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Abuse Tolerant Lithium-ion Cells for Transportation Applications

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What is the Cost of Cell Failure?

- ***Independent of Field Failure vs. Abuse Failure***
- ***Materials, manufacturing & <u>liability</u> costs***
- ***Significant for large format cells and high energy systems***





SNC-Lavalin Gulf Contractors Safety Alert, June 2008

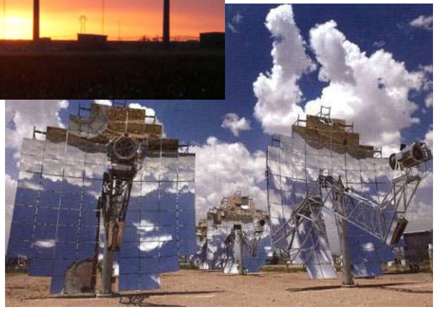
Impact of Scale

Larger batteries in larger quantities:

- ***The numbers of cells used in the automotive industry (EVs and PHEVs) could potentially be huge (billions)***
- ***EV and PHEV battery packs are much higher energy (15-50 kWh)***
- ***Increasing consideration for lithium-ion cells for utility storage (MWh systems)***

6 cells, 50 Wh battery

7000 cells, 50 kWh battery



??? cells, MWh battery

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Impact of Scale

Consumer Cells (0.5-5 Ah) → Large Format Cells (10-200 Ah) → Batteries (1-50 kWh) → Vehicle system

www.nissan.com
www.internationalbattery.com
www.samsung.com

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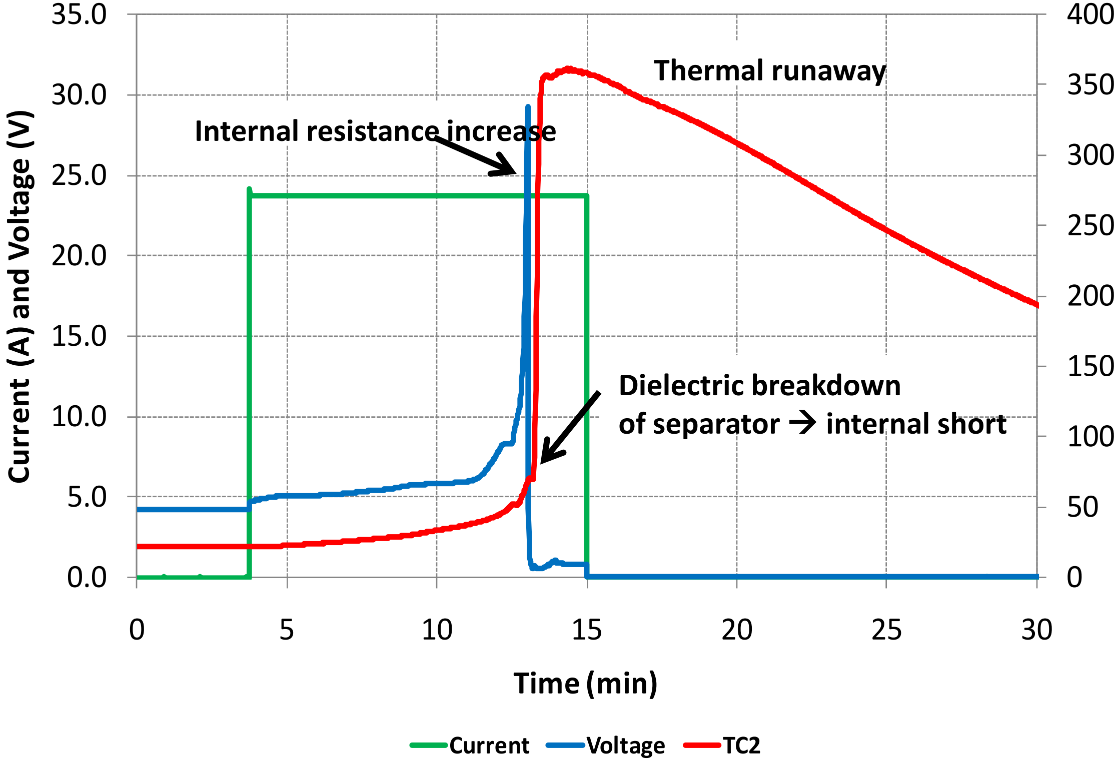
12 Ah (~50 Wh) Pouch Cell Overcharge Abuse



..\..\Movies\PL-8570170-2C_01 fire.mpg

Internal temperature limited due to ejection of cell contents

→ 500 Wh failure…. → 5000 Wh failure….

Mitigating Lithium-ion Safety Issues

Moving forward, we must work on improving safety not only of systems and controls but also inherent safety at the cell-level

Safety Issue	Mitigation Strategy	
	Materials Strategy	Engineering Controls
Thermal exposure	Stable cathode materials Cathode coatings Mimimize electrolyte combustion	PTC Thermal management
Overcharge	Redox shuttle/polymer additives Stable cathode materials Minimize electrolyte combustion	CID Fuses Voltage control electronics
Flammability	Minimize electrolyte decomposition Non-flammable solvents	Gas sensors
Mechanical abuse	Robust materials	Packaging

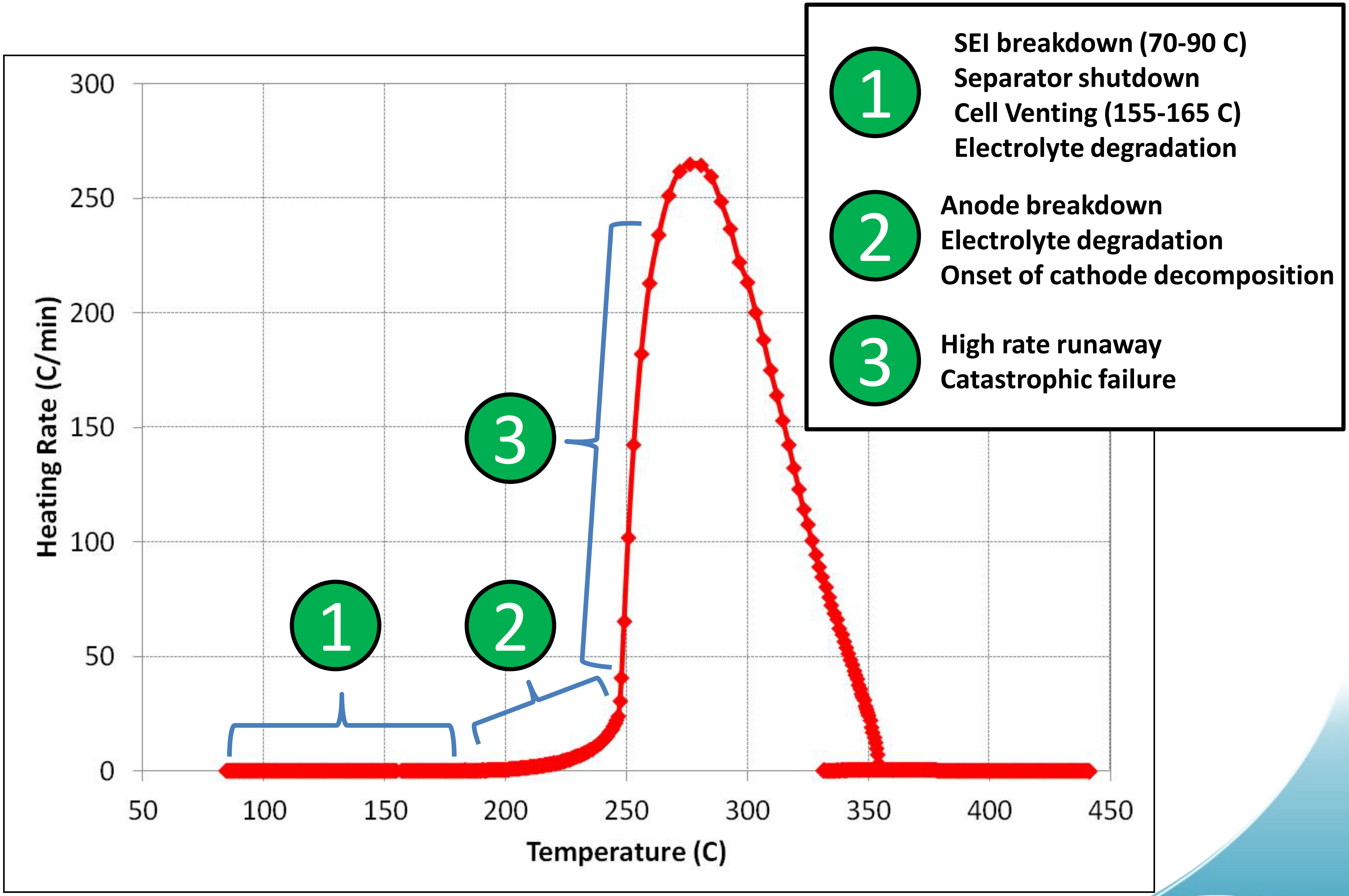
Improvements to inherent safety of lithium-ion cells at the materials scale could minimize complexity of the controls systems & reduce total cost

Technical Challenges

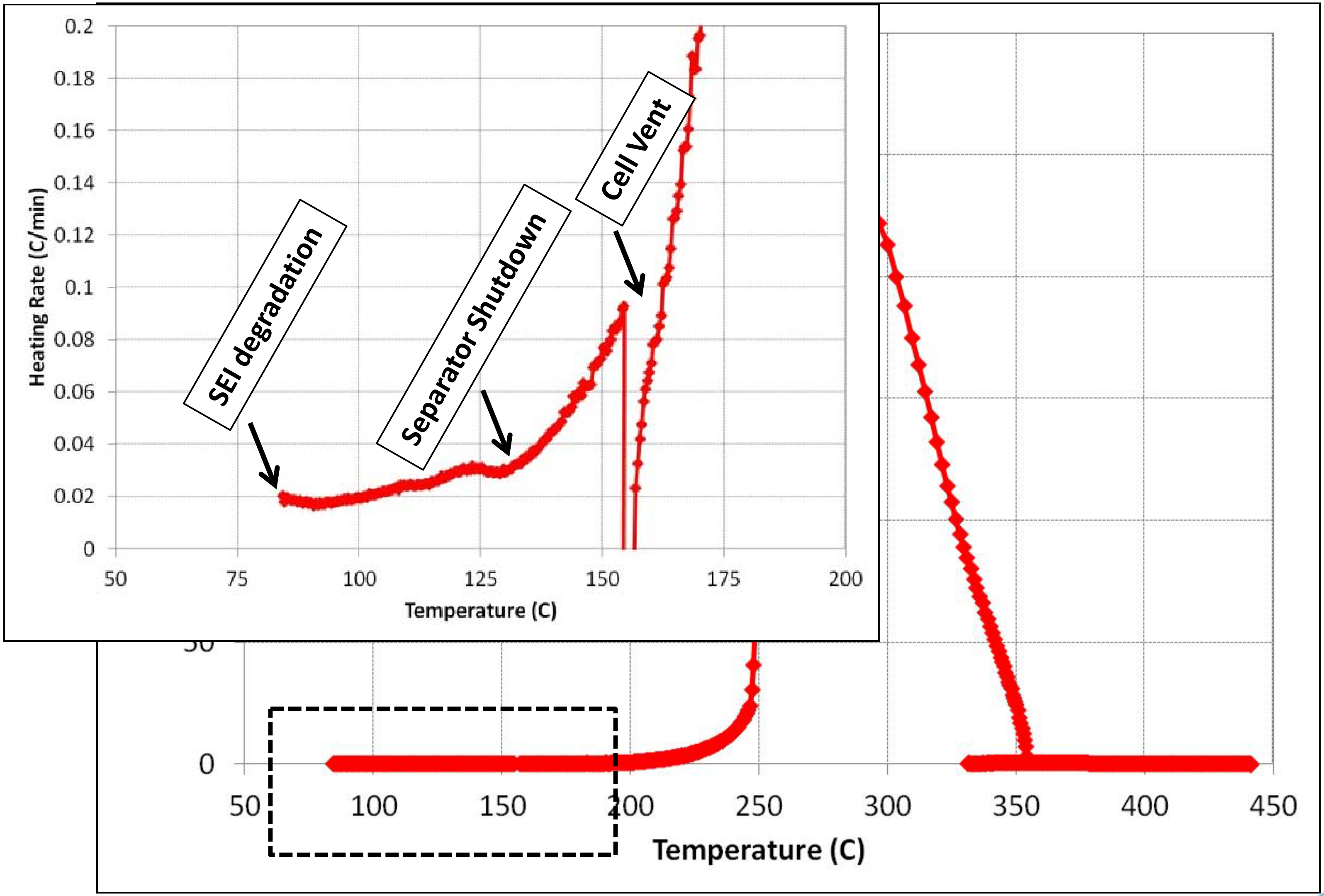
…..toward the development of inherently safe lithium-ion cell chemistries and systems

- ***Energetic thermal runaway of active materials***
  - Exothermic materials decomposition, gas evolution, electrolyte combustion
  - Improvements made by electrode coatings and new materials
- ***Electrolyte degradation & gas generation***
  - Overpressure and cell venting is accompanied by an electrolyte spray which is highly flammable
  - Needs to be improved with electrolyte choices with minimal impact on performance or by minimize electrolyte degradation at electrode interfaces
- ***Abuse response as a function of cell age***
  - The cell age effects on abuse tolerance of cells and cell materials (electrolyte salts, additives, active materials, separators) are largely unknown
  - Systematic approaches to studying cell abuse response as a function of calendar and cycle life

Anatomy of Catastrophic Failure

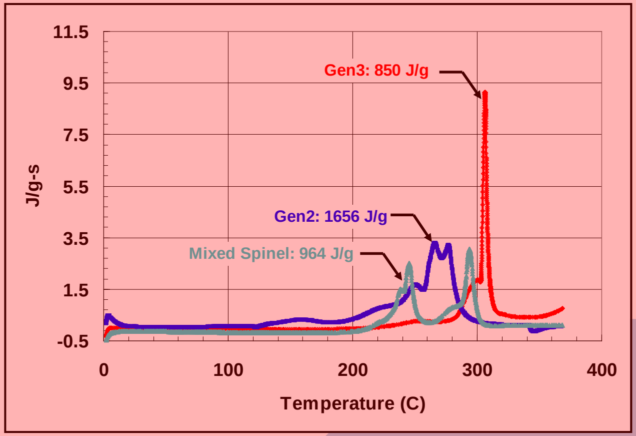


Anatomy of Catastrophic Failure

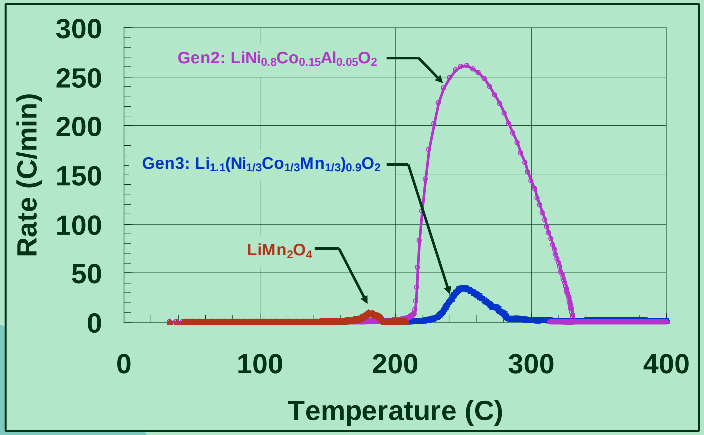


Understanding Failure Mechanisms

Materials Characterization



Cell Performance



Cell and Battery Testing

Identify strategies to mitigate failure or poor abuse tolerance

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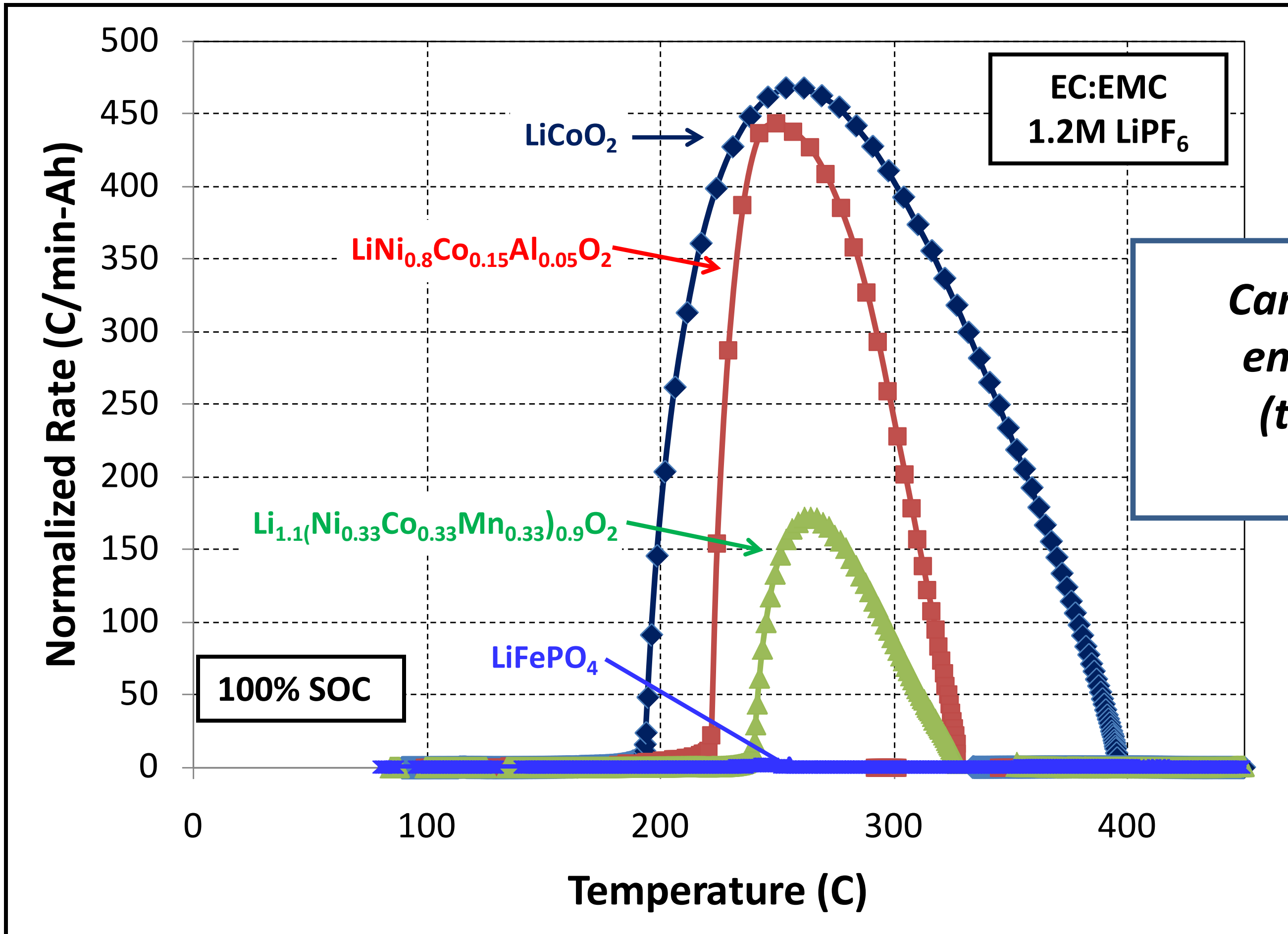
Energetic Cathode Runaway

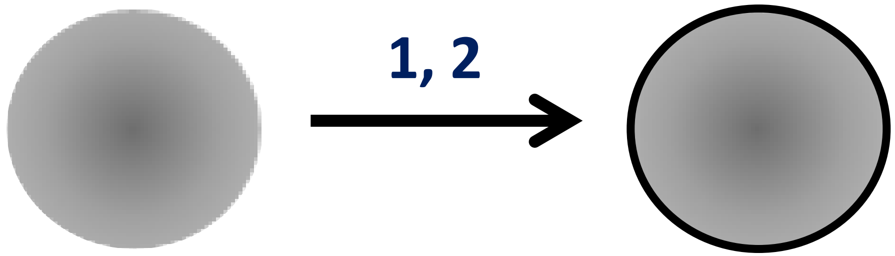
Accelerating Rate Calorimetry of Advanced Materials in Cells



Can we make a high energy cell behave (thermally) like a $LiFePO_4$ cell?

ARC response of high voltage and high capacity cathodes?
ARC response of cells with high capacity anodes (Si-composites)?

Coated Cathodes



Cathode particle
(secondary particle)

Coated-cathode particle

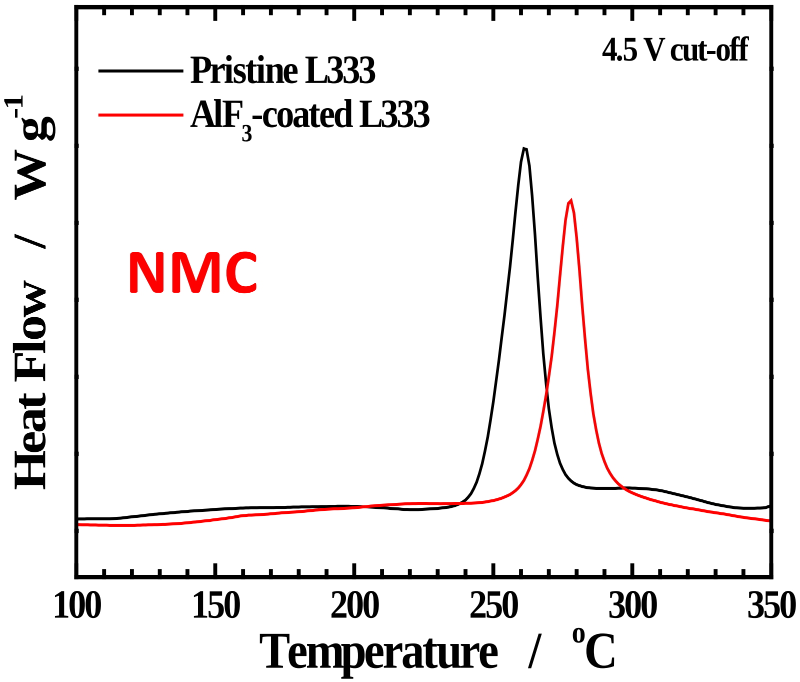
1. **Coating Process – Chemical co-precipitation, surface modification, vapor deposition, ALD, etc.)**
2. **Coating Materials - AlF_3, Al_2O_3, $M_3(PO_4)_x$**

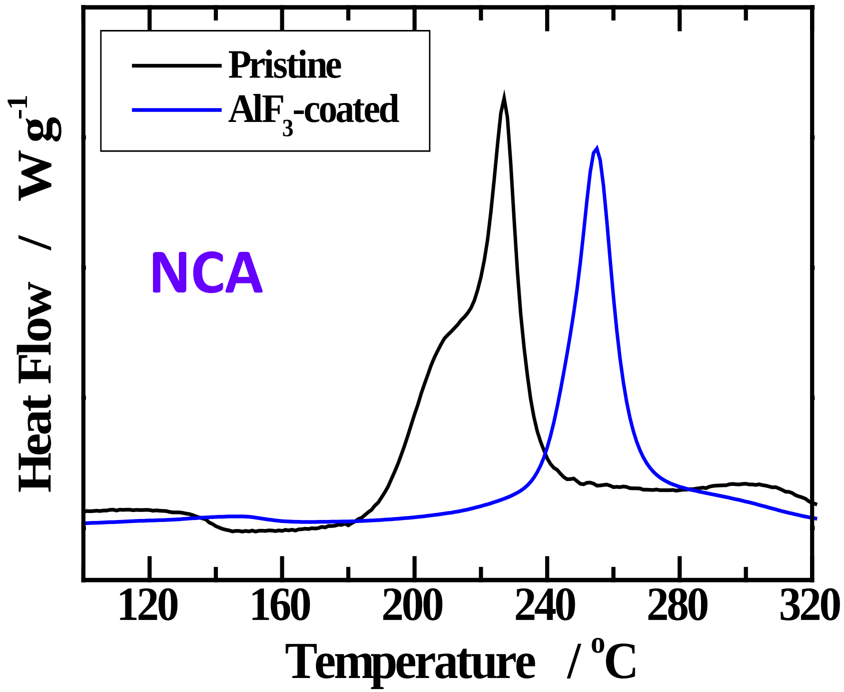
Improvements in cathode performance (capacity fade, cycle life, etc.) and materials stability

Sun, Y. –K. et al. Electrochem. Commun. 2006, 8, 821-826
Hyo, L. S. et al. J. Power Sources, 2008, 184, 276-283
Oh, S. et al. J. Power Sources, 2004, 132, 249-255
Riley, L. A. et al. J. Power Sources, 2011, 196, 3317-3324
Leung, K. et al. J. Am. Chem. Soc., 2011, 133, 14741-14754

Coated Cathodes – AlF_3 coated NMC

Collaboration with K. Amine and Z. Chen at Argonne National Laboratory

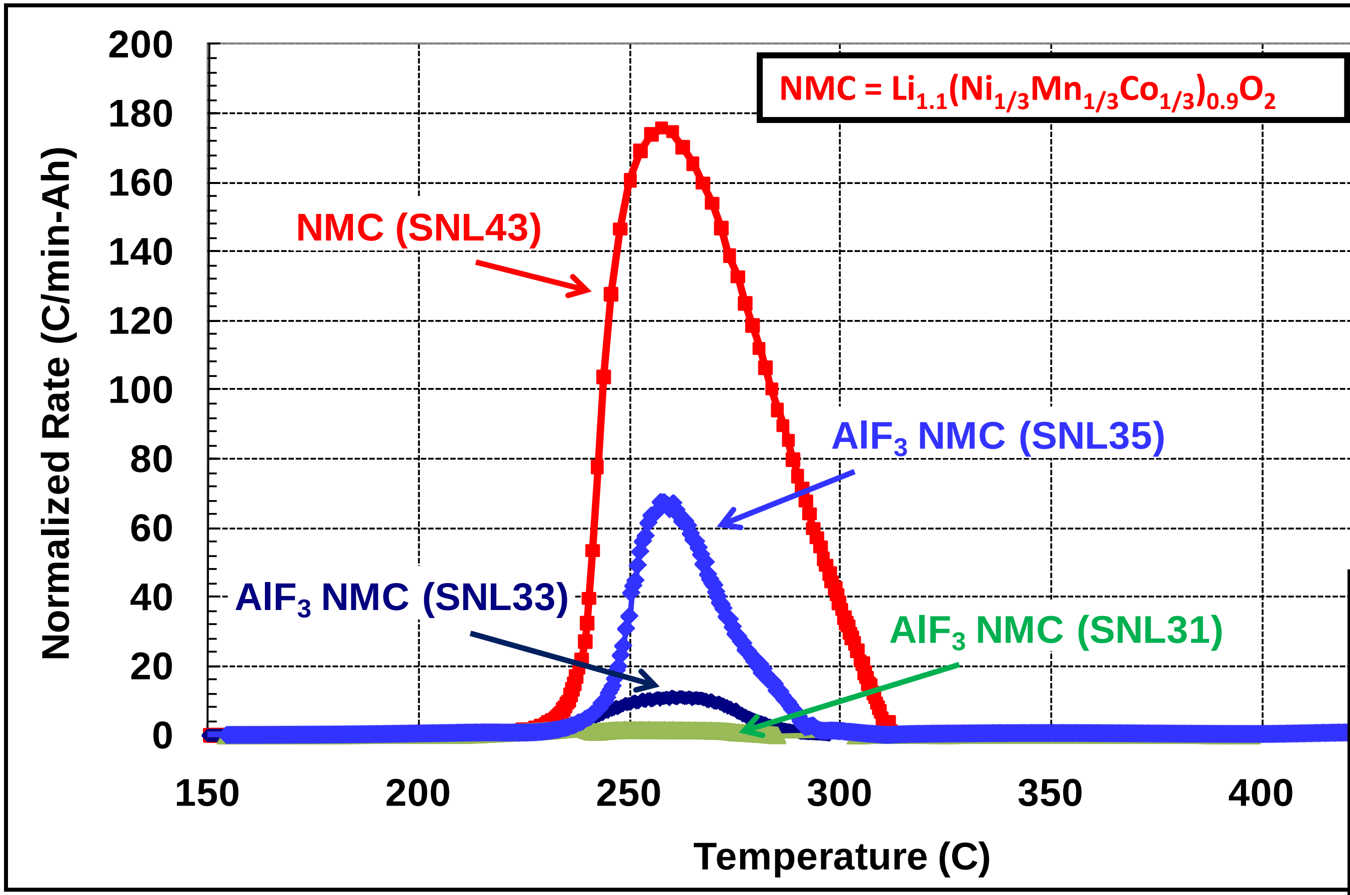


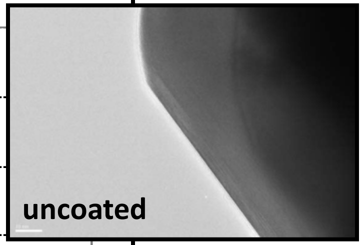


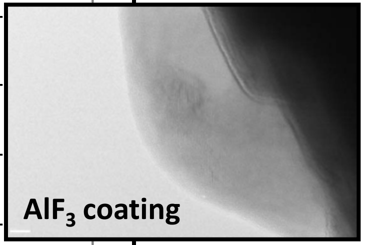
Material	Onset Temp. (°C)
NMC	240
AlF_3-NMC	260
NCA	190
AlF_3-NCA	235

AlF_3-coating improves the thermal stability of NMC and NCA cathodes

Coated Cathodes – AlF_3 coated NMC







- ***Increased stabilization significantly improves the thermal response during cell runaway***
- ***Variability likely due to the material heterogeneity***

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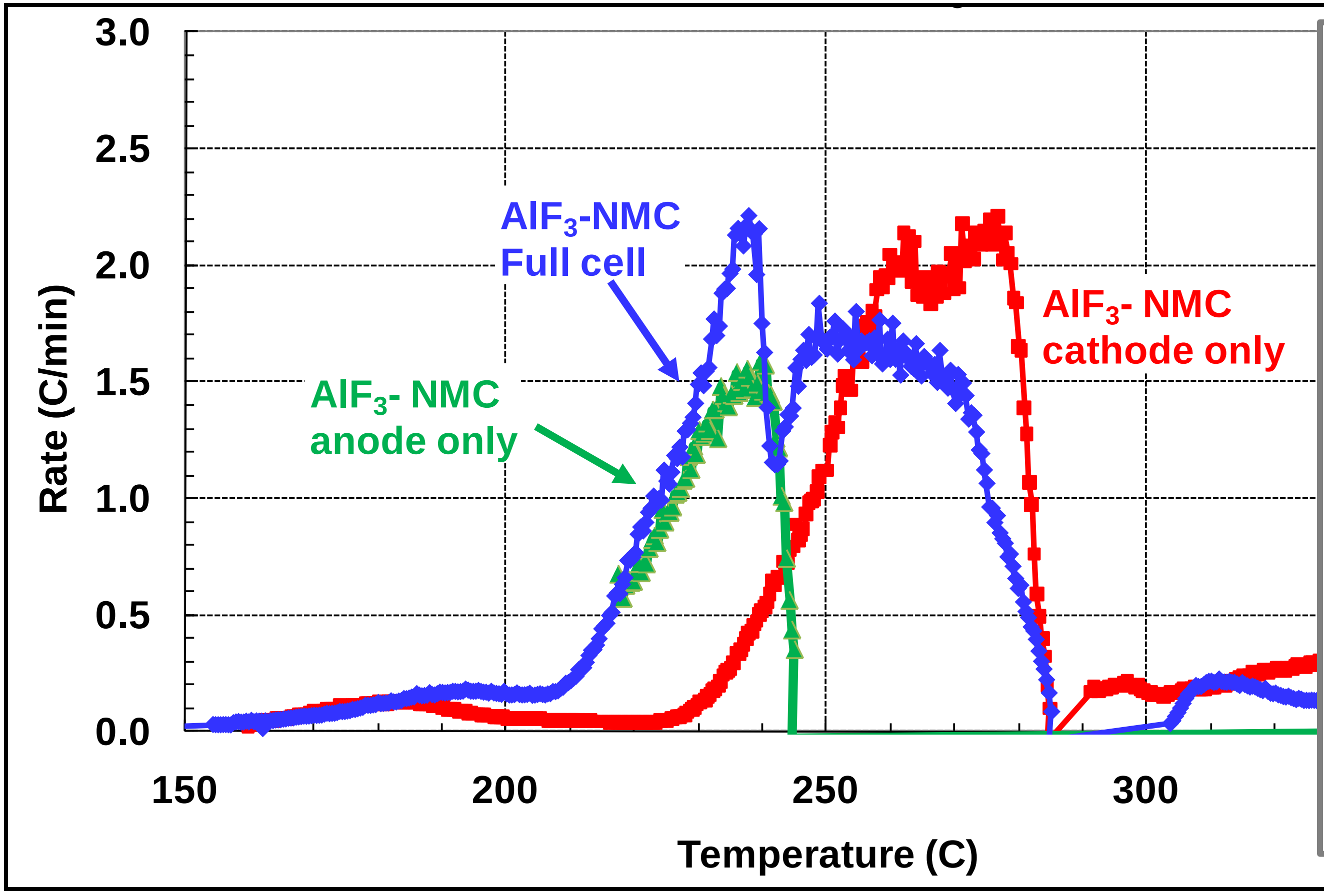
Coated Cathodes – AlF_3-coated NMC



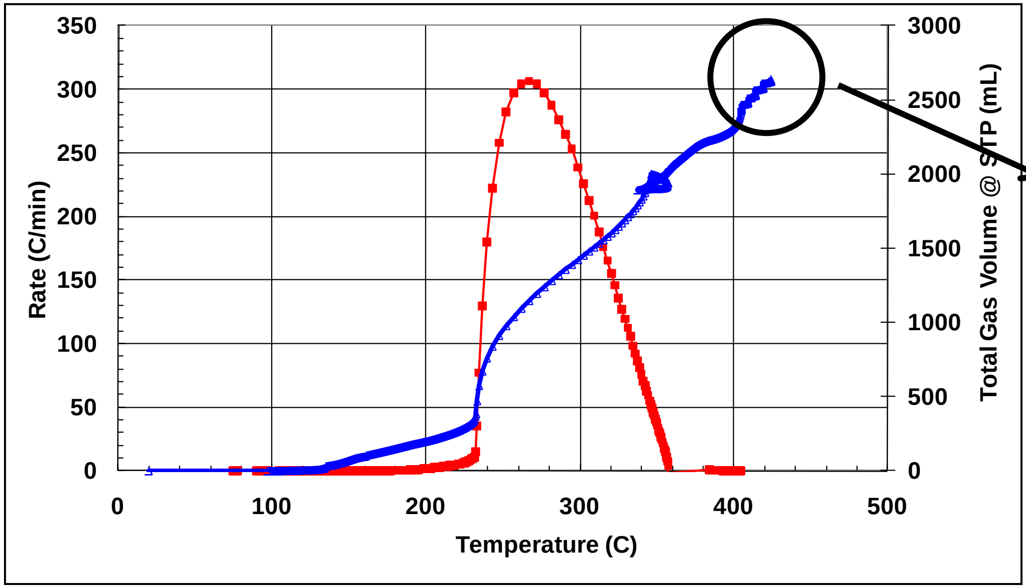
Estimated runaway enthalpy

Cell	ΔH (kJ)
NMC_43	20.6
NMC_44	21.7
AlF3_31	17.5
AlF3_33	18.8
AlF3_35	19.6
AlF3_32c	10.9
AlF3_32a	13.2

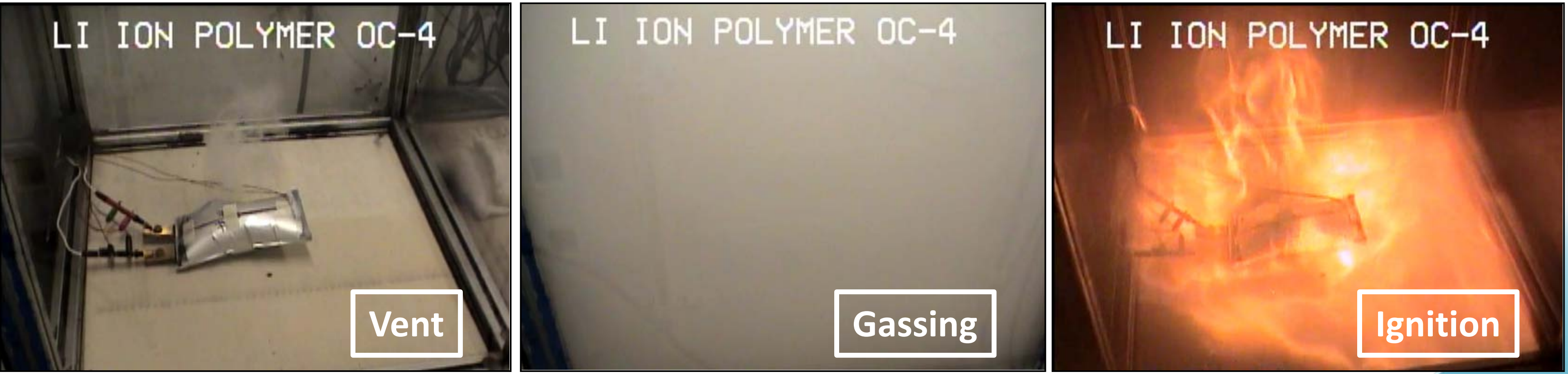
- *Good agreement between individual electrode ARC experiments and full 18650 cells*
- *Total enthalpy is comparable for the coated and uncoated NMC (Gen3) cells*
- *Inert coatings reduce the reaction rates, but the total heat output remains unchanged*

Effects of Electrolyte on Cell Runaway

Electrolyte Degradation & Flammability

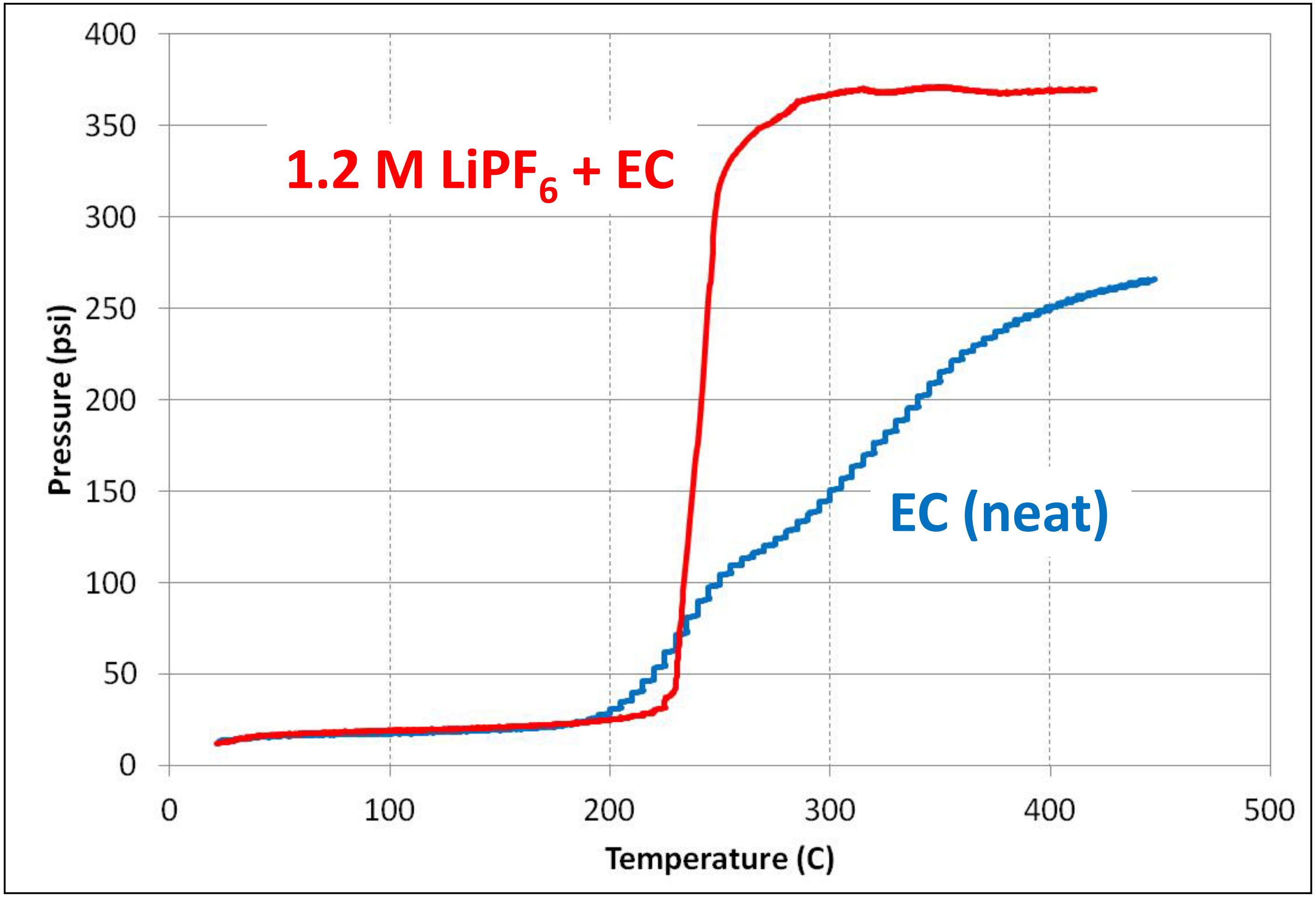


- *Large gas volume - 2.5 L for 18650 cell*
- *Cell vent → solvent aerosol spray (flammable)*
- *Cell vent → spreading particulates (inhalable)*



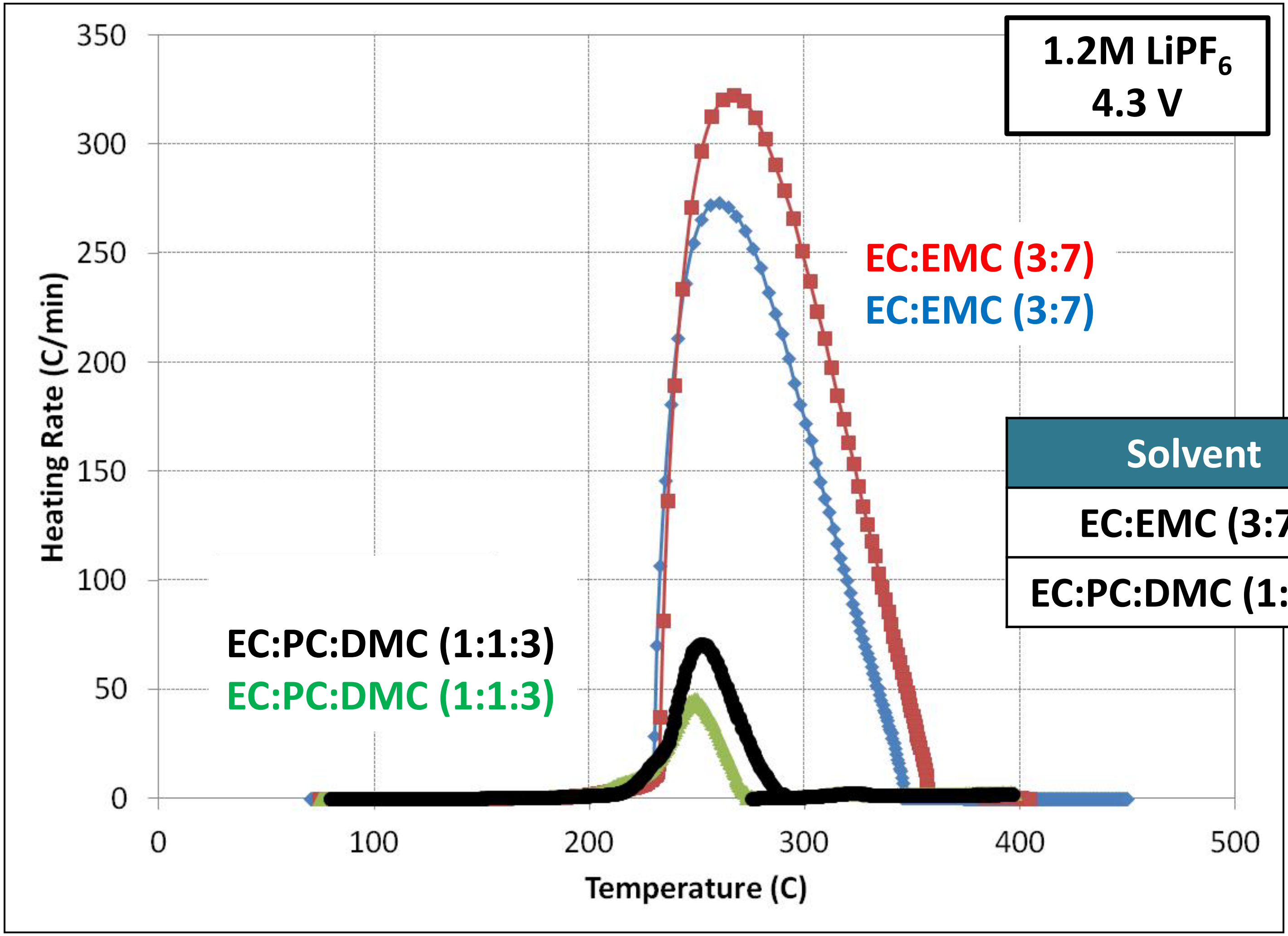
G. Nagasubramanian "Thermally Stable Electrolytes for Li-ion Cells"
Battery Safety 2011, Thursday November 10, 2011

Electrolyte Solvent Decomposition – $LiPF_6$



$LiPF_6$ catalyzes electrolyte solvent decomposition at elevated temperature

Solvent Impact on Cell Runaway



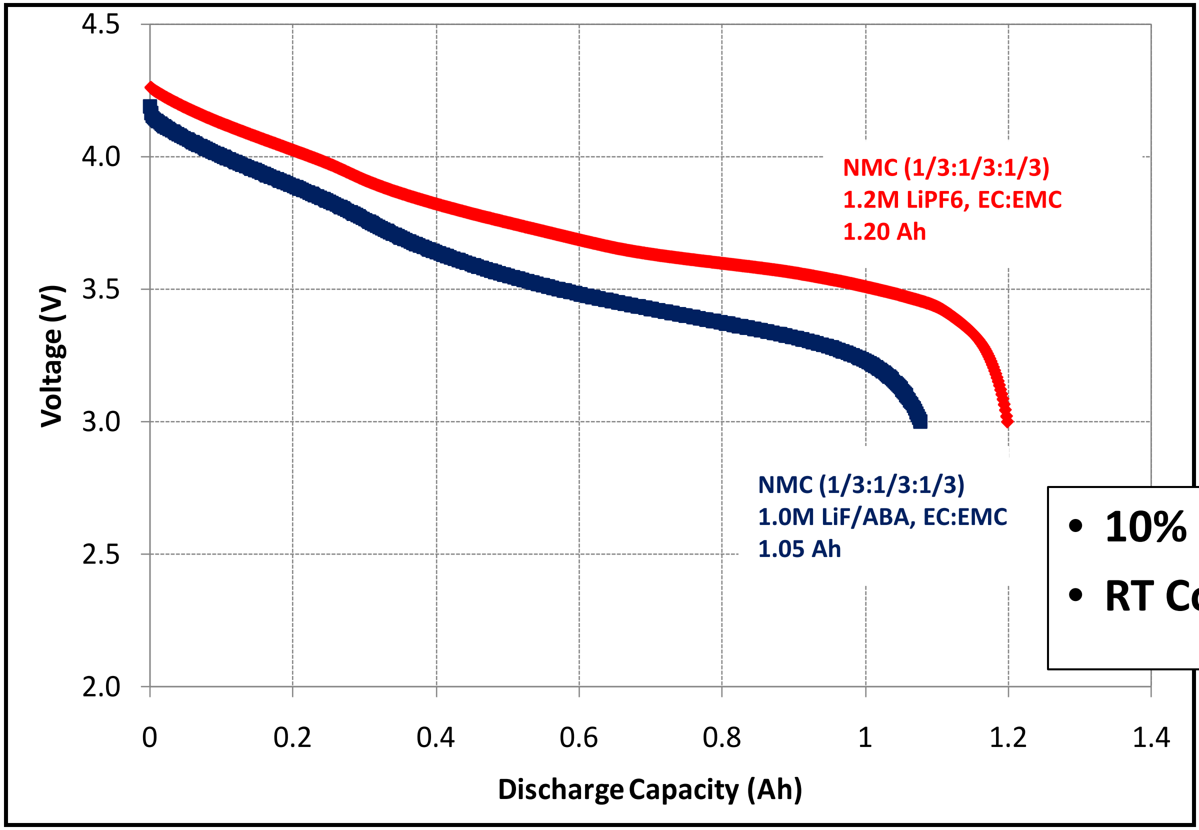
Solvent	$\Delta H_c°$/cell (kJ)
EC:EMC (3:7)	86.5
EC:PC:DMC (1:1:3)	77.8

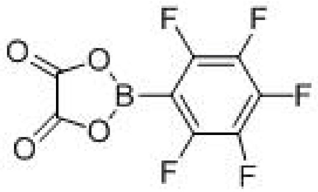
Impact of Electrolyte on Cell Runaway

- Are these really "inactive" components of a cell?
- Can we design electrolytes to passivate cathode reactions?
  - Analogous to inert cathode coatings
- Can we choose electrolyte salts that minimize the catalysis of solvent decomposition?
- Can we identify solvent systems with suitable lower combustion enthalpy than carbonate solvent mixtures?

ABA Electrolyte Development

Objective: Develop ABAs to use with LiF (or non-PF_6 salts)
→ Reduce gas decomposition products
→ Passivate the runaway reactions at the cathode



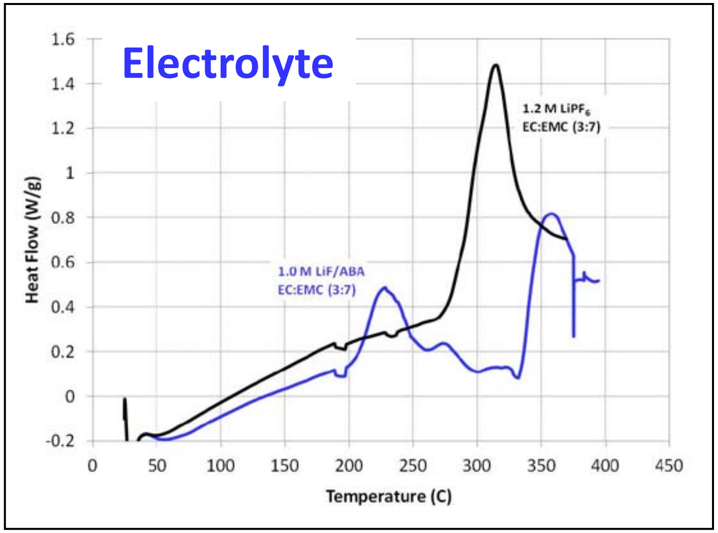


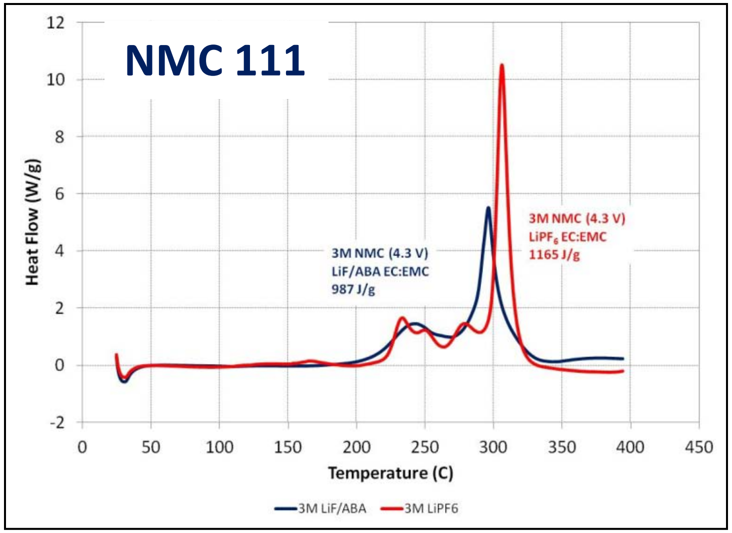
Perfluorophenyloxaltoborate

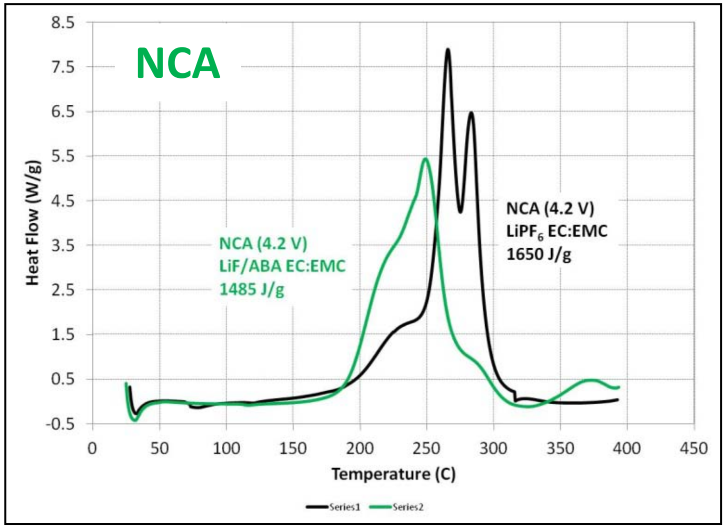
- **10% reduction in total capacity (cell)**
- **RT Conductivity = 2 mS/cm**

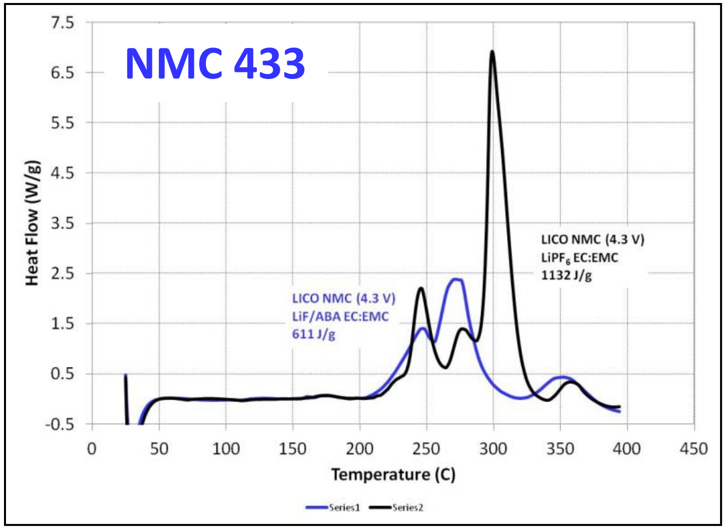
Collaboration with Binrad Industries and X. Q. Yang at BNL on ABA development work

ABA Electrolyte Development



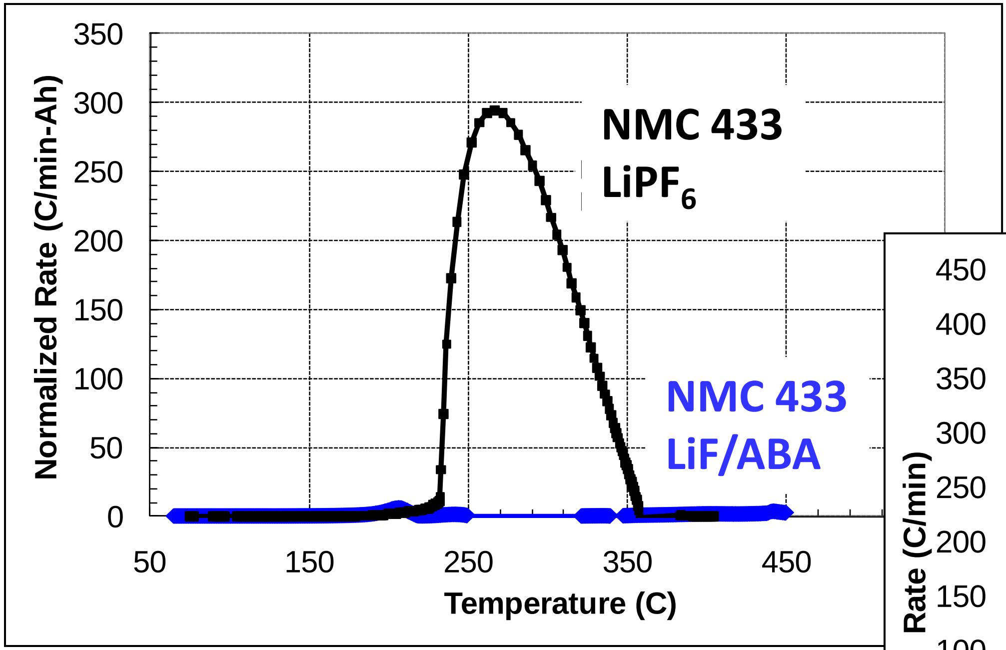


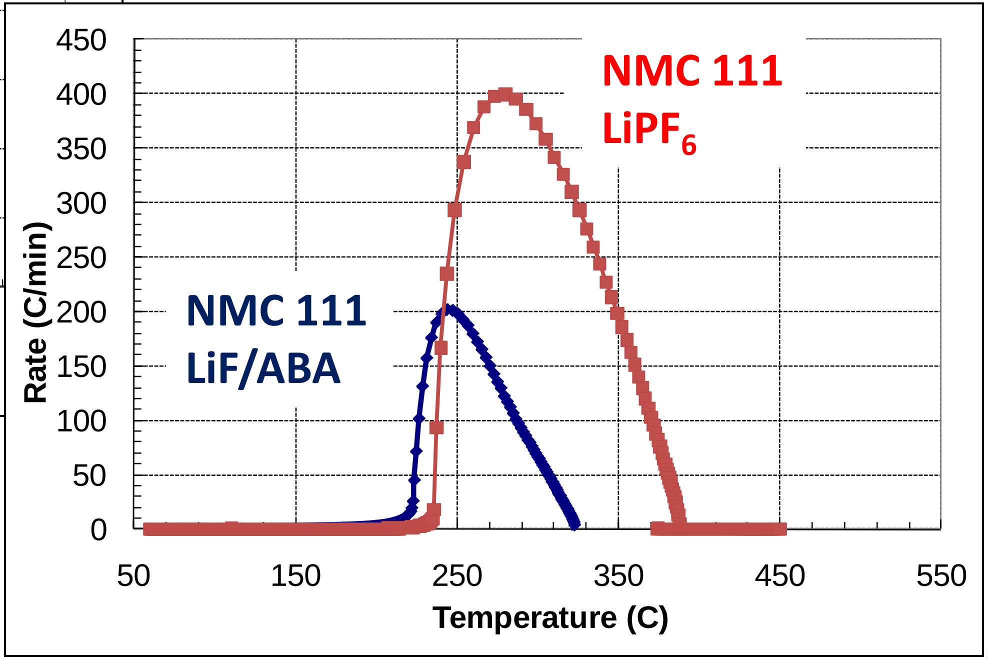




50% reduction in total specific heat output of NMC 433 with LiF/ABA electrolyte

ABA Electrolyte Development





- **Significant reduction in cathode runaway in ARC measurements**
- **Continue work to elucidate passivation mechanism**
- **Synthesis of new ABA molecules**

Effects of Cell Age on Inherent Cell Safety

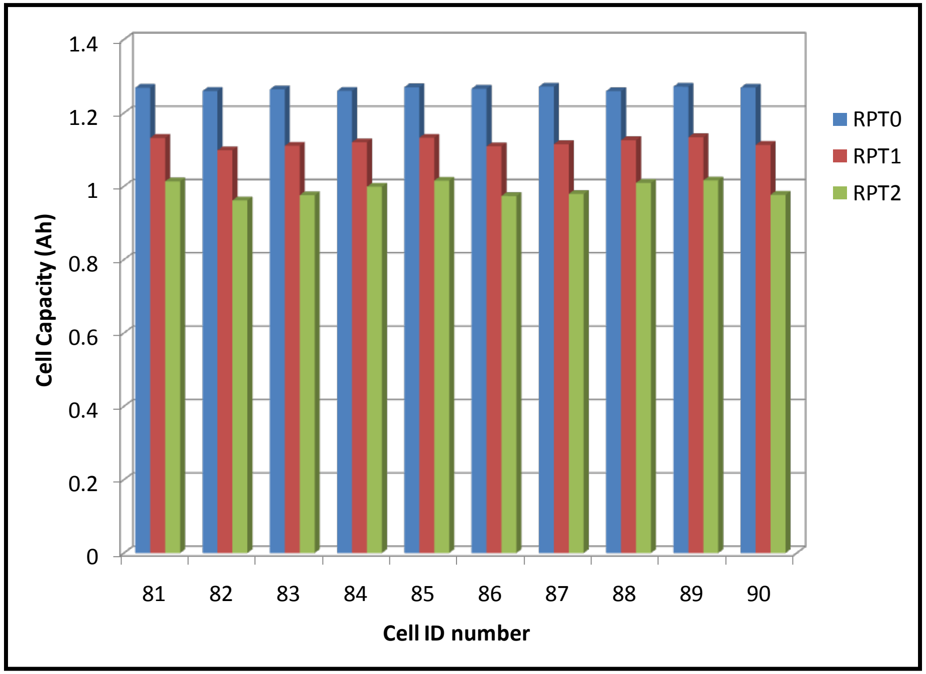
Effect of Age on Cell Abuse Response

Collaboration with J. Belt at Idaho National Laboratory and Bor Yann Liaw at Univ. Hawaii

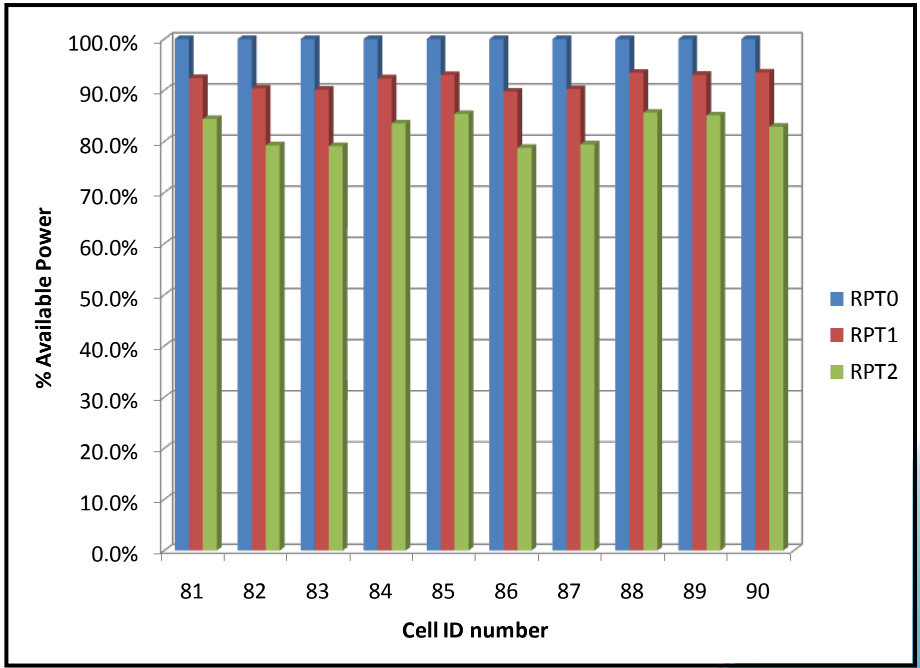
Objectives:

- **Determine the effect of cell age on thermal profile (ARC)**
- **Investigate how cell performance and thermal profiles vary from cell-to-cell and if variations change with cell age (implications in system thermal modeling and performance)**

Capacity fade of aged cells (60 °C storage)



Power fade of aged cells (60 °C storage)



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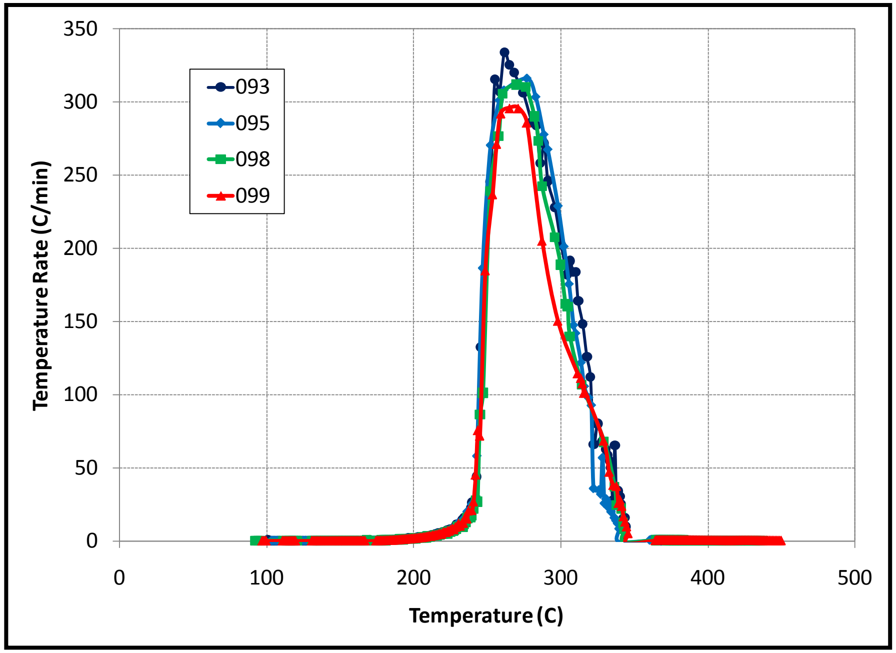
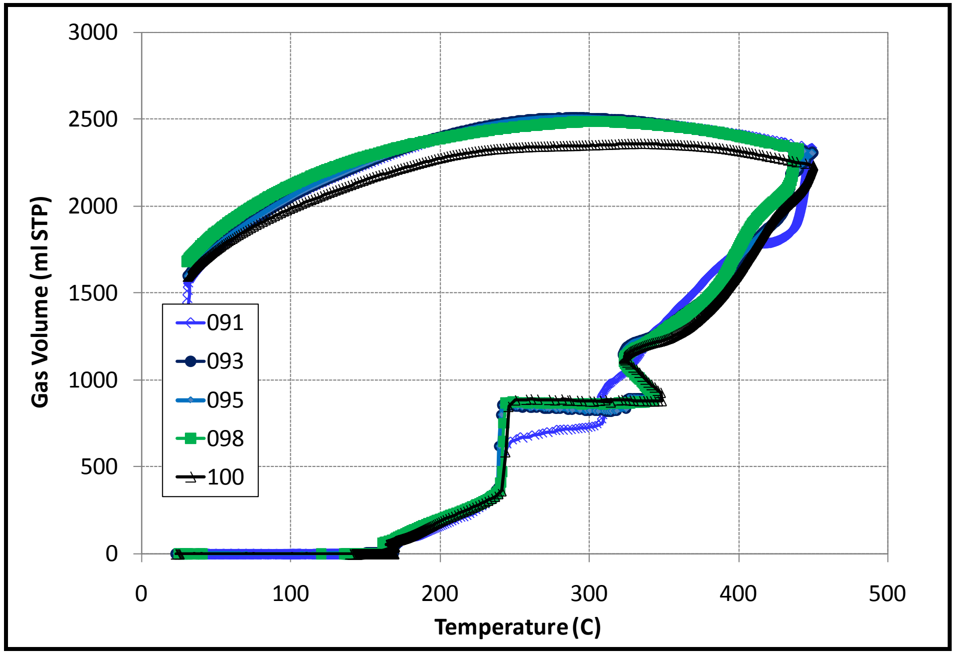
Control (Fresh Cell) Population

ARC thermal runaway profiles of fresh cells



Total gas volume from fresh cells



Good agreement in the thermal response & gas volume of initial cells

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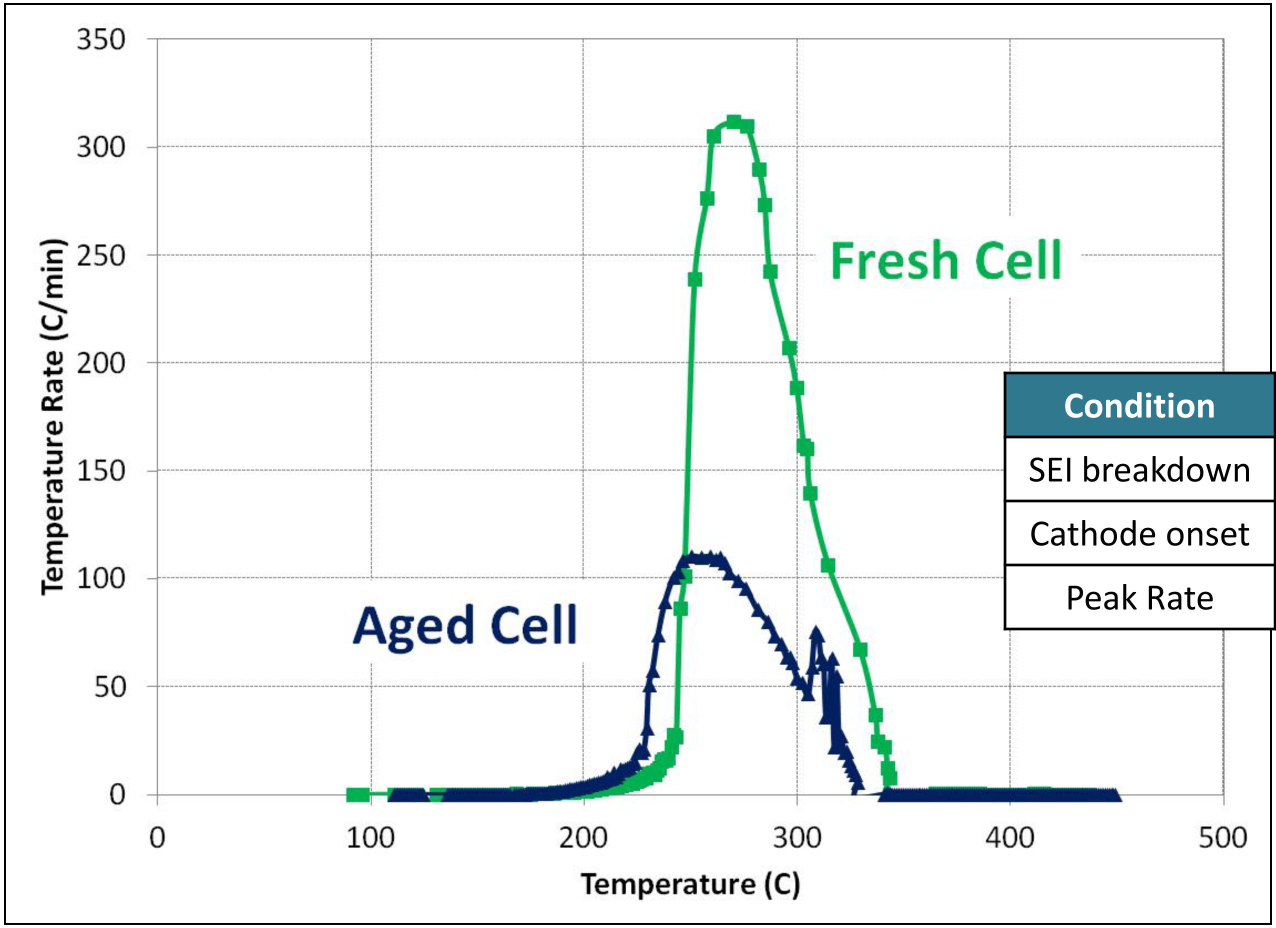
Effect of Age on Cell Abuse Response



Condition	Fresh Cell	Aged Cell
SEI breakdown	90 °C	110 °C
Cathode onset	240 °C	220 °C
Peak Rate	320 (C/min)	110 (C/min)

Significant differences in onset temperatures & heating rates for the aged cells
Consistent with materials changes within the cell

Summary

- **Fielding the most inherently safe chemistries and designs can help addressthe challenges in scaling up lithium-ion**
- **Coated cathodes show measureable improvements in runaway reaction rates in full cells relative to their uncoated analogues**
- **Future work will focus on ionic conducting coatings of advanced high voltage and high capacity materials**
- **Choices in electrolyte salt and solvent can impact the combustion enthalpy, gas generation and flammability of the electrolyte**
- **ABA-based electrolytes can significantly passivate the cathode runaway reaction at the material- and cell-scale**
- **Cell age has a significant impact on abuse response namely onset temperatures (both anode and cathode decomposition) and reaction rates**
- **Future work will continue to look at age effects (calendar vs. cycle age) to better understand mechanisms that lead to changes in abuse response**

Acknowledgements

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