Li-Ion Safety: New Material and Cell Performance

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Advanced Technology Development

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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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Li-Ion Rechargeable Batteries Advanced Technology Development (ATD) Program

- DOE's Advanced Technology Development (ATD) Program addresses the three barriers that remain for batteries in hybrid electric vehicles -
  - ***(1) high cost, (2) short calendar life, and (3) poor abuse tolerance.***
- FreedomCAR is Stakeholder (through USABC)
- Focus is Li Ion Rechargeable Chemistry
- Involves 5 US National Laboratories and 1 DoD Lab
  - Sandia National Labs, Argonne National Lab, Lawrence Berkeley National Lab, Idaho National Engineering & Environmental Lab, and Brookhaven National Lab
  - Army Research Lab
- Technical goal is to
  - **Observe and Characterize** the response of cells and materials
  - **Develop Understanding** of source of thermal output and gas generation
  - **Improve Abuse Performance** with alternate materials or additives.

Cell Chemistries Evaluated in ATD Program

- **Cathode materials:**
  - $LiNi_{0.85}Co_{0.15}O_2$ (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)
- **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 LiPF6
  - LiBOB, LiBETI
- **Additives:**
  - SEI enhancer – Vinyl ethylene carbonate (VEC); Vinylene carbonate (VC)
  - Flame retardants– e.g. Phosphazene-based "Phoslyte" from Bridgestone; phosphate TPP; …

EC = Ethylene Carbonate; PC= Propylene Carbonate EMC = Ethyl (Methyl) Carbonate

Sandia 18650 Cell Build Capability for Thermal Abuse Tolerance Studies

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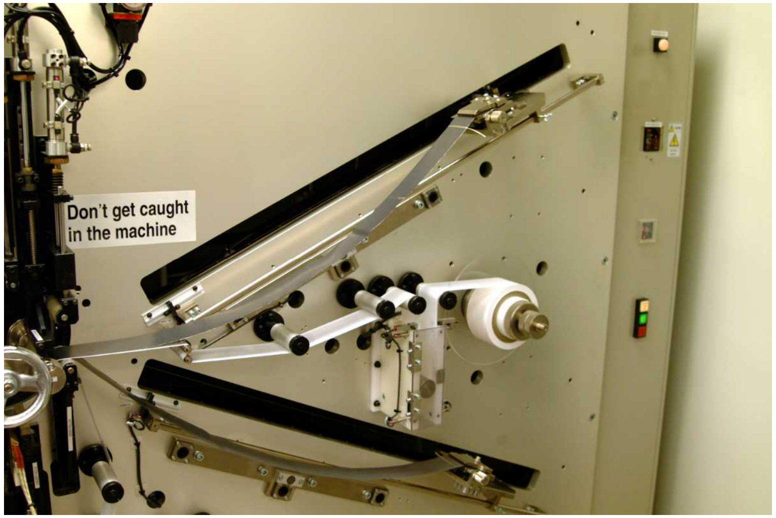
All Cells Built at Sandia Using Custom Coated Electrodes in the 18650 Configuration

Winder System

Electrode/Separator Feed



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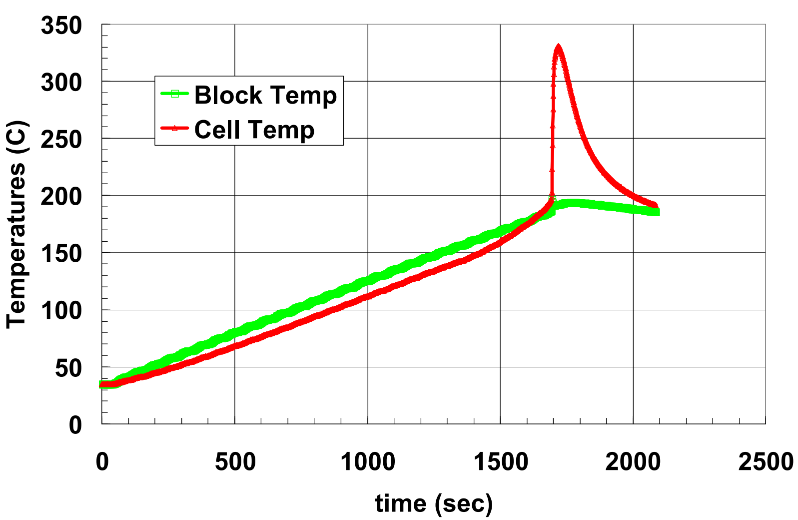
Thermal Runaway Can Be Grouped Into Three Major Temperature Regimes

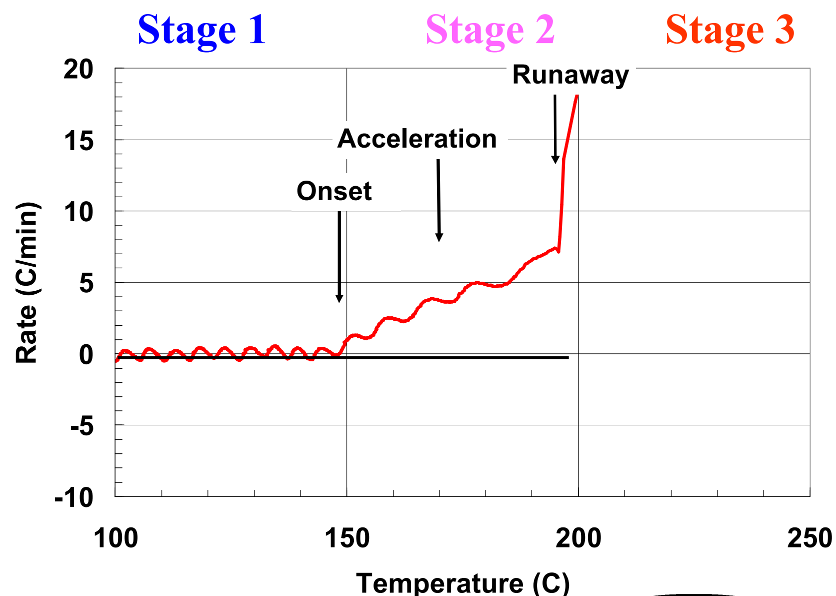
Thermal Ramp Response (100% SOC)

- 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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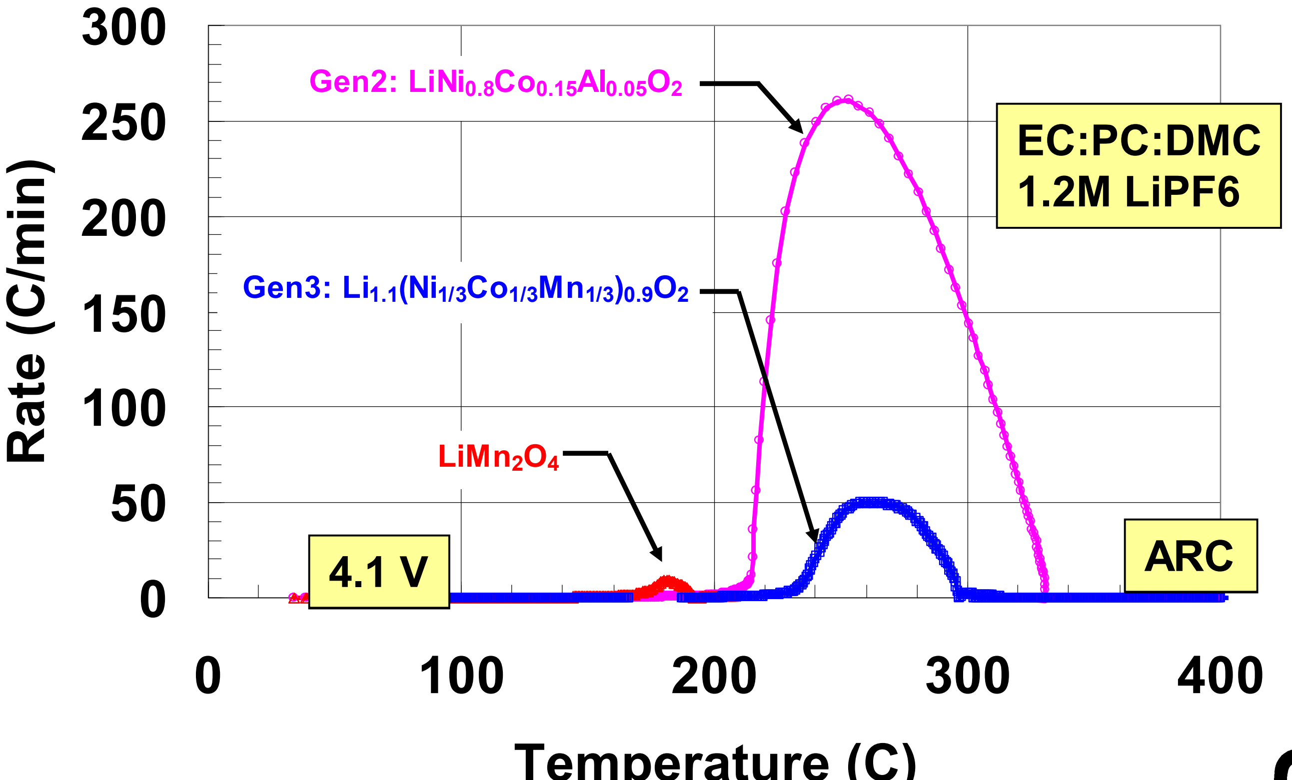
Mechanisms of Runaway Reactions

- **Stage 1 (RT-150°C):**
  - Reaction and breakdown of SEI 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

Thermal Runaway Cathode Comparisons $Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$ / $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2/LiMn_2O_4$

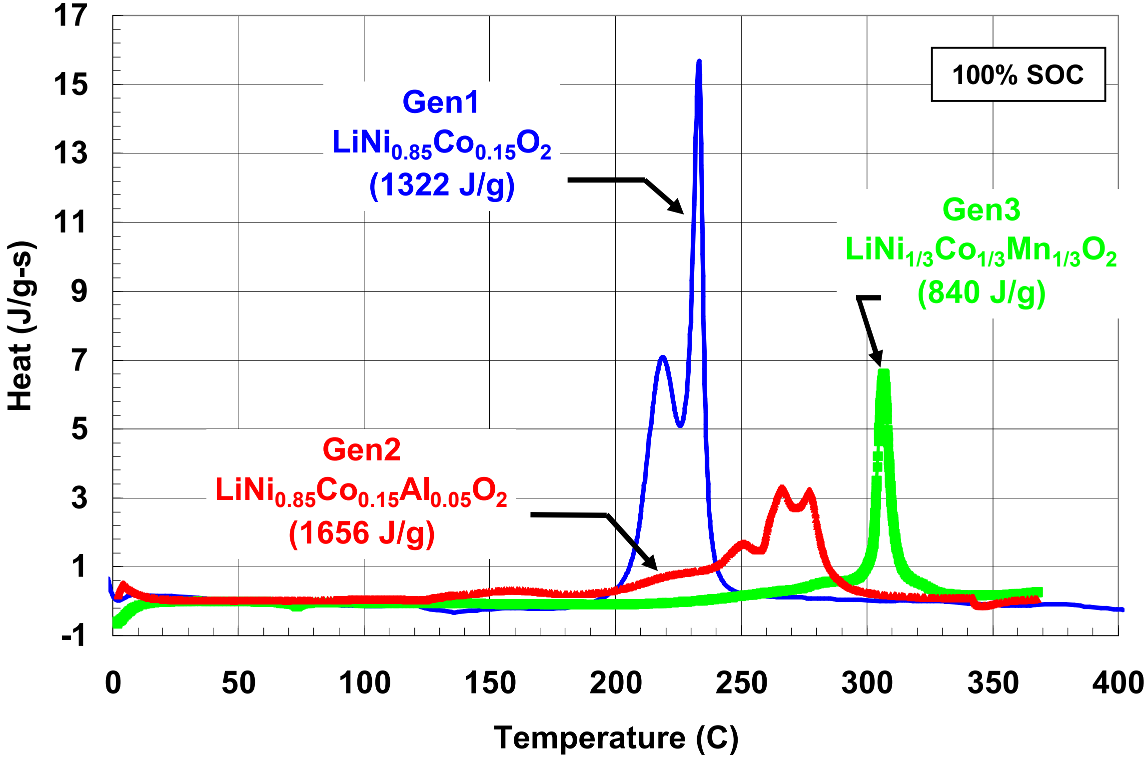
Peak Cathode Reactions Determined by Oxygen Release During Decomposition and Subsequent Electrolyte Oxidation

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



Cathode Reactions Occur at High-Temperature Regime

- Cathode Reactions (> 150°C)
  - Reaction of electrolyte at oxide particle surfaces
  - Decomposition of oxide to release oxygen and subsequently oxidize electrolyte, for example:



$$Ni_{0.8}Co_{0.2}O_2 \rightarrow \frac{1}{3} Ni_{2.4}Co_{0.6}O_4 + \frac{1}{3} O_2$$

$$3O_2 + C_3H_6O_3(DMC) \rightarrow 3CO_2 + 3H_2O$$

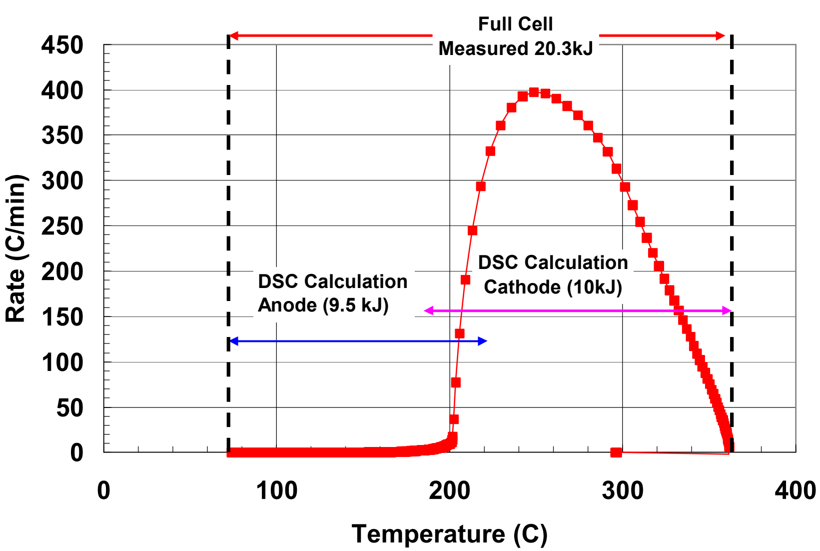
Correlation of DSC and ARC Enthalpy Values for Anode/Cathode Materials

Cathode Accounts for Energy Release During Stage 3 Runaway

Calculations Using DSC Enthalpy Give Excellent Agreement with ARC Profiles

Gen2 LixNi0.8Co0.15Al0.05O2

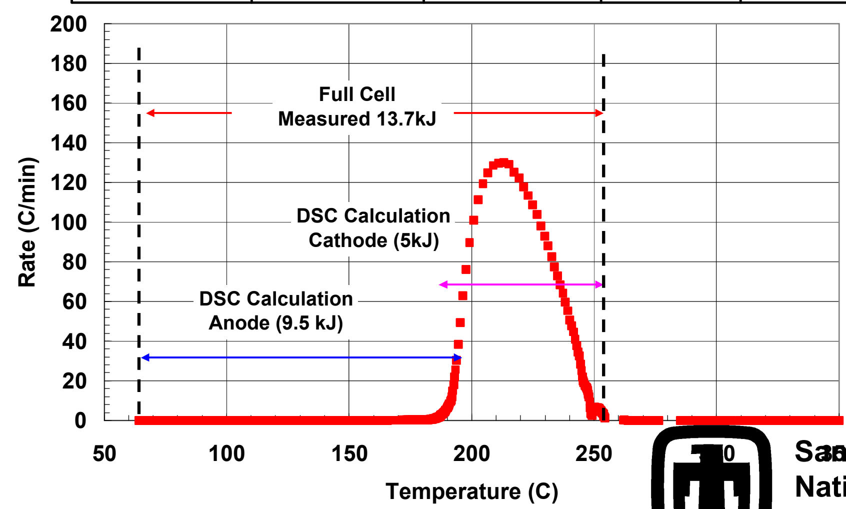
	active material wt. (g)	DSC Specific Enthalpy (kJ/g)	Enthalpy (kJ)	Resulting Delta T(C)
Anode:	4.25	2.22	9.44	131
Gen2 Cathode:	6.1	1.65	10.07	140
		Calculated Total:	19.50	271
		ARC total:	20.30	



Majority of Anode Energy Released During Low Temperature Ramp

LixNi1/3Co1/3Mn1/3O2

	active material wt. (g)	DSC Specific Enthalpy (kJ/g)	Enthalpy (kJ)	Resulting Delta T(C)
Anode:	4.25	2.22	9.44	131
LiNi1/3Co1/3 Mn1/3O2 cathode	6.3	0.78	4.91	68
		Calculated Total:	14.35	200
		ARC total:	13.70	



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Comparison of Gen2 Cathode and Gen2 Full Cell ARC Thermal Runaway Profiles

Cathode Runaway Profile Same as for Full Cell

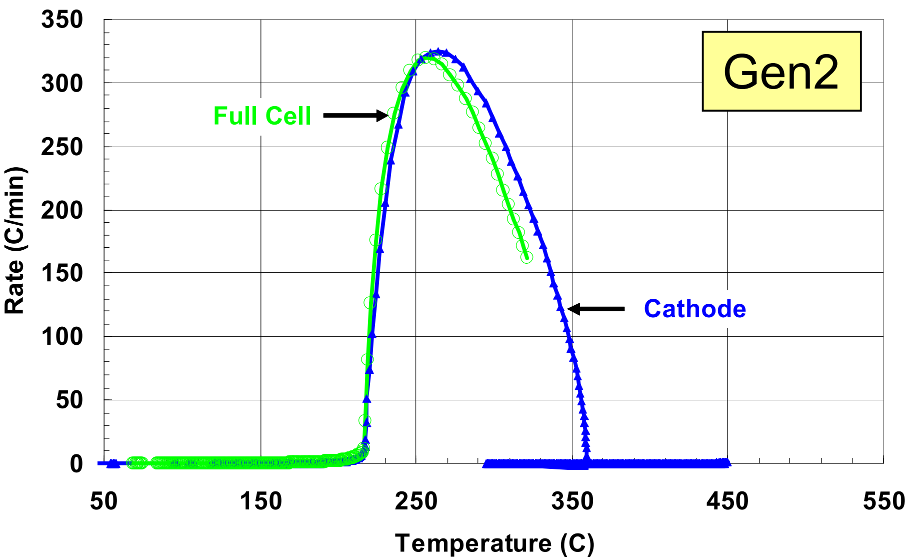
Cathode and Anode Removed from Full Cell at 100%SOC
Resealed in 18650 Cans with Electrolyte

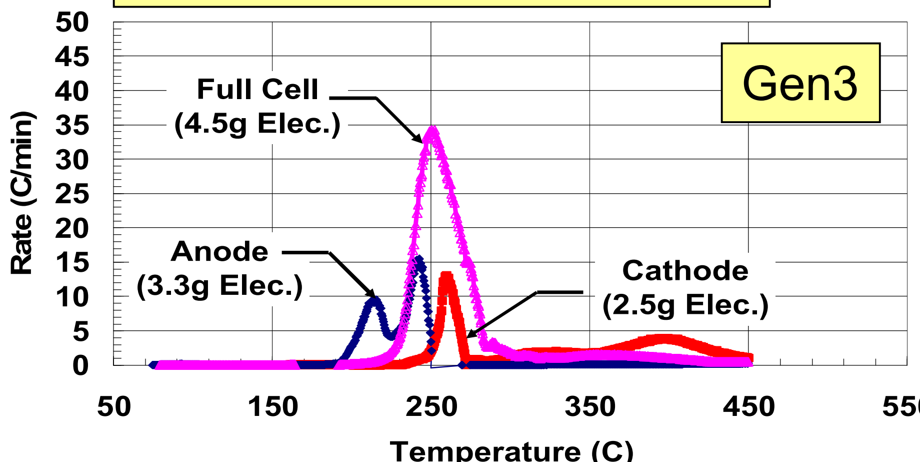
Gen2 Peak Thermal Runaway Profile Determined By Cathode Reactions

Gen3 Peak Thermal Runaway Profile Determined Equally By Anode and Cathode Reactions

Less Oxygen Generation by Cathode reduces Exothermic Electrolyte Combustion

SNL Gen2 Cathode in 18650 Can: 100%SOC





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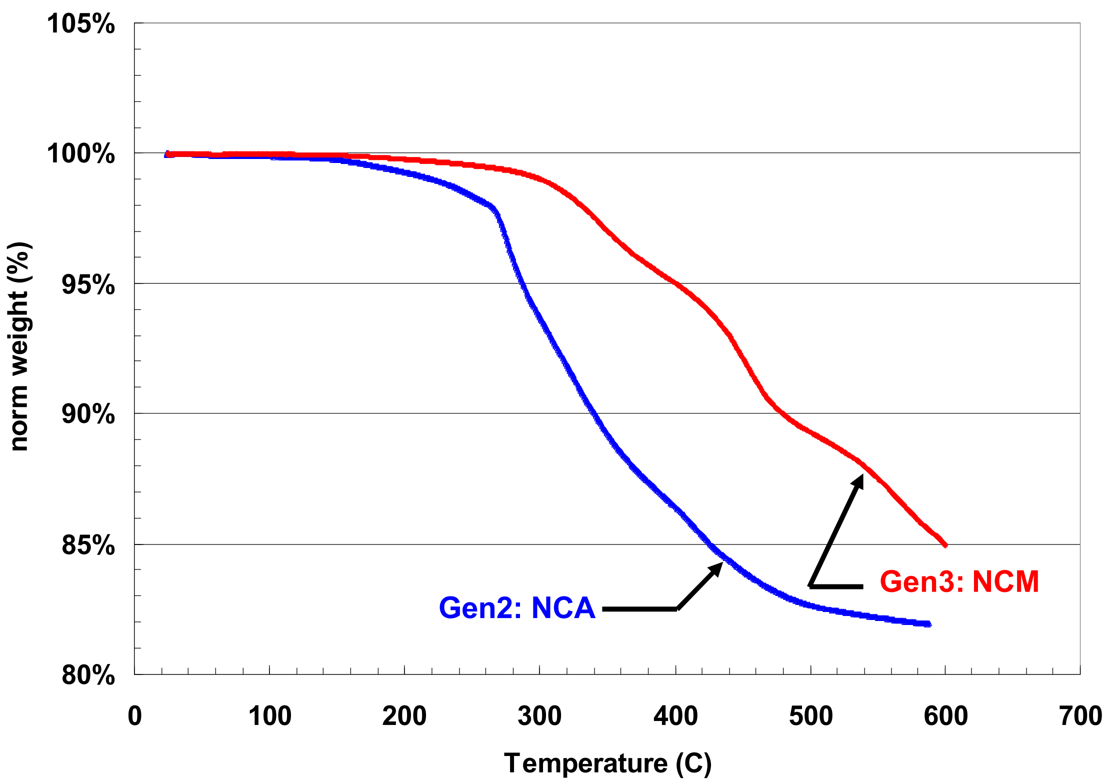
TGA Profiles

Mass Loss From Oxygen Release From Decomposing Cathodes



Oxygen Generation Correlates With ARC Reaction Rate and Enthalpy

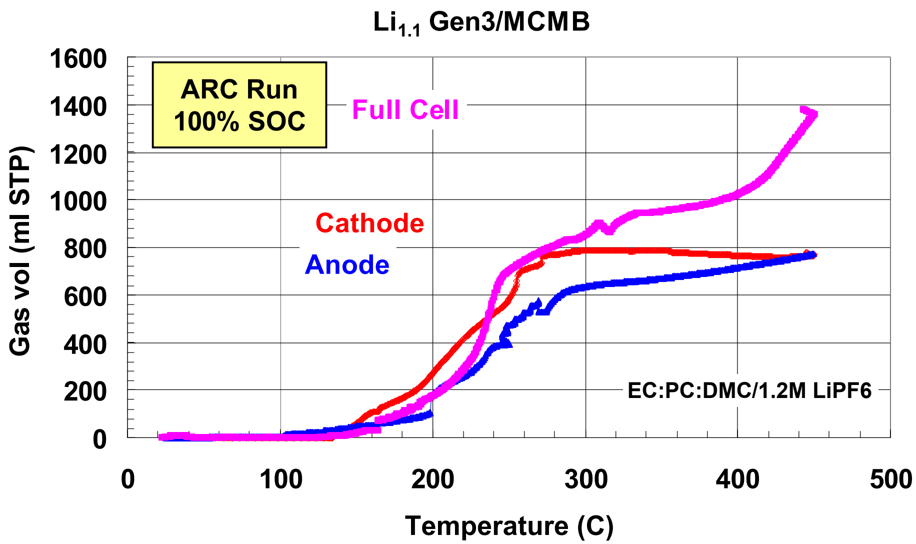
Gen2 Shows Highest Mass Loss and Greatest Reaction Rate

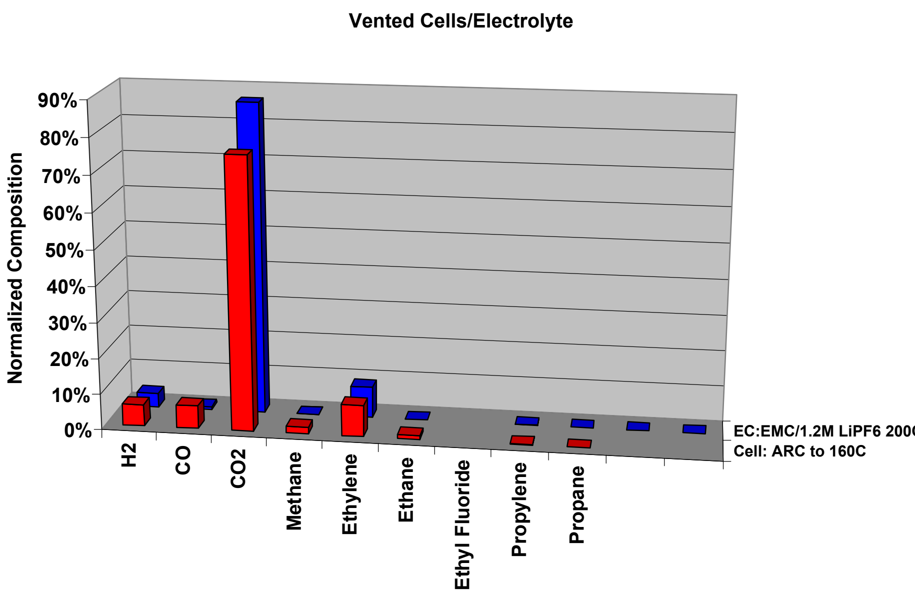
Gas Evolution and Composition

Onset of Gas Generation at Cathode Around 150°C

Total Volume of Gas From Cell Accounted for by Individual Electrodes

Gas Composition Largely CO_2 Both for Full Cell and Electrolyte Decomposition





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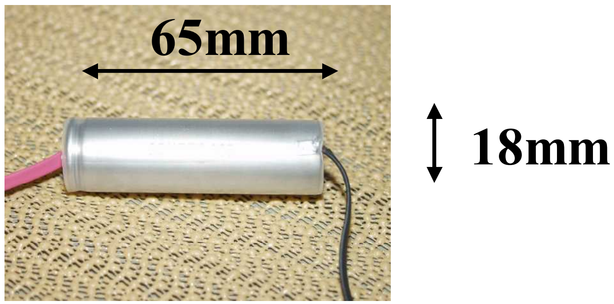
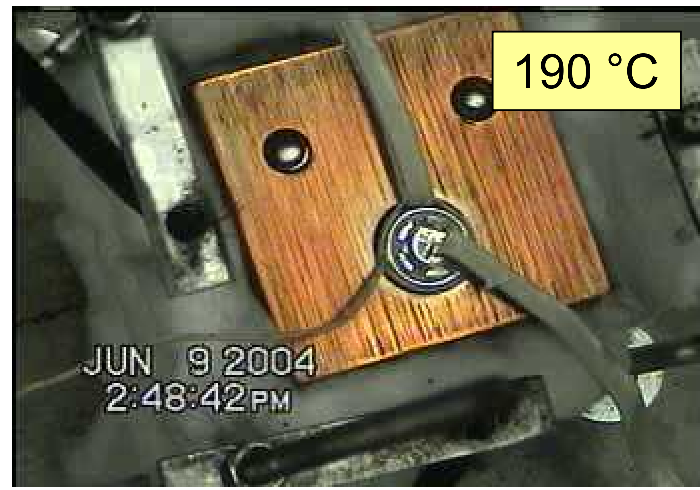
Thermal Ramp Apparatus

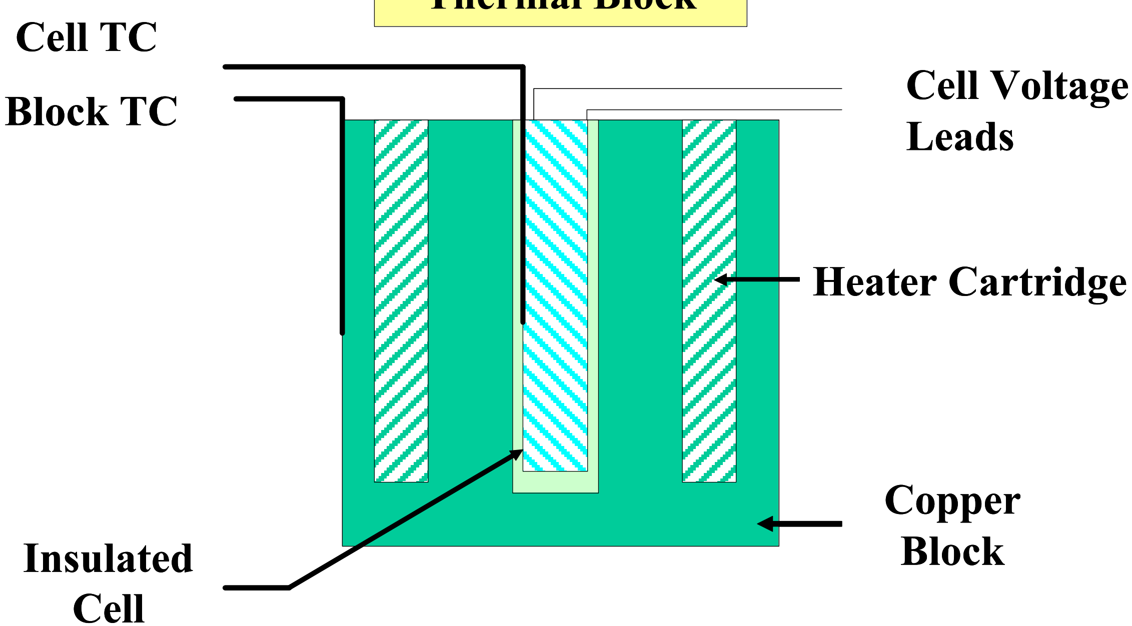
Ramp to runaway in air with external ignition



Ramp at 6 °C/min



Thermal Block



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

Thermal Ramp of Commercial 18650 Cell Similar to Laptop Battery Cell

Ignition of Vented Solvent Vapors

Stage 3 Thermal Runaway

Cell Temperature ~ 190°C

Thermal Ramp

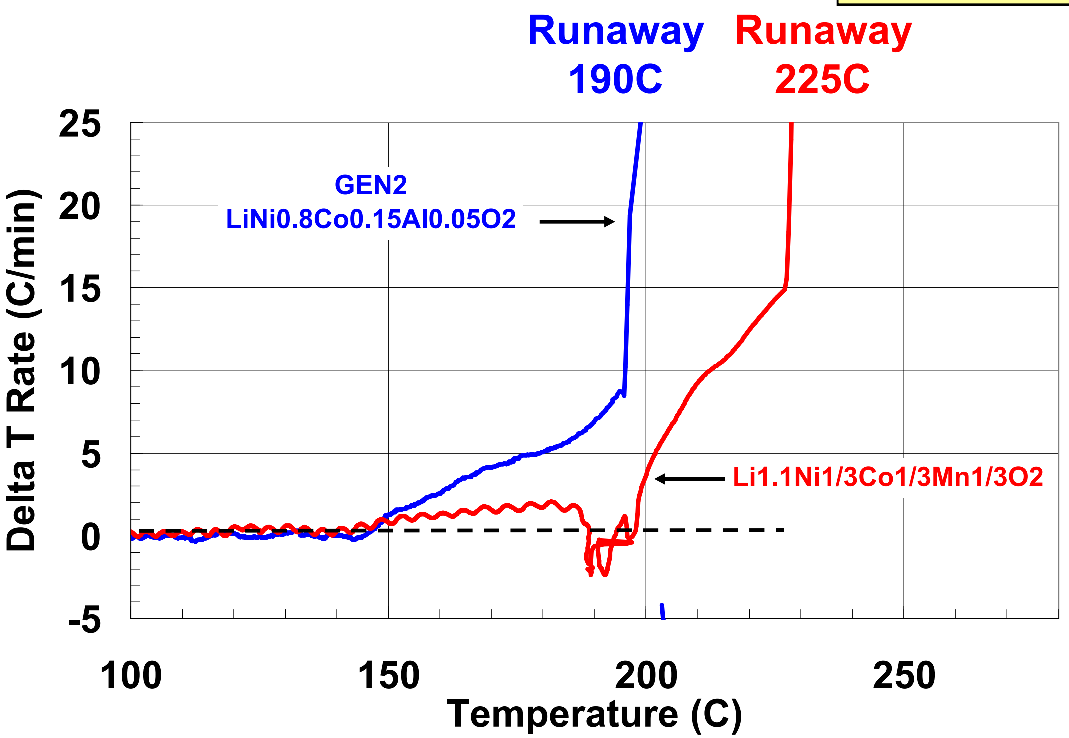
$Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$ 1.2M $LiPF_6$/EC:PC:DMC

Cells Show Delayed Runaway Response

Onset of Thermal Runaway Same as Gen2/GDR Baseline Cell

No Explosive Runaway! Cell Remained Intact

Vapor Flammability not affected by cathode material



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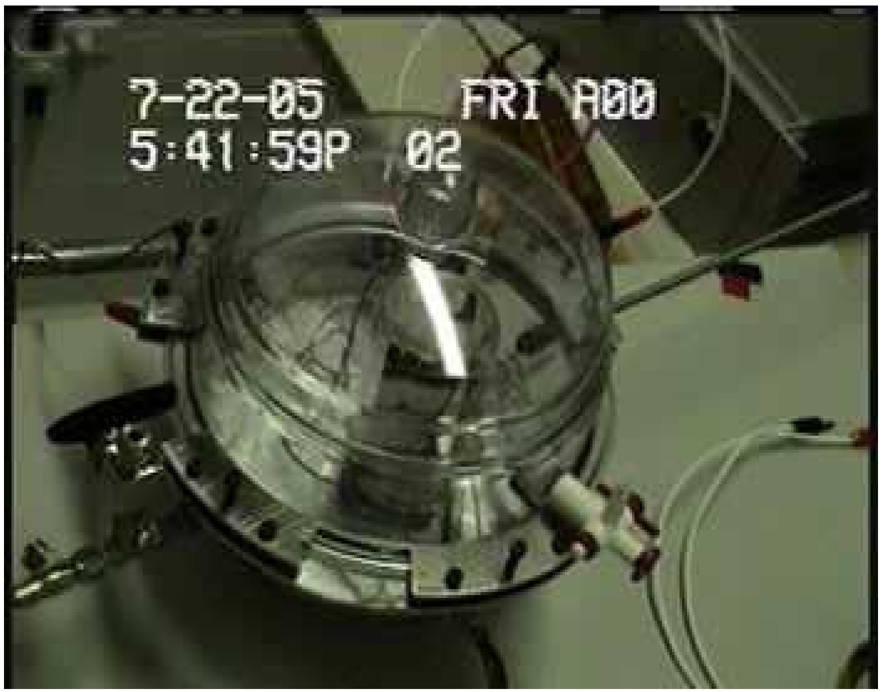
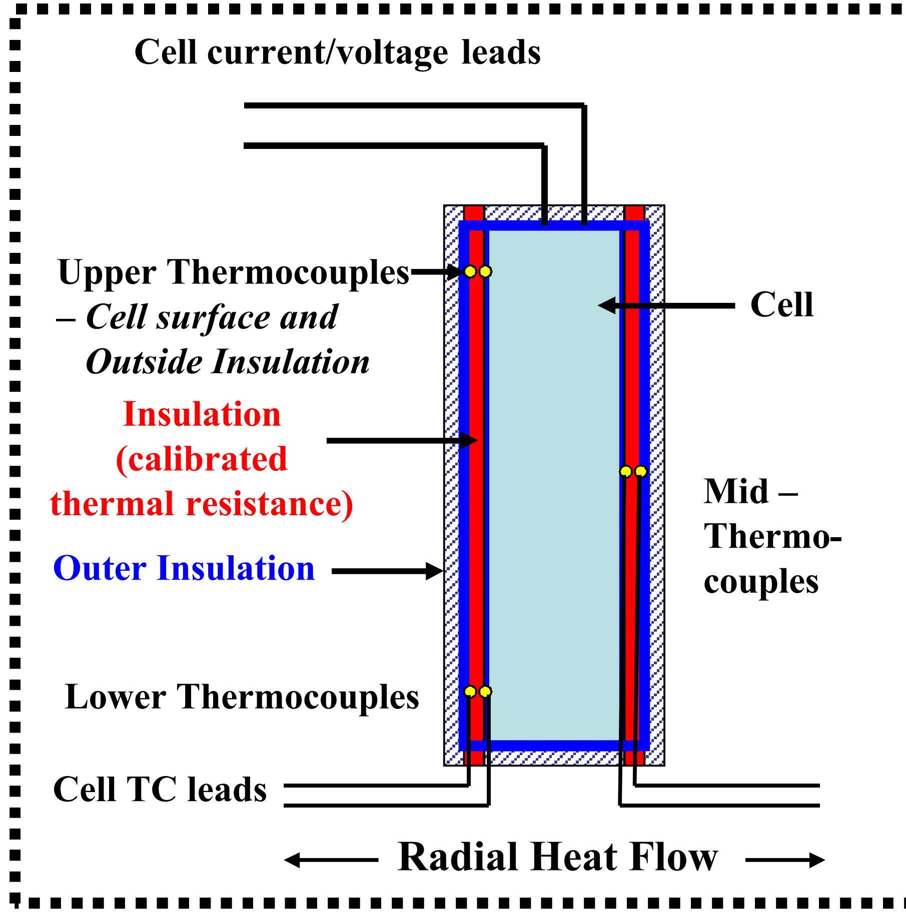
Overcharge Test Setup

Allows Us to Measure Heat Output and Control Temperature Profile



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



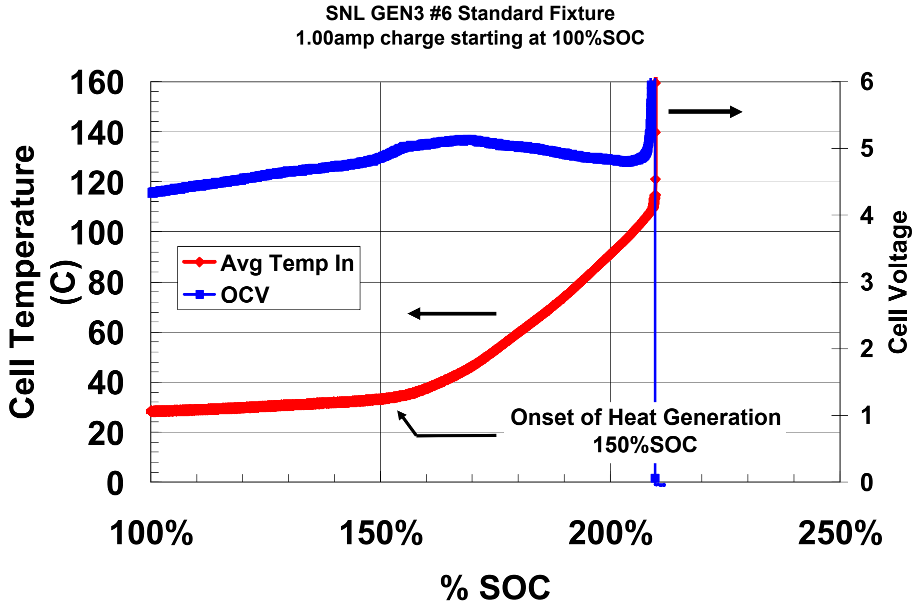
Overcharge Response 1C Rate $Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$

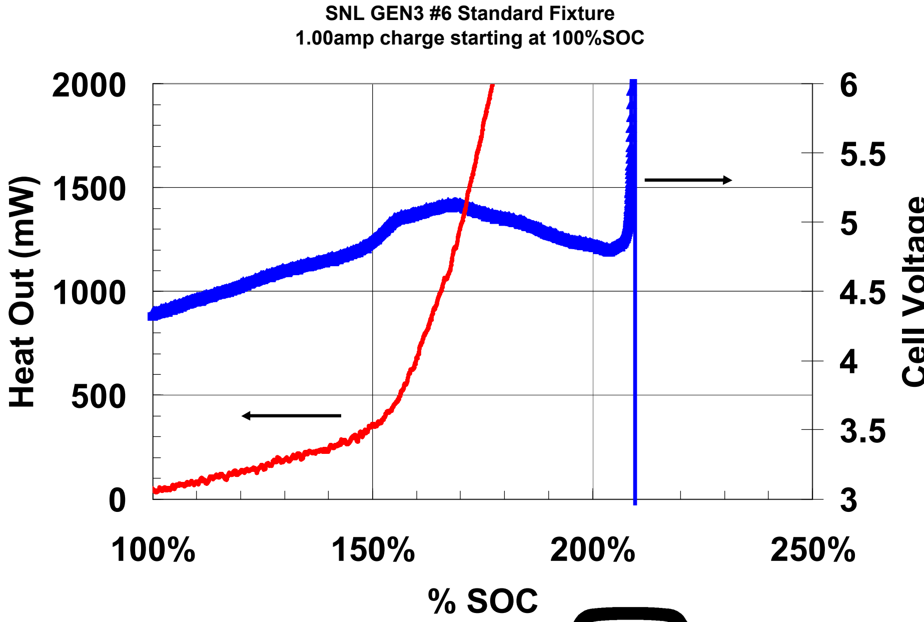
1C Overcharge Rate/4.3V 100%SOC (Air Atmosphere)

Heat Output Increases at 150% SOC

Cell Thermal Runaway at Surface Temperature of 120ºC

(internal Temperature ~135ºC)





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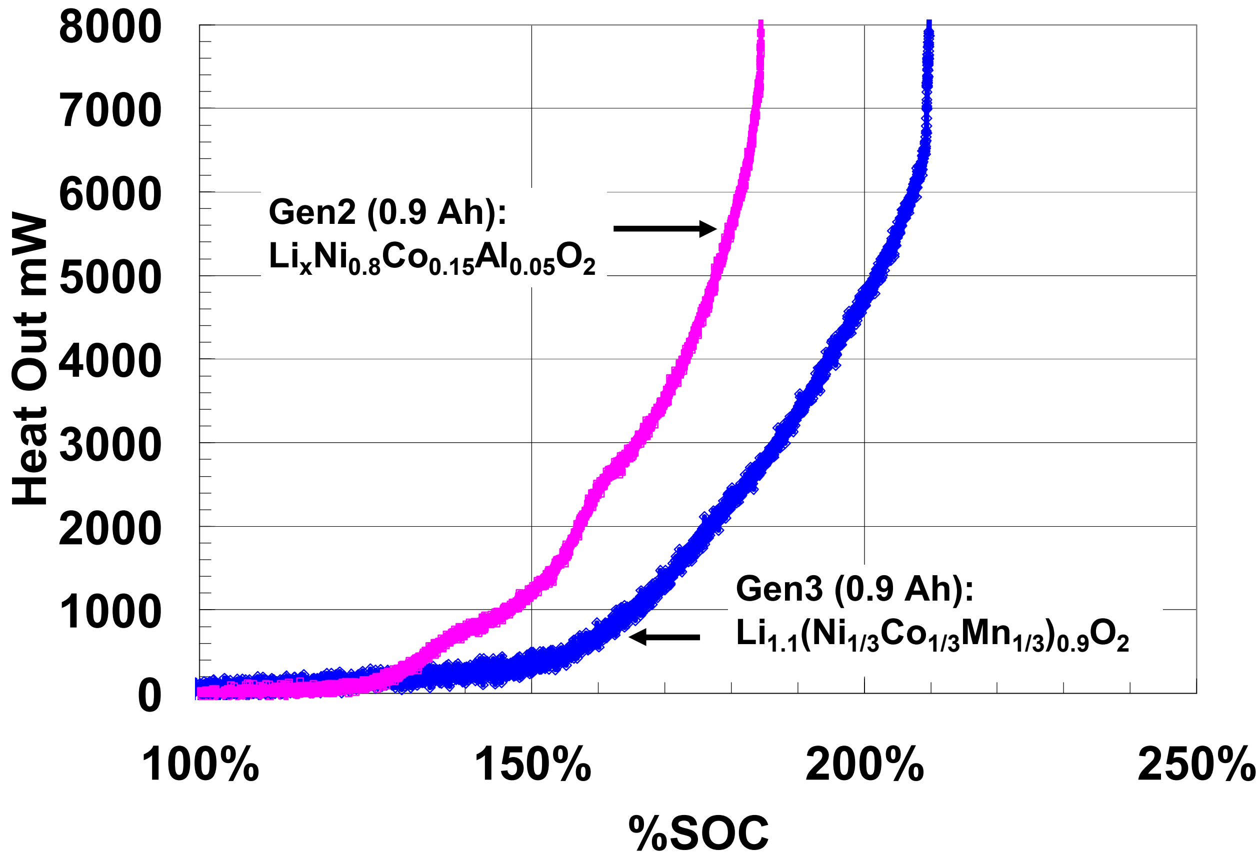
More Stable Cathodes Improve Overcharge Response



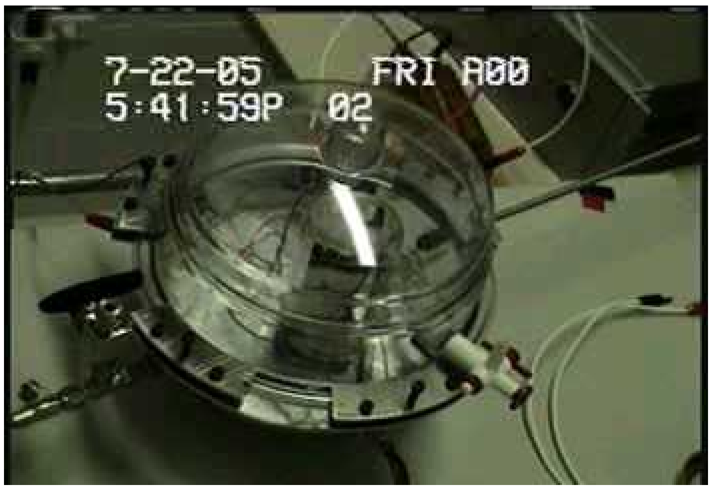
Overcharge Runs

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

Thermal Runaway Occurs After Separator Shutdown and Loss of Separator Integrity

No vapor ignition

Fuel/air explosion in confined space

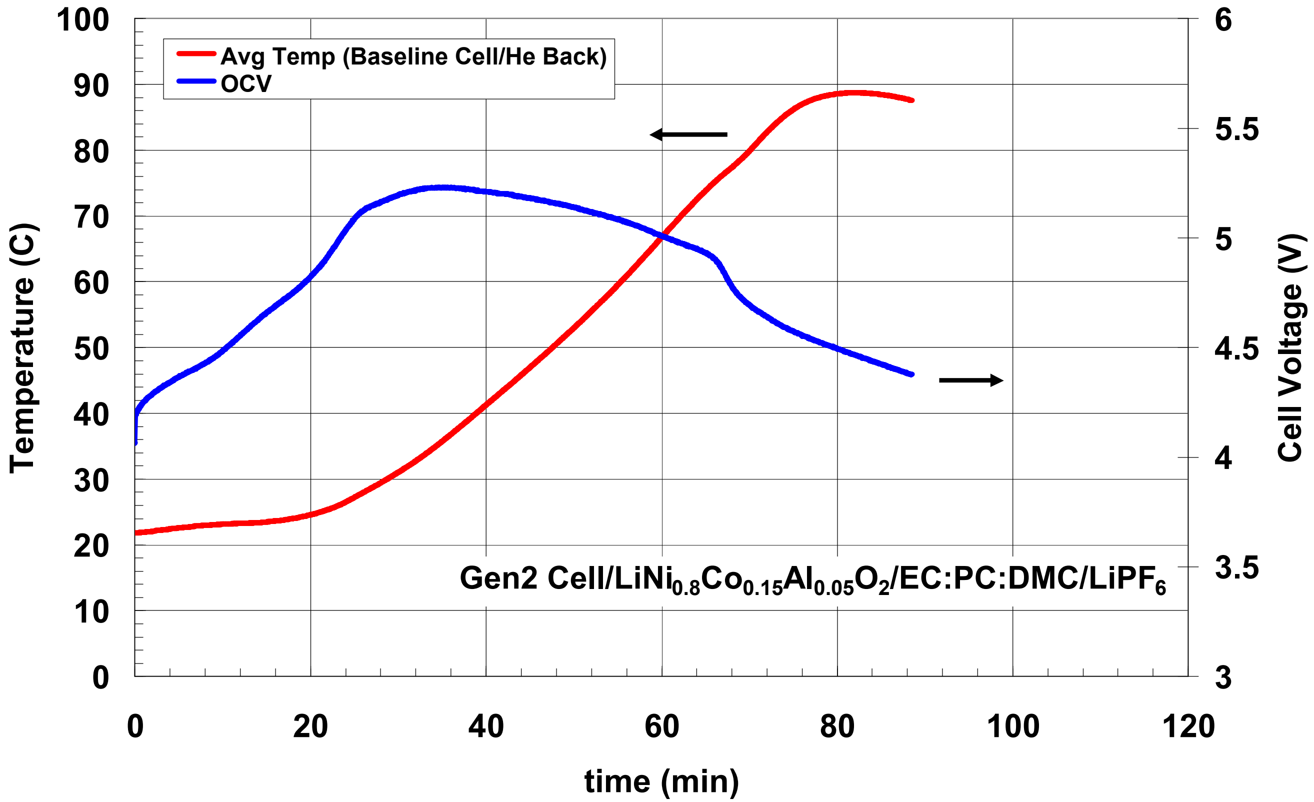


Nitrogen Atmosphere

Air Atmosphere

Overcharge in He Cover Gas

Cell Temperature Remains Below Separator Shutdown



What Gases Are Generated During Overcharge?

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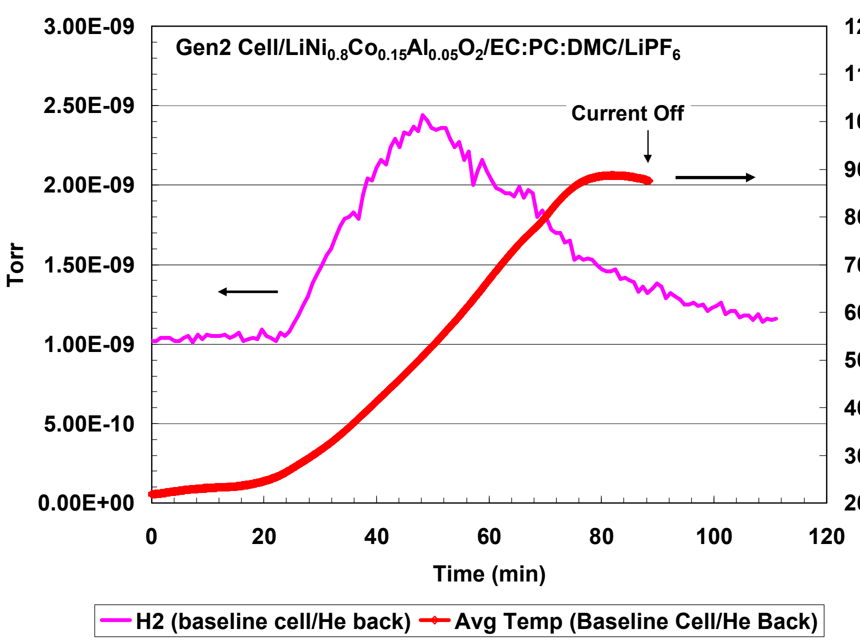
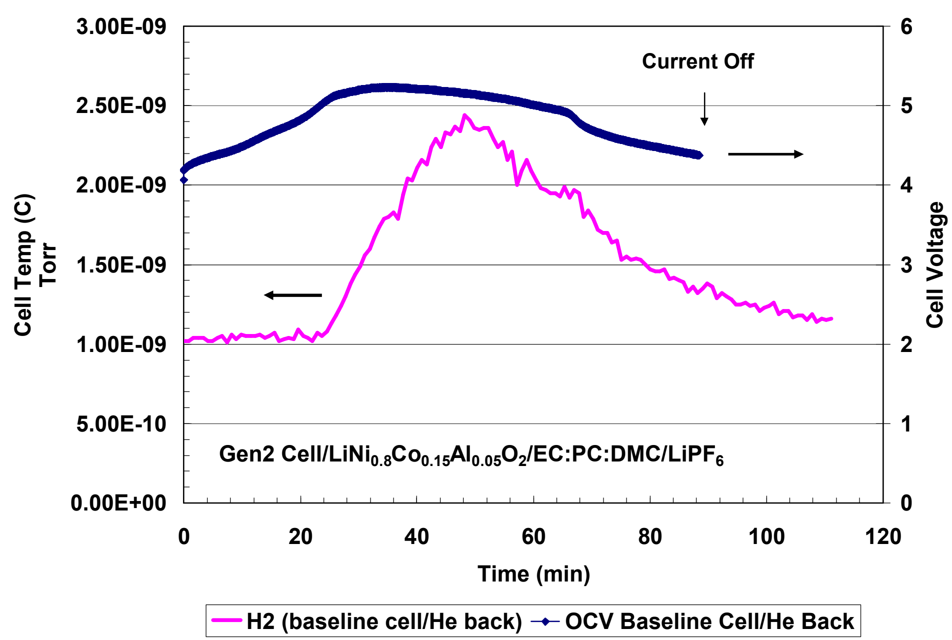
Hydrogen Generation Associated with Increased Heat Generation and Start of Voltage Turnover





Opening in Cell Can to Allow Gas Monitoring

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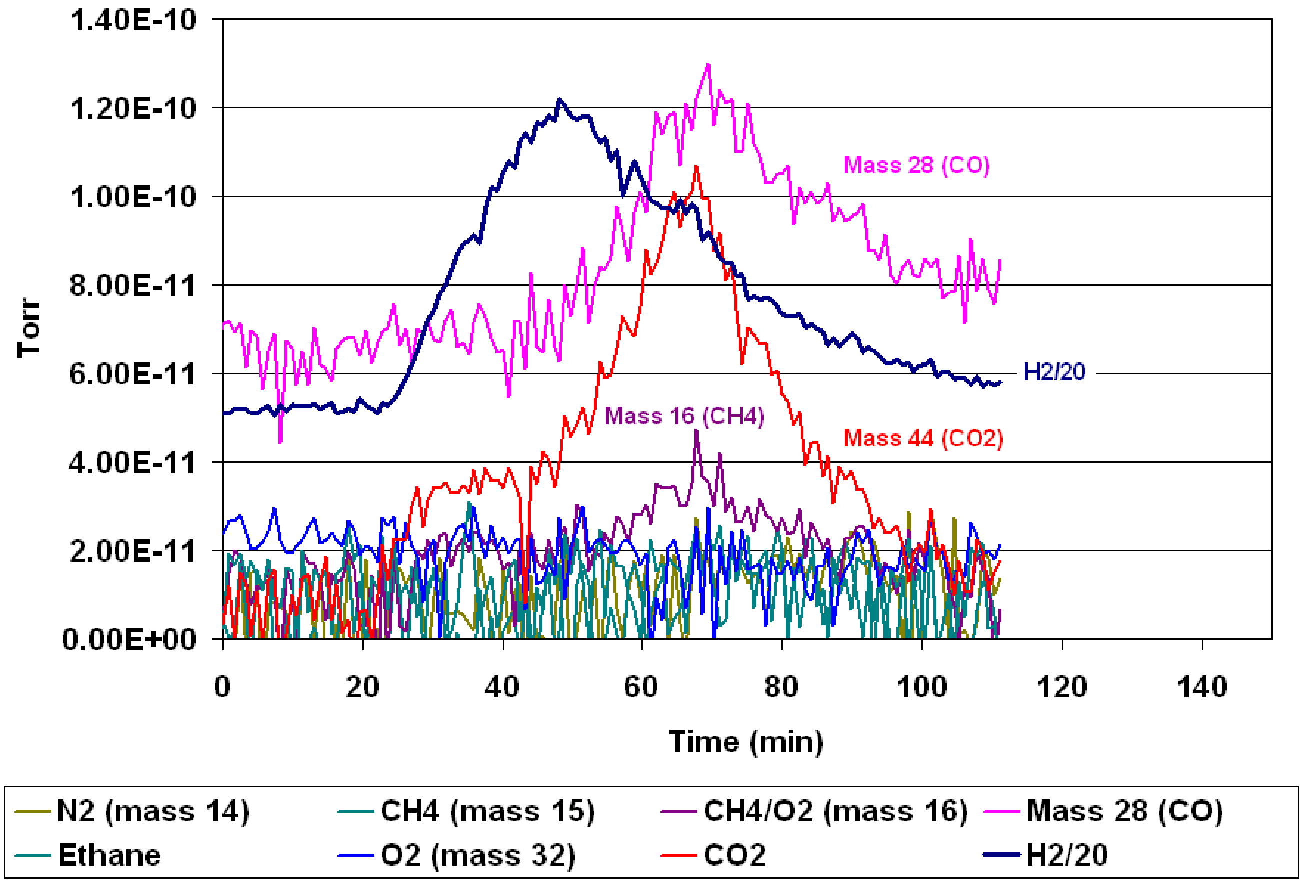
Other Gas Species Observed After Initial Hydrogen Generation



Summary

Our work on *Abuse Tolerance* continues to shed light on mechanisms that control cell response.

- Anode and cathode effects are being understood.
- Separator integrity and breakdown is important influence.
- Additives & improved cathode materials show promise for increased thermal stability.

Understanding and Control of Cell and Battery Abuse Response Will Be Even More Important as New Higher Energy Cells Are Developed for Plug-In Hybrids and Electric Vehicles

Acknowledgements

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