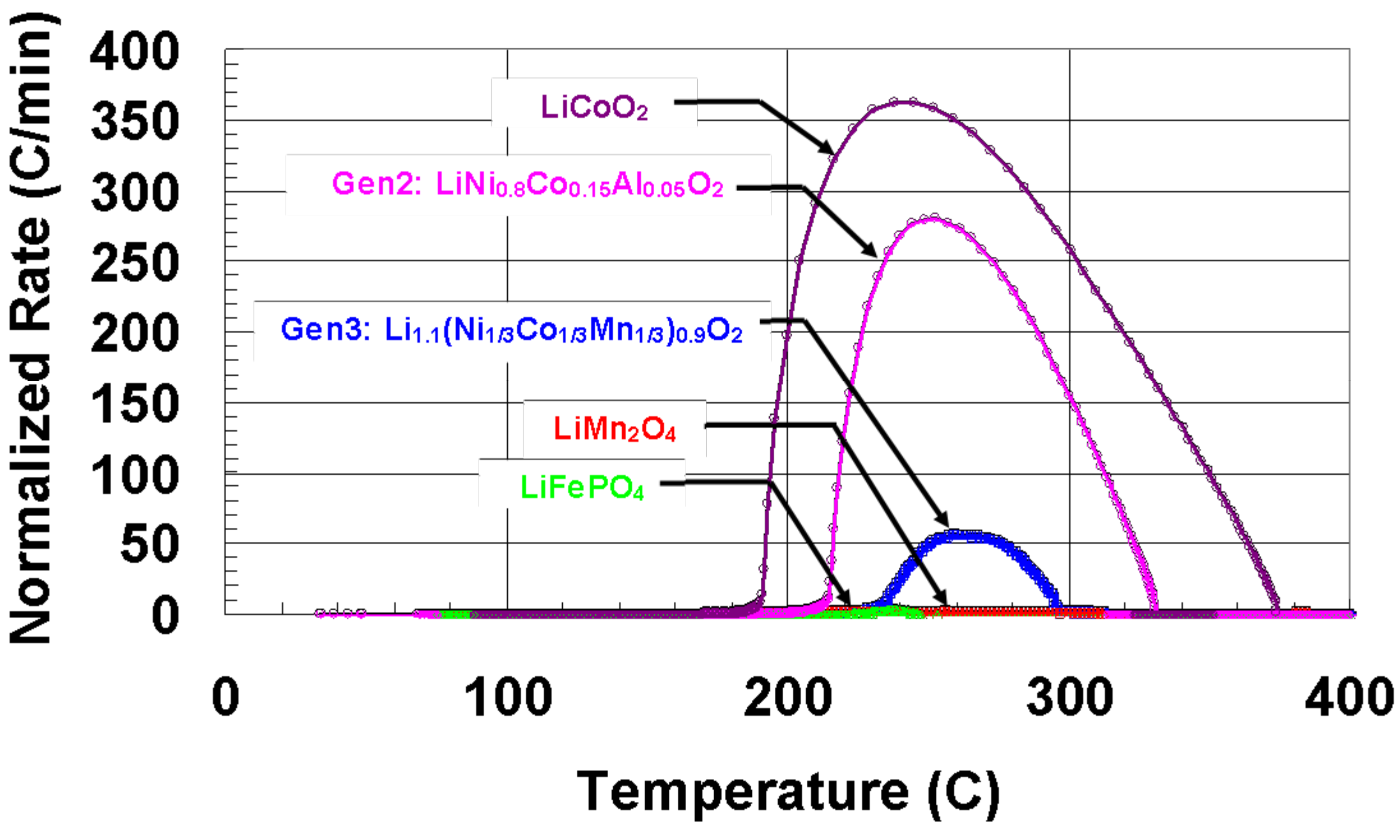
Technical Accomplishments/ Progress/Results (cont.)

- Shown that cells with $LiFePO_4$ cathodes, though thermally stable, have higher heat generation during overcharge compared to other cathode oxides and heat generation starts immediately above 100% state of charge resulting from the low cathode Li level at full SOC
- Developed new techniques and equipment to study separator integrity and internal cell short circuits by introducing defect particles at the separator layer
- Constructed 18650 Cells with fluorinated LiBOB electrolyte additive and shown them to have reduced thermal reactions during high temperature abuse testing

Thermal Runaway Cathode Comparisons

Improved Cathode Stability Results in Increased Thermal Runaway Temperature And Reduced Peak Heating Rate for Full Cell

Decreased Cathode Reactions Associated with Decreasing Oxygen Release



EC:PC:DMC
1.2M $LiPF_6$

ARC

100% SOC

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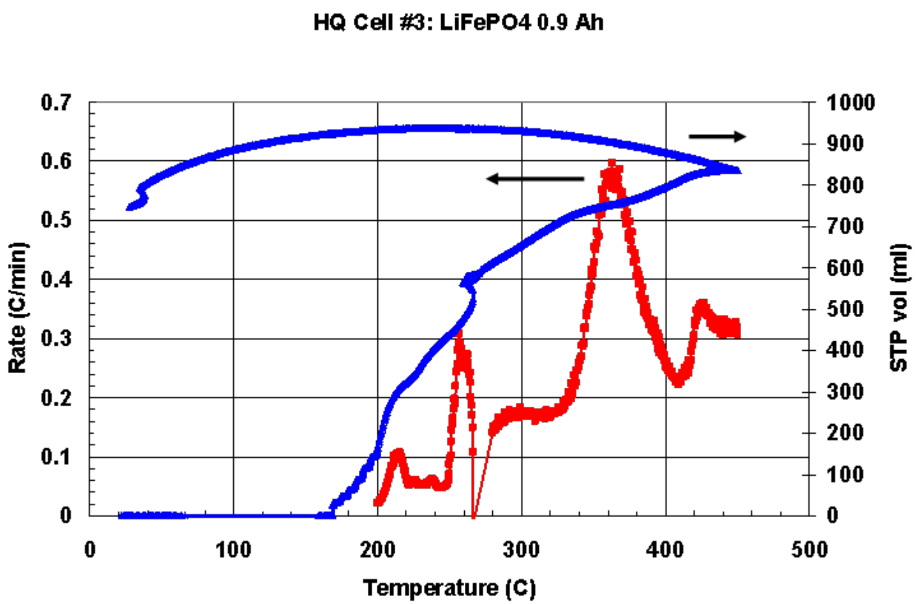
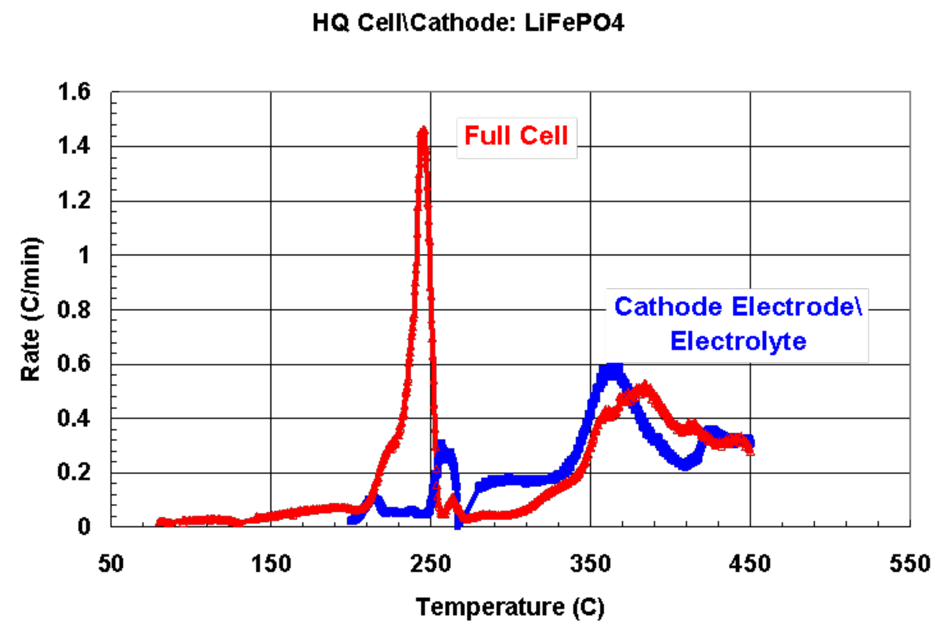
ARC Profile $LiFePO_4$: Full Cell and Cathode Electrode\Electrolyte

Cathode\Electrolyte

Full Cell
Cathode\Electrolyte





Anode Reactions Dominate Cell Response

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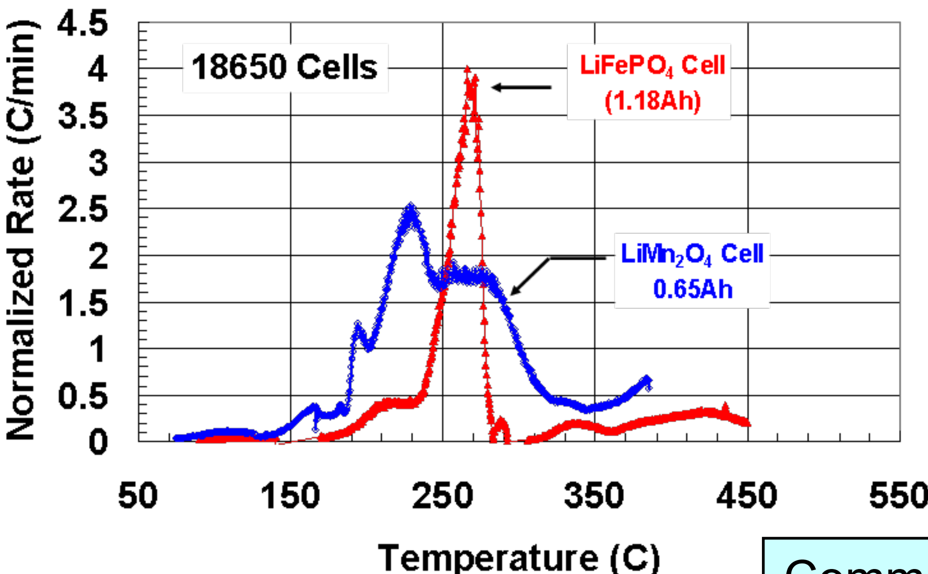
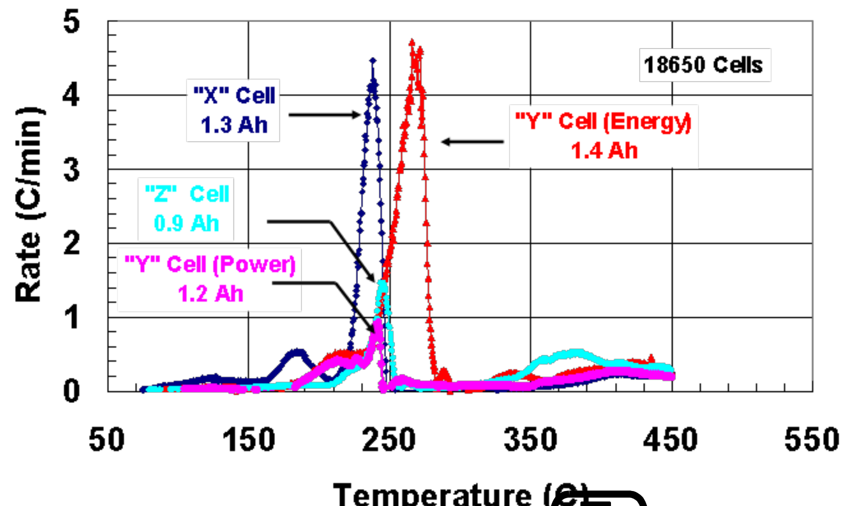
$LiFePO_4$ Cells Show Lower Reaction Kinetics and Reaction Enthalpy Compared to $LiMn_2O_4$ Cells

$LiFePO_4$ Does Not Release Oxygen and Shows the Lowest Thermal Reactions

Different Source $LiFePO_4$ Cells Show Similar Onset Thermal Response Which Are Greatly Reduced Compared to Layered Ni Oxides





Commercial Cells "X" and "Y"
Cell "Z" built at Sandia

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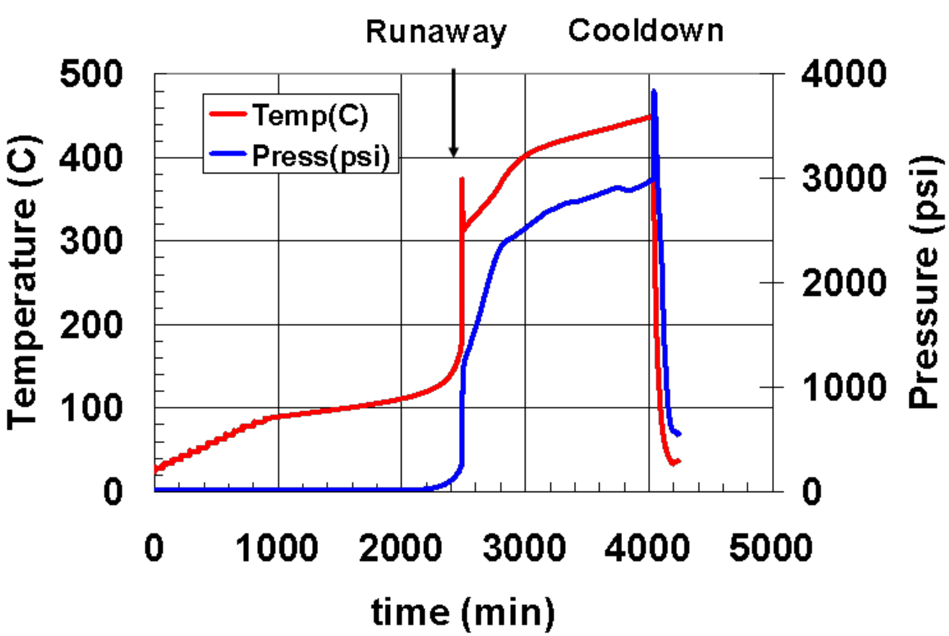
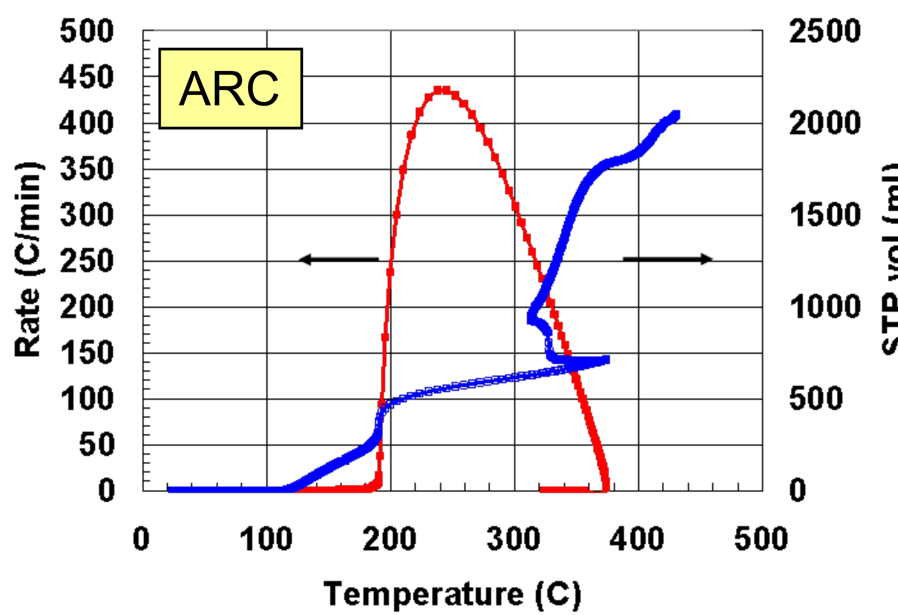
Gas Evolution is a Critical Property Affecting Safety

Gas Evolution Begins ~ 150°C from Electrolyte Decomposition
Gas Evolution During Peak Runaway Has Greatest Safety Impact





1.2 Ah MCMB/$LiCoO_2$ EC:PC:DMC/1.2M $LiPF_6$

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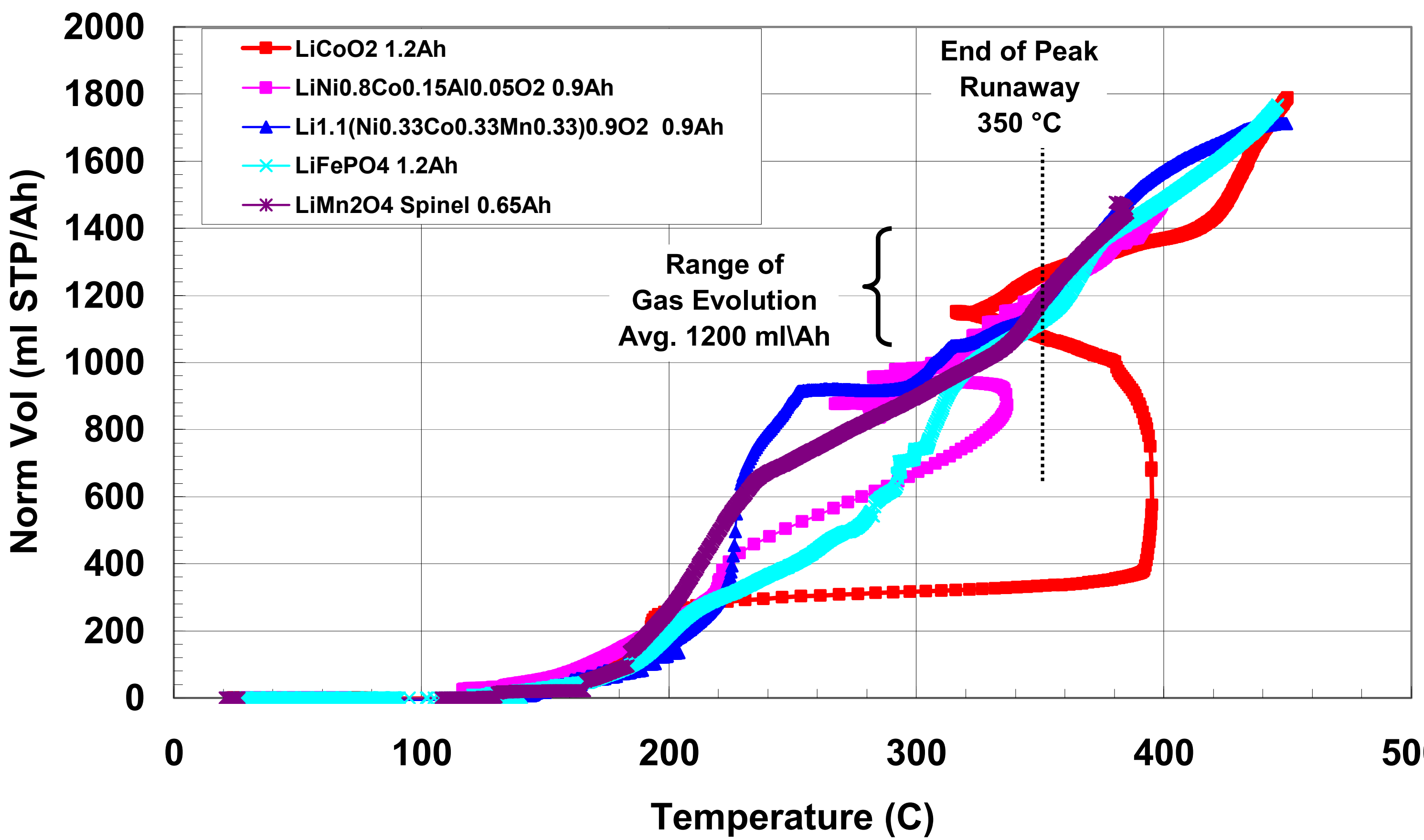
Gas Evolution for Different Cathode Chemistries

Peak Gas Evolution Independent of Cathode Chemistry
Determined by Quantity of Electrolyte



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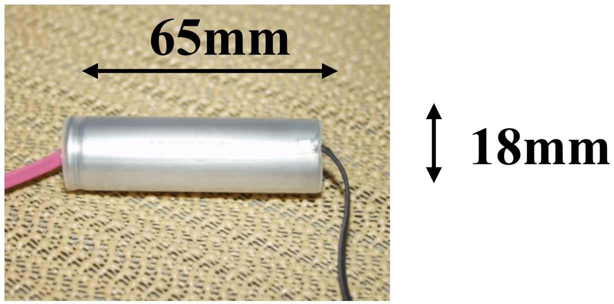
Thermal Ramp Apparatus

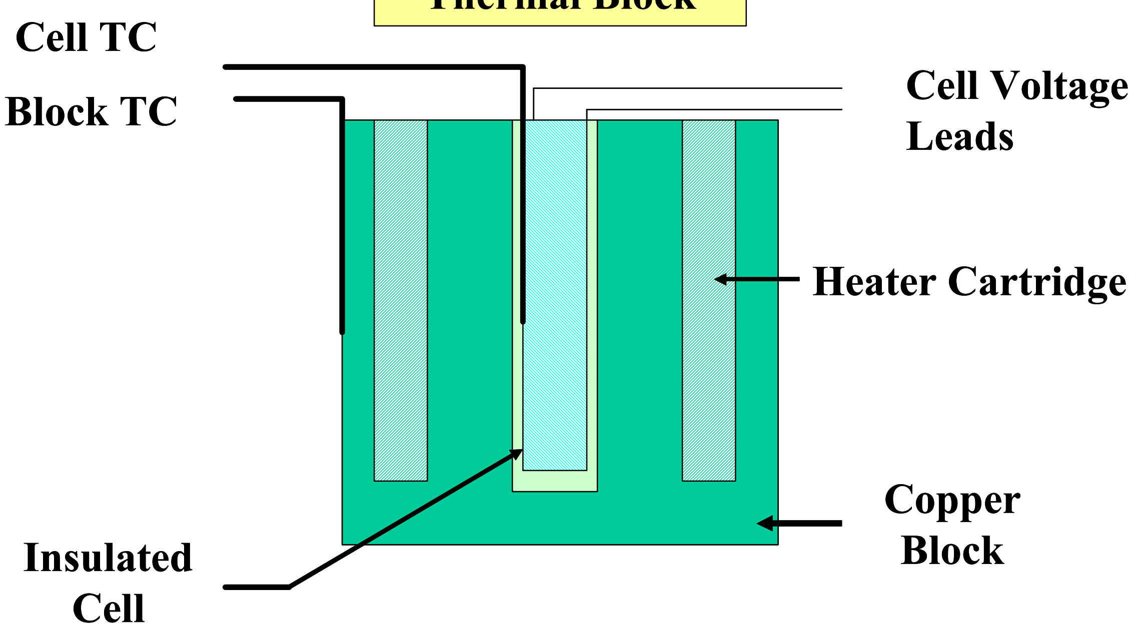
Ramp to runaway in air with external ignition



Ramp at 6 °C/min

190 °C

Thermal Block



Heat Block with External Ignition Sources
Cell has vented and is about to enter explosive decomposition stage.

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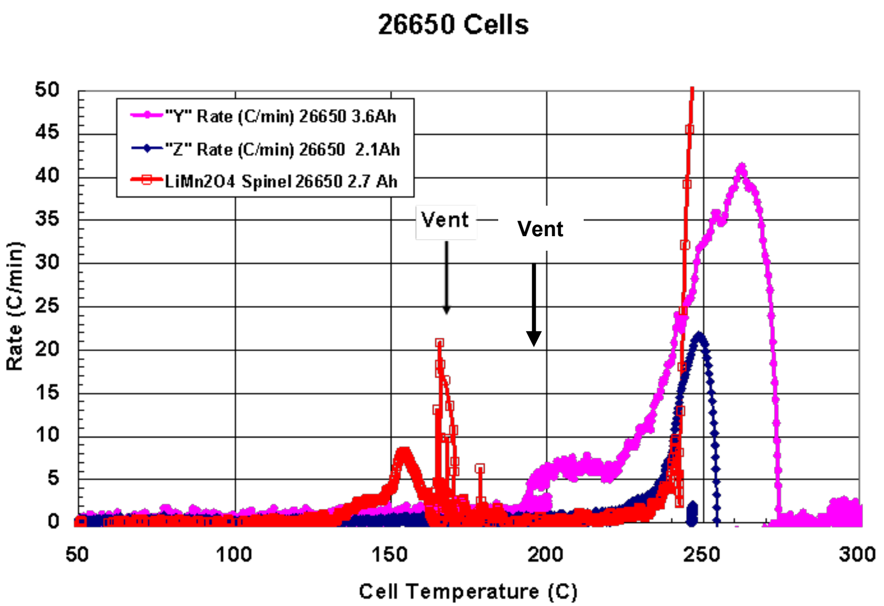
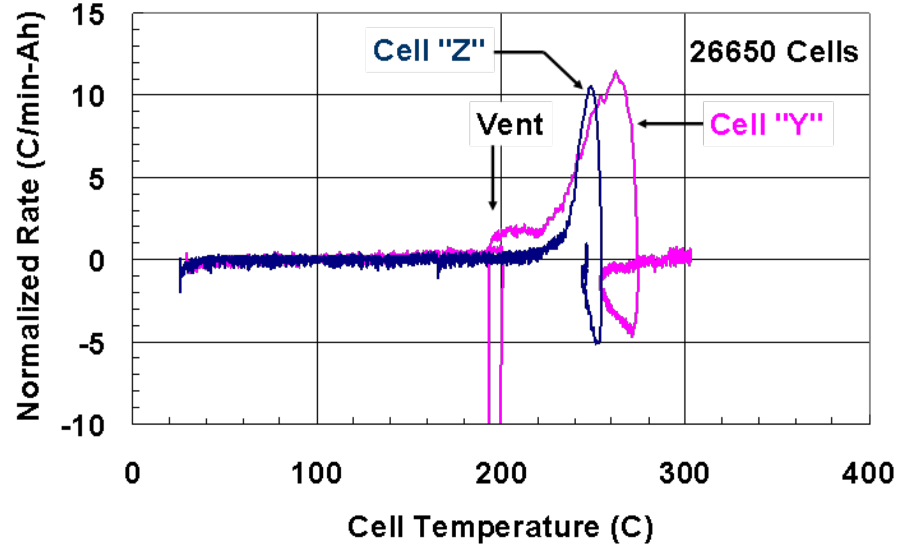
Comparison of Commercial $LiFePO_4$ Cells with $LiMn_2O_4$ Cell

Cell Thermal Response Scales With Capacity as Expected

Normalized Cell Response Very Similar for Different Cell Capacities





Cells Remained Intact During Thermal Runaway

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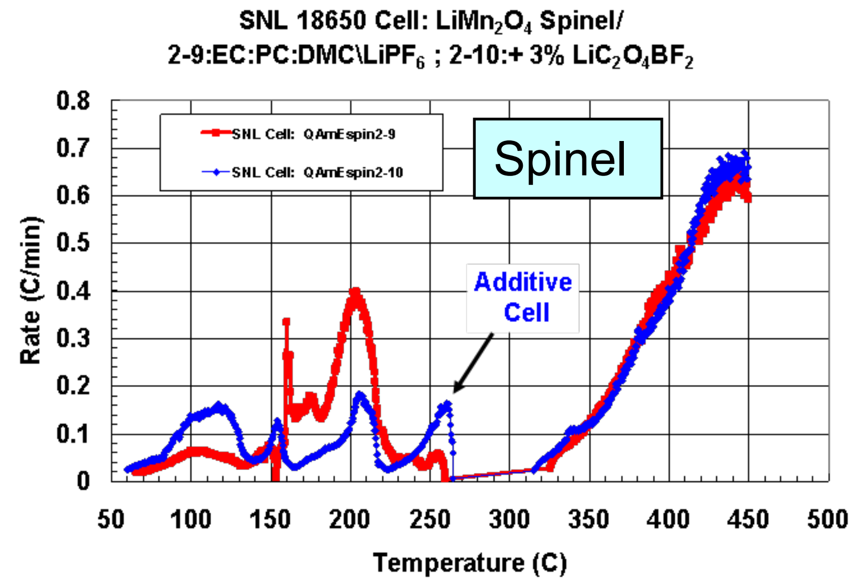
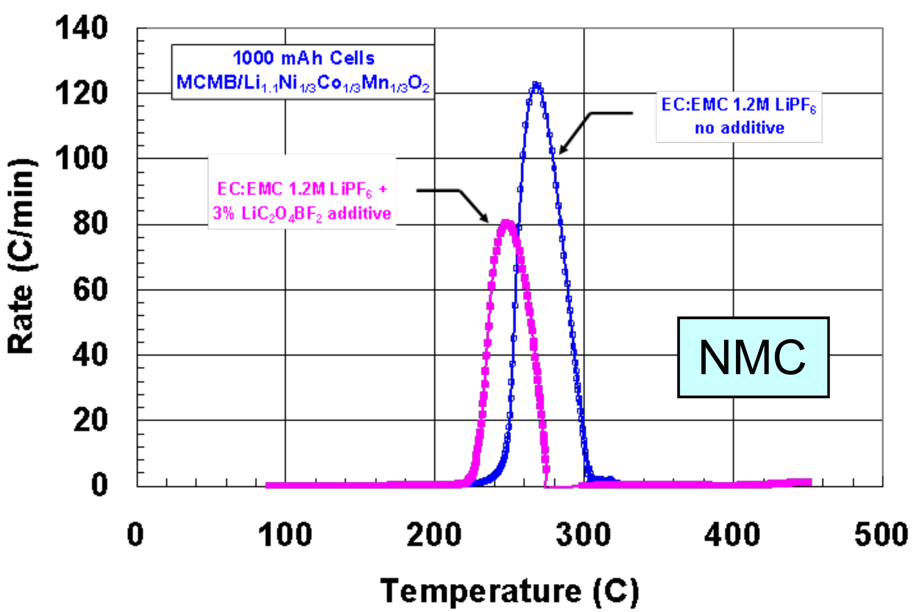
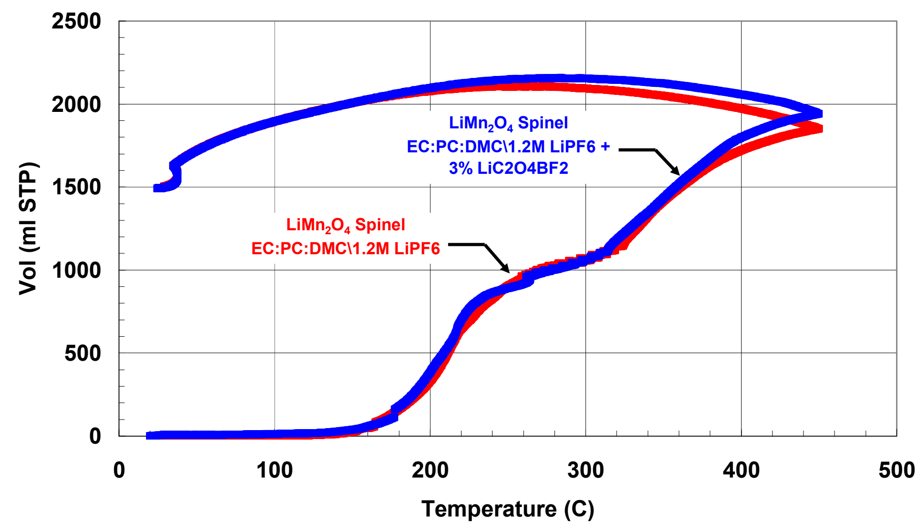
Reduced High-Temperature Thermal Reactions with Fluorinated LiBOB Additives

Addition of 3% $LiC_2O_4BF_2$ Reduces Low Temperature and High Temperature Reactions with No Increase in Gassing







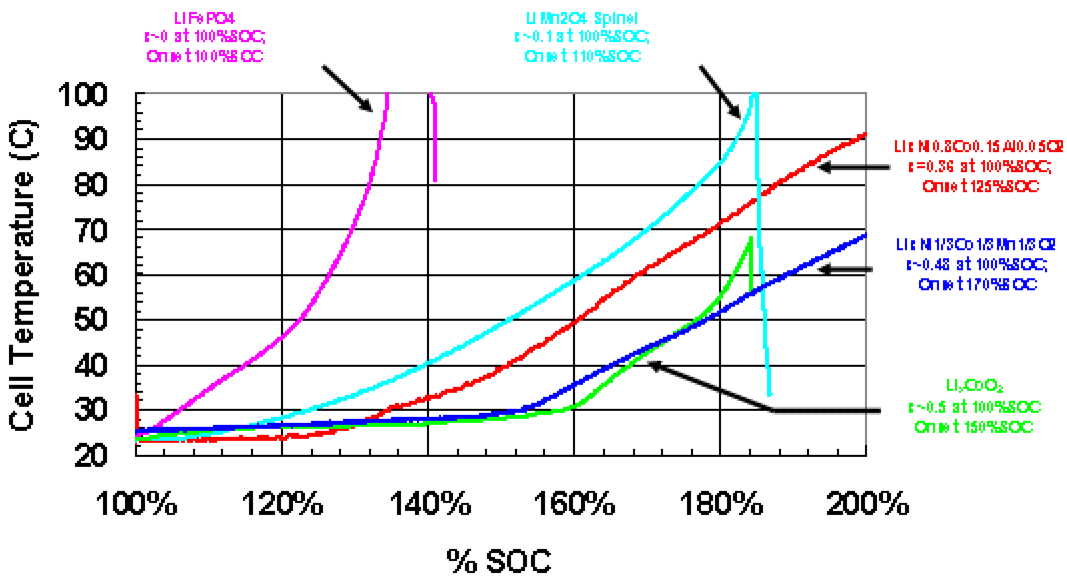
Overcharge Response

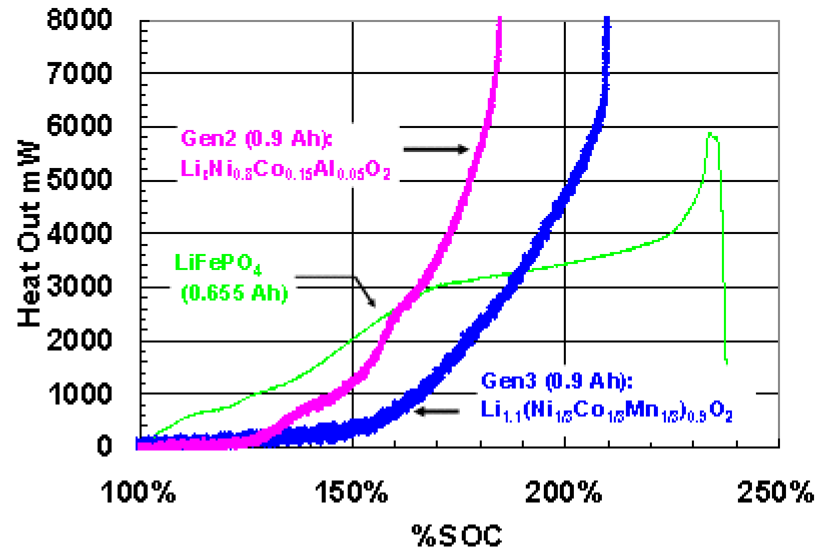
- Overcharge is one of the most energetic abuse conditions
  - Highly reactive, unstable cathode
  - Highly lithiated anode
- High levels of heat generation
  - Separator shutdown and possible internal short
  - Initiation of thermal decomposition runaway
- Flammable gas generation
  - Hydrogen
  - Venting of solvent vapors

$LiFePO_4$ Cells Show Greater Heating During Overcharge Compared to Other Cathode Oxides

Heat Generation Begins Immediately On Overcharge of $LiFePO_4$ Cells

Heat Generation Begins When Li Has Been Removed From Cathode





1C Overcharge

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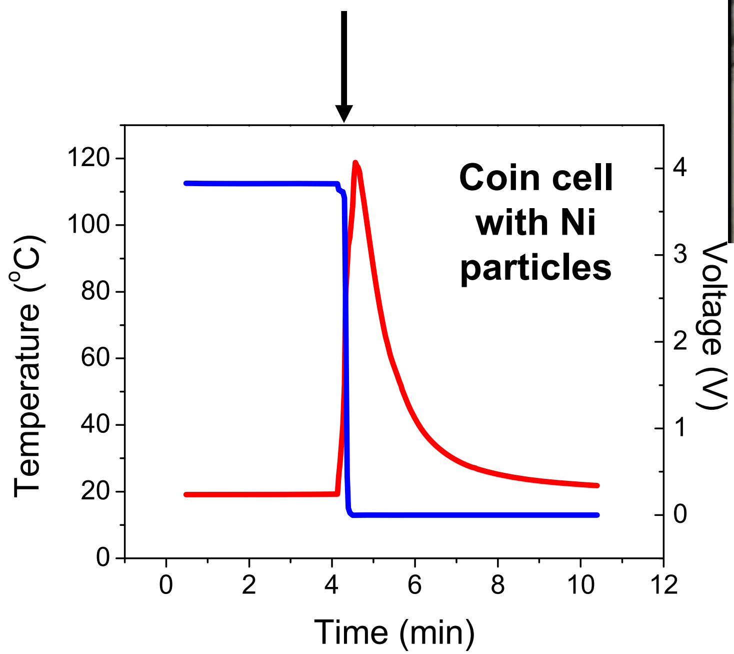
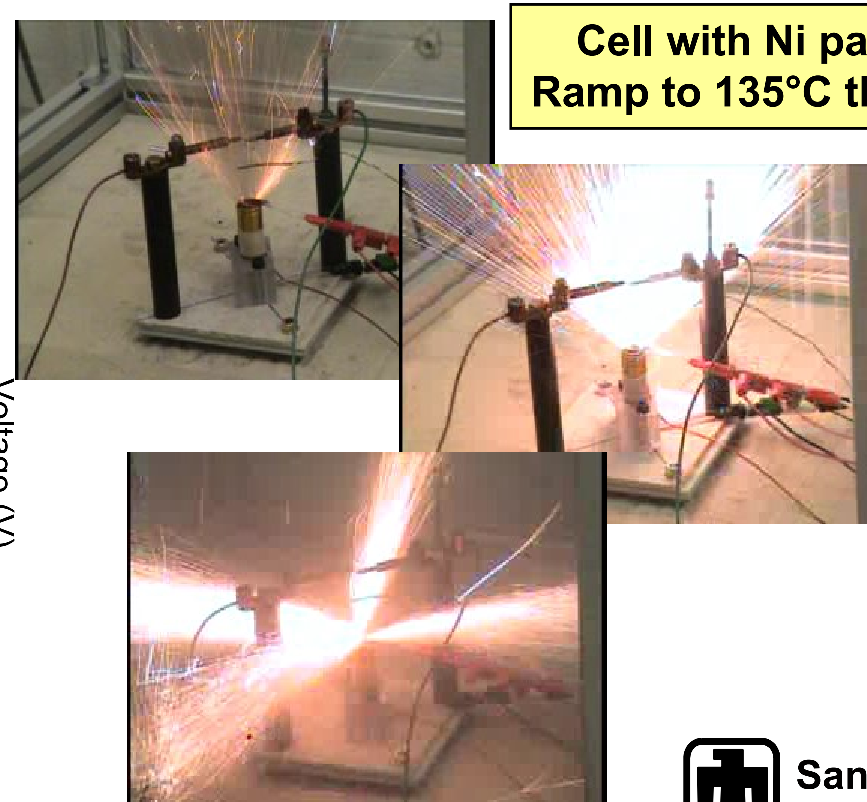
Induced Internal Shorts

Internal shorts have been induced in coin cells and full 18650 cells using defect particles and external stimulation

Ultrasonic pulse applied





Cell with Ni particles: Ramp to 135°C then short

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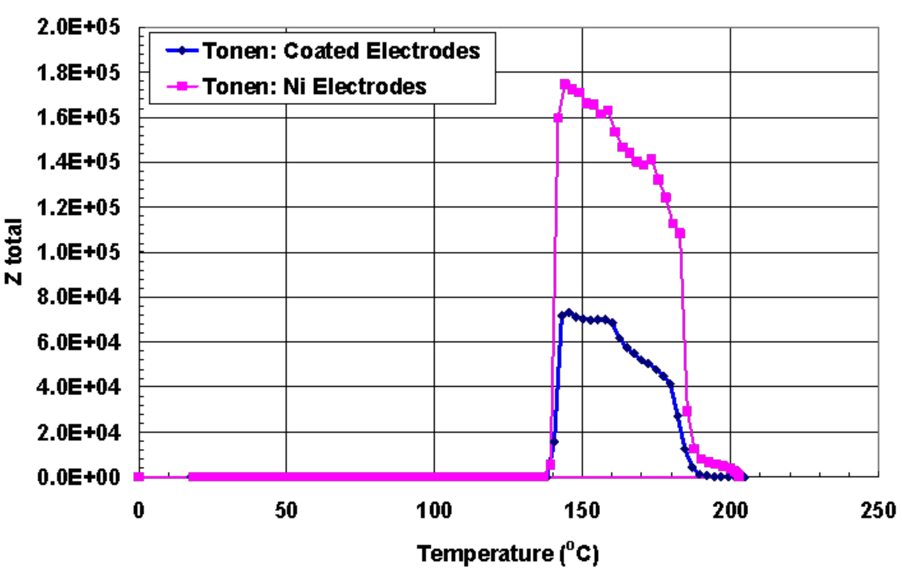
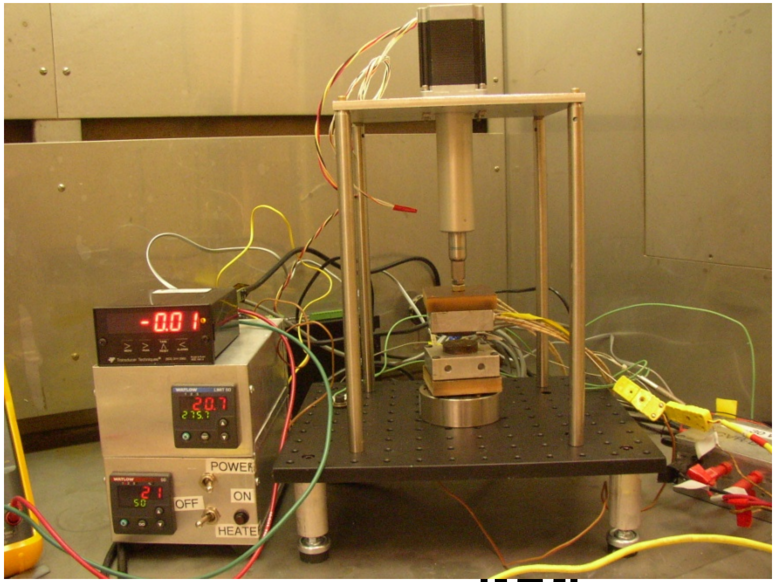
Separator Failure Characterization

Shutdown temperature is well defined.

Shutdown integrity affected by pressure and surface irregularities

Upgraded separator characterization apparatus with programmable load fixture to test for pressure induced separator failures with and without defect particles





Future Work

Emphasis On New PHEV, High Energy Density Materials

- Develop an enhanced stability cell by conducting quantitative cell-level abuse studies to verify material enhancements (e.g. AlF_3 coated NMC cathodes).
- Demonstrate improved overcharge abuse tolerance in full cells with new materials and additives.
- Demonstrate reduced electrolyte gas generation under full-cell abuse conditions using non-PF_6 salts with increased temperature and voltage stability.
- Support development of an abuse model using measured cell material properties that will allow prediction of cell abuse response for any given cell design and failure mode (e.g. internal short).

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Summary

- Increased thermal stability has been demonstrated with more stable cathodes ($LiMn_2O_4$ Spinel and $LiFePO_4$)
  - Improved stability results from decreased oxygen generation
- Anode reactions are still important to provide better abuse tolerance
- Certain additives can reduce thermal reactions under abuse conditions
- Electrolyte gas generation and flammability still a critical issue
- Separator integrity is a critical to cell abuse tolerance and safe operation