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Cell Level Abuse Tests Of HEV\PHEV Li-Ion Chemistries

Advanced Technology Development

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Li-Ion Safety Issues

Abuse Tolerance is a Critical Requirement for Li-Ion Battery Development and Application

There are two main modes for failure:

- **Field Failures**
  - Failures during normal use
    - Rare (less than one in a million)
    - Not predictable
    - Abrupt, high-rate reactions often resulting in cell disassembly and fire
    - Cause usually attributed to manufacturing defects
- **Abuse Failures**
  - Failures due to external factors exceeding normal design limits
    - Mechanical (crush, nail penetration, shock)
    - Thermal (over temperature)
    - Electrical (short circuit, overcharge)

Cell Chemistries Evaluated in DOE Advanced Technology Development (ATD) Program

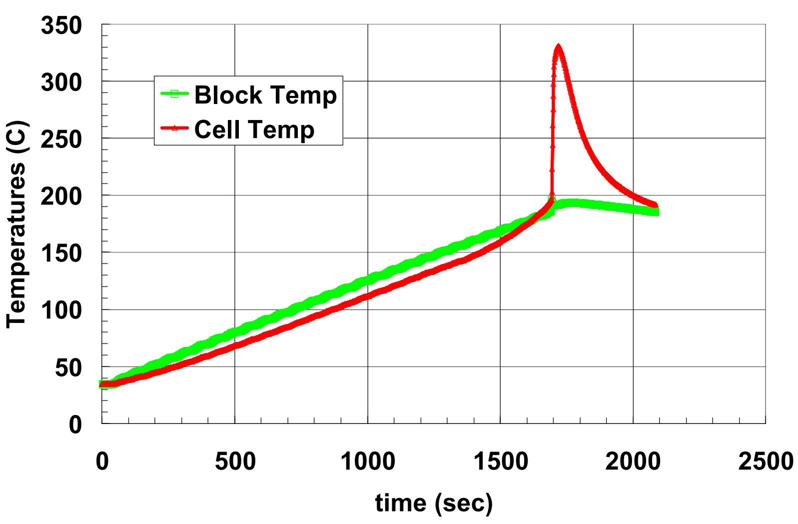
- **Cathode materials:**
  - $LiCoO_2$
  - $LiNi_{0.85}Co_{0.15}O_2$ (Gen1)
  - $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (Gen2);
  - $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$; $Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$ (Gen3)
  - $LiMn_2O_4$ (Spinel)
  - $LiFePO_4$
- **Anode materials:**
  - MCMB (Gen1 and 3)
  - 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; …

Thermal Runaway Can Be Grouped Into Three Major Temperature Regimes

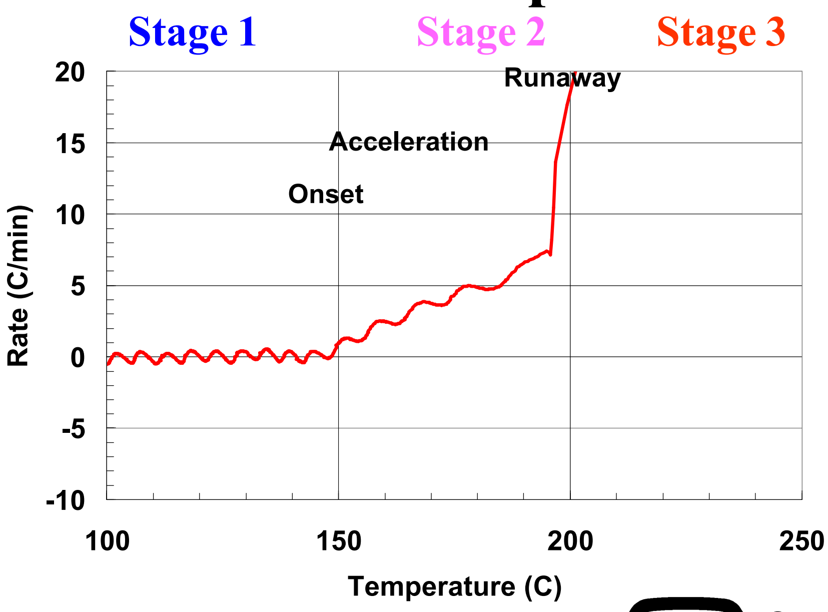
Thermal Ramp Response (100% SOC)

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

Ramp Temperatures



Differential Temperature Rate



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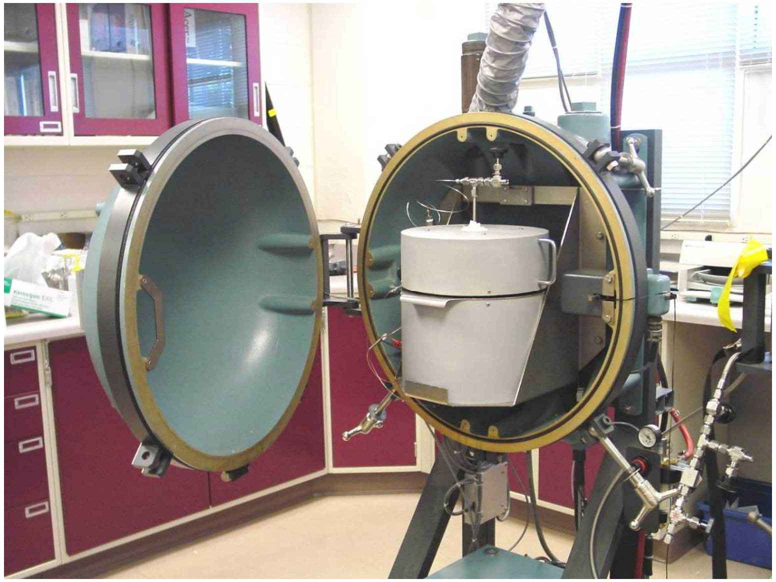
Thermal Runaway Characterization by Accelerating Rate Calorimetry (ARC)

ARC Apparatus for Measurement of Full Cells with Gas Capture



Top Heater

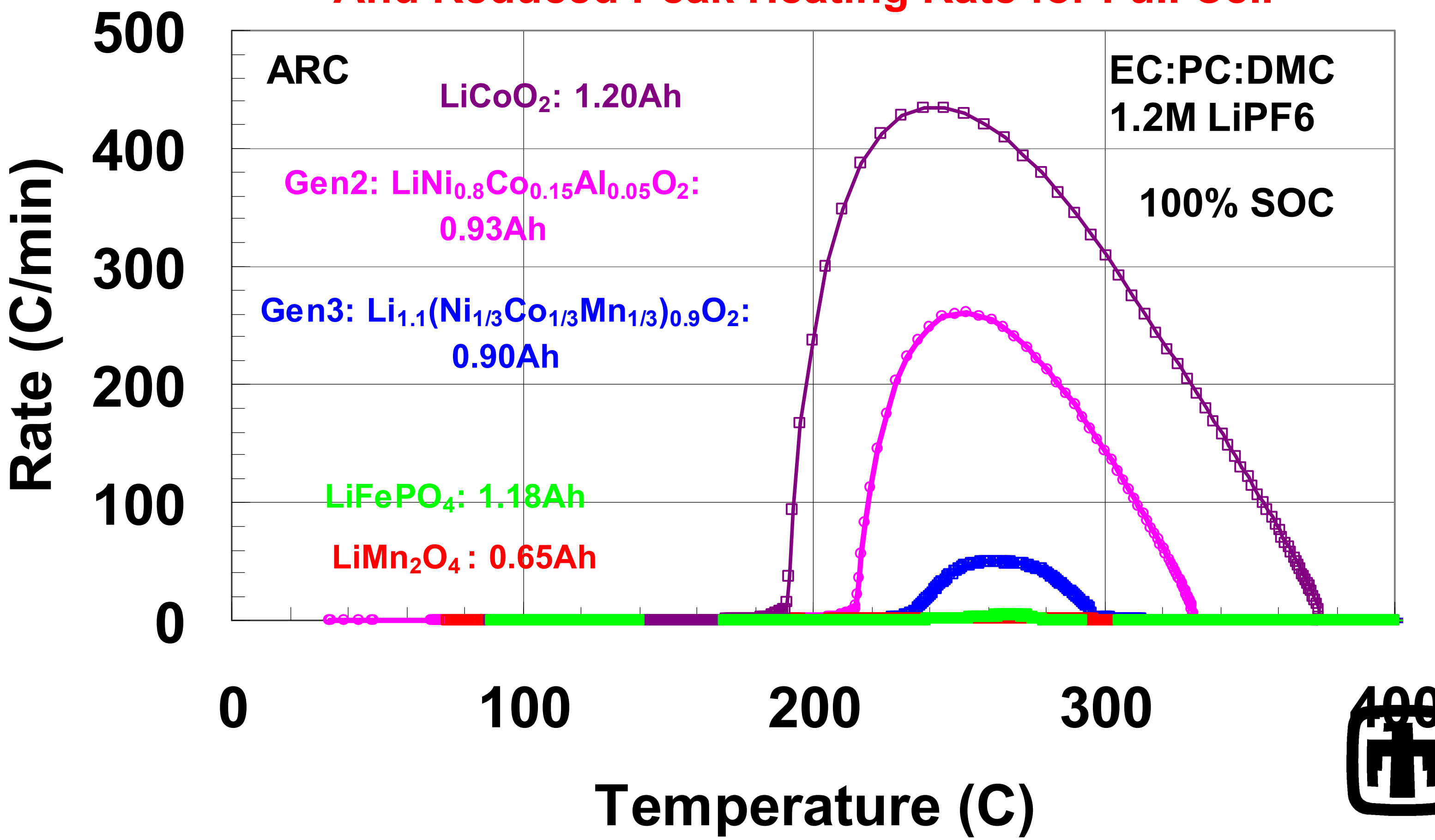
Gas Tight Cell Holder

Clam Shell Blast Shield

Heating Unit

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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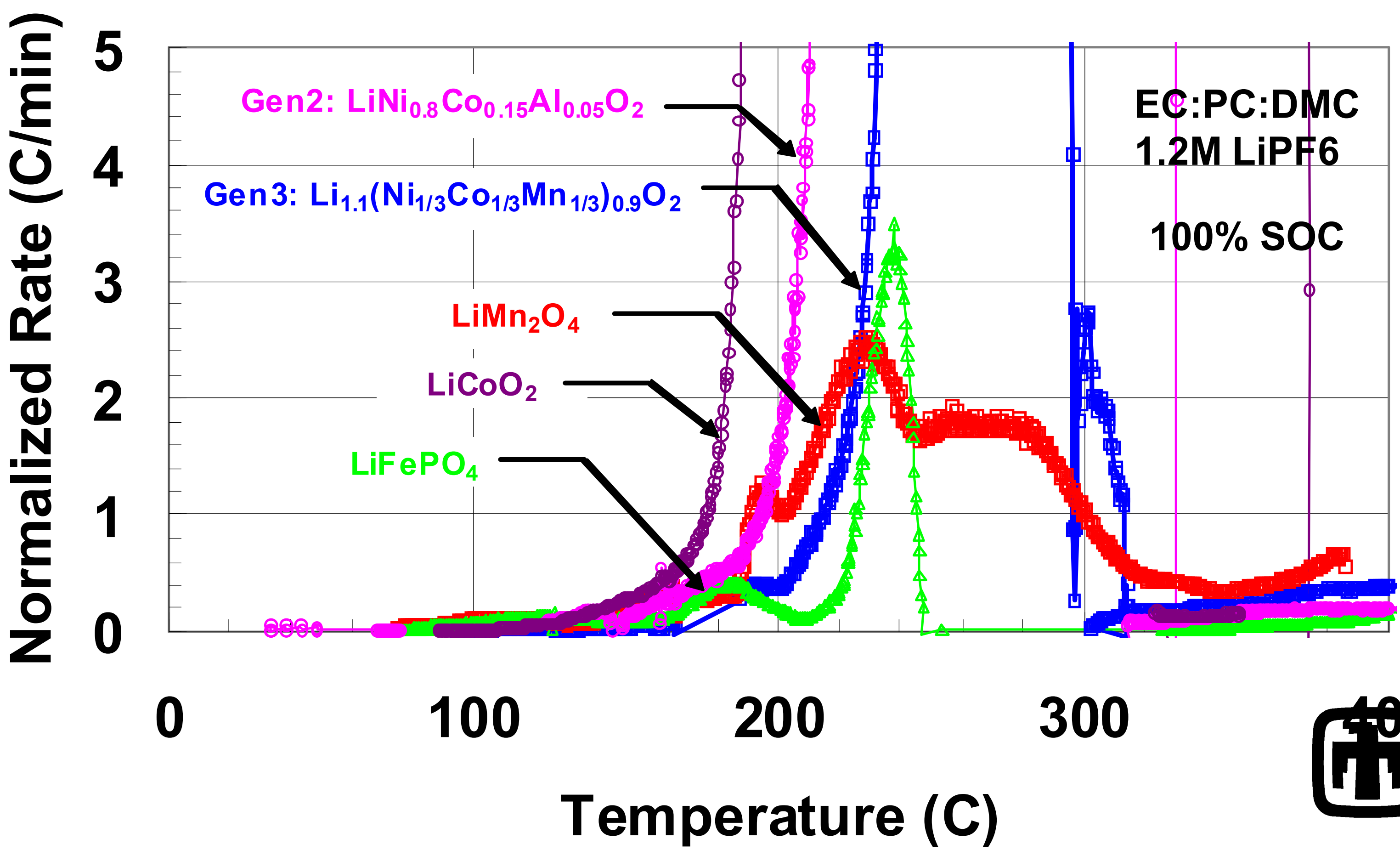
Thermal Runaway Cathode Comparisons (Expanded View)

Initial Onset Reactions Dominated by Anode



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TGA Profiles

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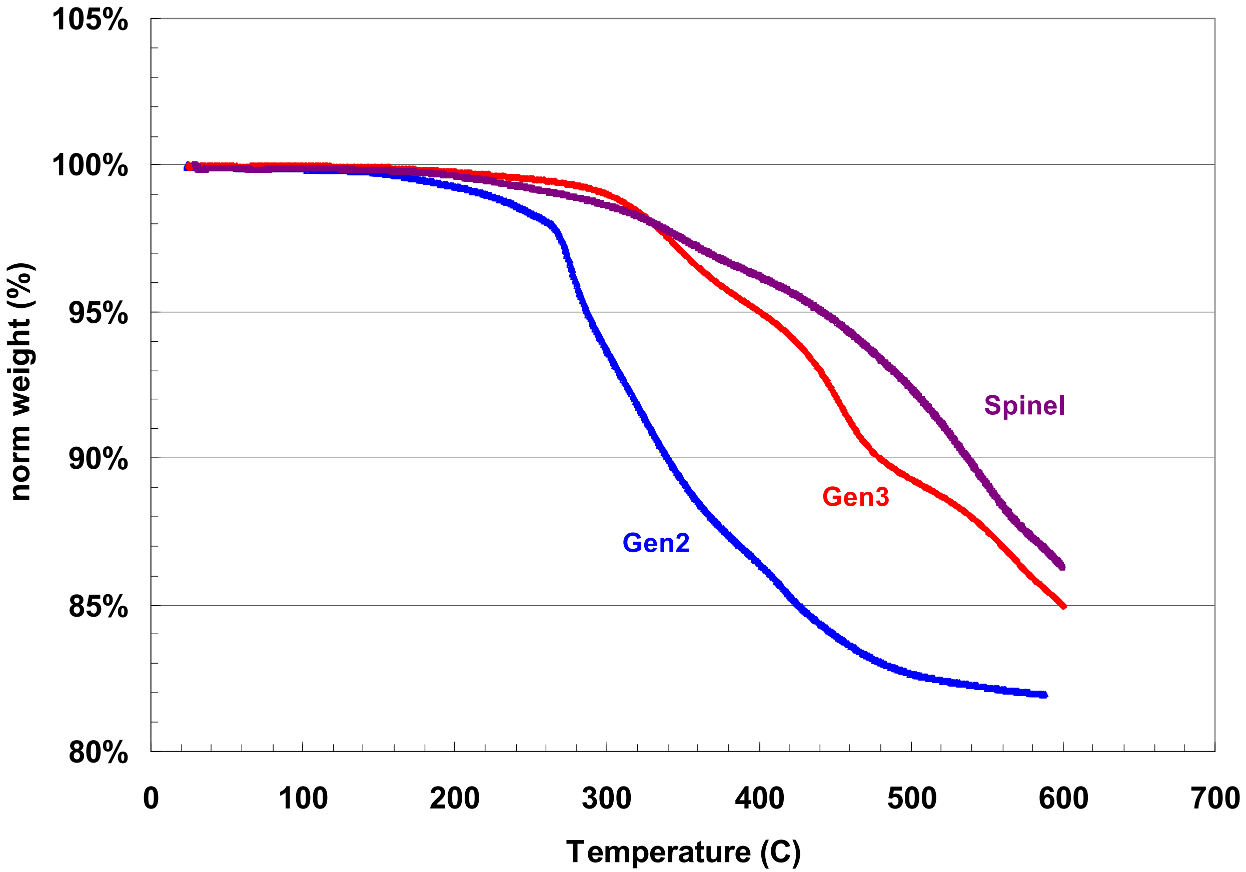
Mass Loss From Oxygen Release
From Decomposing Cathodes



Oxygen Generation Correlates With ARC Reaction Rate and Enthalpy

Gen2 Shows Highest Mass Loss and Greatest Reaction Rate

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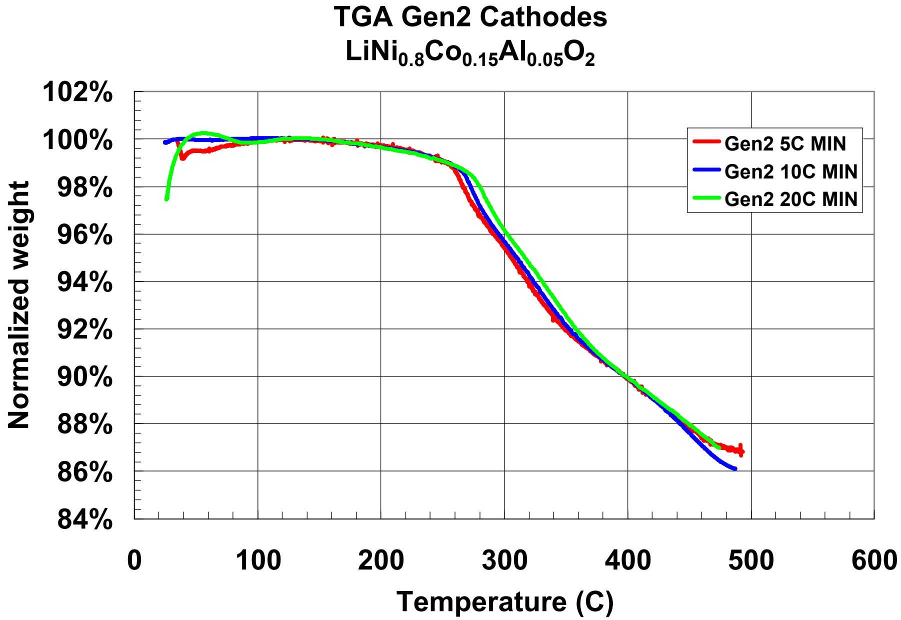
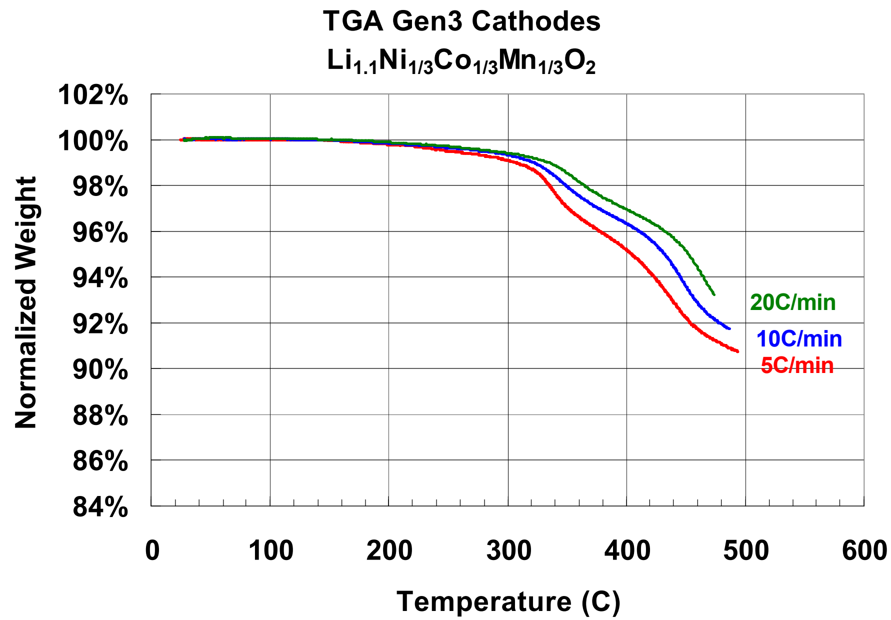
Reaction Kinetics Also Determine Peak Runaway Response

TGA Curves Show Fast Gen2 Decomposition Kinetics



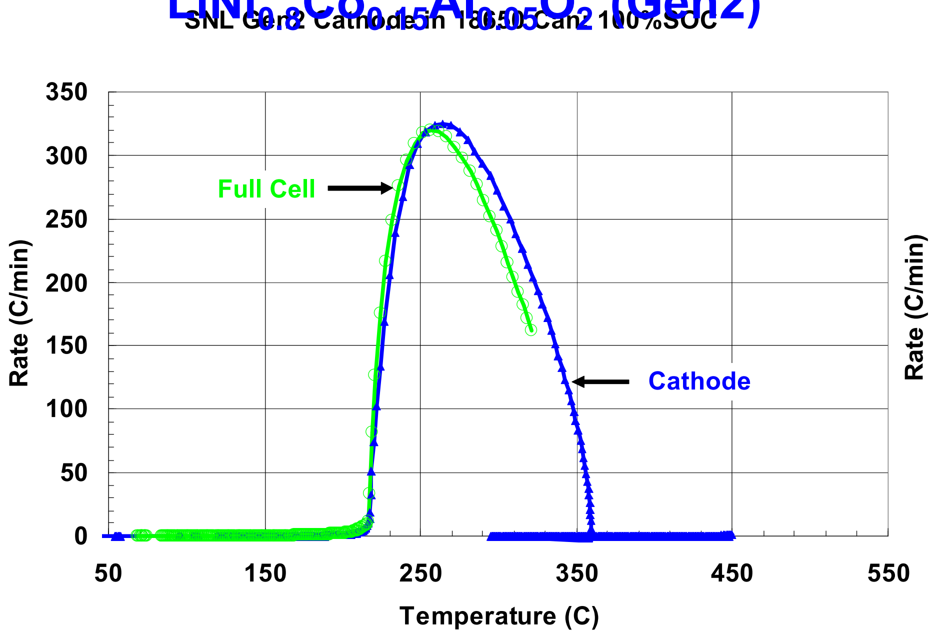
TGA Curves Show Slower Gen3 Decomposition Kinetics



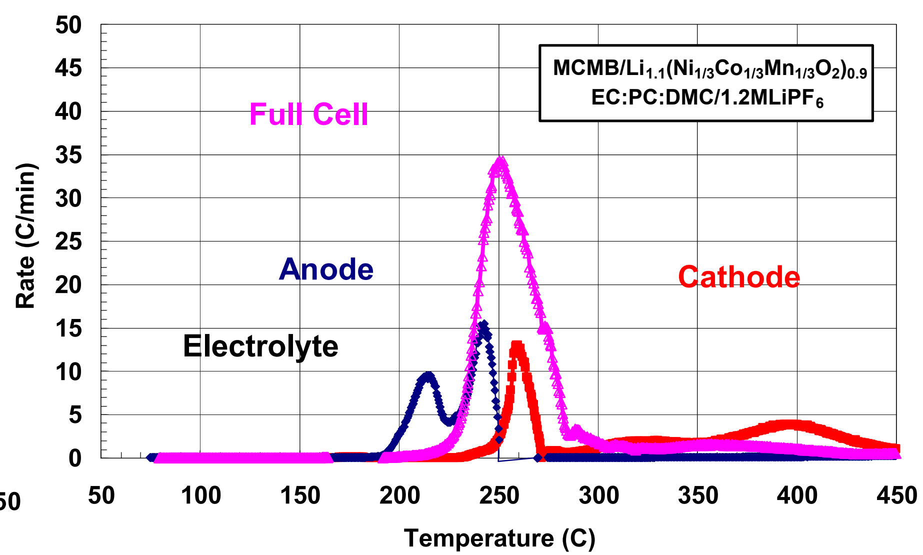
Comparison of Gen2 and Gen3 Cathodes Full Cell ARC Thermal Runaway Profiles

Peak Thermal Runaway Profile Determined By Cathode Reactions

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



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



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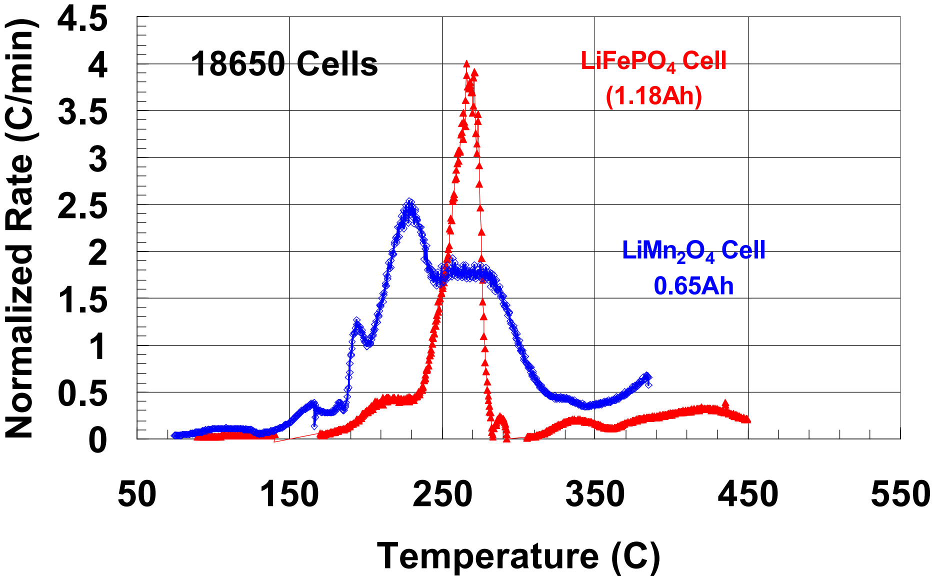
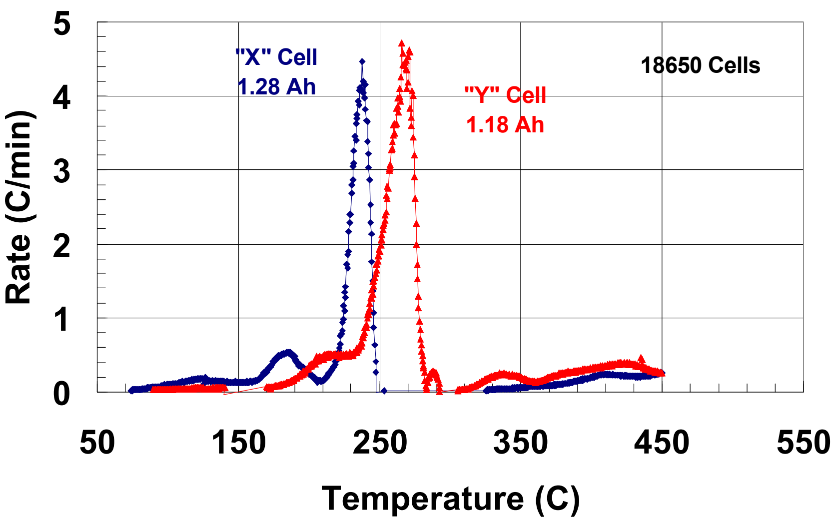
$LiFePO_4$ Cells Show Lower Reaction Kinetics and Reaction Enthalpy Compared to $LiMn_2O_4$ Cells

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

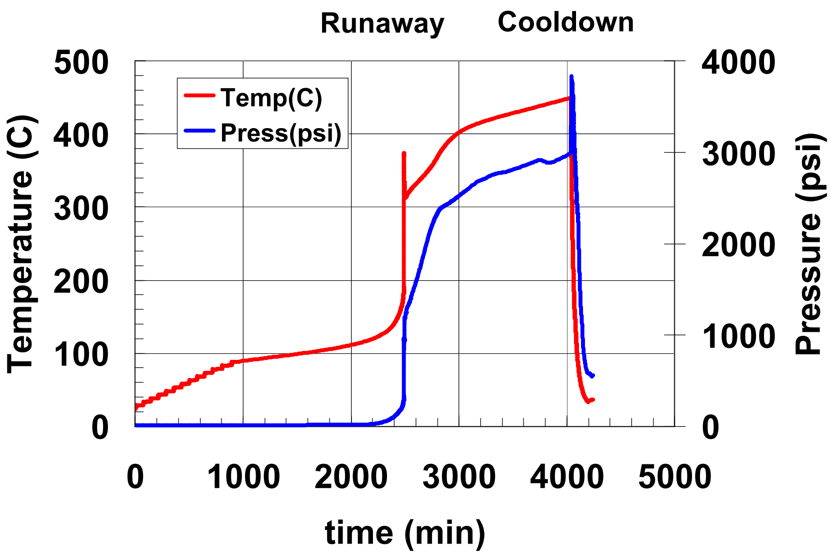


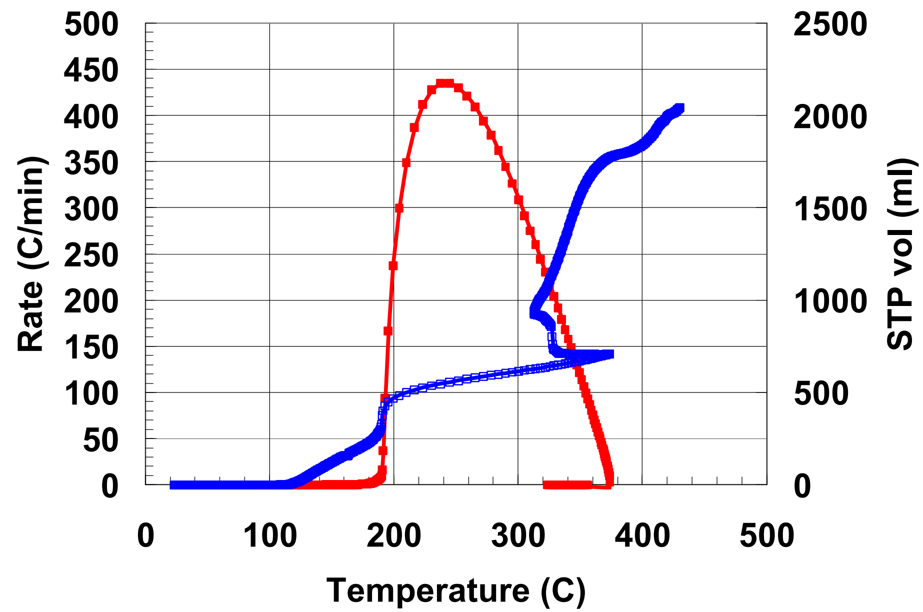
Cell from Two Manufacturers (X and Y) with $LiFePO_4$ Cathodes Both Show Similar Responses



Gas Evolution is a Critical Property Affecting Safety

ARC





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

Gas Generation During Thermal Runaway

Thermal Ramp Test to Runaway (~200°C)

Gas Evolution and Composition

Cathode and Anode Removed from Full Cell at 100%SOC
Resealed in 18650 Cans with Electrolyte

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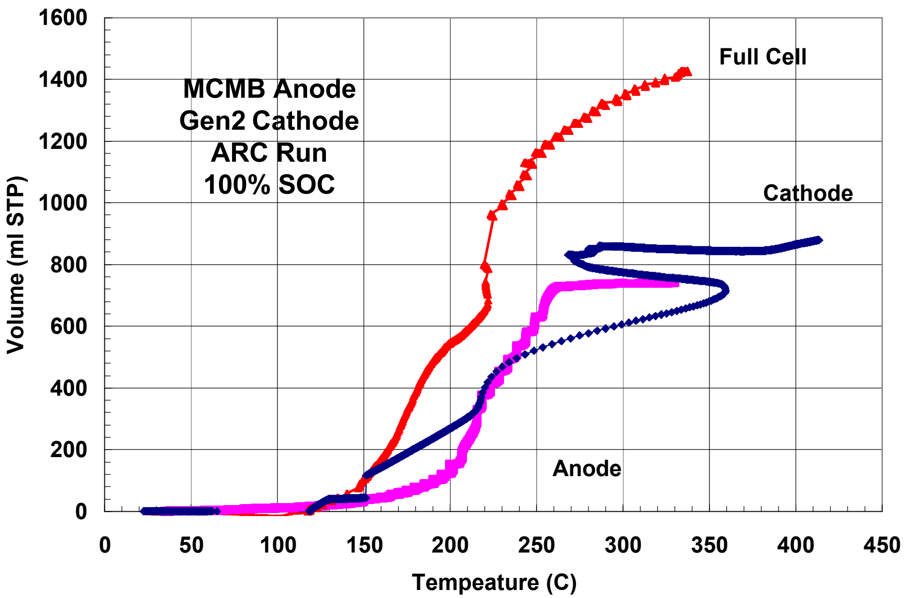
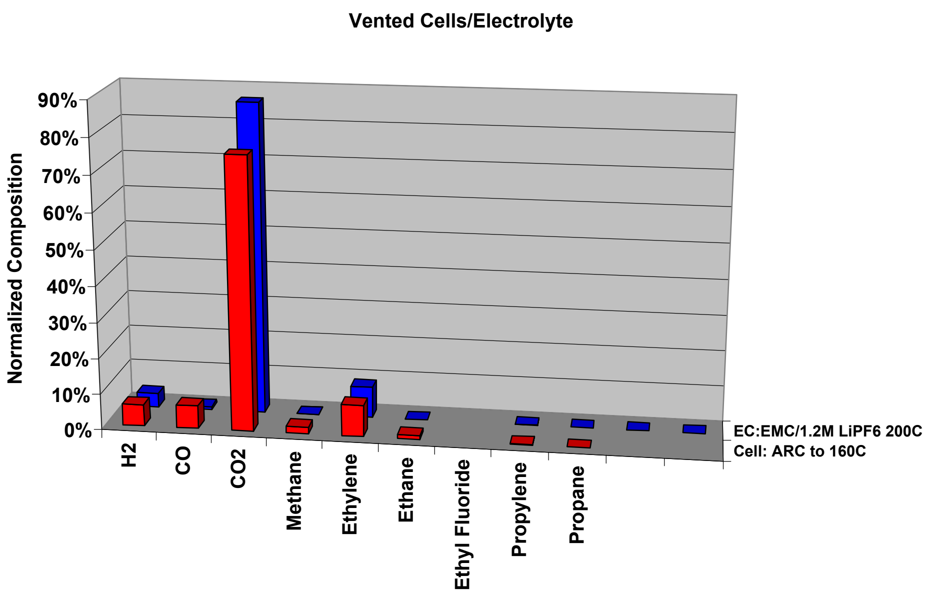
Onset of Gas Generation at Cathode Around 150°C

Equal Gas Volumes for Reactions at Cathode and Anode



Gas Composition Largely CO_2 Both for Full Cell and Electrolyte Decomposition



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

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Gas Evolution for Different Cathode Chemistries

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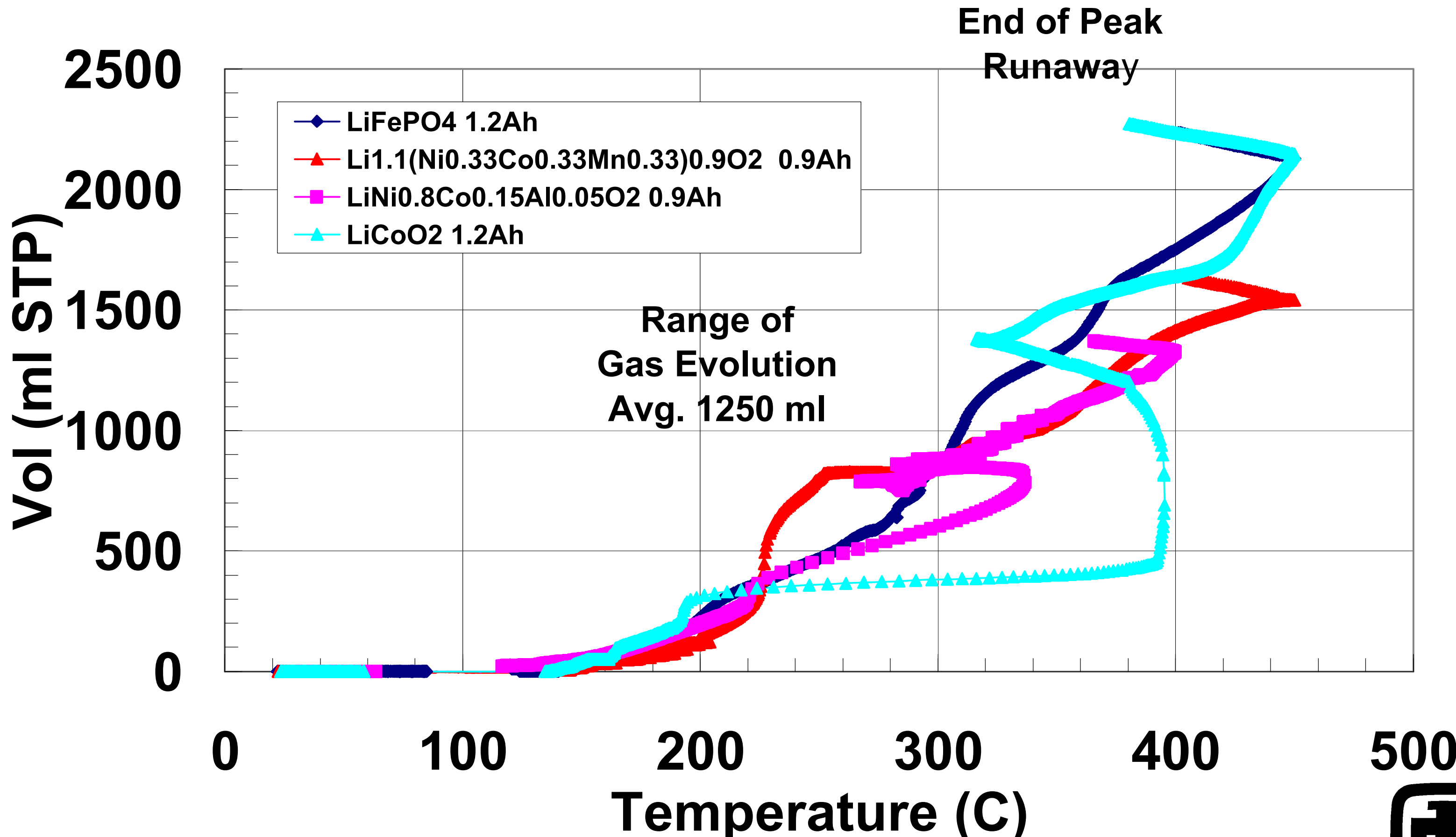
Gas Evolution Largely Determined by Quantity of Electrolyte



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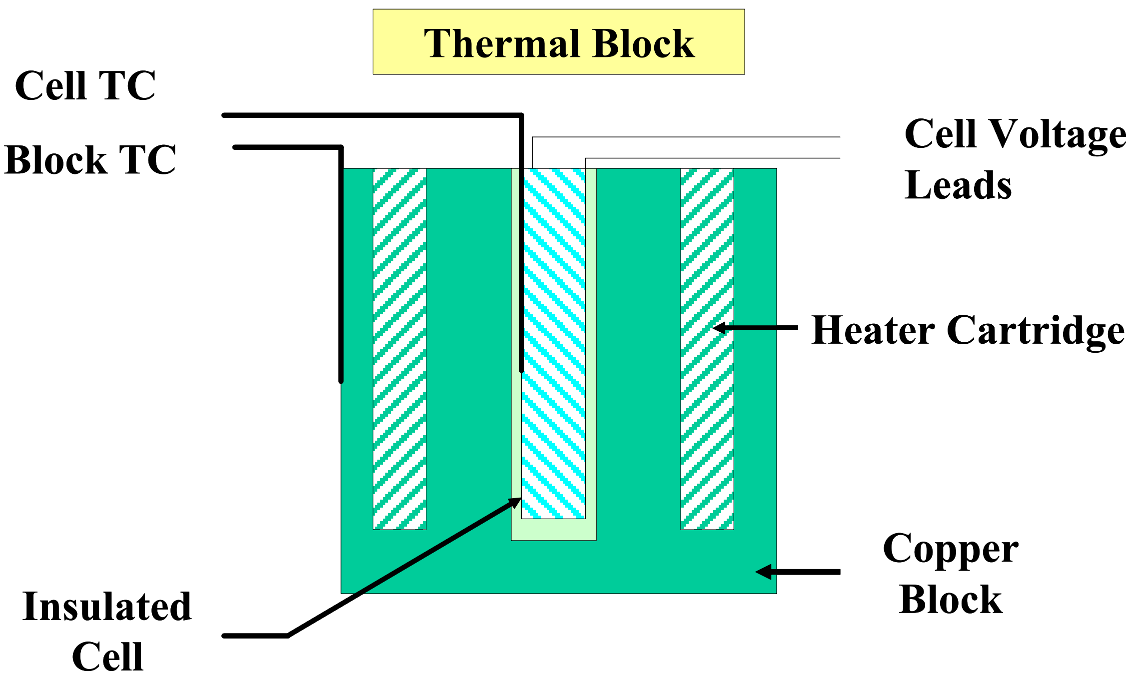
Thermal Ramp Apparatus

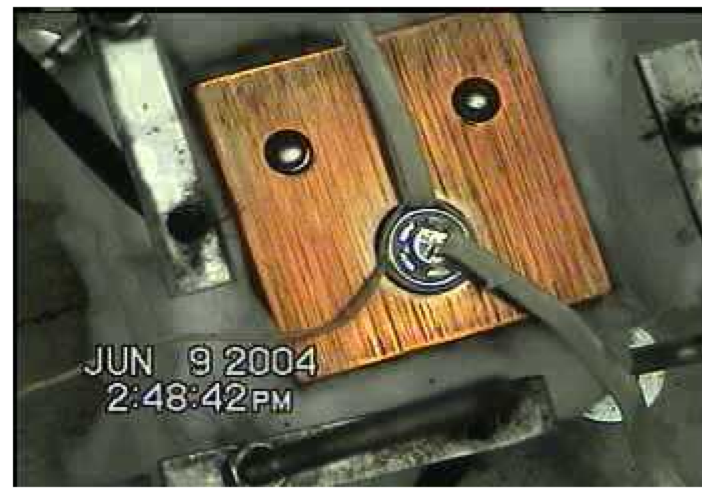
Ramp to runaway in air with external ignition

18mm

Ramp at 6 °C/min

190 °C





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

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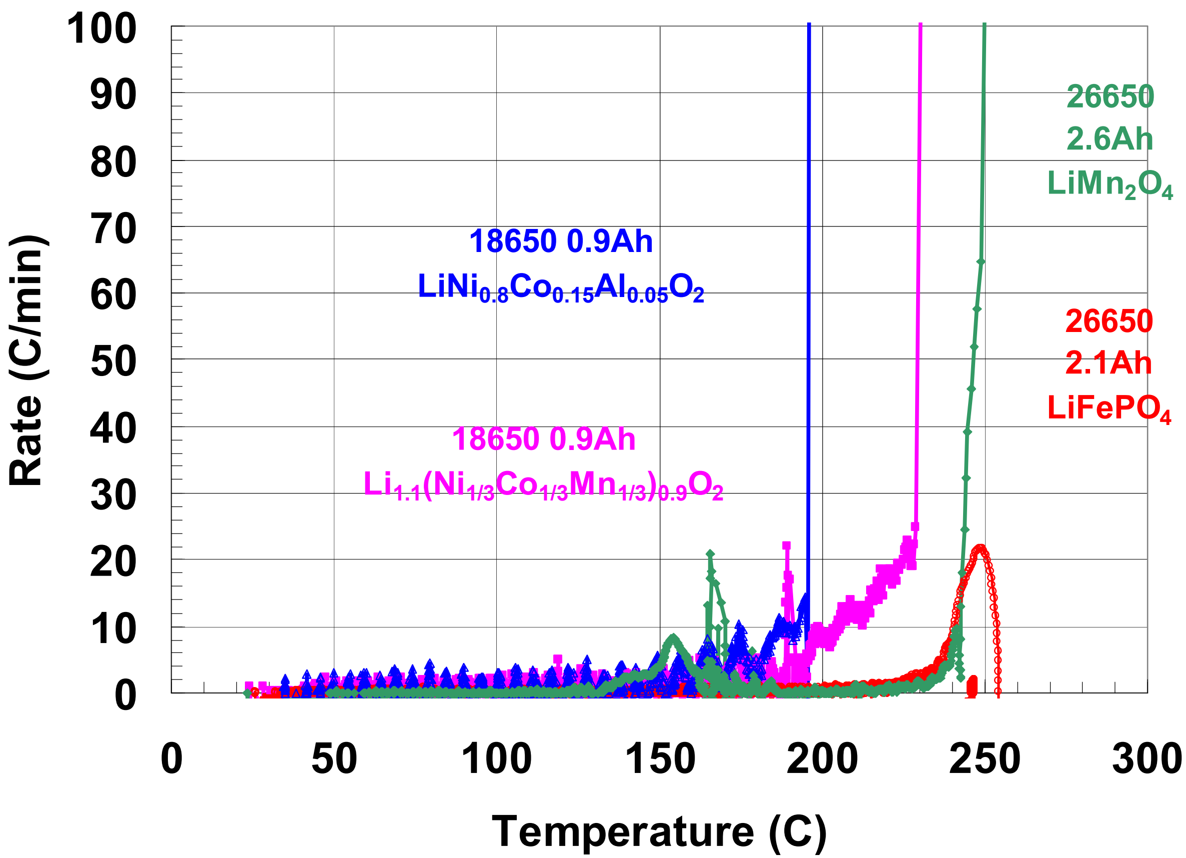
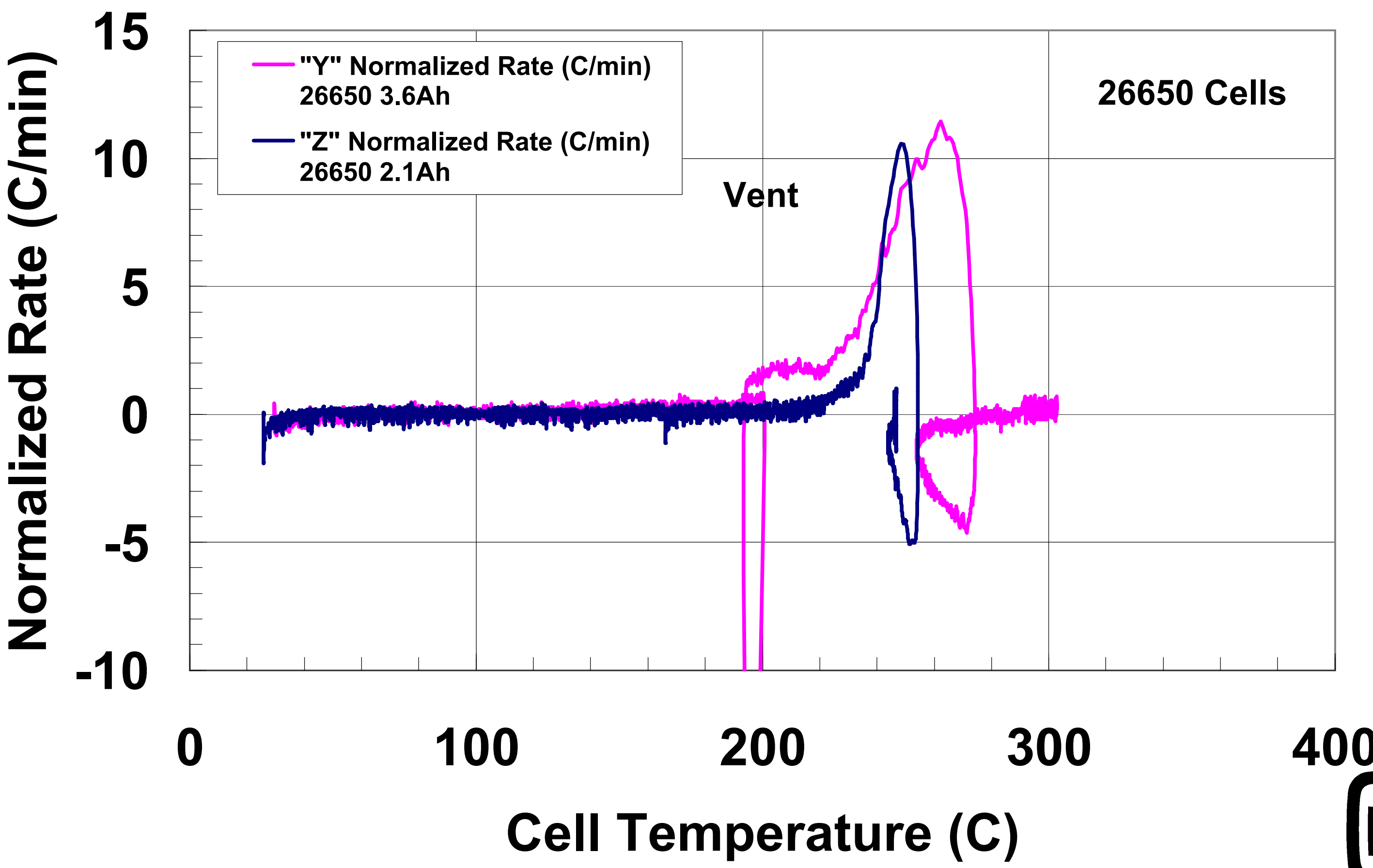
Greater Abuse Tolerance Shown for New Chemistries with Reduced or No Cathode Oxygen Release

Anode Reactions Still Contribute to Runaway



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

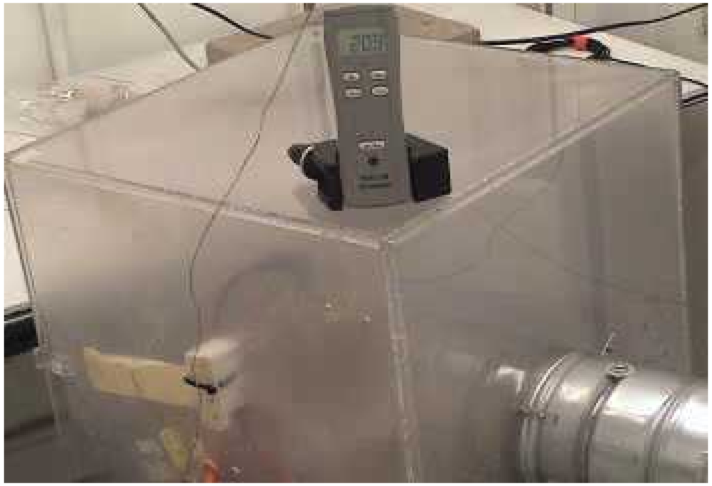
Comparison of Two Commercial $LiFePO_4$ Cells



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

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

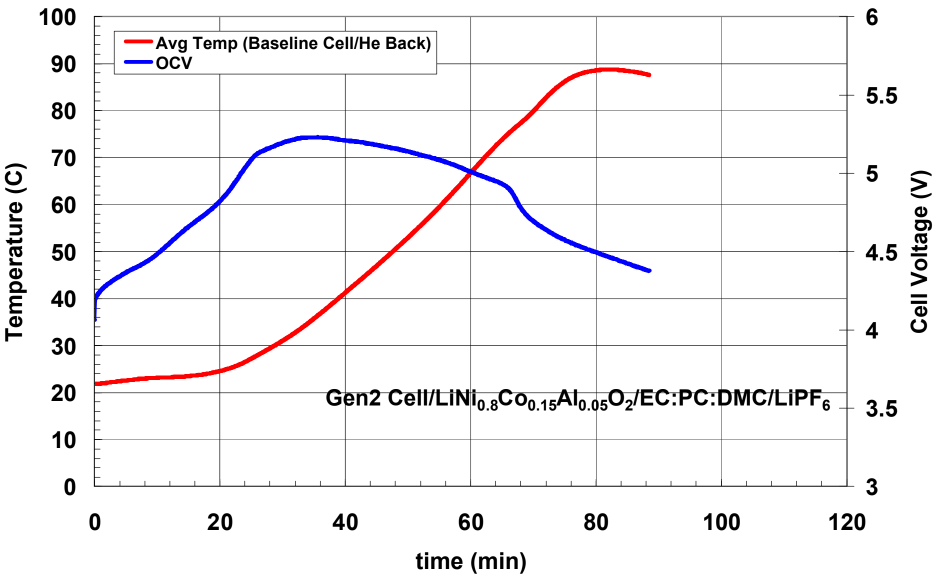
Overcharge Gas Generation

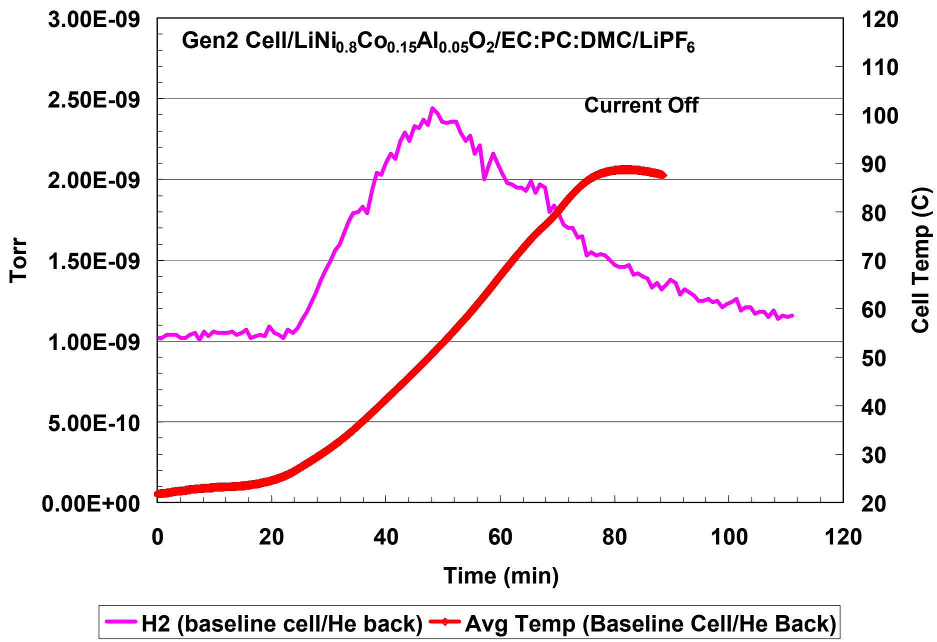
We have previously shown that explosive gases are generated during overcharge: Hydrogen and flammable solvent vapors

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





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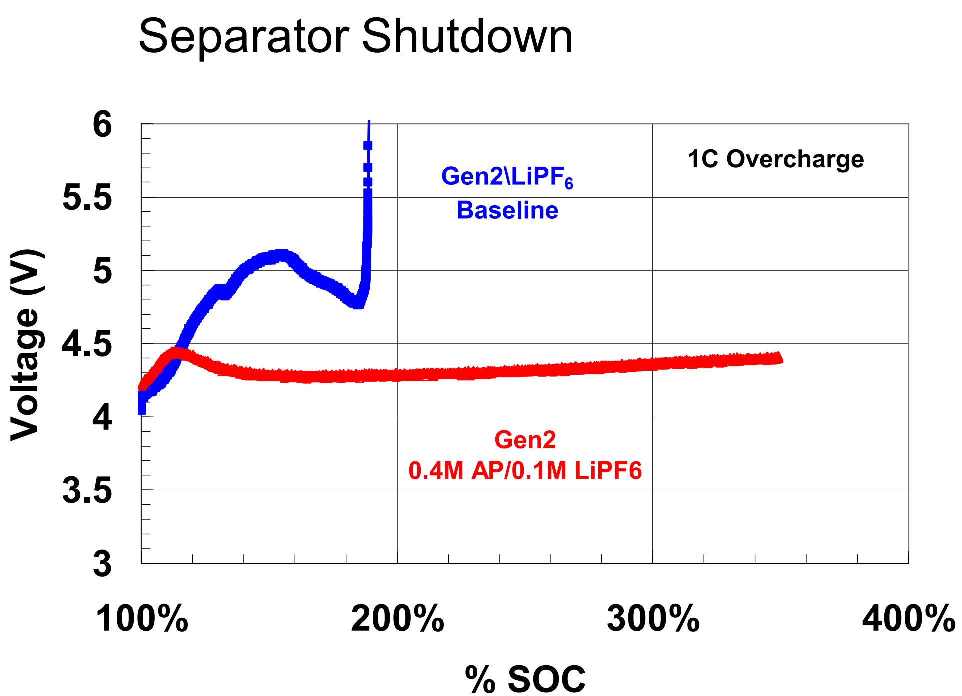
Abuse Response Improved with Electrolyte Additives

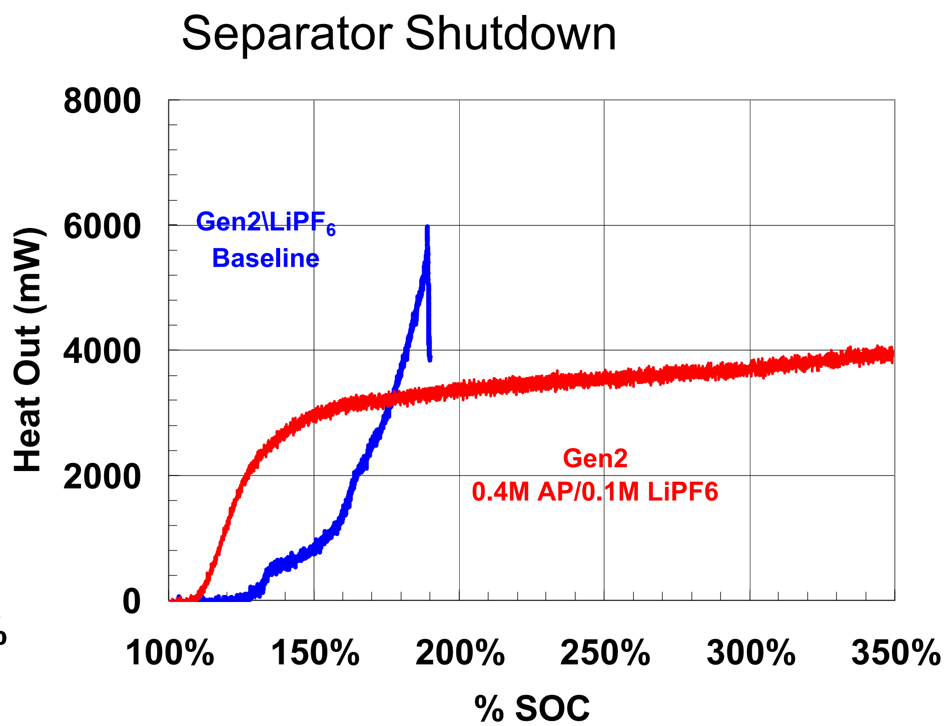
- Additives to improve:
  - SEI
    - VEC, VC
  - Electrolyte stability
    - LiBOB, LiBETI
  - Overcharge
    - **Shuttle Additives**
  - Flammability
    - Phosphazenes
    - Phosphates

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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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 $LiFePO_4$)***
  - ***Improved stability results from decreased oxygen generation***
- ***Anode reactions are still important to provide better abuse tolerance***
- ***Some additives have shown improvements in thermal and overcharge abuse response***

Acknowledgements

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