Abuse Tolerance Studies on Li-Ion Cells and Modules

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Advanced Technology Development

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FreedomCAR & Fuel Partnership

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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DOE Advanced Technology Development (ATD) Program

- The *FreedomCAR Program* is developing hybrid electric vehicles to reduce the US dependence on Foreign Oil Supplies

- DOE's Advanced Technology Development (ATD) Program addresses the three barriers that remain for batteries in hybrid electric vehicles -
  - high cost, short calendar life, and poor abuse tolerance.

- Involves 5 US National Laboratories
  - Argonne National Lab, Sandia National Labs, Lawrence Berkeley National Lab, Idaho National Engineering & Environmental Lab, and Brookhaven National Lab

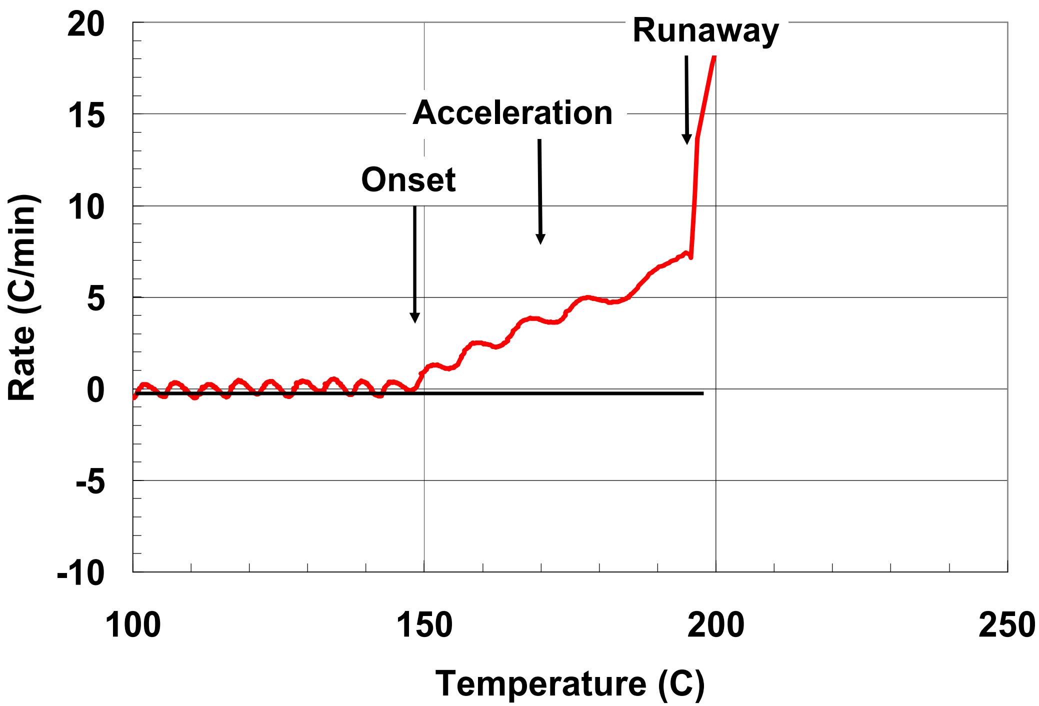
- Technical goal is to
  - Develop improved diagnostic techniques at National Labs.
  - Identify life-limiting mechanisms for failure of lithium-ion cells during abuse and aging

Thermal Abuse Response
This is the Behavior That Must Be Understood and Mitigated

There are three main temperature regimes during thermal runaway:

- Stage 1: Room Temperature to 150°C – Onset of thermal runaway occurs at the anode
- Stage 2: 150°C - 180°C – Venting and accelerated heating (cathode and anode participate)
- Stage 3: 180°C and above – High-Rate Reaction (largely cathode with driven anode reaction)

Stage 1 **Stage 2** **Stage 3**



Cell self-generated heating during thermal ramp

Mechanisms of Runaway Reactions

- **Stage 1 (RT-150°C):**
  - Reaction and breakdown of passivation layer on anode results in exothermic reduction of electrolyte by lithiated carbon
- **Stage 2 (150°C- 180°C):**
  - Continued electrolyte reaction at anode
  - **Onset of oxidation of electrolyte at cathode surface**
- **Stage 3 (180°C and above):**
  - **Cathode decomposition releasing oxygen which exothermically reacts at high rate with electrolyte**
  - Final breakdown of anode passivation layers and subsequent reaction
  - Exothermic decomposition of free electrolyte

ATD Li-Ion Cell Chemistries

Cell Chemistry Greatly Determines Cell Performance and Abuse Response

- **Anodes:** natural or synthetic carbons
  - MCMB, GDR, MAG10
- **Cathodes:** metal oxides with vacant sites for Li incorporation
  - $LiCoO_2$ (most common in commercial Li-Ion cells)
  - $LiNi_{0.8}Co_{0.2}O_2$
  - $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
  - $Li_{1.1}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$
  - $LiMn_2O_4$ (spinel)
- **Electrolytes:** mixture of cyclic and linear alkyl carbonates with Li salt
  - Solvents:
    - ethylene carbonate (EC), propylene carbonate (PC)
    - diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC)
  - Salts:
    - $LiPF_6$, $LiB(C_2O_4)_2$ or LiBOB
  - Additives:

    SEI enhancer – Vinyl ethylene carbonate (VEC)

    Flame retardants – Phosphazene-based "Phoslyte™", Triphenyl Phosphate

Thermal Analysis Techniques

- Thermal Ramp
  - Constant heating rate up to thermal runaway
  - Measurement of heat generation onset
  - Open venting with spark ignition source for flammability determination
- Accelerating Rate Calorimetry (ARC)
  - Adiabatic Temperature Conditions
  - Measures cell heat and gas output as a function of chemistry and State of Charge (SOC)
- Differential Scanning Calorimetry (DSC)
  - Measure material thermal reactions at constant heating rate
  - Determine reaction enthalpies and activation energies

Cell Baseline Chemistries

Cells Produced at Sandia in 18650 Configuration

Gen2:

Anode: GDR carbon
Cathode: $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
Electrolyte: EC:EMC (3:7) 1.2M LiPF6

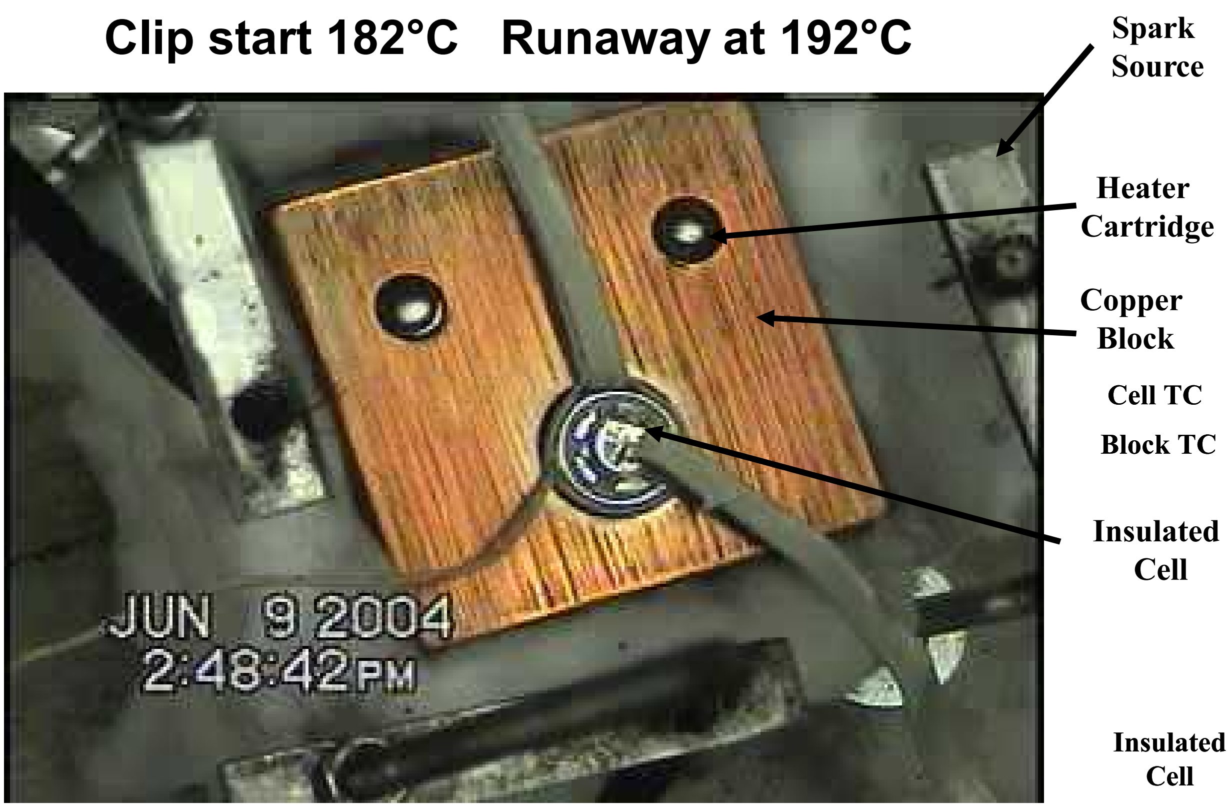
Gen3: Improved Thermal Stability Compositions

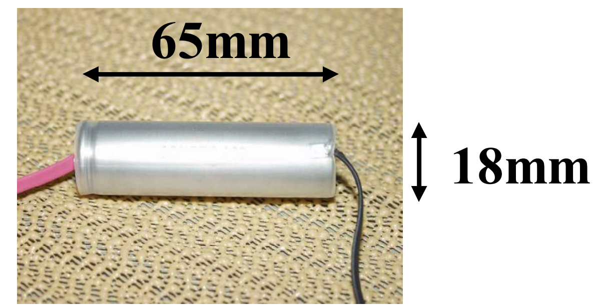
Anode: MCMB carbon
Cathode: $Li_{1.1}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$
Electrolytes: EC:EMC (3:7) 1.2M LiPF6
EC:PC:DMC (1:1:3) 1.2M LiPF6

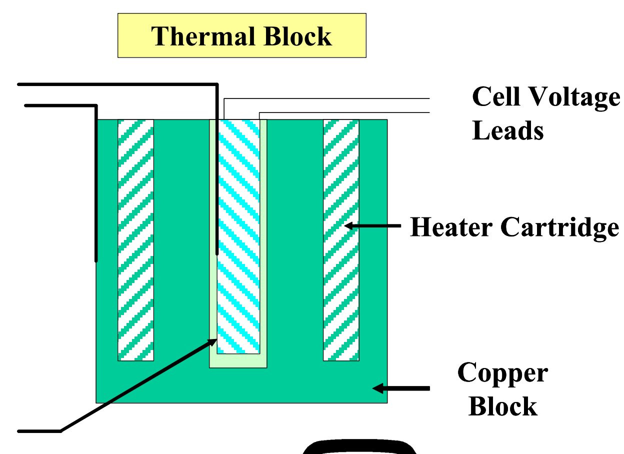
Thermal Runaway Under Ramp Conditions for 18650 Cells

Heat Generation Followed by Venting of Flammable Solvent Vapors and Eventual Rapid Cell Disassembly

Clip start 182°C Runaway at 192°C







Spark Ignition Sources to Test for Flammable Vapors

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Thermal Ramp

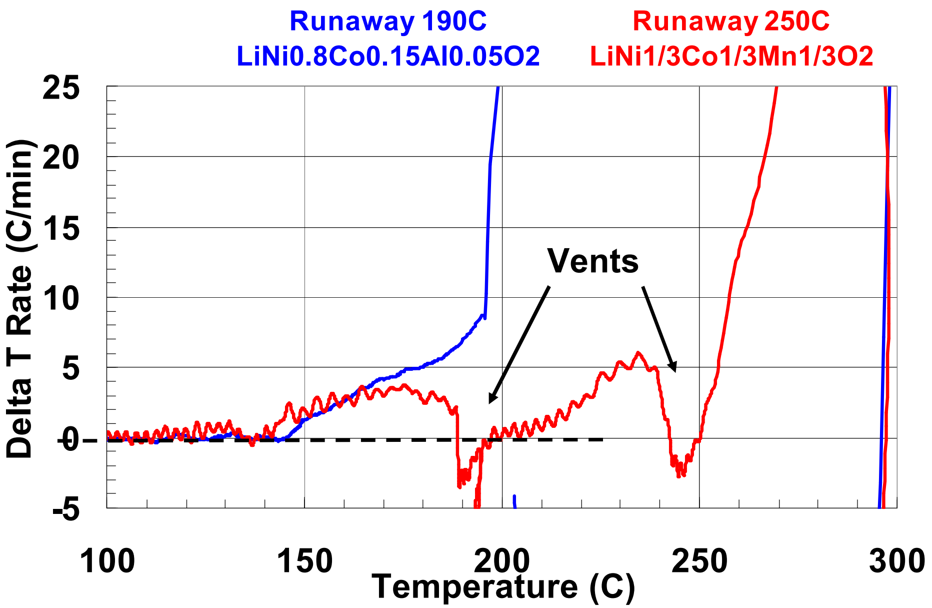
$Li_{1.1}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ 1.2M $LiPF_6$/EC:PC:DMC

Cells Show Delayed Runaway Response

Onset of Stage 2 Reactions Same as Gen2/GDR Baseline Cell

No Explosive Runaway! Cell Remained Intact

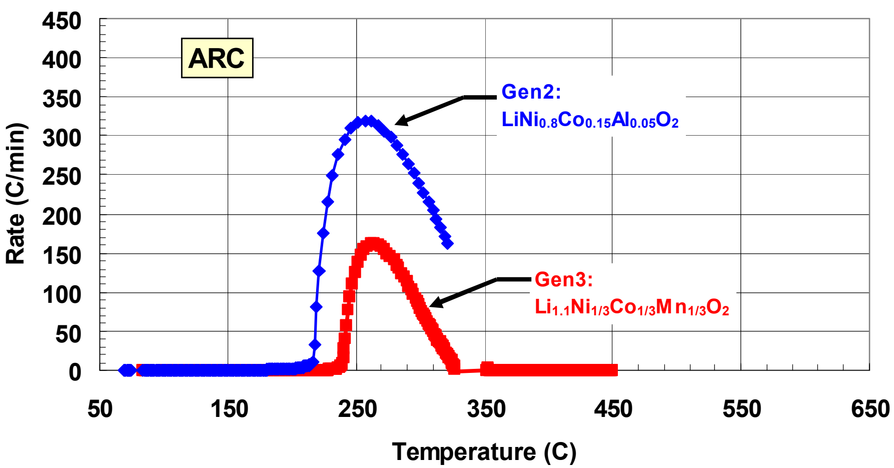
Vapor Flammability Not Affected by Cathode Material

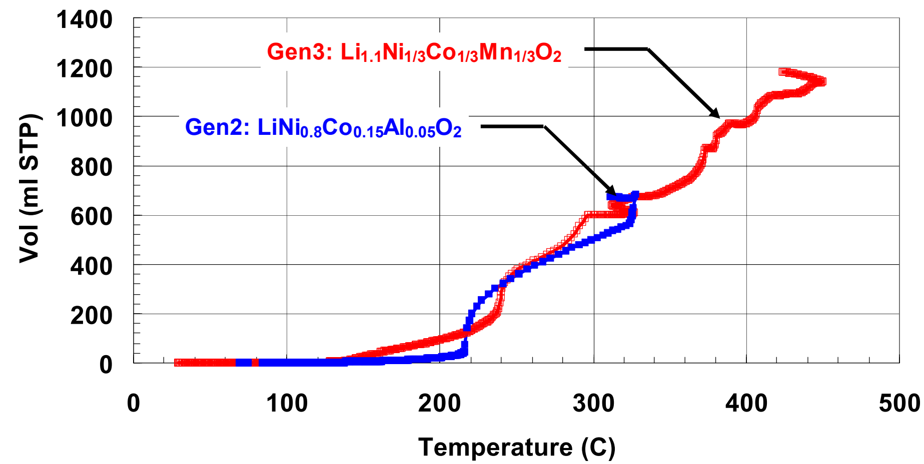


ARC Thermal Runaway Comparison $Li_{1.1}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ / $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$

Gen3: $Li_{1.1}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$
- **Higher Runaway Temperature**
- **Reduced Peak Heating Rate**
- **Lower Enthalpy of Reaction**

Gen3/Gen2:
- **Similar Gas Volumes Generated**





EC:EMC/1.2M LiPF6

Evolved Gas Species from Thermal Decomposition

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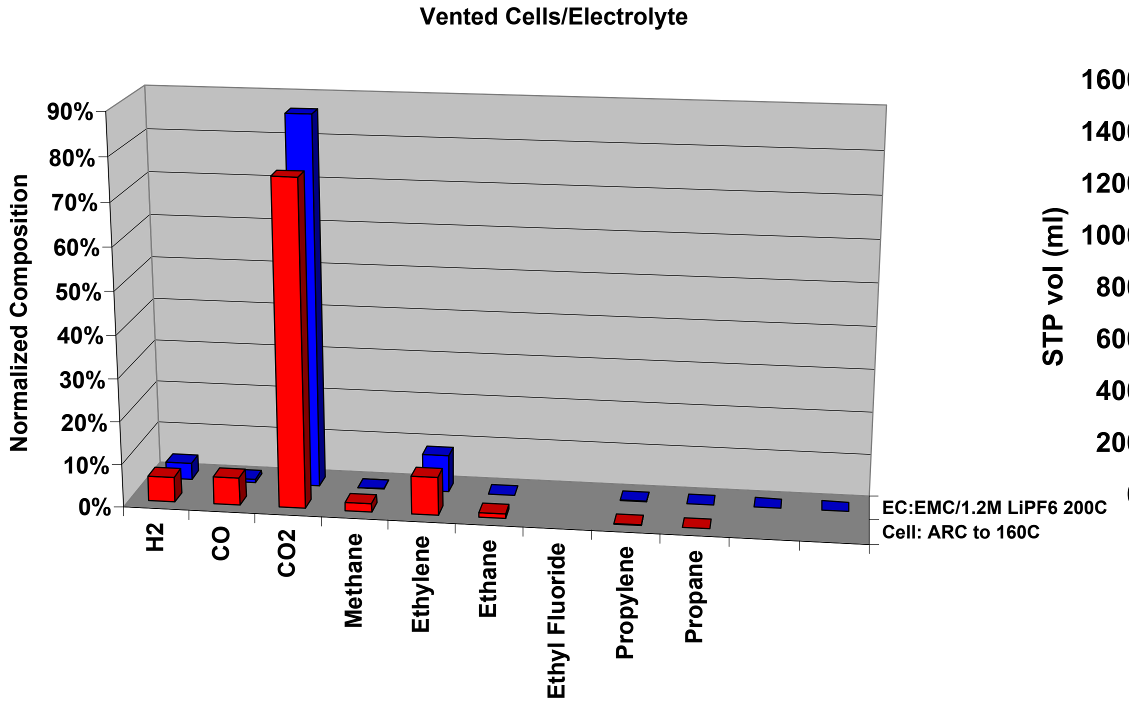
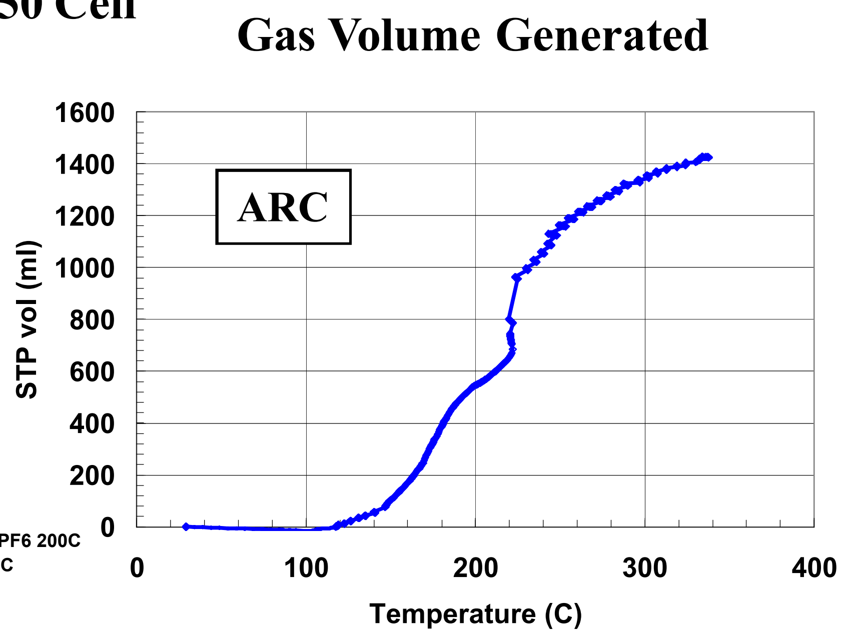
CO_2 is the Dominant Evolved Gas Species
Gases Are Primarily From Electrolyte Decomposition and Reaction with Cathode-Generated Oxygen

1Ahr 18650 Cell





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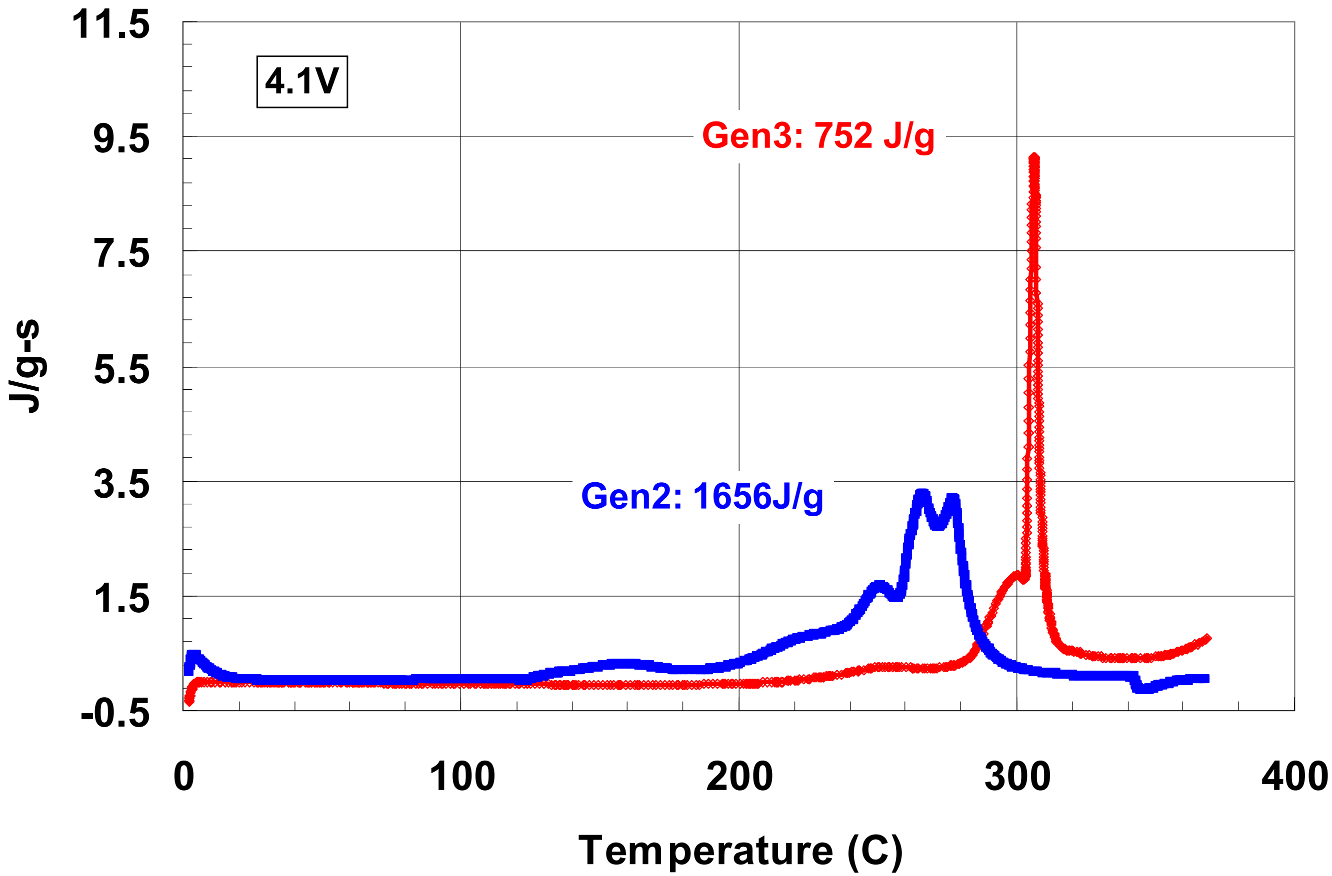
DSC Analysis Comparisons

Gen3 $Li_{1.1}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ /Gen2 $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$

Gen3 cathode material shows 50% reduction in total enthalpy and higher decomposition onset temperature



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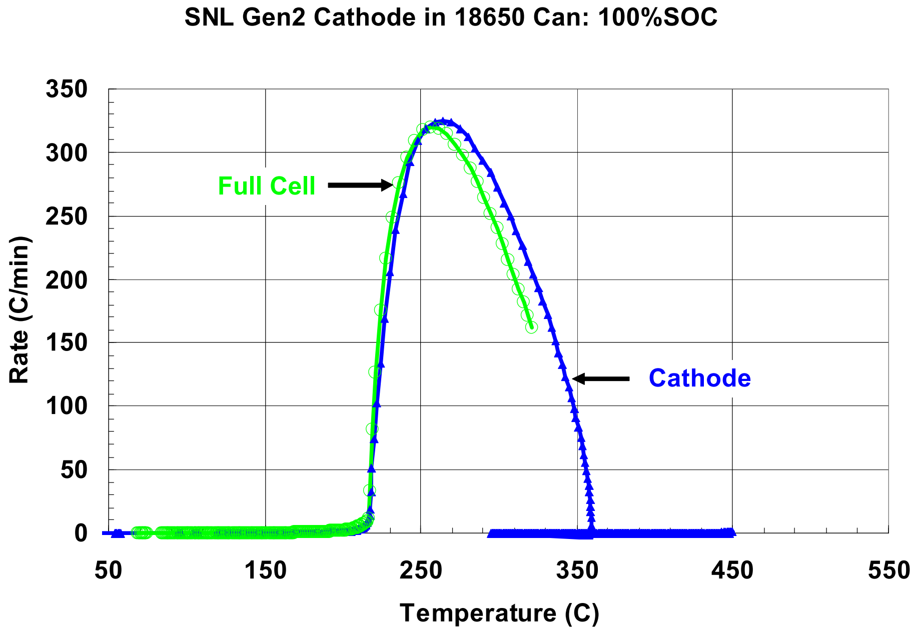
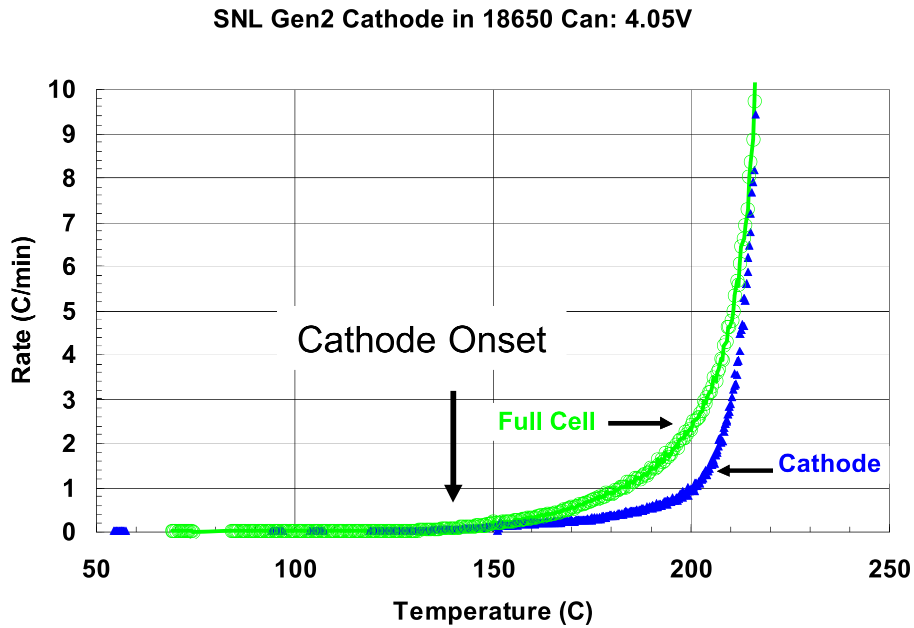
Comparison of Cathode and Full Cell ARC Thermal Runaway Profiles

Cathode Runaway Profile Same as for Full Cell

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

Peak Thermal Runaway Profile Determined By Cathode Reactions



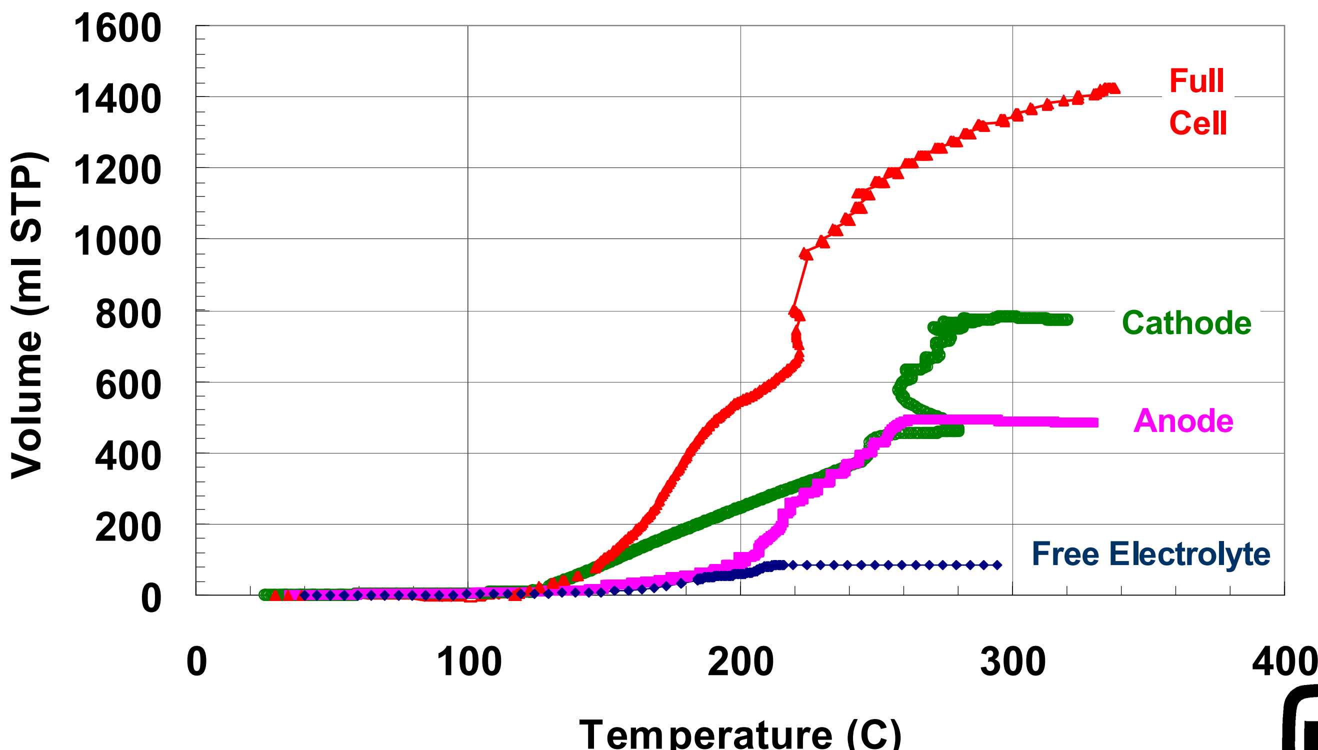


Gas Generation
Cell Components and Full Cells

Total Volume of Gas Can Be Accounted for by Sum of Individual Electrode Gas Volumes

Electrolyte Distribution: 55% Anode, 37% Cathode, 8% Free
Gas Evolution: 40% Anode, 60% Cathode

Greater Relative Gas Generation at Cathode



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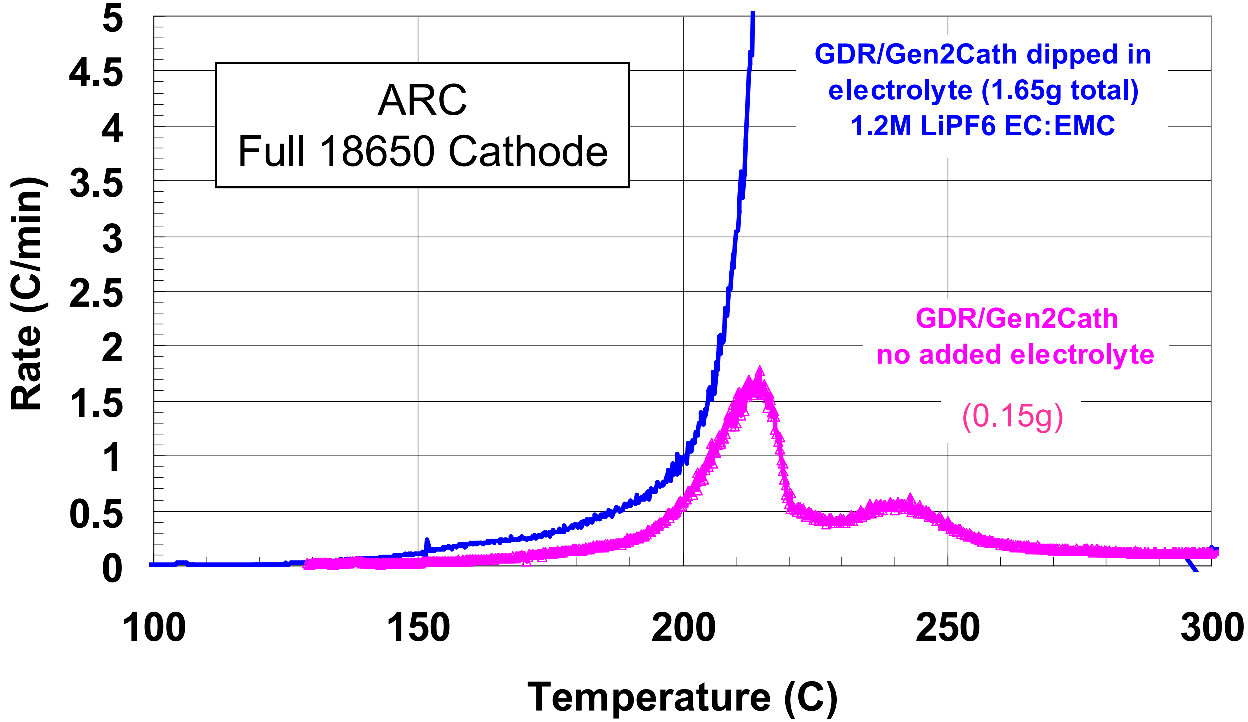
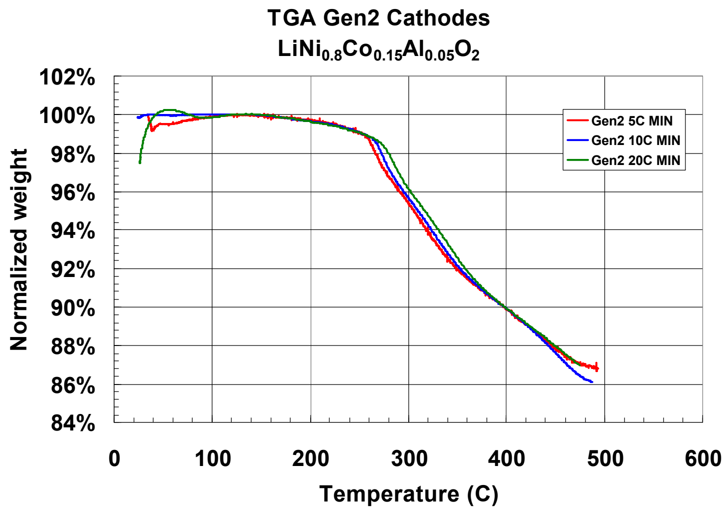
Gen2: $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
Reaction with Electrolyte

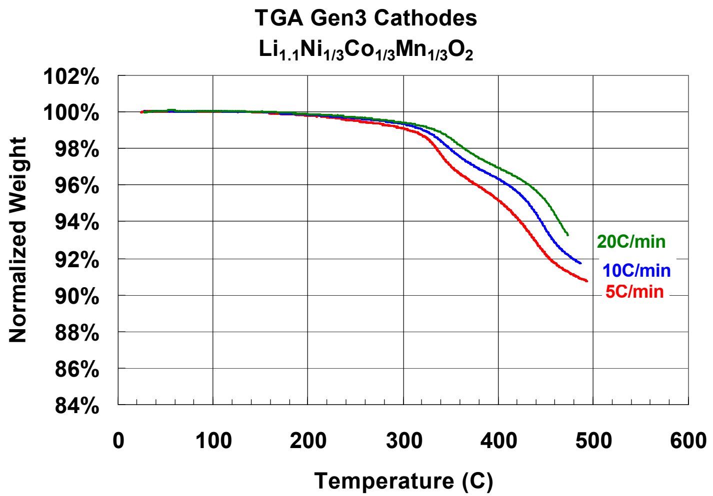
Similar Onset Reaction at Cathode Surface
Reaction Stops with Depletion of Electrolyte

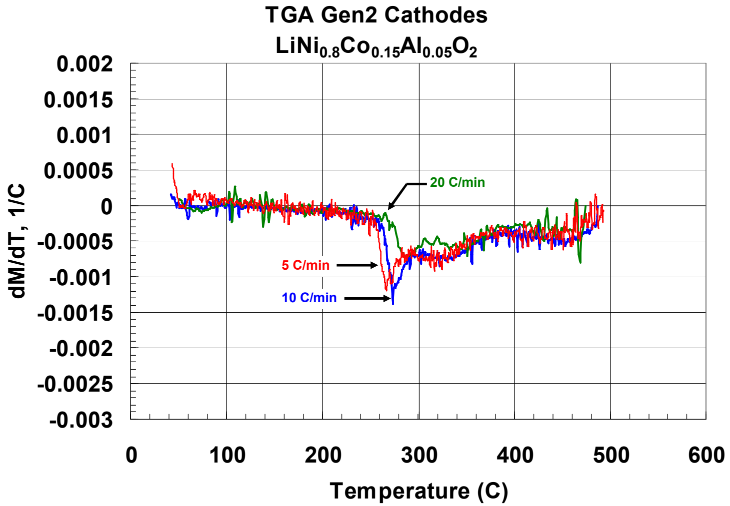


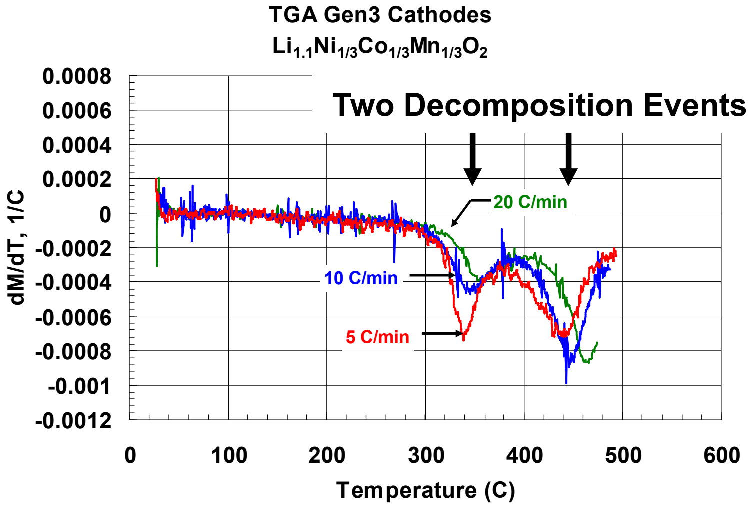
Cathode Decomposition: TGA

Gen2 Cathodes Show Earlier Decomposition, Higher Reaction Rates and Greater Mass Loss









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Source of High-Rate Cathode Reaction: Solvent Combustion by O_2 from Cathode

Solvent combustion reactions for several of the most used solvents:

EC: $C_3H_4O_3 + \frac{5}{2}O_2 \rightarrow 3CO_2 + 2H_2O$ DH= 1161 kJ/M

DEC: $C_5H_{10}O_3 + 6O_2 \rightarrow 5CO_2 + 5H_2O$ DH= 2715 kJ/M

DMC: $C_3H_6O_3 + 3O_2 \rightarrow 3CO_2 + 3H_2O$ DH= 1440 kJ/M

EMC: $C_4H_8O_3 + \frac{9}{2}O_2 \rightarrow 4CO_2 + 4H_2O$ DH= 2000 kJ/M
(estimated from DEC and DMC)

EC: 2/5 x 1161 kJ/M = 464 kJ/MO2

DEC: 1/6 x 2715 kJ/M= 452 kJ/MO2

DMC: 1/3 x 1440 kJ/M= 480 kJ/MO2

EMC: 2/9 x 2000 kJ/M= 444 kJ/MO2

Average of 460 kJ/MO$_2$ for the solvent combustion reaction (ΔH_S)

Cathode Decomposition Reaction:

$$Li_xMO_2 \rightarrow (1+x)Li_{\frac{x}{1+x}}M_{\frac{1}{1+x}}O + \frac{(1-x)}{2}O_2$$

For our Gen2 stoichiometry, x=0.38 at 100%SOC giving 0.31M O_2/Mpos.
TGA measured a total of 12% loss of mass from 180°C-500°C giving 0.32M O_2/Mpos.

Cathode reacting over the 320°C temperature range gives 1.44 kJ/g.
DSC measurements have given 1.35-1.46 kJ/g.

Cathode Decomposition/Electrolyte Combustion Accounts for Measured Energy Release

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Effect of Flame Retardant Additives

$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$;0.7M LiBOB/EC:PC:DMC

No Explosive Vapor Ignition!

Additive C Shows Similar Onset Response To Baseline Cell But With No Explosive Gas Generation

Bridgestone Phoslyte™ Flame Retardant: Phosphazene Based Additive

Cycled Cells (>30)
4.1V full charge

No additive

10% Phoslyte Additive C

Thermal Abuse Test Observations

- ***Increased thermal stability has been demonstrated with more stable cathodes ($Li_{1.1}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$)***
- ***Cathodes dominate peak heating rate thermal runaway***
- ***Cathode oxygen generation and solvent combustion accounts for observed high-temperature reactions***
- ***Still no "magic bullet" for producing completely stable Li-ion cells***
  - **Thermal abuse tolerance will result from informed choices of improved cell materials, additives and cell design.**

Objectives

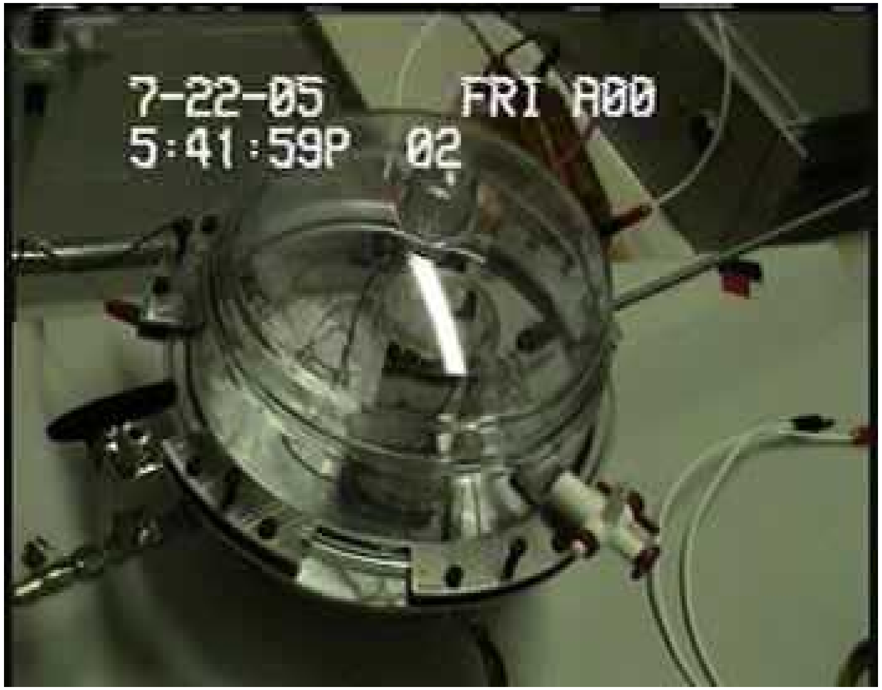
- Determine the relative importance of electrochemically-derived and thermally-derived decomposition pathways.

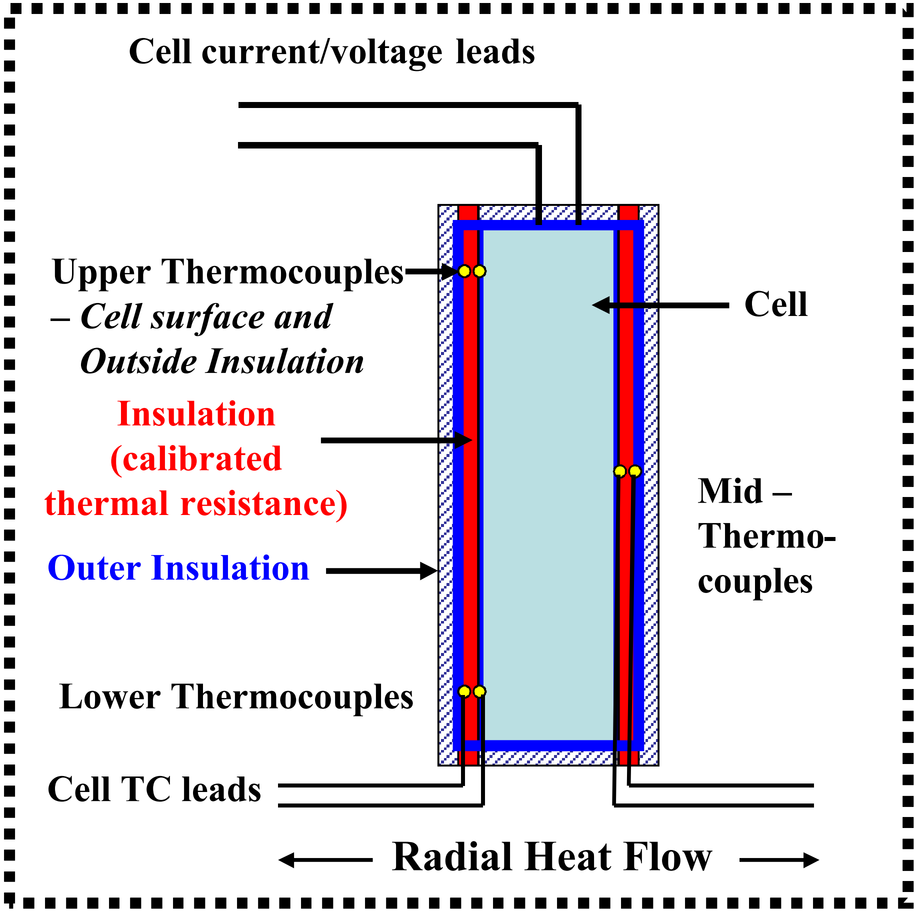
  Under what conditions does Overcharge trigger thermal runaway?

  Compare different overcharge profiles and cell conditions resulting in different SOC and temperature states.

Overcharge Test Setup

Allows Us to Measure Heat Output and Control Temperature Profile





Helium, N_2 or air flow through Lexan® enclosure for real time gas sampling

Overcharge Response $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

- **18650 SNL Cells**
  - **MCMB Anodes**
  - **EC:PC:DMC/1.2M LiPF6**
- **4.1V: 910 mAh**
- **4.3V: 1100 mAh**

Overcharge Response 1C Rate
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

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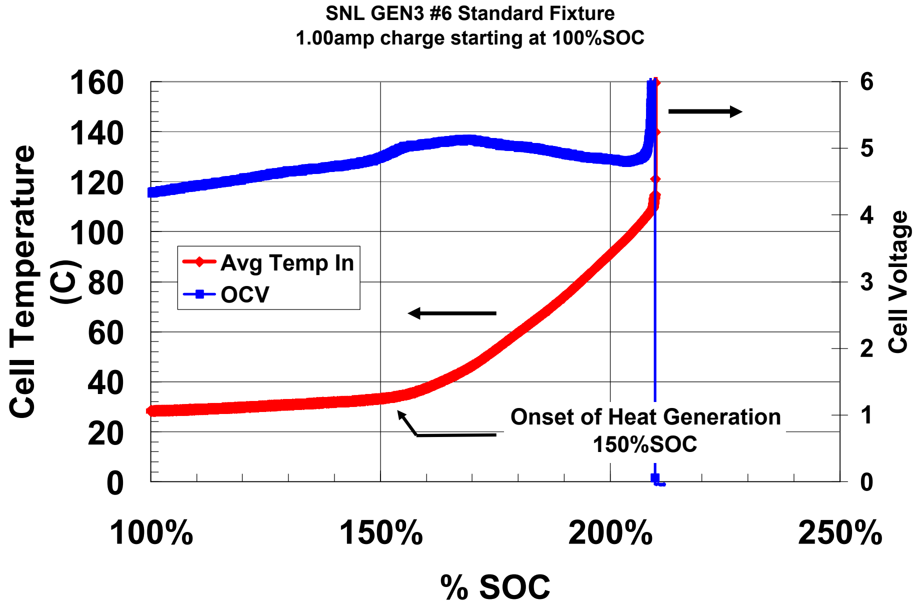
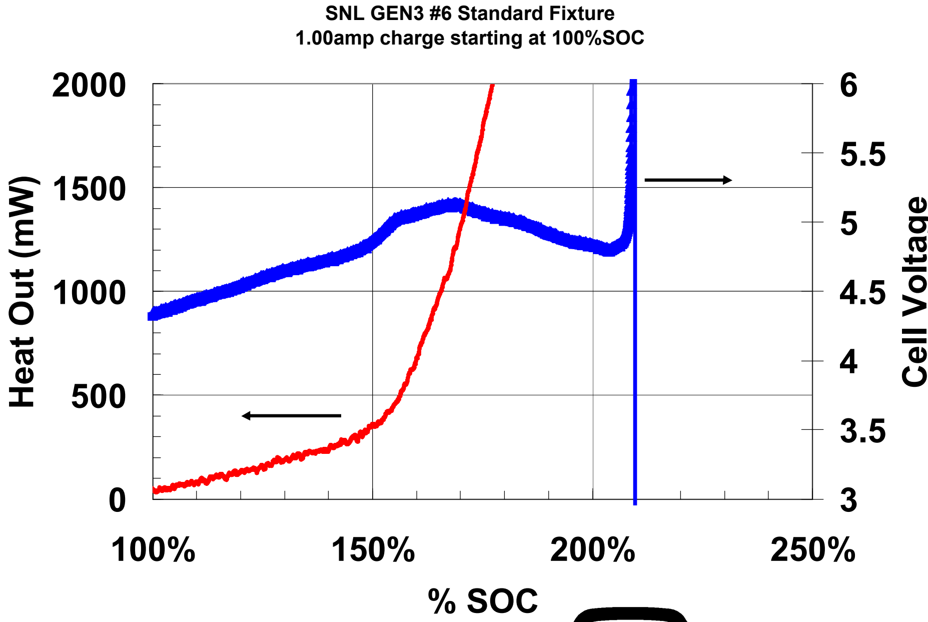
1C Overcharge Rate/4.3V 100%SOC (Air Atmosphere)

Heat Output Increases at 150% SOC

Cell Thermal Runaway at Surface Temperature of 120ºC

(internal Temperature ~135ºC)





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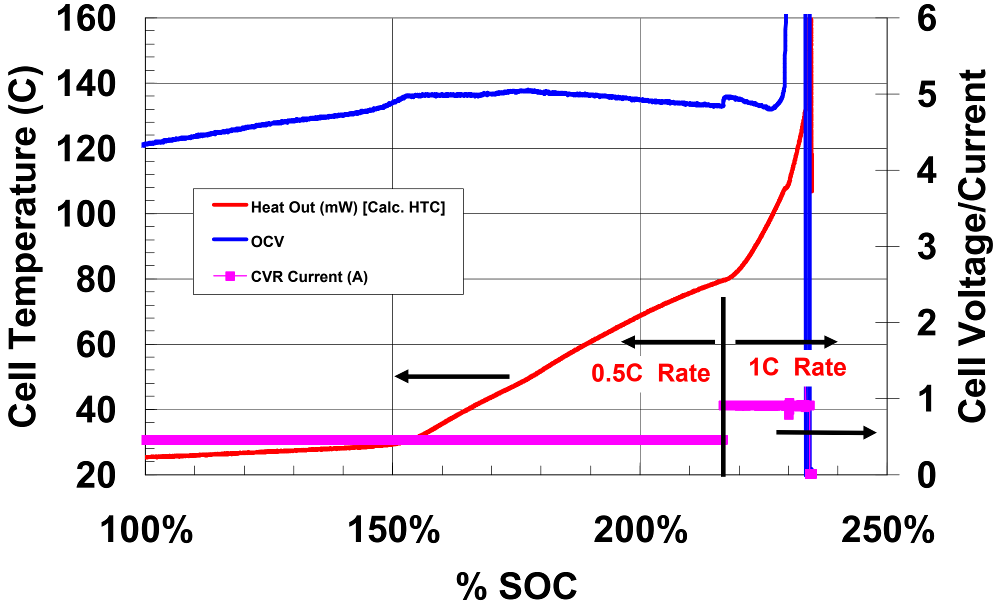
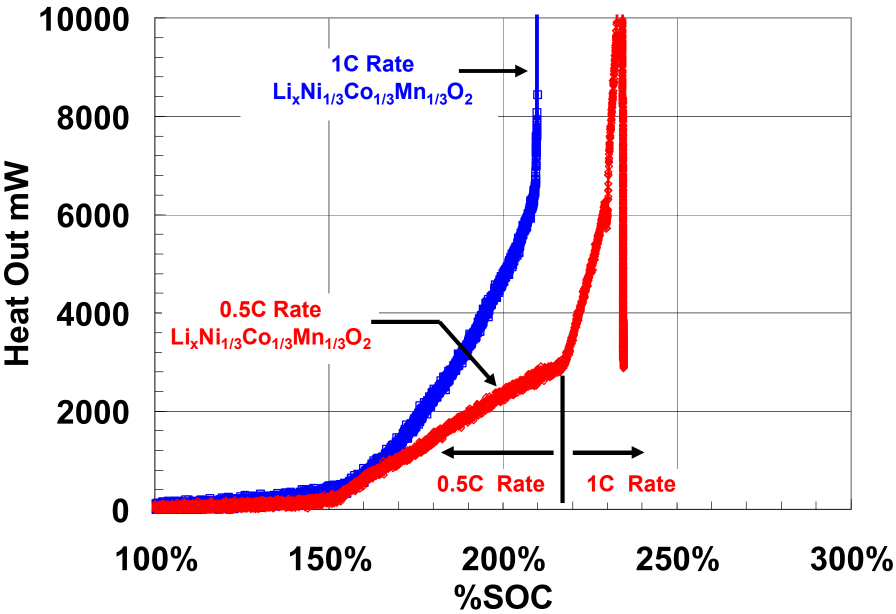
Overcharge Response: 0.5C/1C Rate $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

No Runaway at 0.5C at over 200%SOC

Same level of heat output up to 165%SOC for 0.5C and 1C Rates

Runaway at 1C/Cell Temp 130ºC (Separator Shutdown)

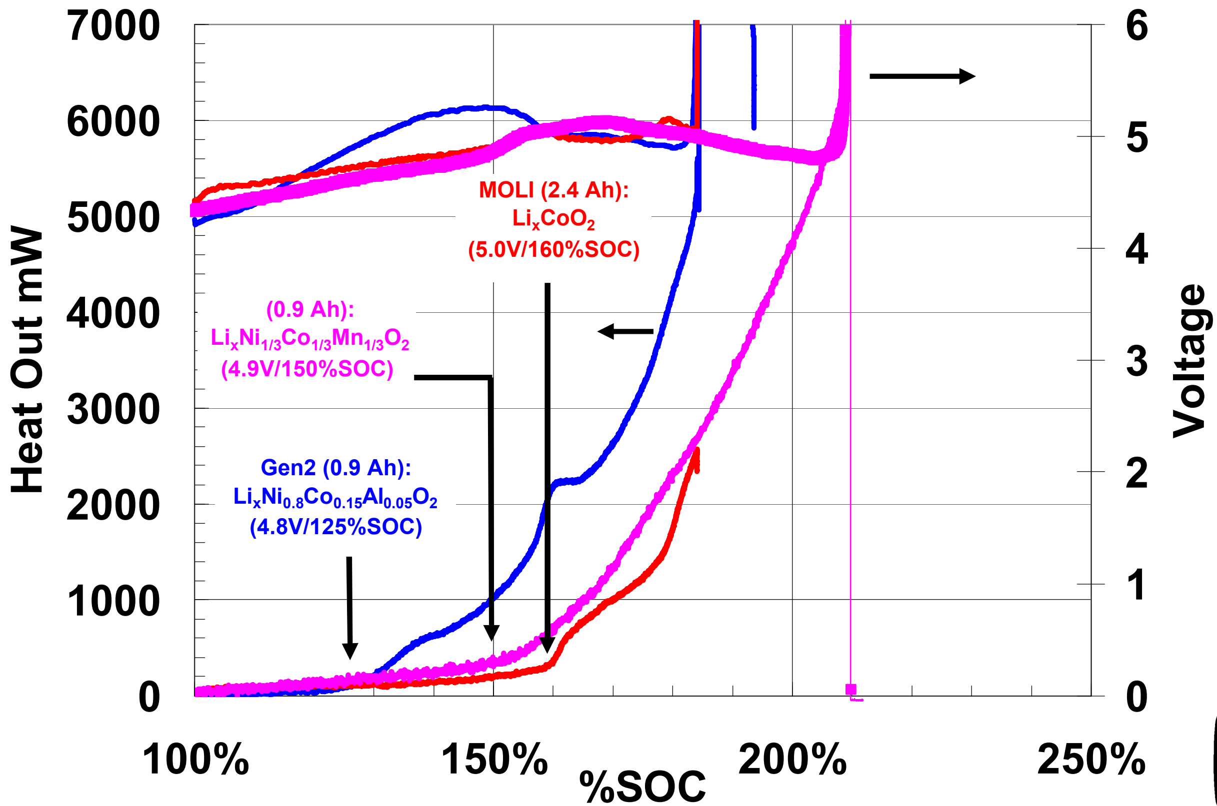




Overcharge Response Comparisons
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$

New Cathode Shows Improved Overcharge Response

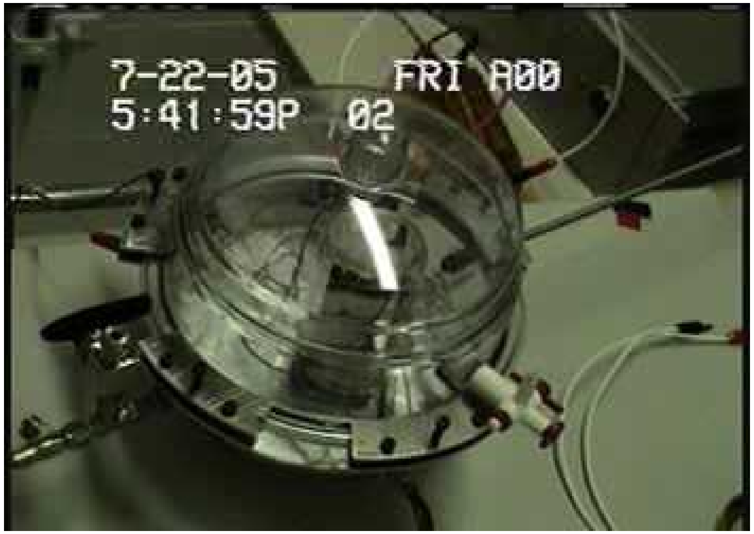
Heat Generation at Higher State of Overcharge



Overcharge Runs
MCMB Anode/$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Cathode

Nitrogen Atmosphere

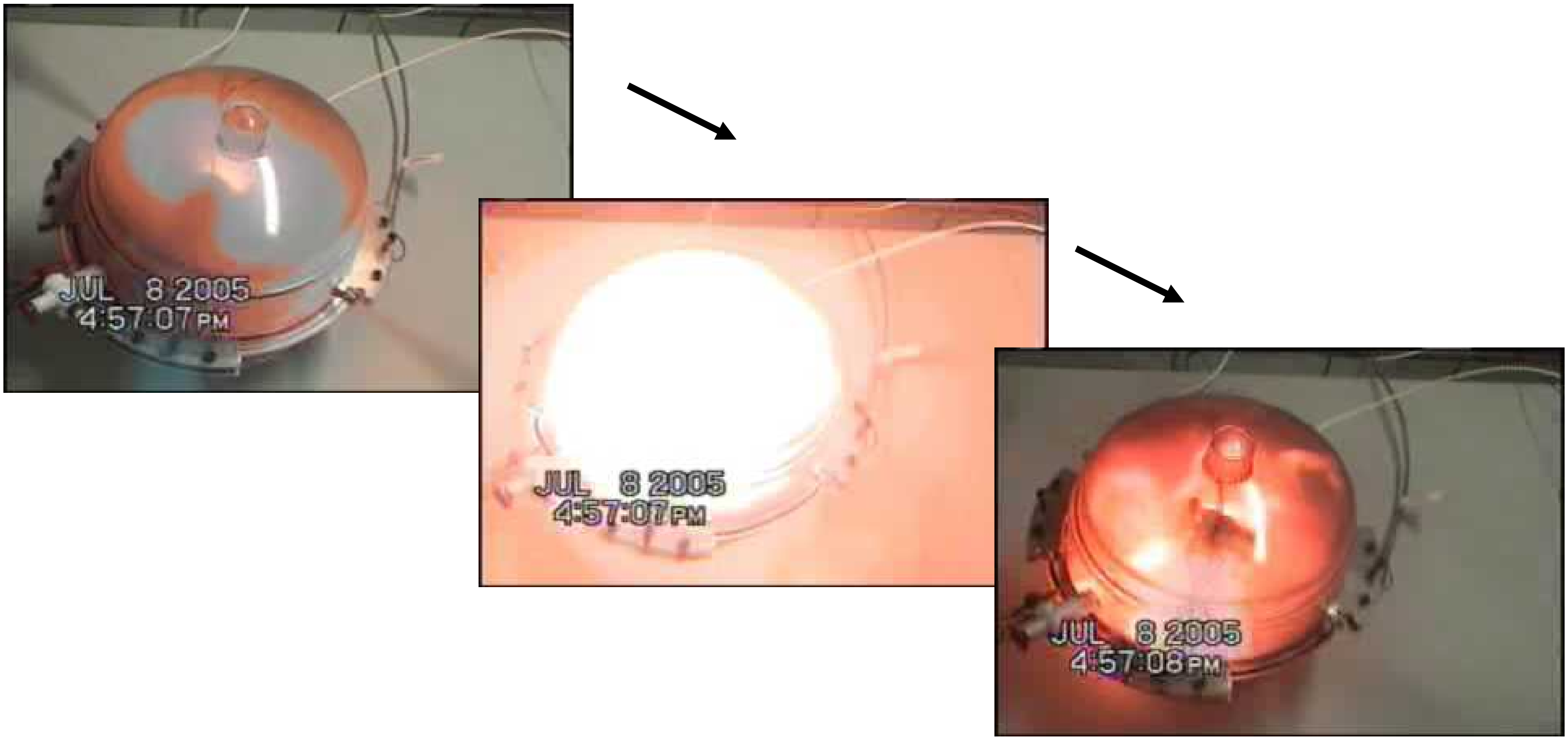
No vapor ignition



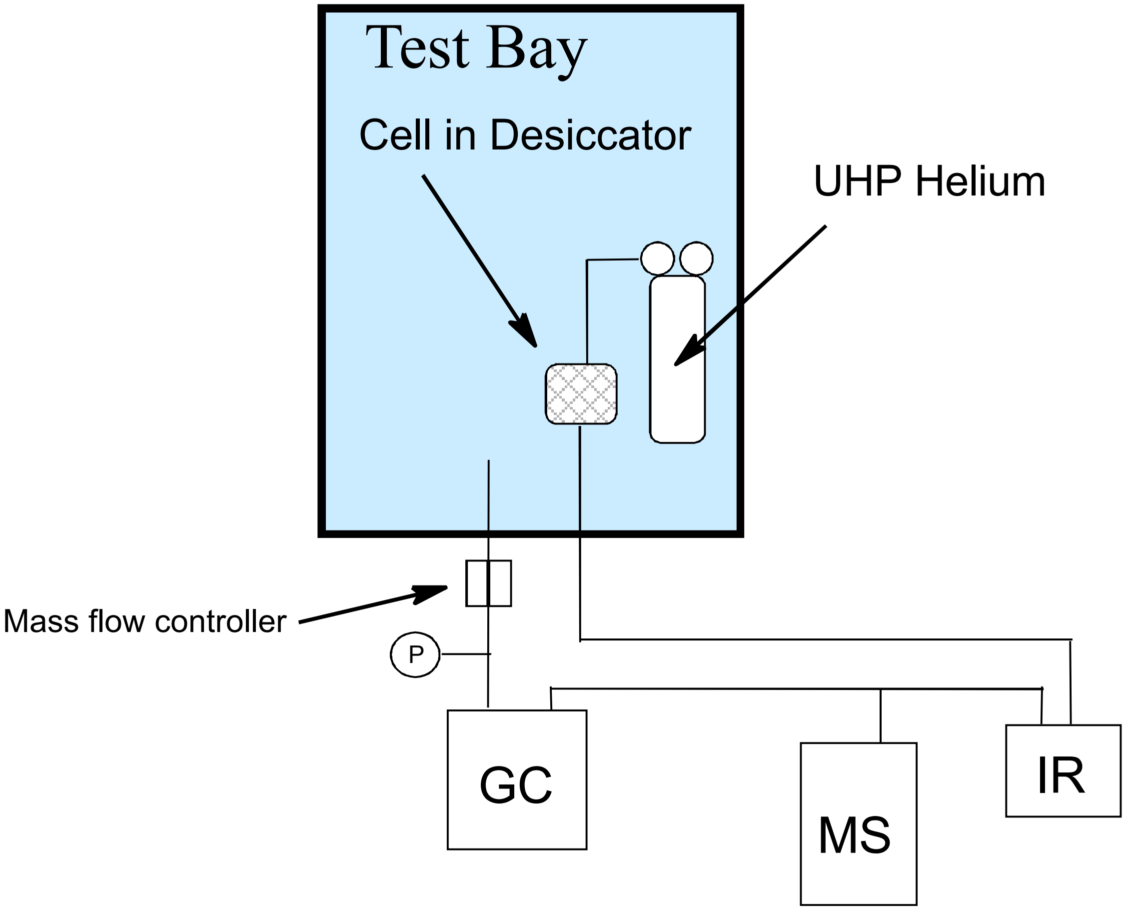
Air Atmosphere

Fuel/air explosion in confined space

Overcharge Explosion in Air



Overcharge Run in Nitrogen Real-Time Gas Analysis



Sampling Intervals

FTIR - 15 sec

MS - continuous

GC - 20 min
(new system 6 min)

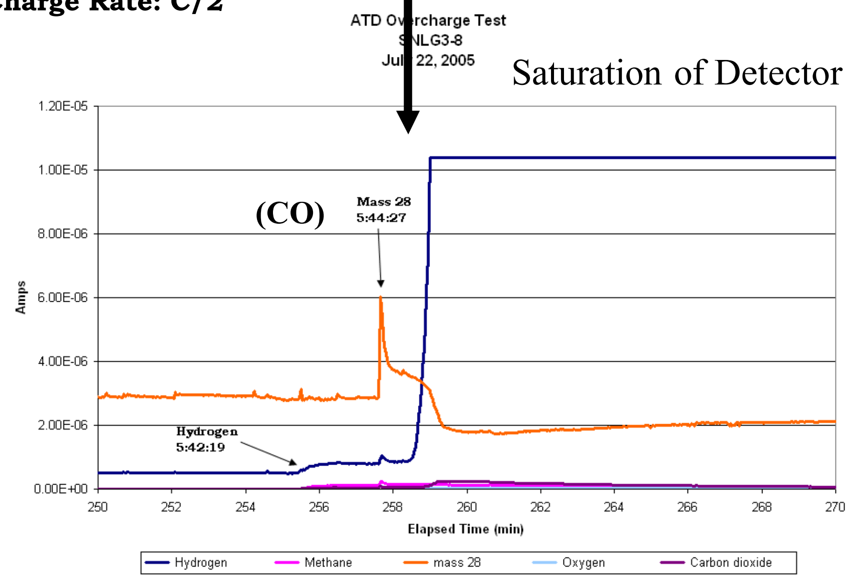
Gas Analysis of Overcharge Run

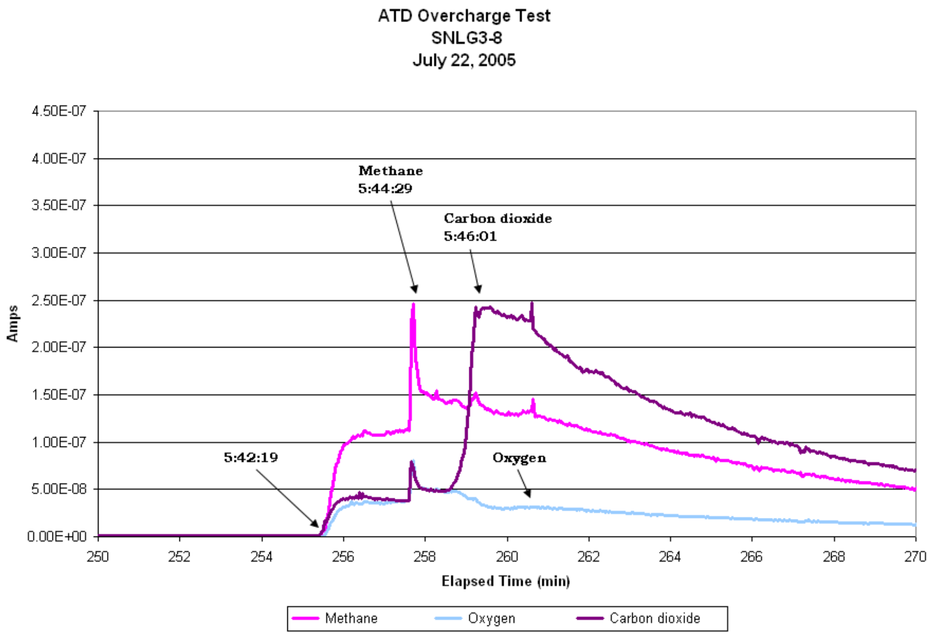
High Level of H_2 Generation

Runaway

Charge Rate: C/2

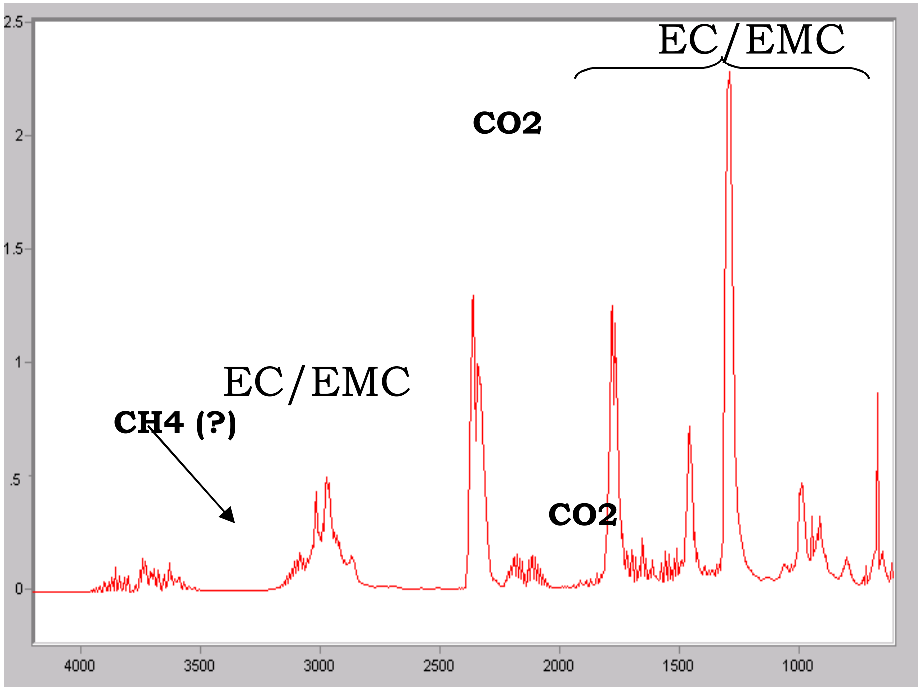
Saturation of Detector

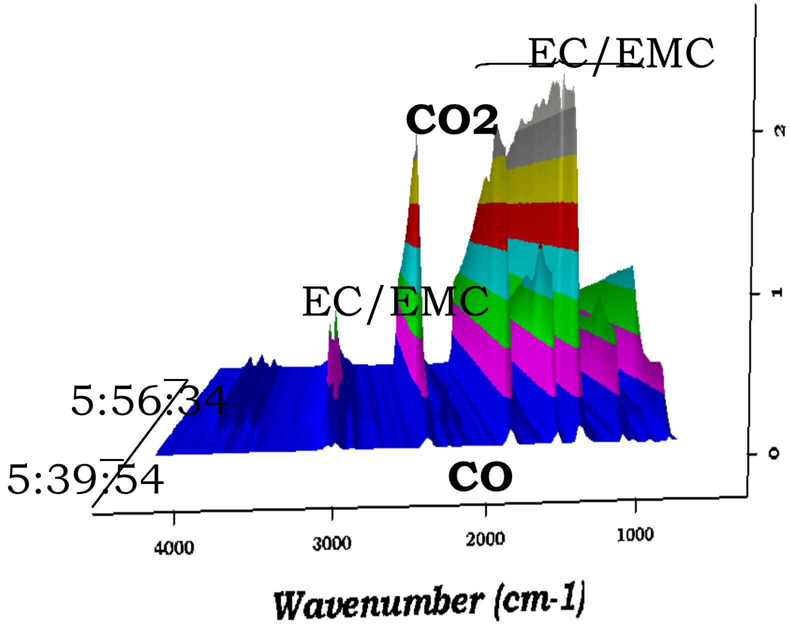




FTIR Analysis of Thermal Runaway Gases Confirmation of MS Gas Species

Incombustible Gases: CO_2, CO
Combustible Gases: CH_4, solvent vapors





Separator Response During Shutdown

How does the separator respond to applied potentials after thermal shutdown and at higher temperatures?

Does the separator breakdown at a definite potential as a function of temperature?

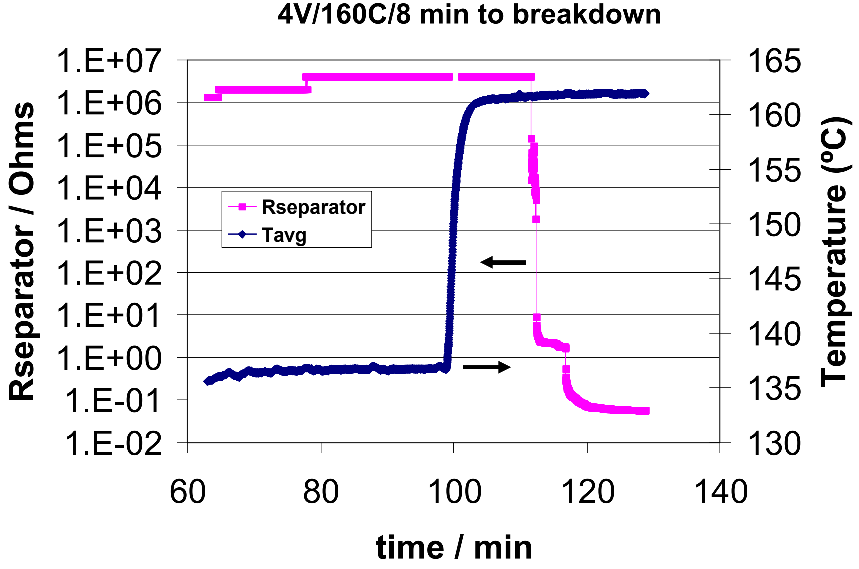
Does breakdown always result in an internal short?

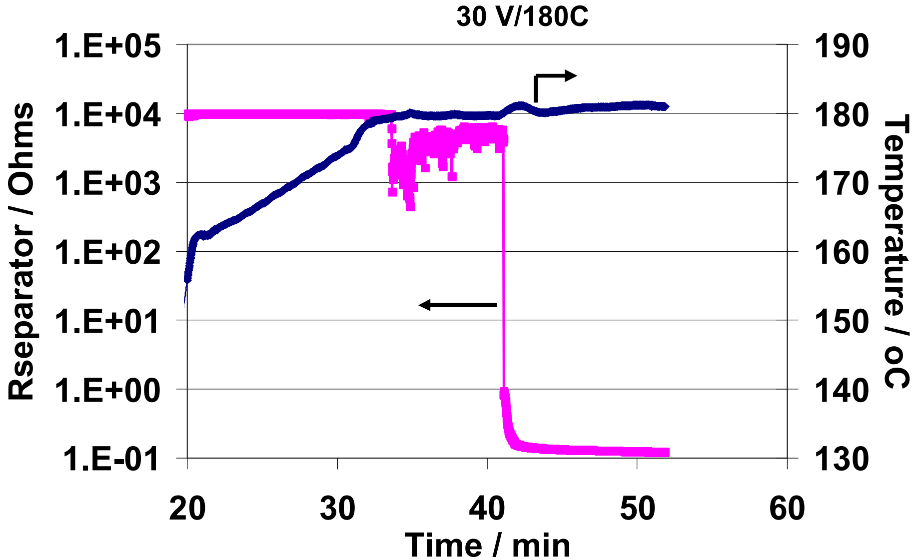
Breakdown Does Not Occur Immediately On Application of Potential Even at High Temperatures

Celgard 2325 Tri-layer Separator

Breakdown 49 min after applying 4V; 8 min after reaching 160ºC

Breakdown 24 min after applying 30V potential; 7 min after reaching 180ºC





Module Abuse Response

Shutdown Separator Response is Critical to Module Abuse Response

Separator Shutdown in a Series String of Cells Results in Cell Failure That Can Cascade into the Full Module

Thermal Runaway of Module

Interactions Between Cell Leads to a Cascading Failure and Multiplication of Cell Runaway Response

Overcharge Response of Single 18650 Cell

Overcharge Response of 84V/20 Cell Module

Summary

- Thermal Response of Full Cells Can Be Understood From Individual Cell Thermal Properties
  - Anodes Responsible for Initial Low Rate Runaway
  - Cathodes Responsible for High Temperature, High Rate Runaway
  - New Cathode Materials Result in More Stable Cells and More "Graceful" Failures
  - Additives Can Reduce Flammability of Cell Vapors and Mitigate Thermal Runaway Reactions
  - Overcharge Response is Largely a Thermal Runaway Reaction Initiated by Separator Shutdown
- Collections of Cells Lead to Cell to Cell Interactions
  - Cascading Failures
  - Multiplication of Cell Abuse Response

Acknowledgements

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