Abuse Tolerance Improvement

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Albuquerque, NM

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

FreedomCAR & Fuel Partnership

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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.

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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.**

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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)

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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

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Summary of Accomplishments

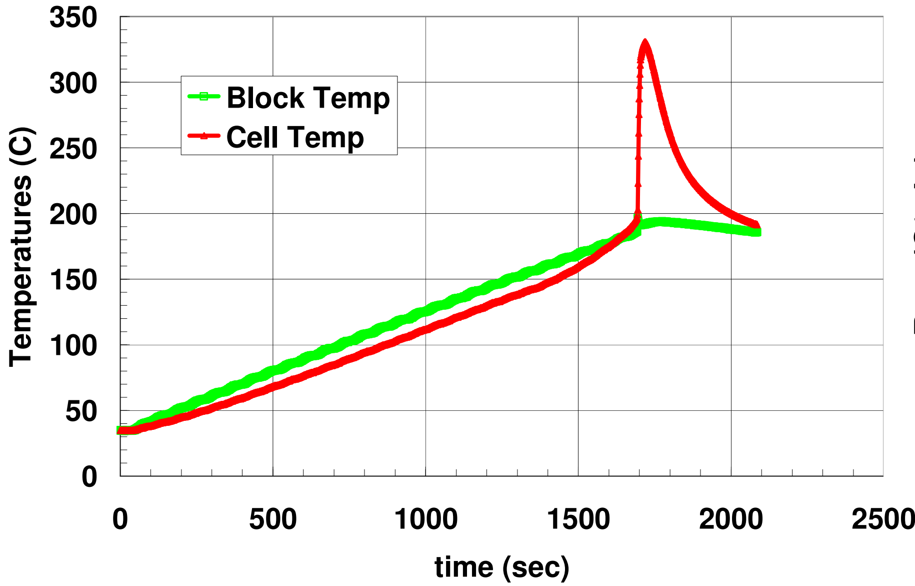
- Demonstrate Improved Thermal Abuse Response in High Power Cells
  - Expanded quantitative measurements of thermal runaway over a broader range of materials ($LiCoO_2$, Spinels, $LiFePO_4$) demonstrating much reduced reactions
  - Characterized electrolyte composition and additives that reduce peak 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 H_2 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

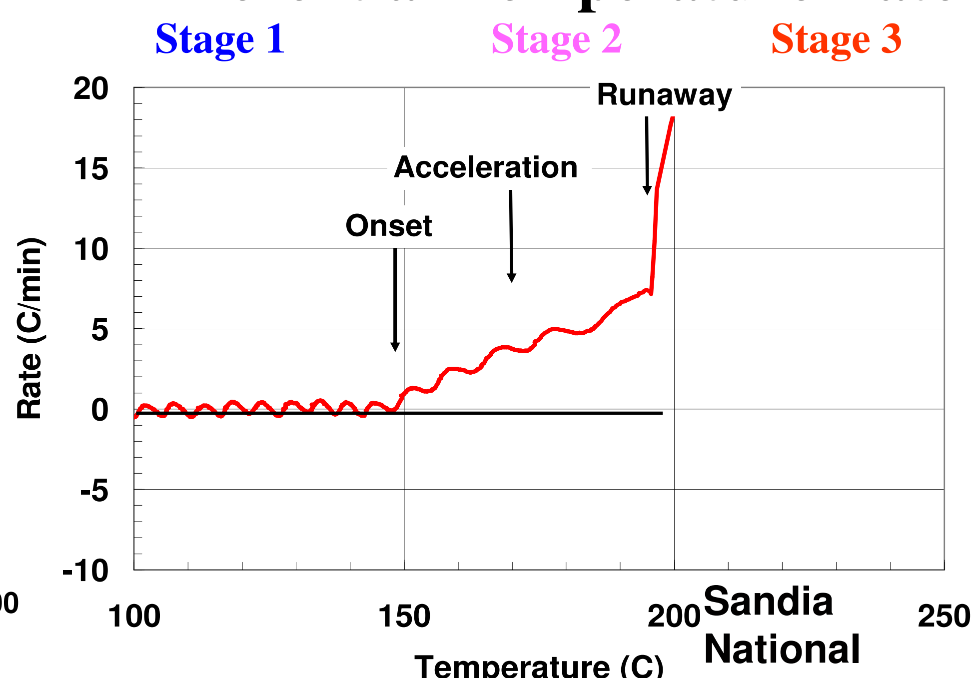
Thermal Ramp Response (100% SOC)

- 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



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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

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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)
  - $LiMn_2O_4$ (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; …

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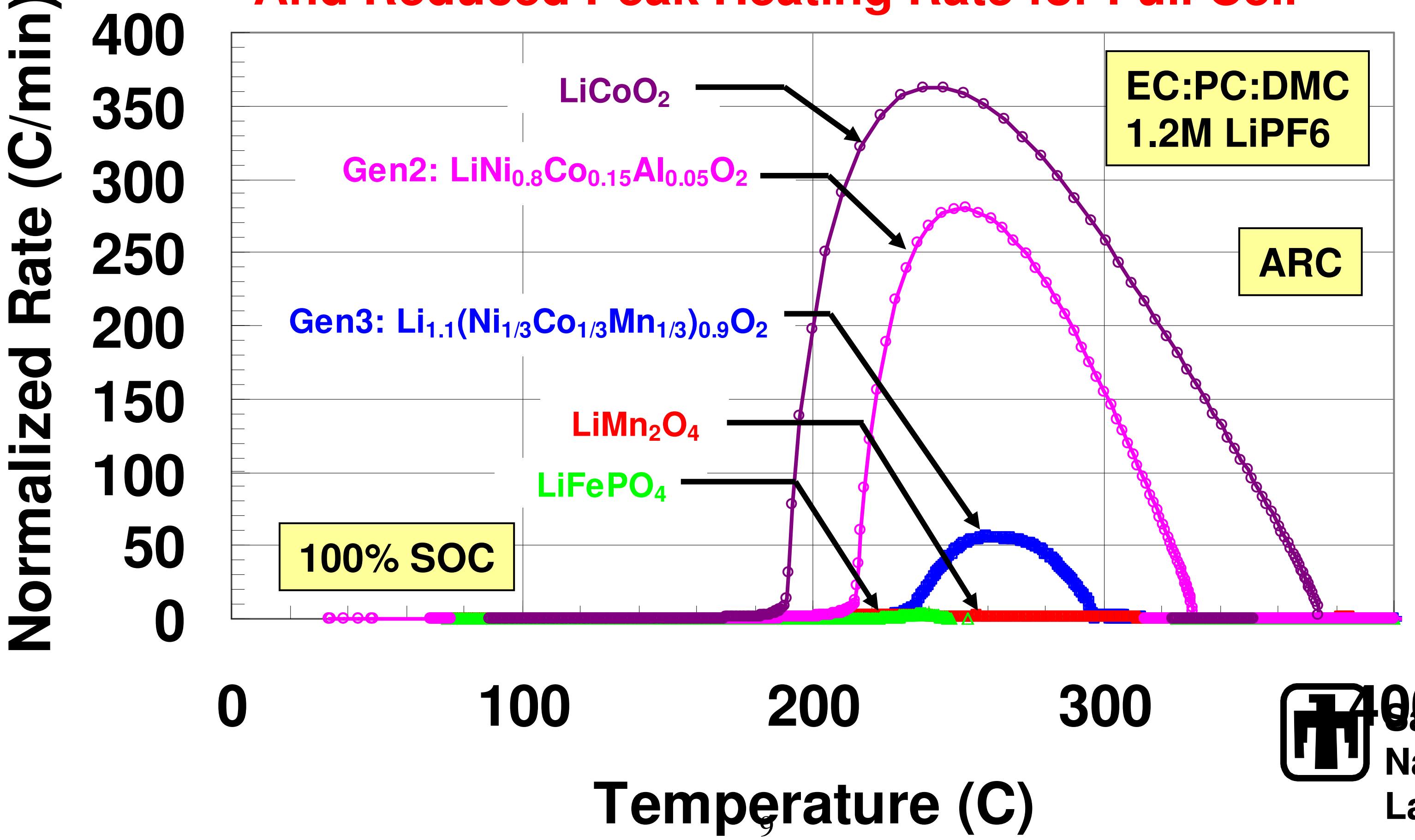
Thermal Runaway Cathode Comparisons

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



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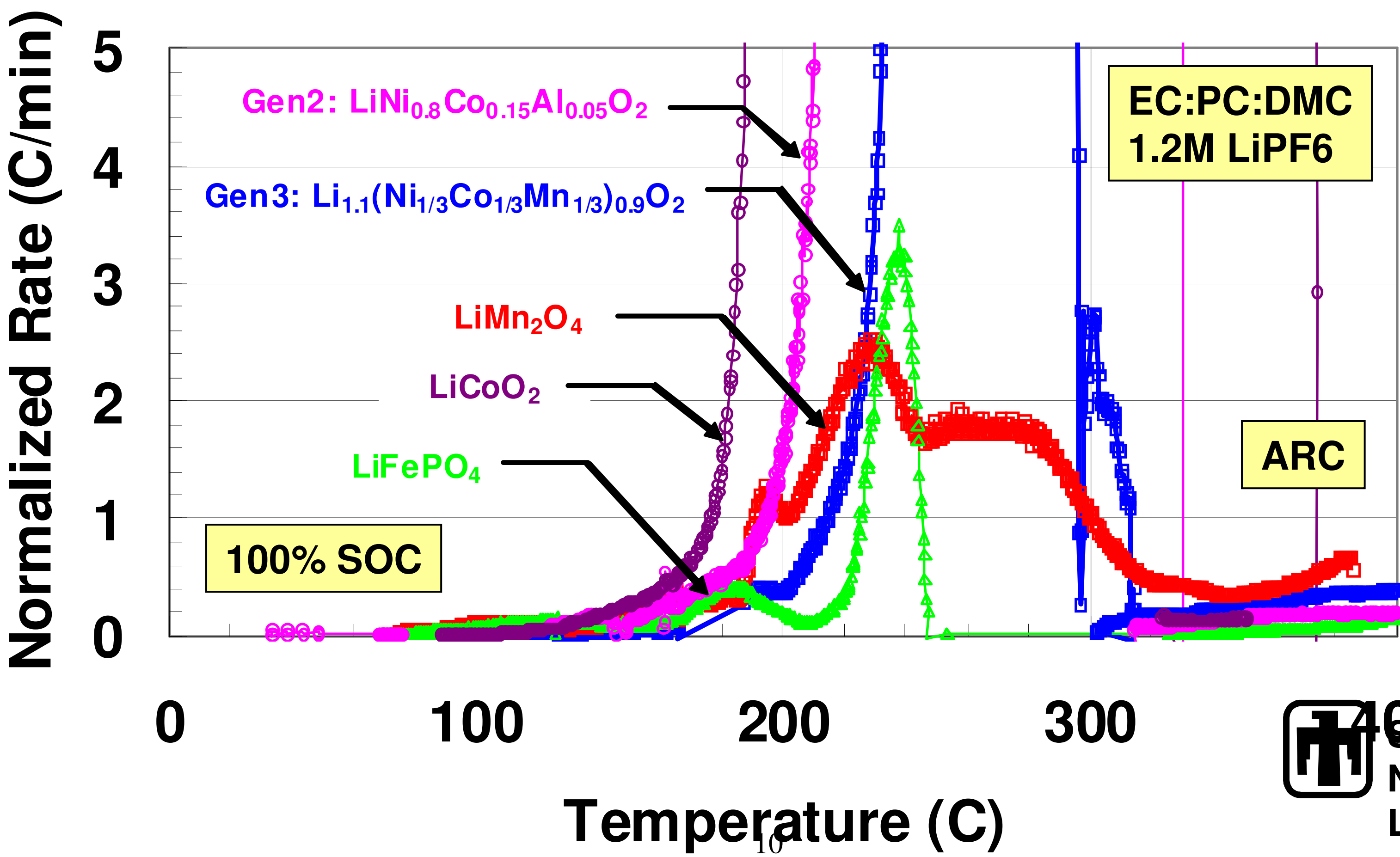
Thermal Runaway Cathode Comparisons (Expanded View)

Initial Onset Reactions Dominated by Anode

Cathode Reaction Onset 160℃-180℃



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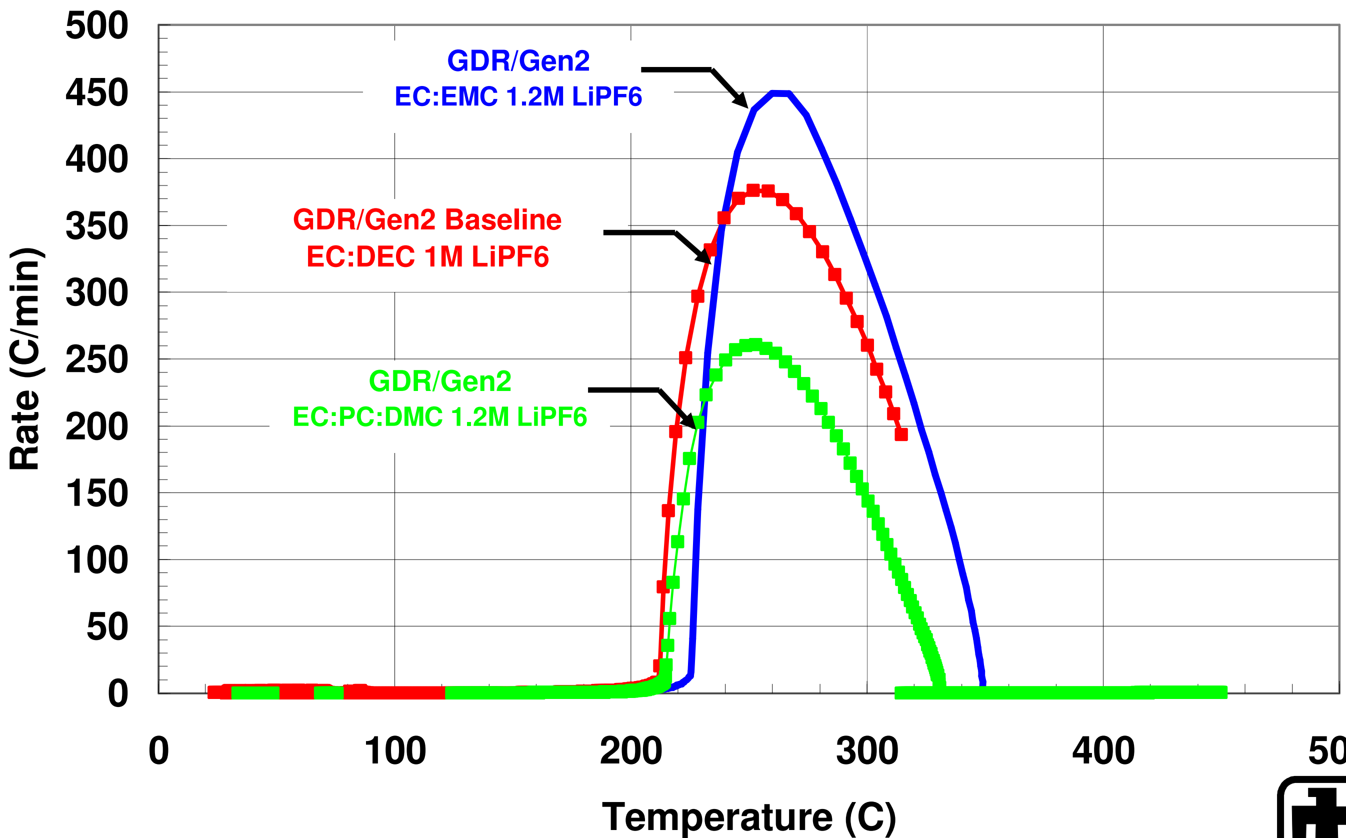
Solvent Composition Affects Peak Reaction Kinetics

EC:PC:DMC\LiPF$_6$ electrolyte has shown the greatest reduction in reaction rate



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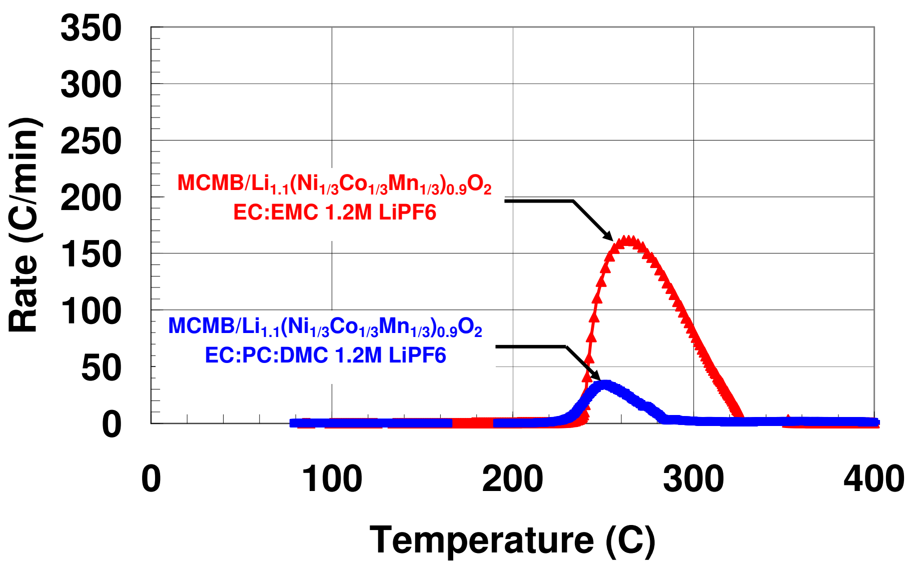
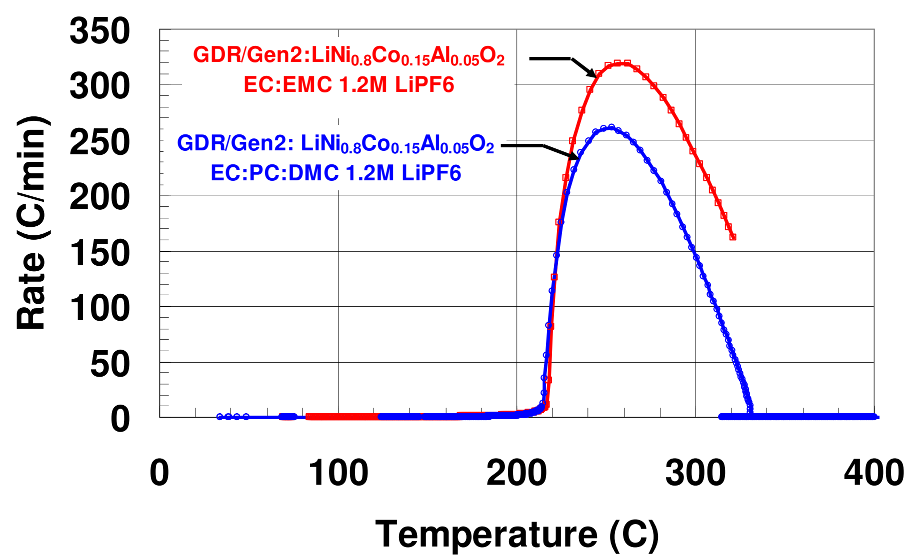
Reduction in Enthalpy and Reaction Rate with EC:PC:DMC Solvents

EC:PC:DMC\LiPF$_6$ electrolyte has shown reduction in reaction rate for the two main cathode chemistries studied

(Gen3)
$Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$



(Gen2)
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$



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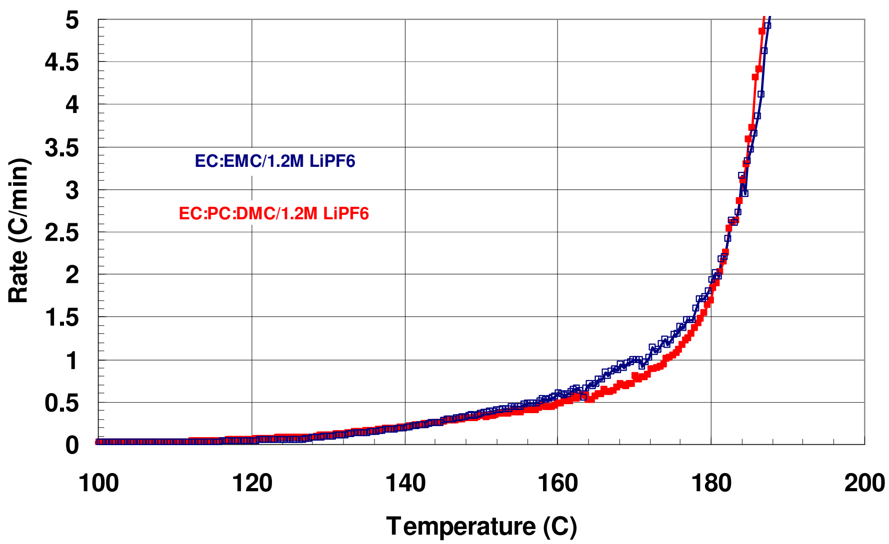
Reduction in Electrode\Electrolyte Reactions Seen for $LiCoO_2$ with EC:PC:DMC Solvents

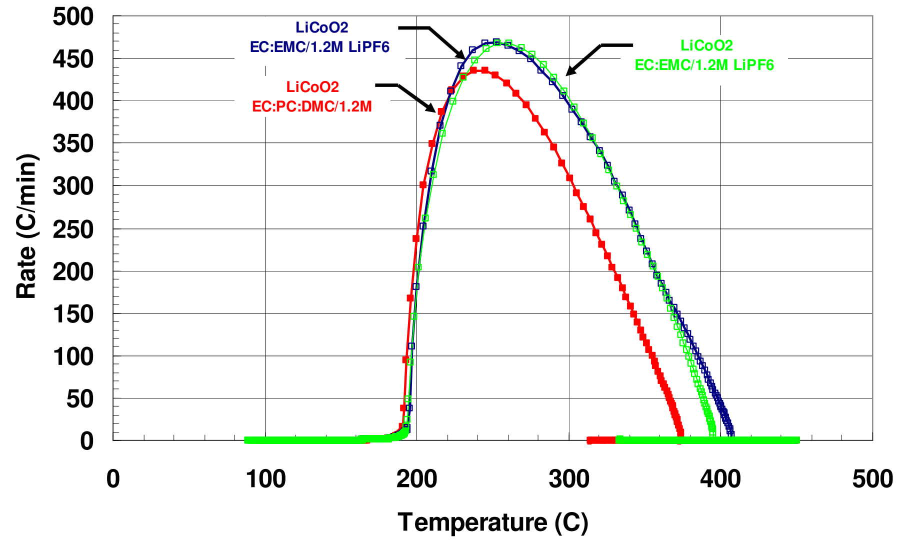
Little Difference in Reaction Rate at Temperatures Below 200°C Implies Difference in Reaction not at Cathode Surface Prior to Cathode Decomposition

LiCoO2



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

$LiCoO_2$



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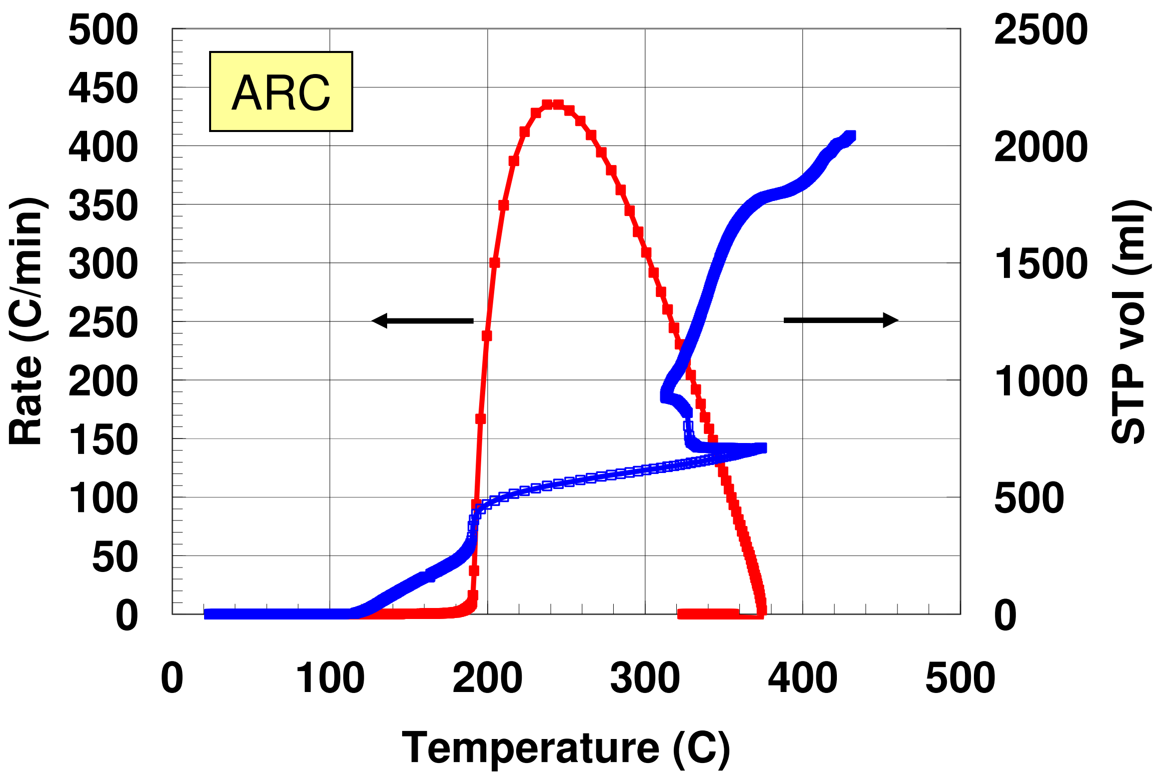
Gas Evolution is a Critical Property Affecting Safety

Peak Gas Generation Volume Similar for Different Cathodes with Same Electrolyte (EC:PC:DMC\$LiPF_6$)

Total Gas Generation up to 450°C Comparable for all Chemistries



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

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

Cathode	Peak Gas Vol.
$LiCoO_2$	900-1000 ml
Gen2	600-900 ml
Gen3	900-1000 ml
$LiMn_2O_4$	700 ml
$LiFePO_4$ (Elec. ?)	500 ml

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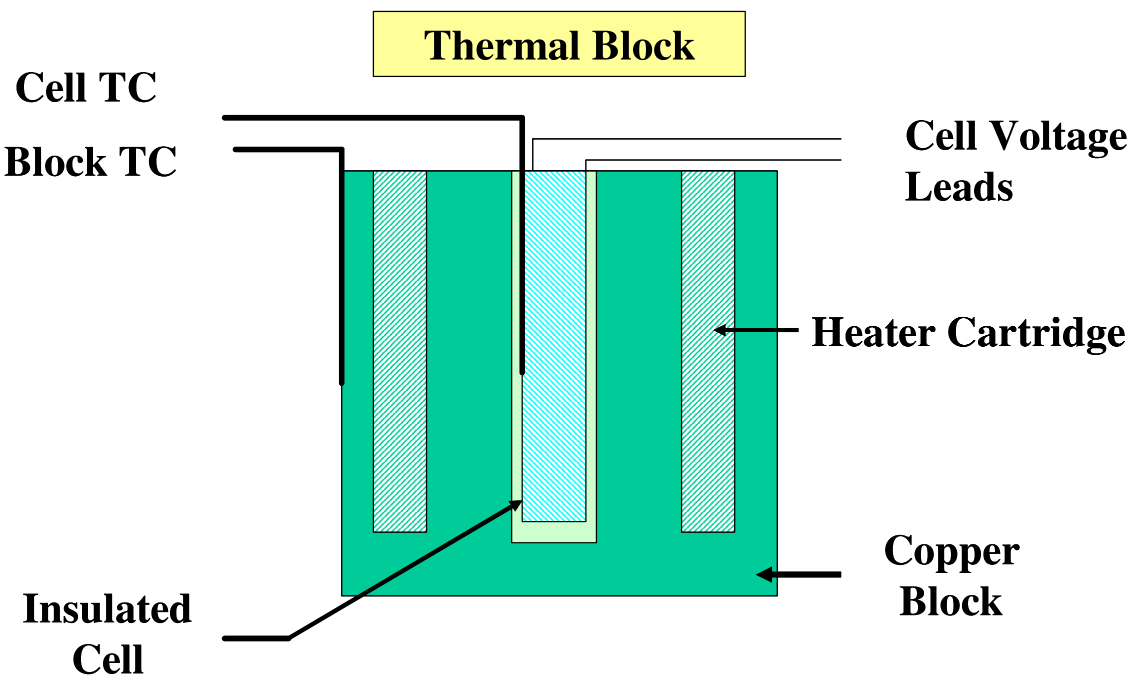
Thermal Ramp Apparatus

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.



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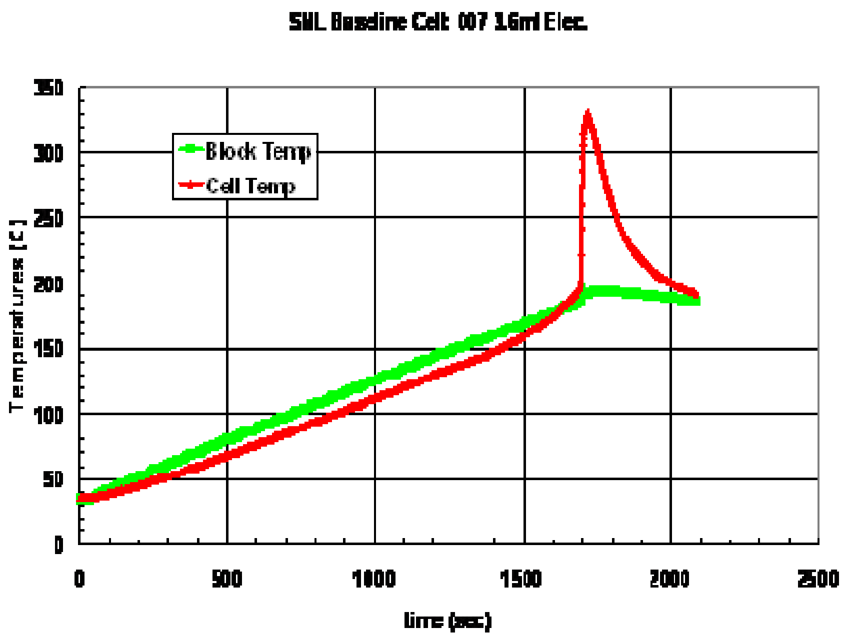
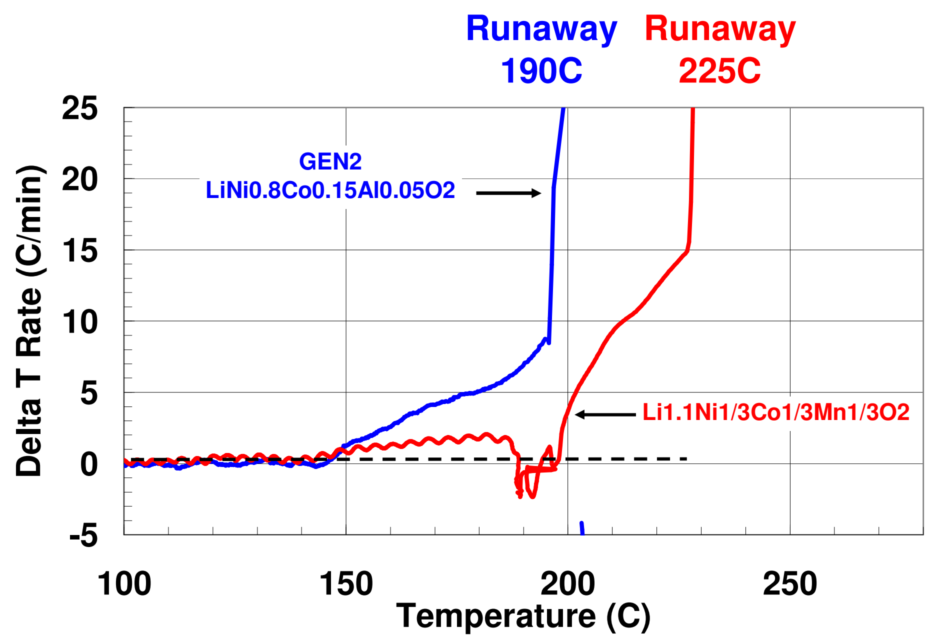
Thermal Ramp Shows Improved Abuse Response For Gen3 Cells as Seen by ARC Measurements

Heating Block and Cell Temperatures



Cell Heating Rates



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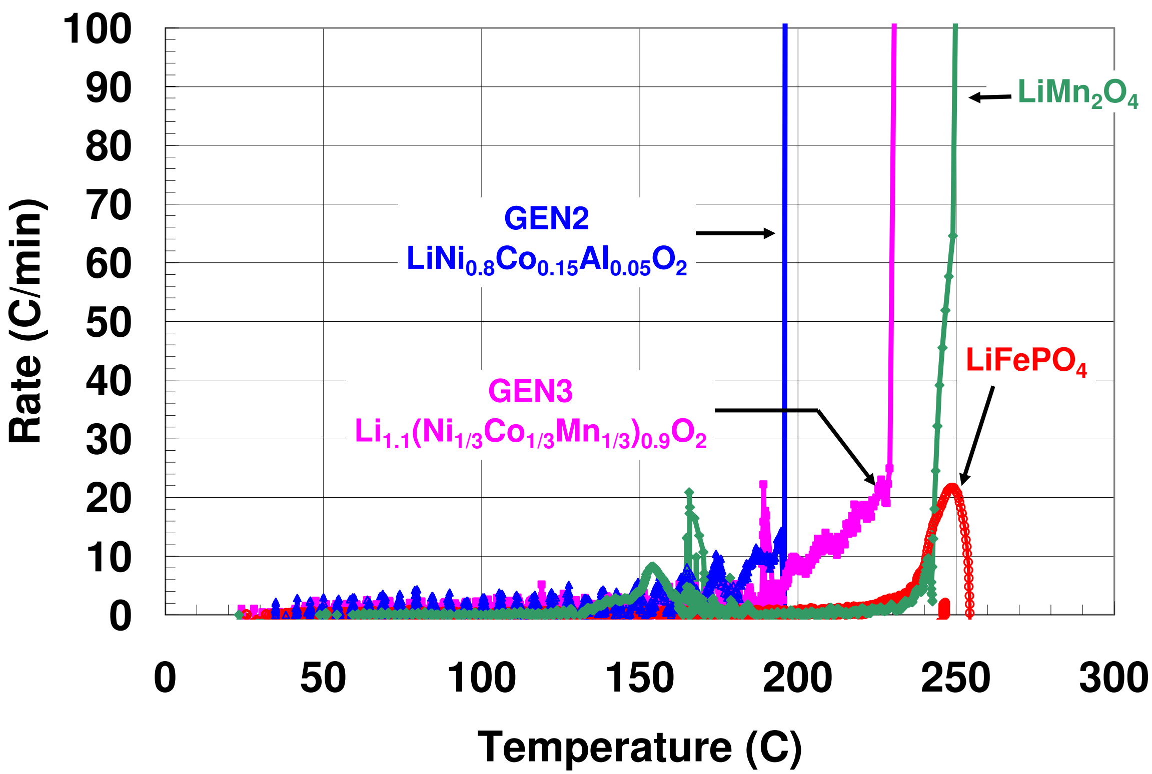
Greater Abuse Tolerance Shown for New Chemistries with Reduced or No Cathode Oxygen Release

Anode Reactions Still Contribute to Runaway



$LiFePO_4$ Nanophosphate Cells Provided by A123

$LiFePO_4$ olivine cathodes show the greatest reduction in heating rate and increased onset temperature for runaway

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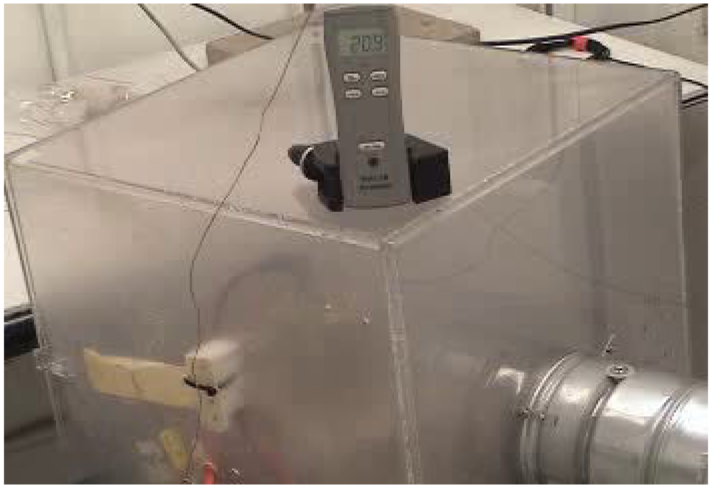
Movie Clips of Cell Thermal Runaway Showing Improved Response of $LiFePO_4$

50% Li/Ni/Co/Mn and 50% $LiMn_2O_4$ Cell

A123 $LiFePO_4$ Cell



Explosive Combustion of Vent Gases (mostly solvent vapors)

100% SOC

26650 Commercial Cells

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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

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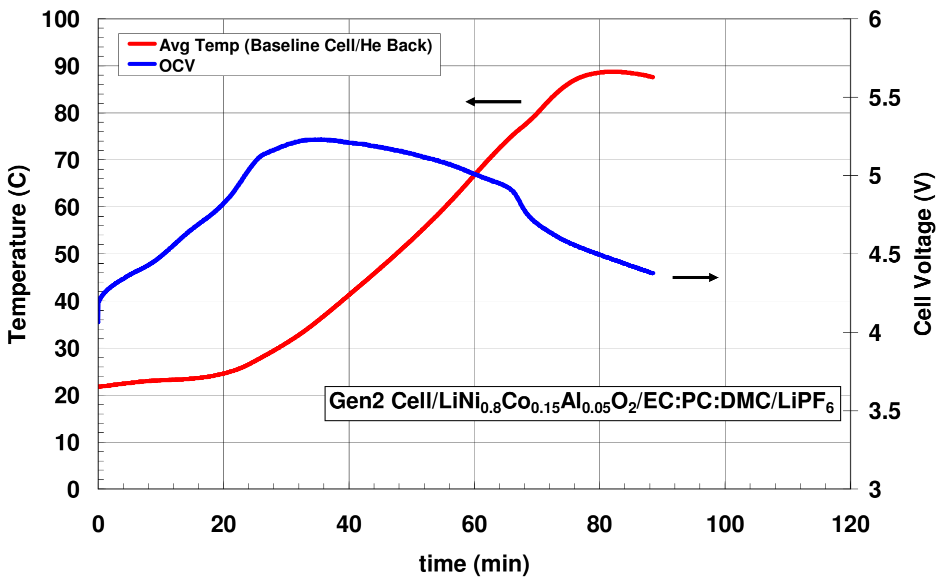
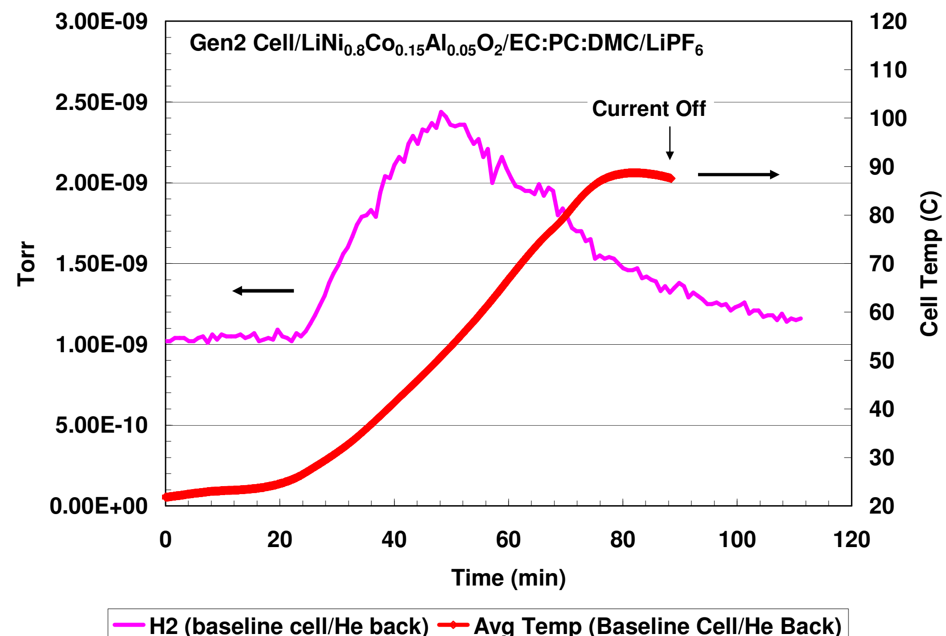
Sequence of Gas Generation During Overcharge

- 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





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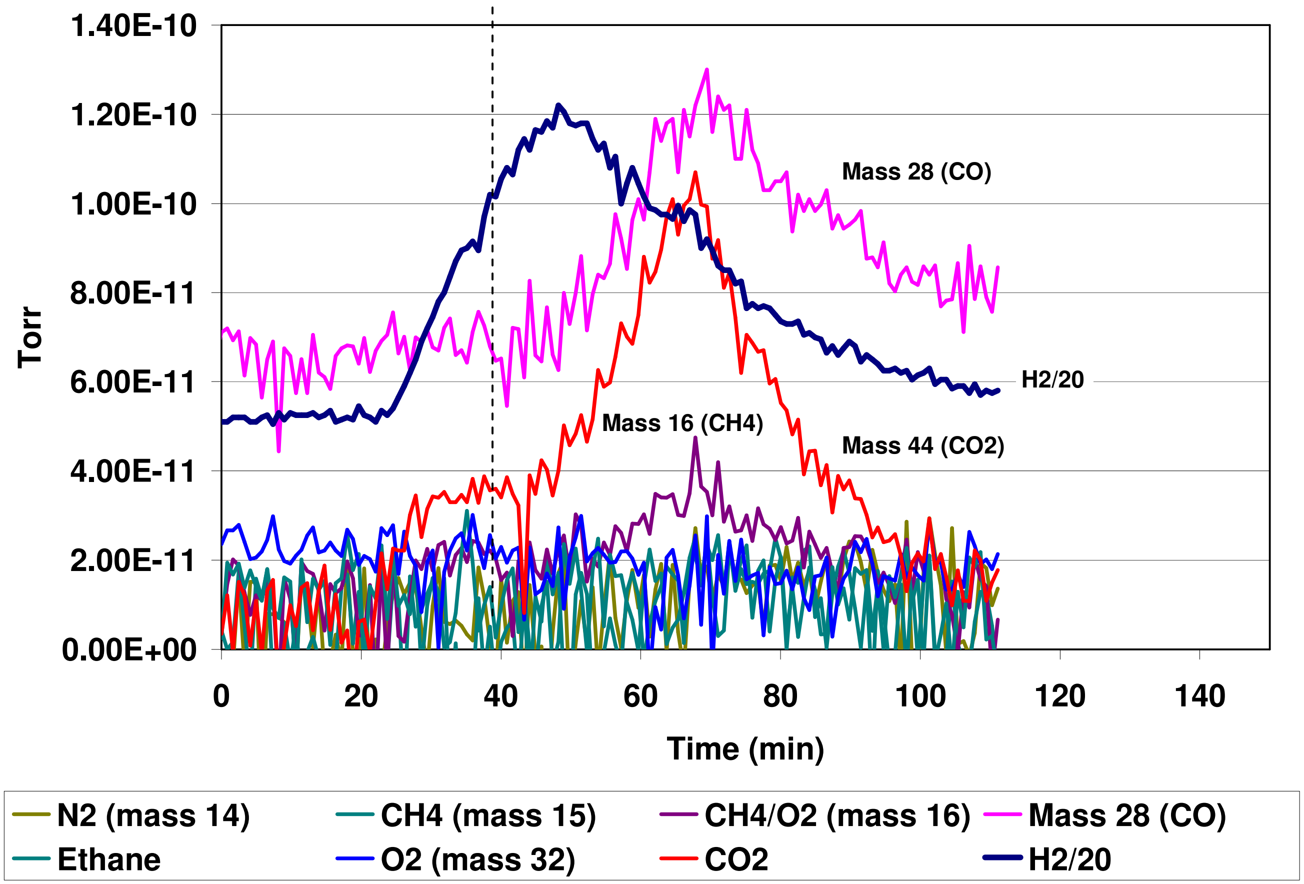
Gas Species Detected

Hydrogen\\CO_2 Generation Precedes Generation of Other Gas Species



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Abuse Response Improved with Electrolyte Additives

- Additives to improve:
  - SEI
    - VEC, VC
  - Electrolyte stability
    - LiBOB, LiBETI
  - Overcharge
    - **Shuttle Additives**
  - Flammability
    - Phosphazenes
    - Phosphates

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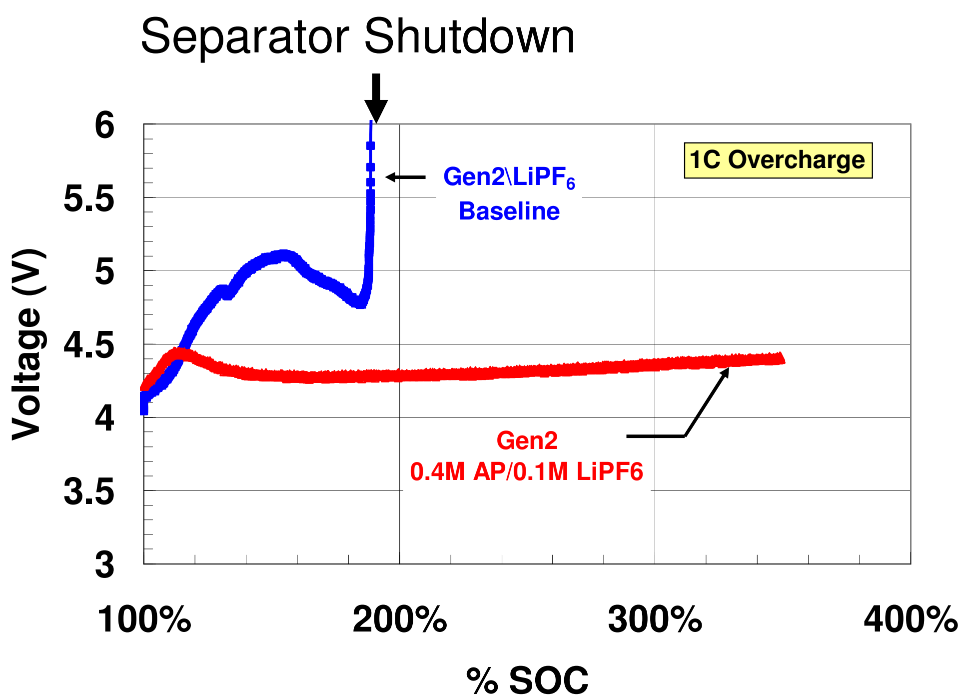
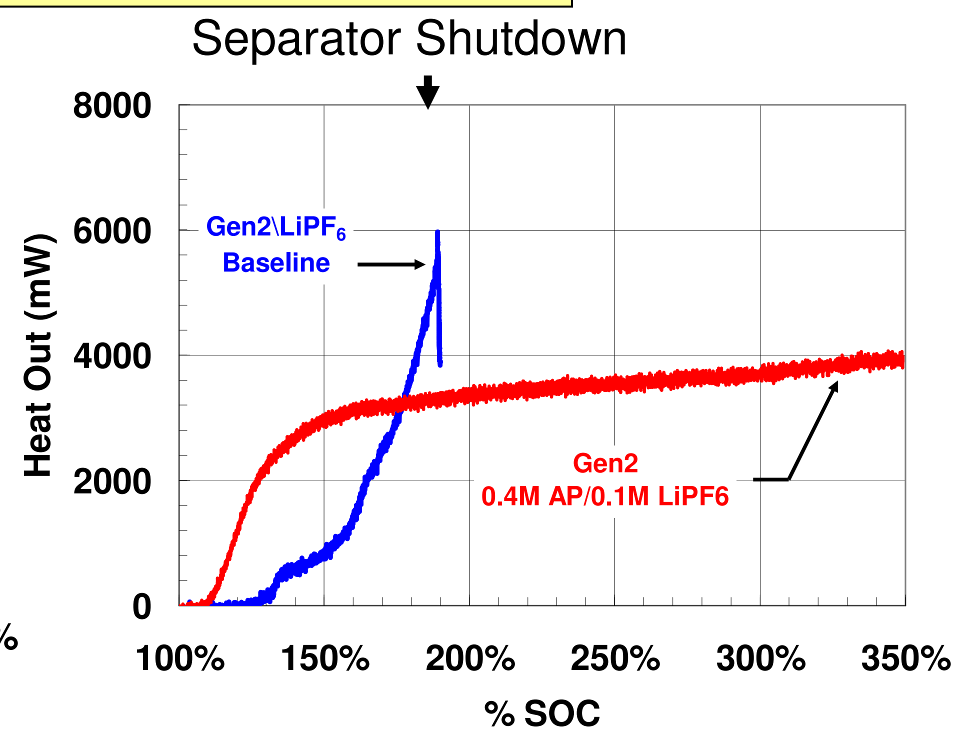
Overcharge is One the Most Abusive Conditions for Li-ion Cells: Improved Response with Overcharge Additive

0.4M $Li_2B_{12}F_9H_3$ and 0.1M $LiPF_6$ in EC/DEC (3:7)

Shuttle Mechanism Limits Cell Voltage and Peak Heating Rate During Overcharge





Material developed by Air Products and Chemicals, Inc.

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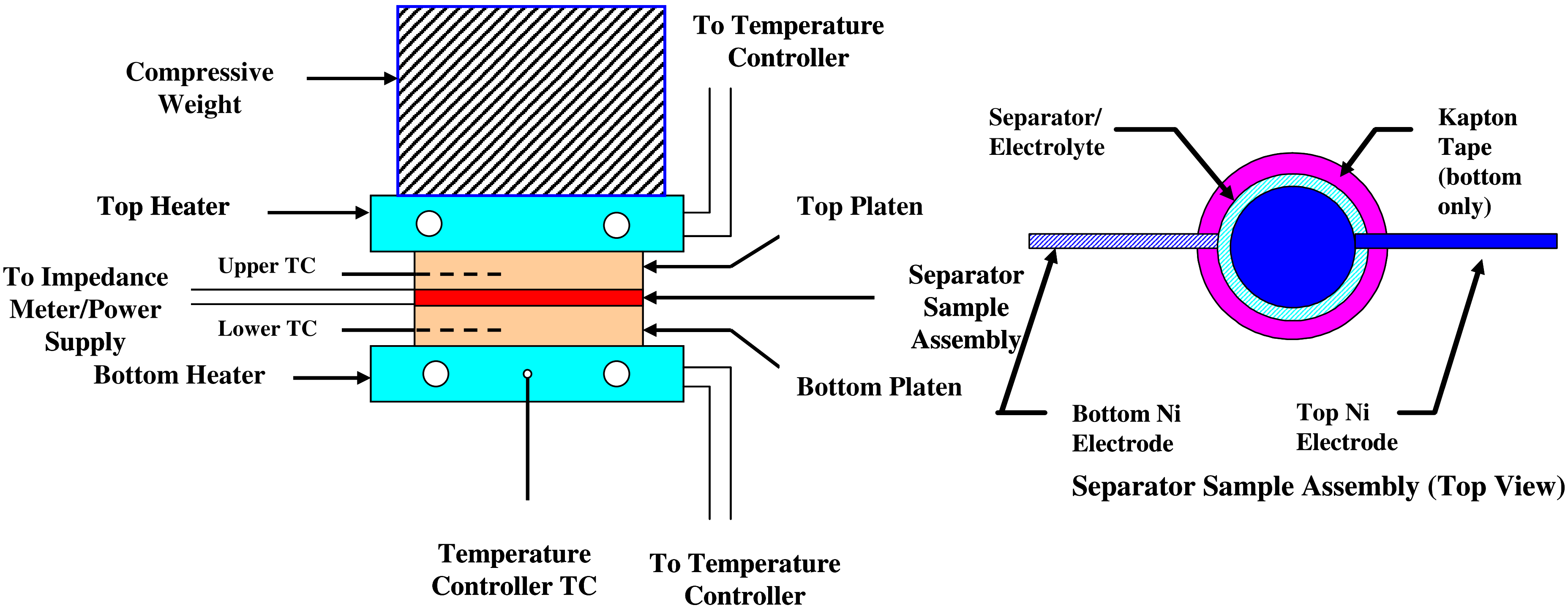
III. Separator Failure
Results in High-Rate Cell Failure for Several Abuse Conditions

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



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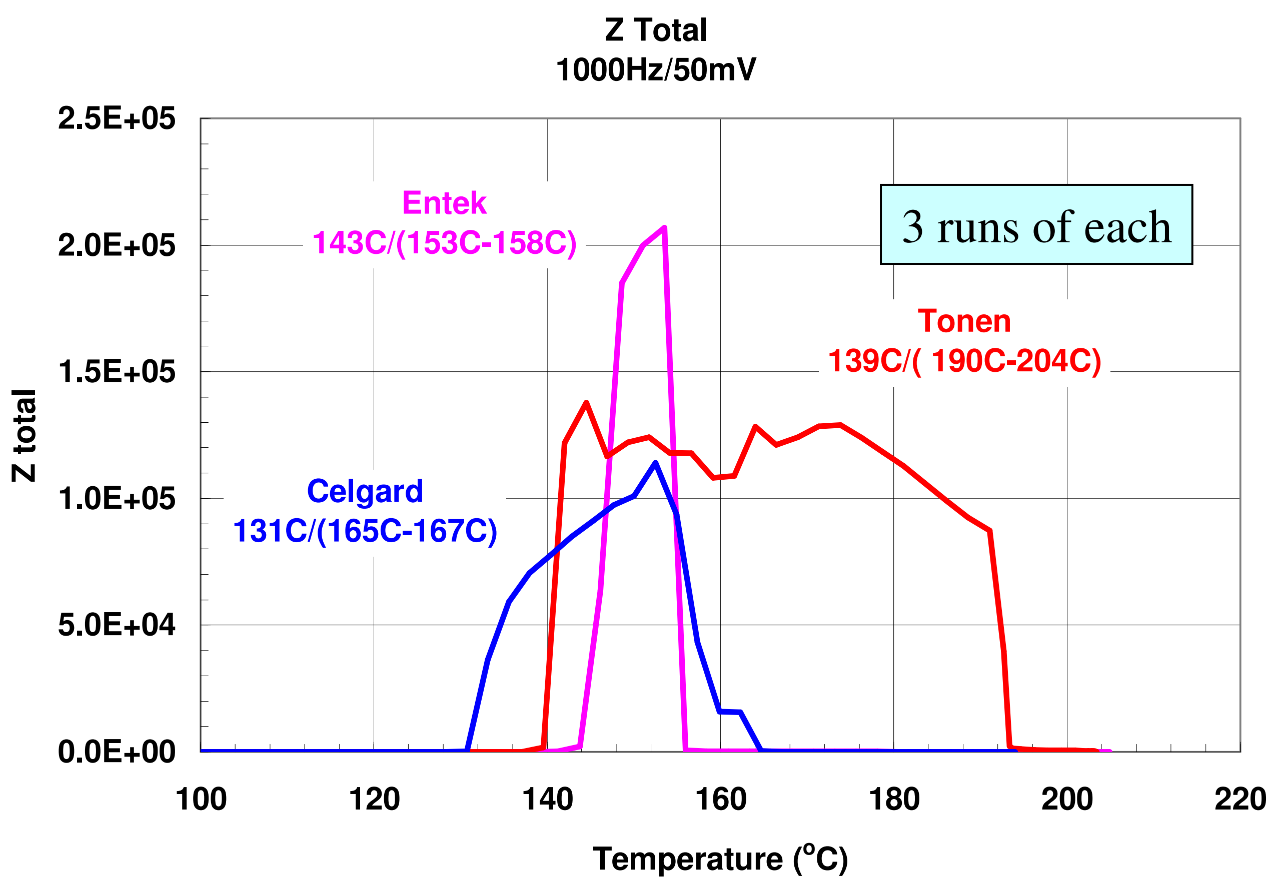
Separator Impedance During Thermal Ramp

Polyethylene-based shutdown separators



Shutdown temperature is well defined.

Upper integrity temperature varies over broader temperature range, affected by pressure and surface irregularities.

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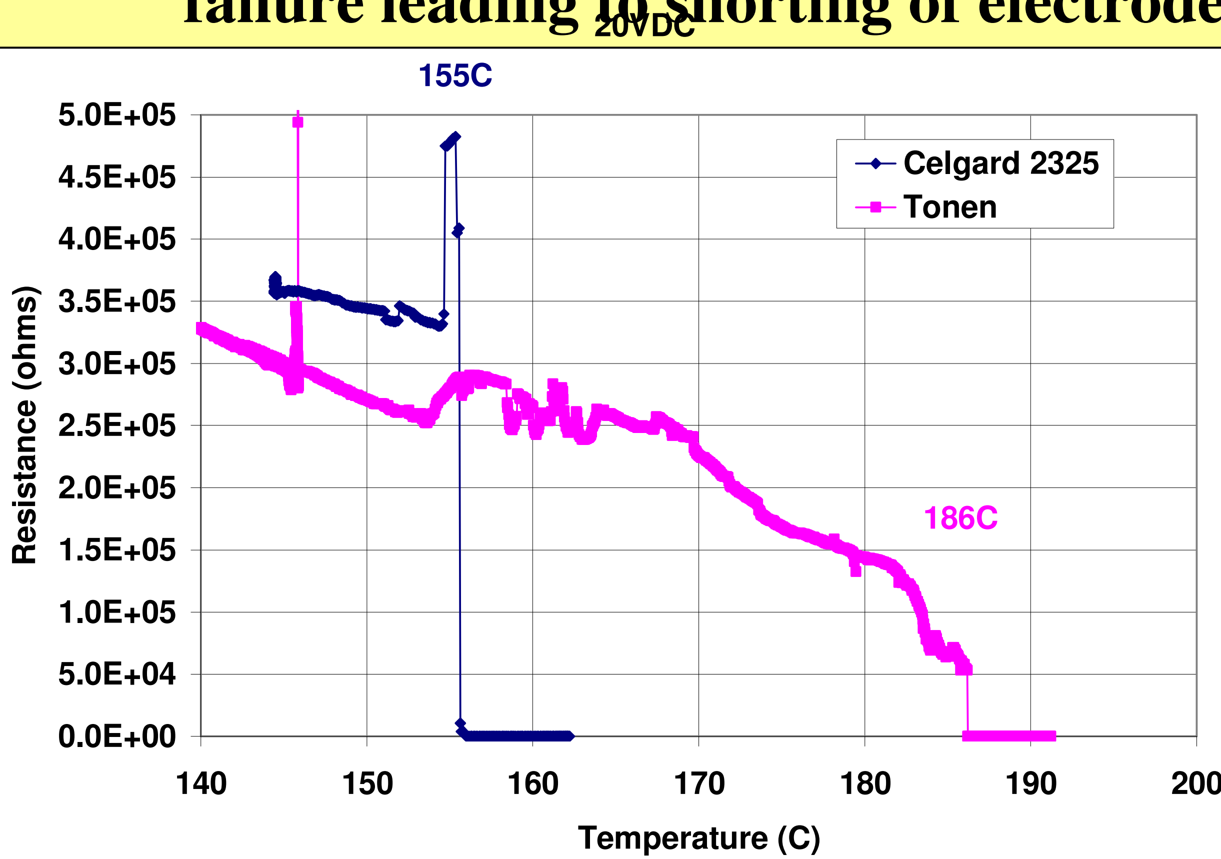
Separator Voltage Integrity

DC Resistance Above Shutdown

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



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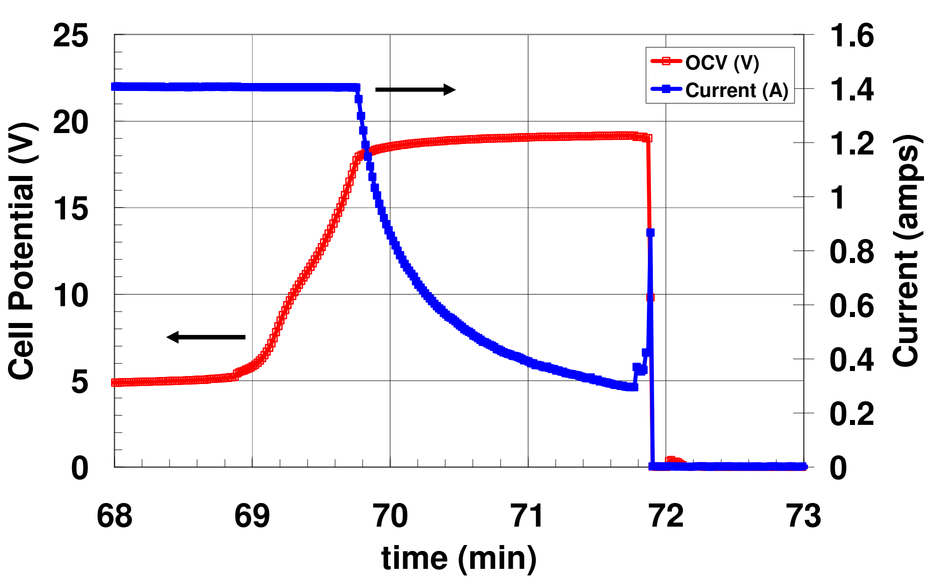
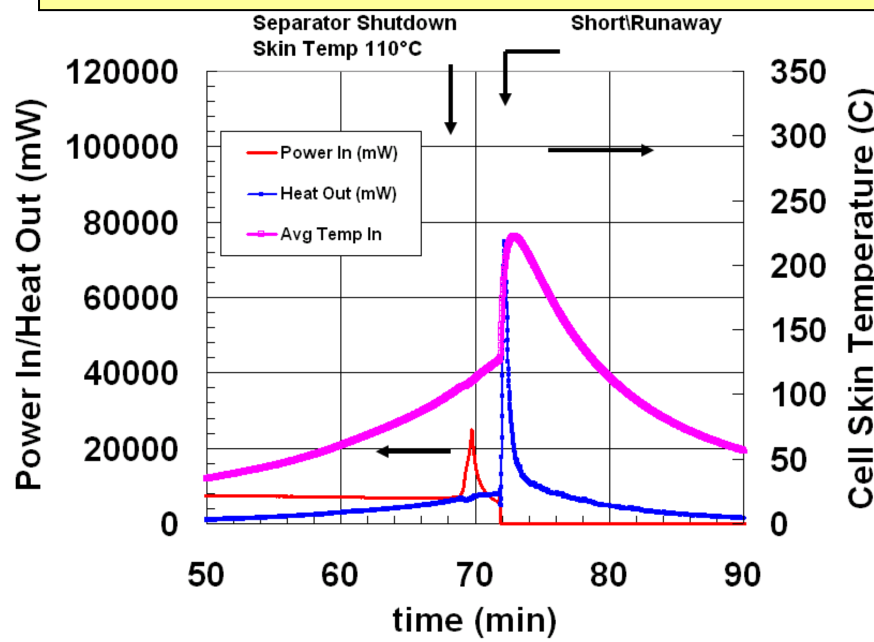
Separator Breakdown and Cell Thermal Runaway

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

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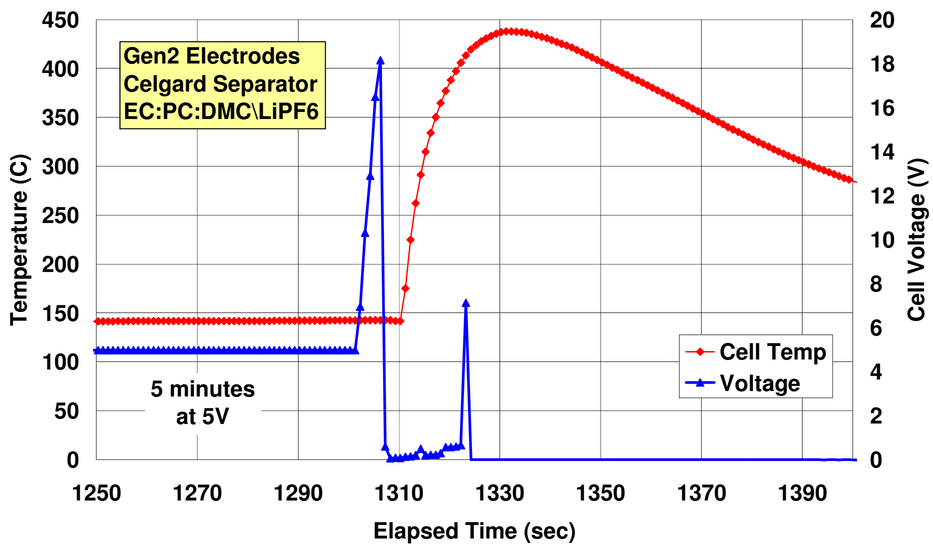
Forced Internal Shorts

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

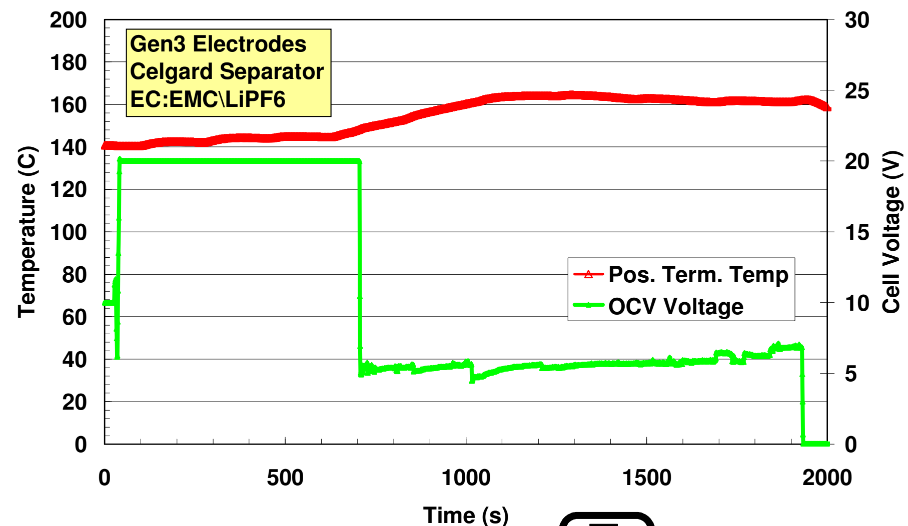
Hard Short Leading to Thermal Runaway

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)



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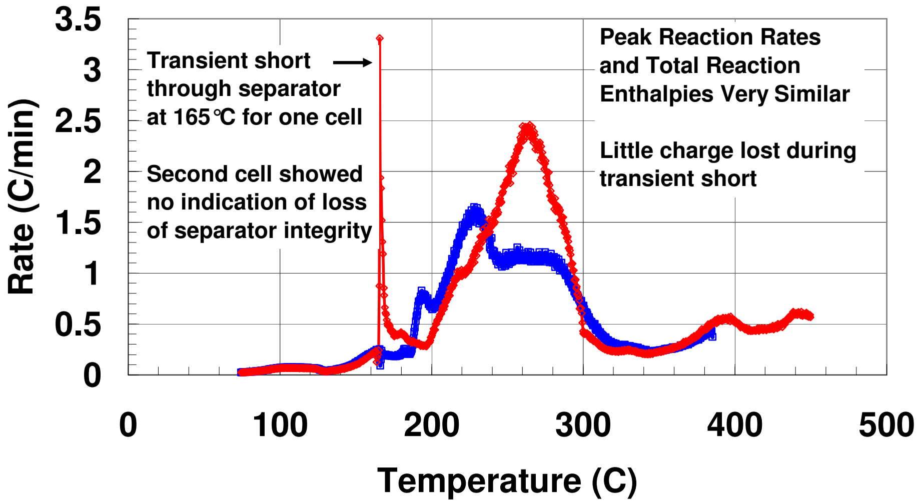
Internal Short With Self-Healing

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

MCMB/$LiMn_2O_4$ Spinel/EC:PC:DMC\1.2M $LiPF_6$
Two Identical Cells: 0.65 Ah



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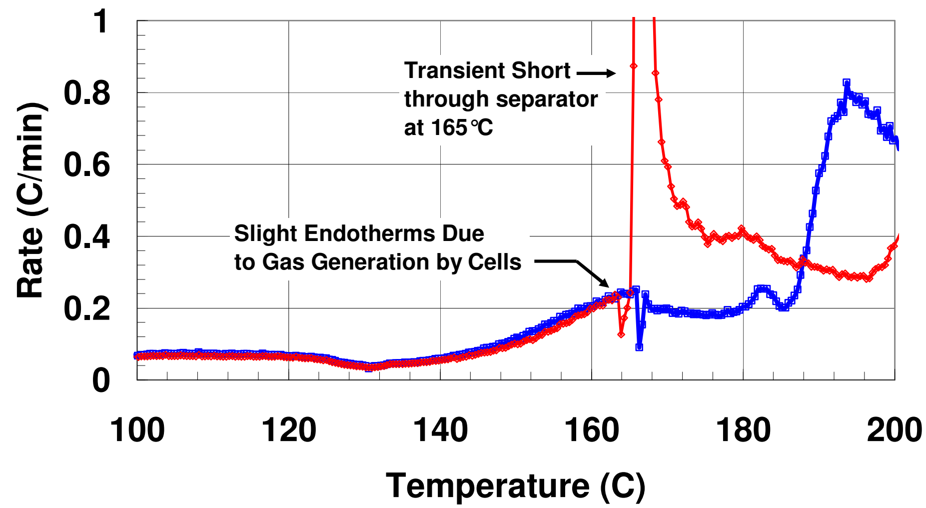

ARC

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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 ($Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$; $LiMn_2O_4$ Spinel and LiFePO4)*

– *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*

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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)

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Publications and Presentations FY07 - Present

- **Publications**
  - Effects of Separator Breakdown on Abuse Response of 18650 Li-Ion Cells, E.P. Roth, D.H. Doughty, D.L. Pile, *Journal of Power Sources,* 174 (2007) 579-583
  - 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
  - Abuse Tolerance Issues for Li Ion Cells, Lithium Mobile Power 2007, E. P. Roth, Chapter 6, 2nd Edition Proceedings.
- **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 Battery Abuse Tolerance Testing - An Overview , E. P. Roth, D. H. Johnson, 75th Battery Safety Mtg., Feb. 21-22, 2007, Albuquerque, NM
  - Li-Ion Batteries: Safety and Abuse Tolerance Issues, E. P. Roth, MIT/Industry Consortium on Advanced Automotive Electrical/ Electronic Components and System Program Review Meeting, Apr. 11-13, 2007, Seattle, WA
  - 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.,
  - Abuse Tolerance Issues for Li-Ion Cells, E. P. Roth, 3rd Annual Conference - LITHIUM MOBILE POWER 2007 - Advances in Lithium Battery Technologies for Mobile Applications, San Diego, CA, Oct. 29-30, 2007

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.

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