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# SNL Battery Safety R&D Program


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# Battery Safety R&D Program at SNL

*Mission Statement: The Laboratory is committed to serving the energy storage community and the National interest with cutting edge research programs, the highest quality testing results, leadership in battery safety and reliability R&D*

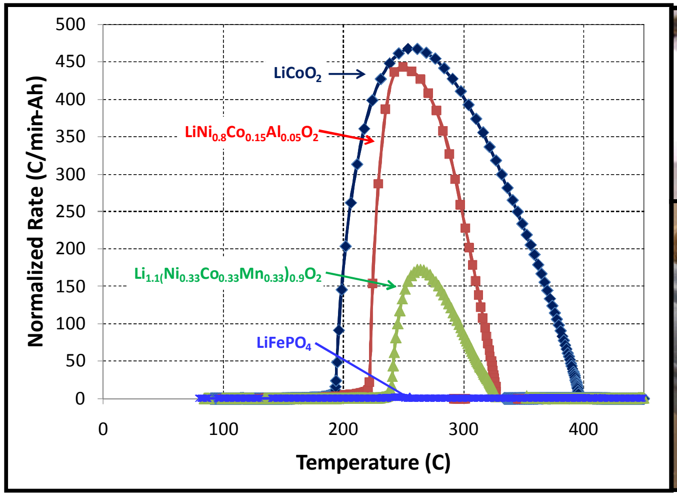
- **Understanding failure mechanisms in cells and battery systems for the emerging global transportation markets**
- **Safety evaluation of the next generation electrode materials for lithium-ion batteries**
- **Development of advanced materials and electrolytes that are abuse tolerant, non-flammable and can mitigate high rate thermal runaway reactions**
- **Develop testing and analytical techniques to better understand critical safety concerns with lithium-ion chemistries and large format cell designs**
- **Facilities include:**
  - **Battery Calorimetry Center**
  - **Battery Abuse Testing Laboratory**
  - **Cell Prototyping Facility**

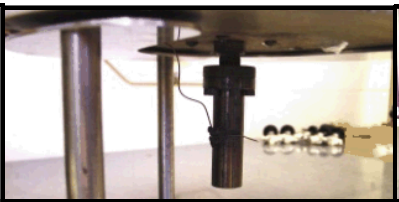
# Battery Safety R&D Program Support

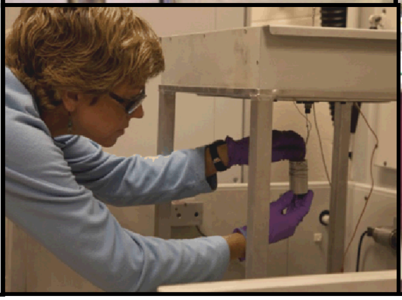
- DOE Office of Vehicle Technologies (OVT) support: USABC/Testing Program, Advanced Battery Research (ABR) Program, ARRA (FY10-12)
- The BATLab has had a number of partnerships over the years including cooperative research and development agreements (CRADA) and work for others (WFO) programs with industry and government agencies to study battery safety and reliability. Our current partners include:
  - NASA
  - Nissan Motors
  - SK Corp.
  - Hitachi
  - A123
  - Enerdel
  - Quallion
  - Eaton Corp.
  - Air Products
  - Exxon/Tonen
  - Dow Chemical
  - Solvay
  - University of Rhode Island
  - SEEO Corporation
  - BASF Corporation
  - Society for Automotive Engineers (SAE)
  - Ford Motor Company
  - USCAR, Crash Safety Working Group
  - NHTSA

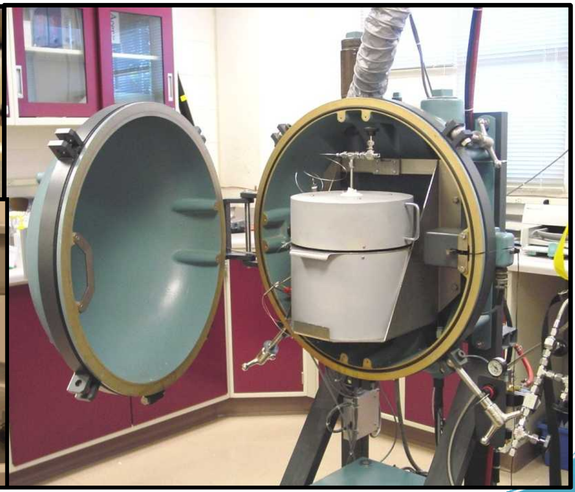
# Battery Calorimetry Center

- **One of the world's largest dedicated battery calorimetry facilities**
- **Six accelerating rate calorimeters (ARCs) for materials and cell-level measurements**
  - Gas volume measurements for decomposition gas products
  - Quantitative gas analysis capabilities from ARC samples
  - Measurements on 1 to 150 Ah cells
- **Two isothermal battery calorimeters**
- **Microcalorimetry for materials analysis**
- **Modulated DSC**









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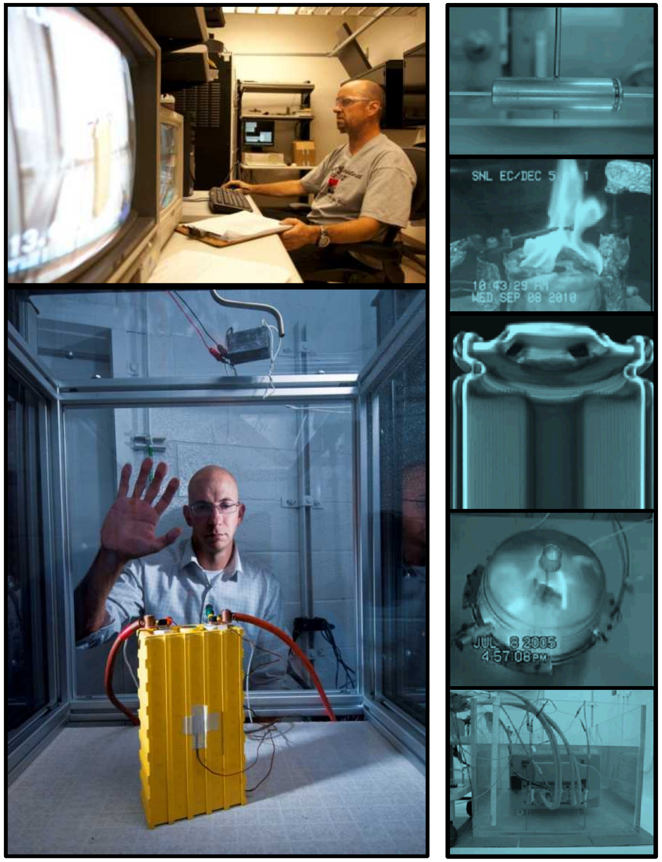
# Battery Abuse Testing Laboratory (BATLab)

- **Comprehensive abuse testing platforms for safety and reliability of cells, batteries and systems from mWh to kWh**
- **Mechanical abuse**
  - Penetration
  - Crush
  - Impact
  - Immersion
- **Thermal abuse**
  - Over temperature
  - Flammability measurements
  - Thermal propagation
  - Calorimetry
- **Electrical abuse**
  - Overvoltage/overcharge
  - Short circuit
  - Overdischarge/voltage reversal
- **Characterization/Analytical Tools**
  - X-ray computed tomography
  - Gas analysis
  - Surface characterization
  - Optical/electron microscopy



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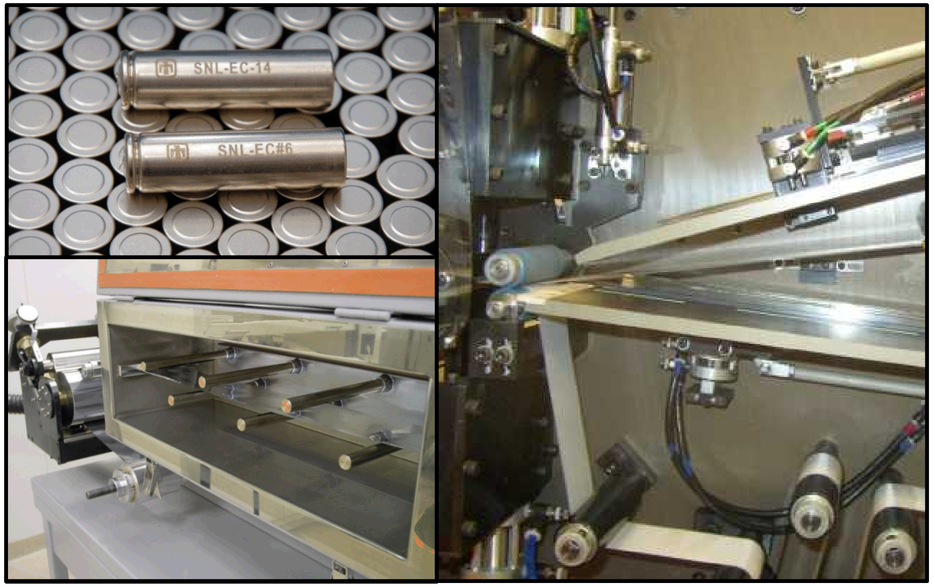
# Cell Prototyping Facility

- **The SNL cell prototyping facility largest DOE dedicated R&D facility equipped to manufacture small lots of lithium-ion cells of various sizes including 2032 coin cells, 18650s, D-cells, and prismatic cells**
  - 1000 sq. ft. of dry room space in two separate dry rooms
  - Two prototype electrode coaters, 20-30 meter coating run capacity
  - Three 18650 cell winders
  - One multiformat cell winder for 18650, D-cell, and prismatic cell formats
  - Electrolyte filling and associated cell hardware and packaging equipment
  - 96 channels for battery performance testing and formation cycling




- **Experience with numerous lithium-ion chemistries including natural and synthetic graphite anodes, $Li_4Ti_5O_{12}$, $LiCoO_2$, NMC, LFP, and spinel cathodes ($LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$).**

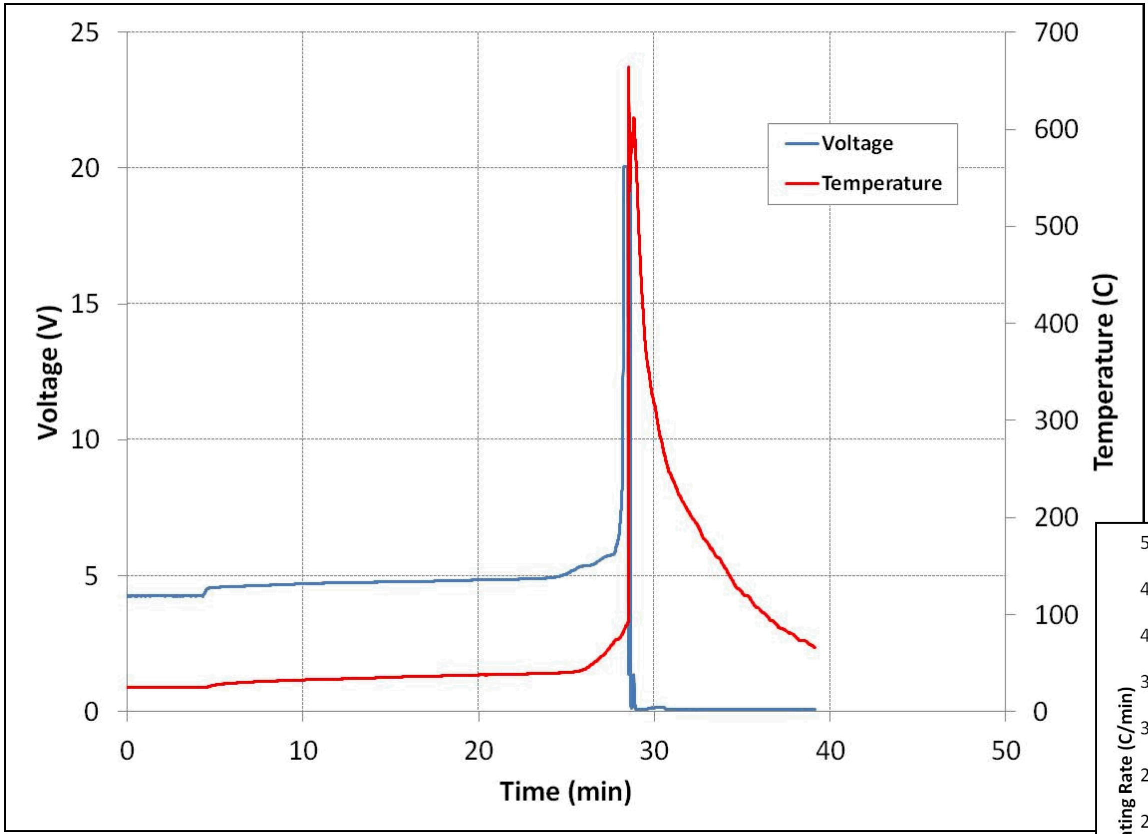
# Battery Safety Testing at Sandia

# Battery Safety Testing Programs

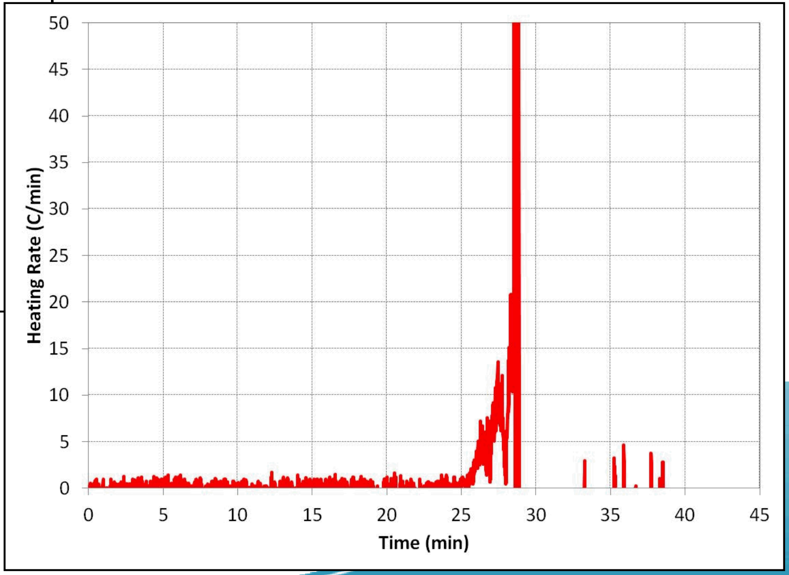
- **Full abuse testing capabilities**
  - mAh cells to kWh systems
    - *Mechanical/environmental (crush, nail, immersion)*
    - *Electrical (overcharge, overdischarge, short circuit)*
    - *Thermal*
    - *Propagation (battery system)*
- **Testing in support of USABC**
  - Testing in accordance to SAE J2464 and USABC Abuse Testing Manual
- **WFO projects**
- **Test development**
  - Electrolyte flammability testing (cell)
  - Gas analysis diagnostics
  - Separator testing
  - Internal short circuit test development
  - Collaborations to develop testing standards/procedures for EV batteries and vehicles

# Overcharge Testing - COTS 12 Ah Cell

- **Overcharged at 24 A (2C), compliance voltage of 20 V, no external ignition**

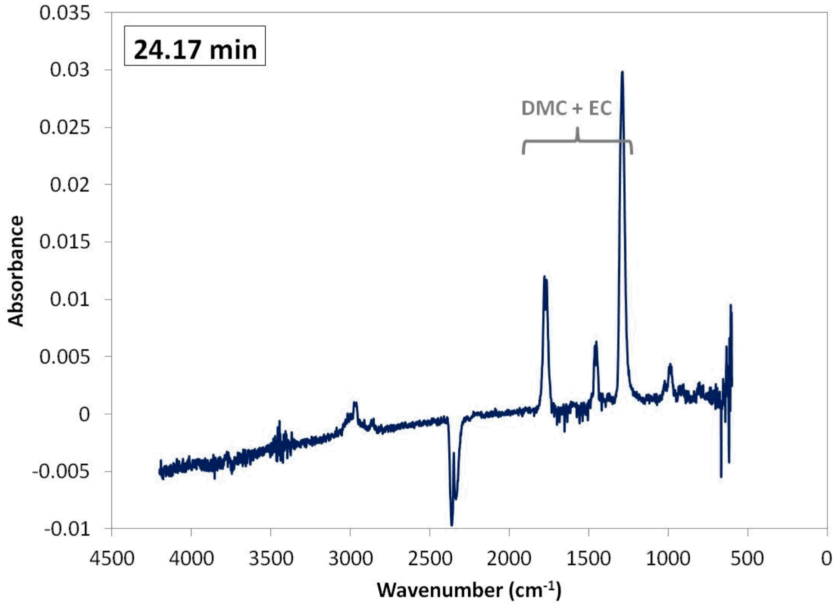


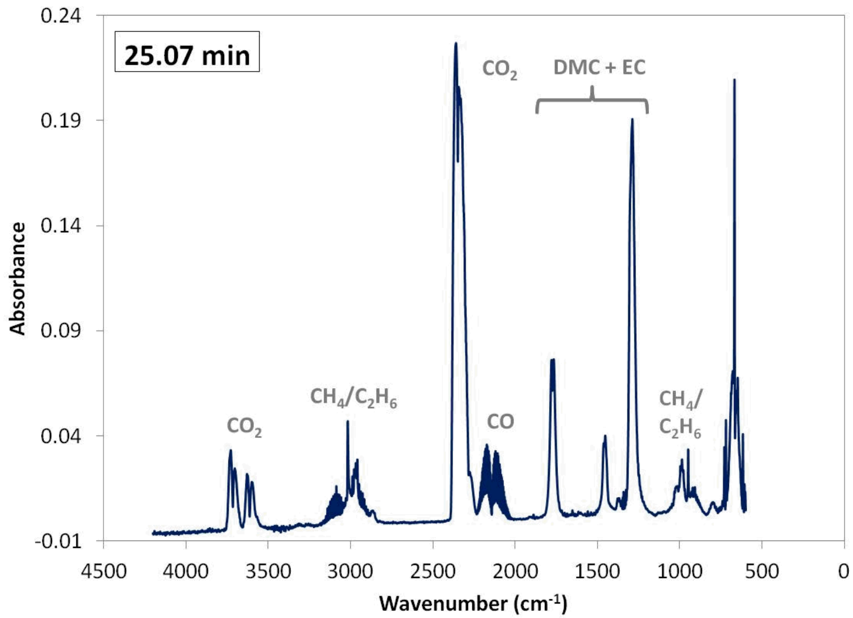

**Battery space 1290142**

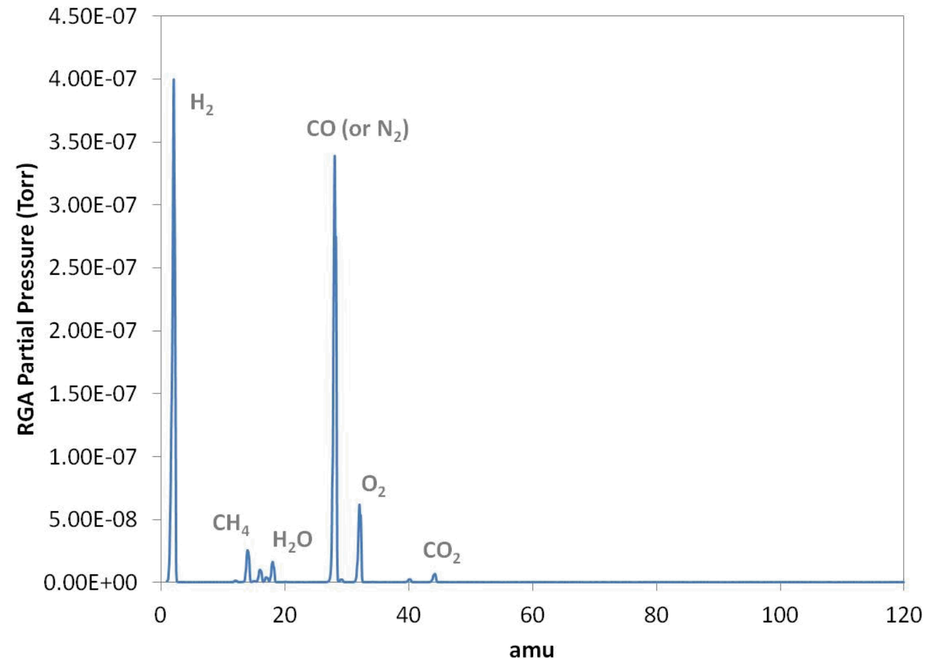



***Gas evolution increases cell resistance, followed by increasing heating, venting, shorting and failure***
***Failure observed at 181% SOC***

# Overcharge Testing - COTS 12 Ah Cell



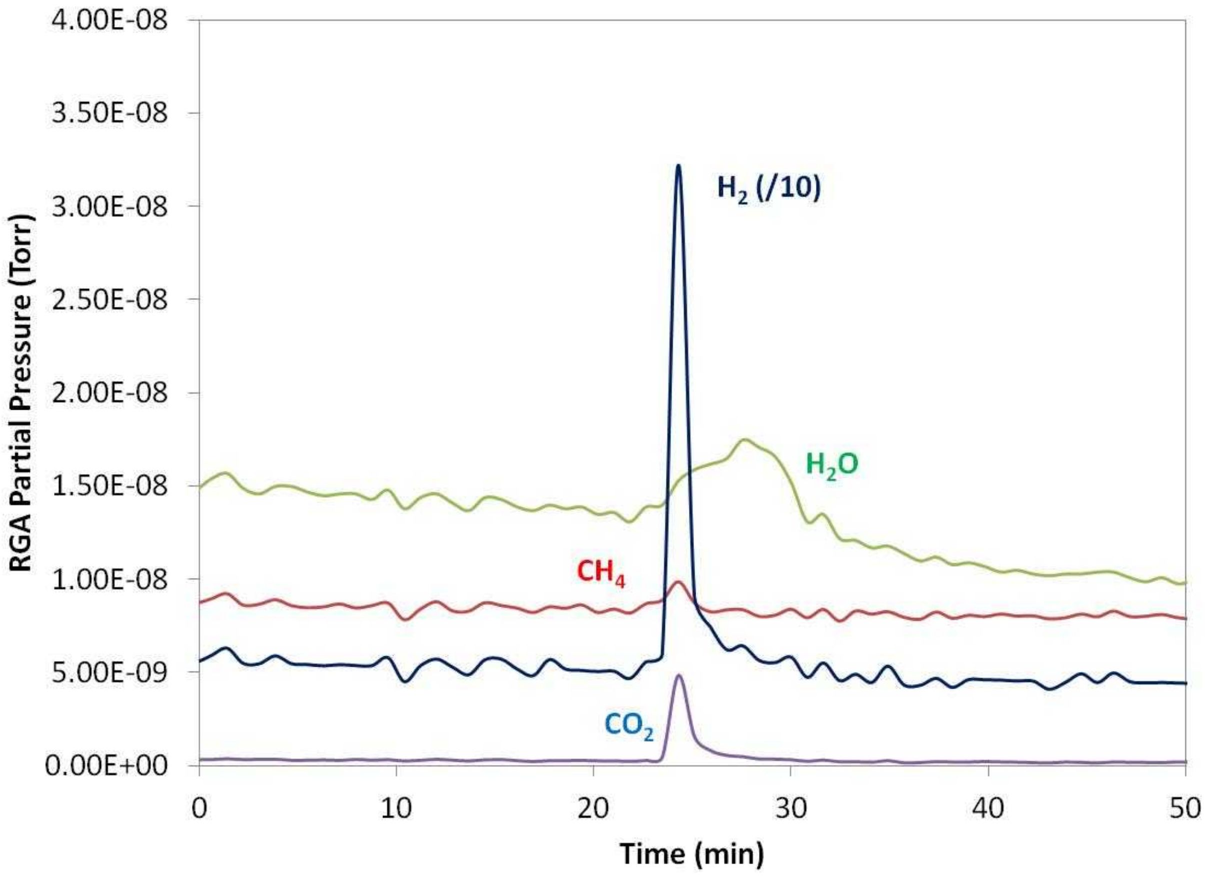




***Initial gas species dominated by electrolyte solvent vapor and $H_2$***

***Gas data provide a real-time analysis of gas products during abuse testing (diatomics, solvents, fixed gases, etc.)***

# Overcharge Testing - COTS 12 Ah Cell

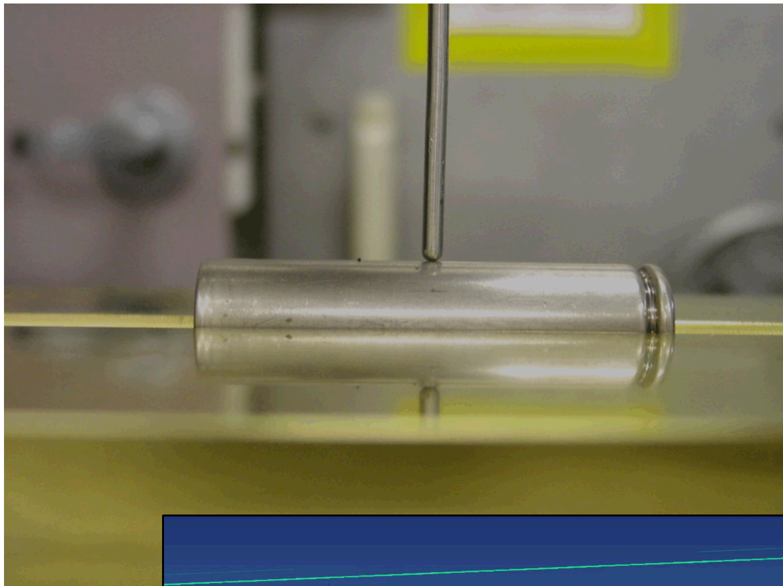


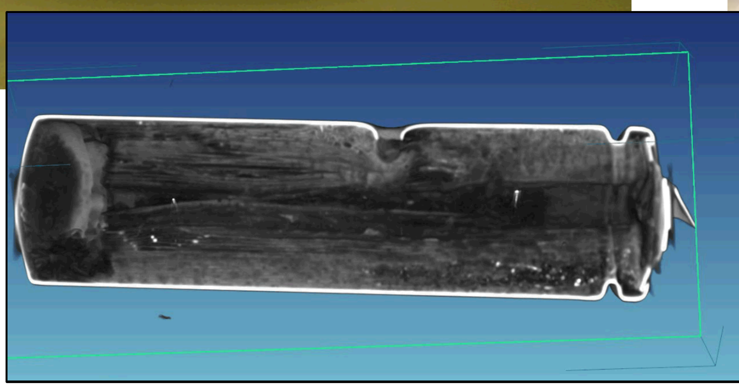

***The initial vent gas consists of largely solvent vapor, solvent decomposition products ($H_2$, $CO_2$, $CH_4$)***

***After the ignition, spectra show the appearance of combustion products (CO, $H_2O$)***

# Overcharge Testing - COTS 12 Ah Cell

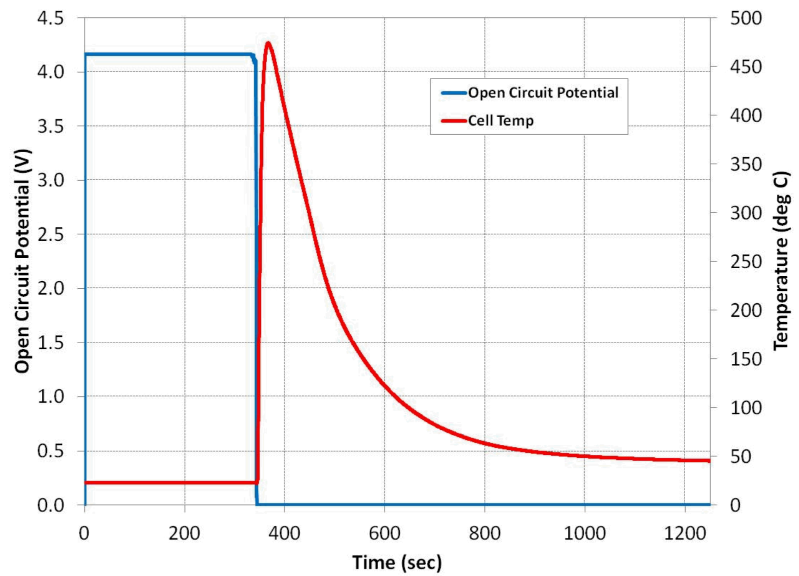

# Mechanical Testing – Blunt Nail Testing

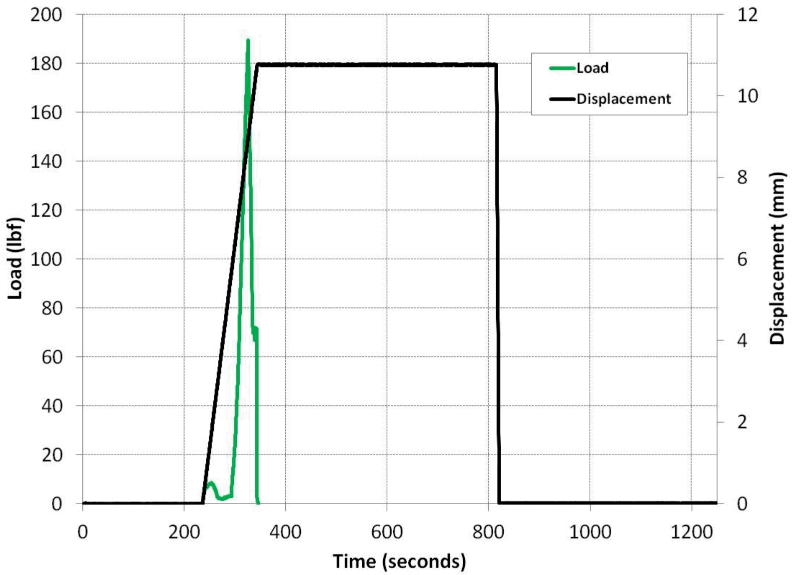





*0.05 mm/s travel speed*
*3 mm nail (rounded tip)*
*The idea is to short before the cell is punctured*
*(Continue with nail travel until cell shorting)*

# Mechanical Testing – Blunt Nail Testing



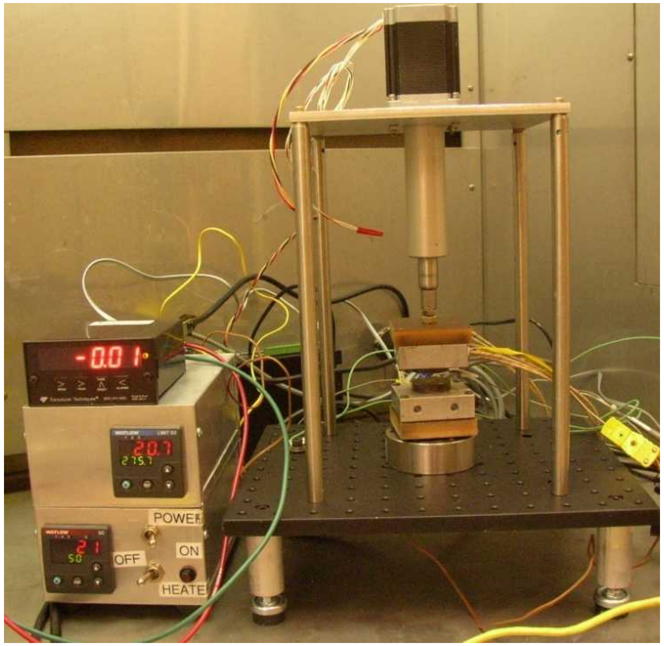



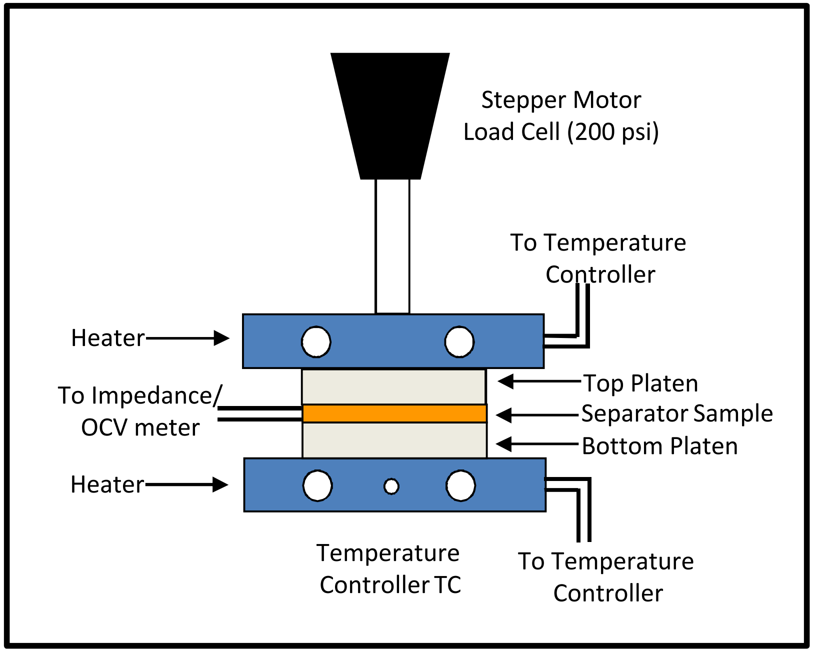


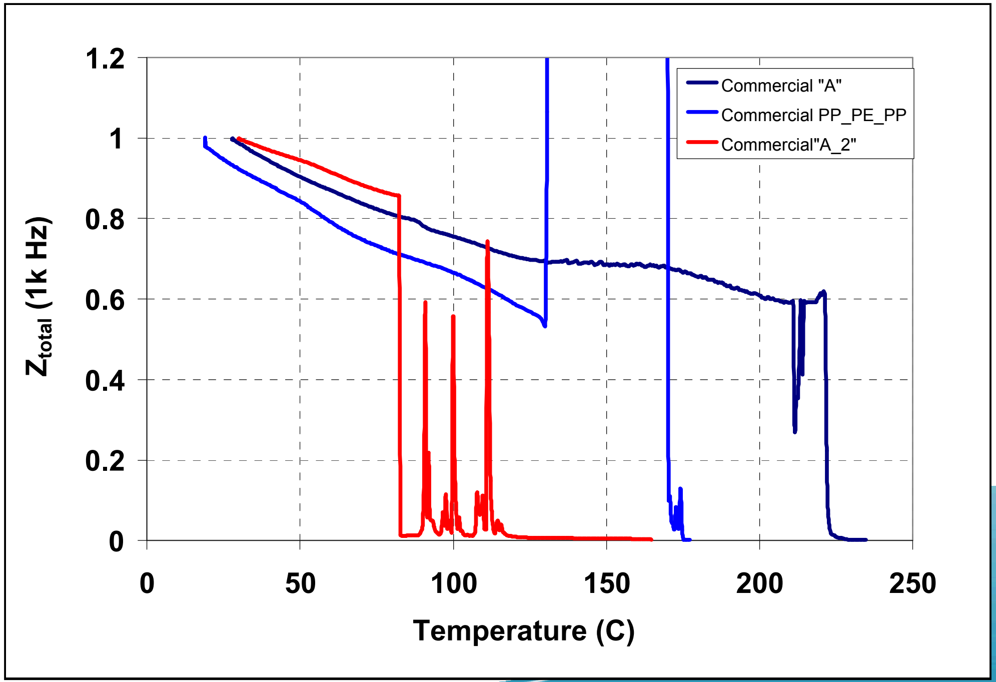
***Cell rupture and shorting at ~9 mm deflection (190 lbf)***

# Separator Testing

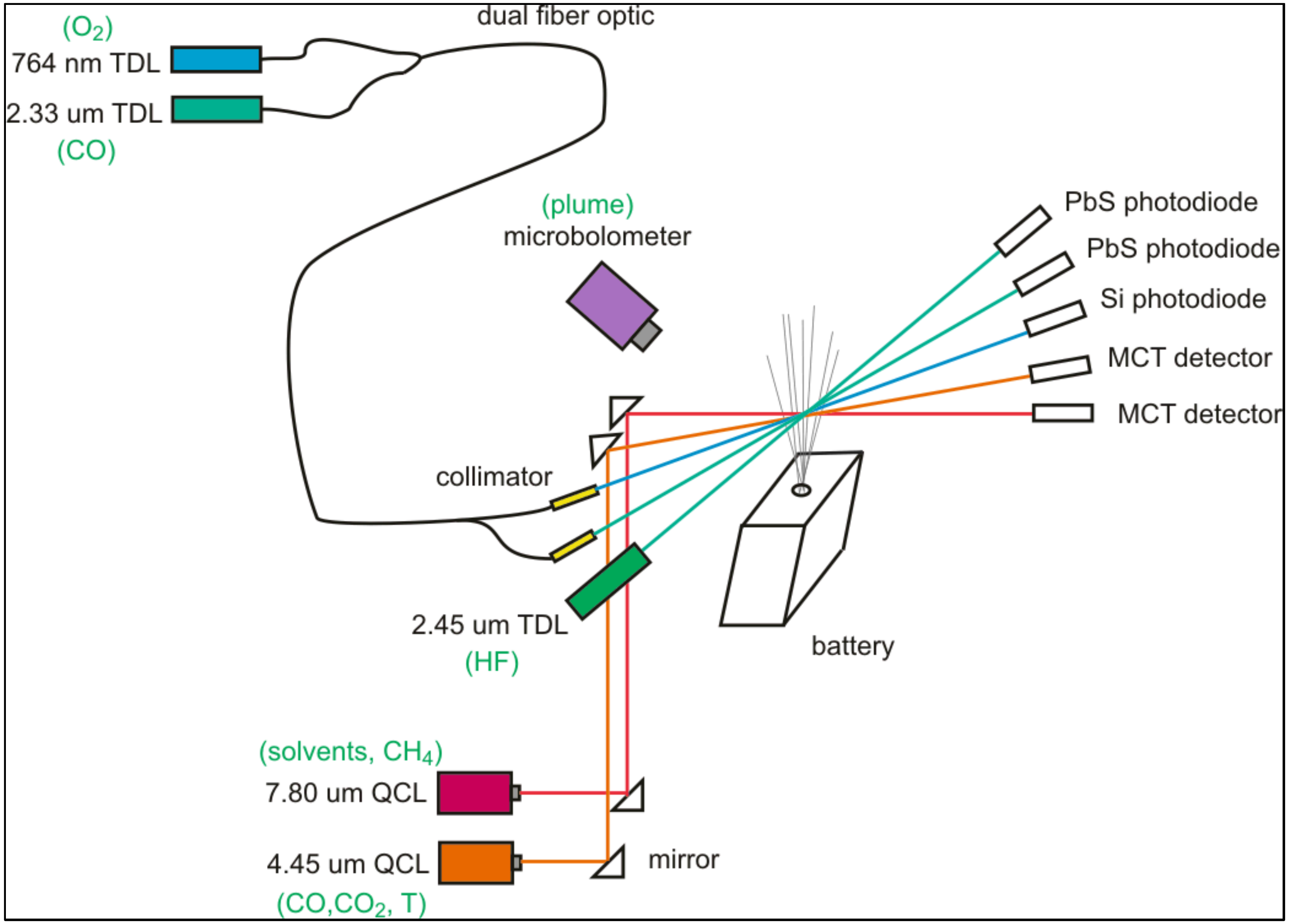
- Physical characteristics (porosity, permeability, bulk strength, etc.)
- Thermal stability (impedance)
- Mechanical stability/resistance to particle puncture





# IR Absorption Gas Diagnostics




***Collaboration with the Combustion Research Facility (SNL Livermore, CA)***
***Construction of the IR absorption system to measure quantitative gas compositions in time and space (ARRA)***

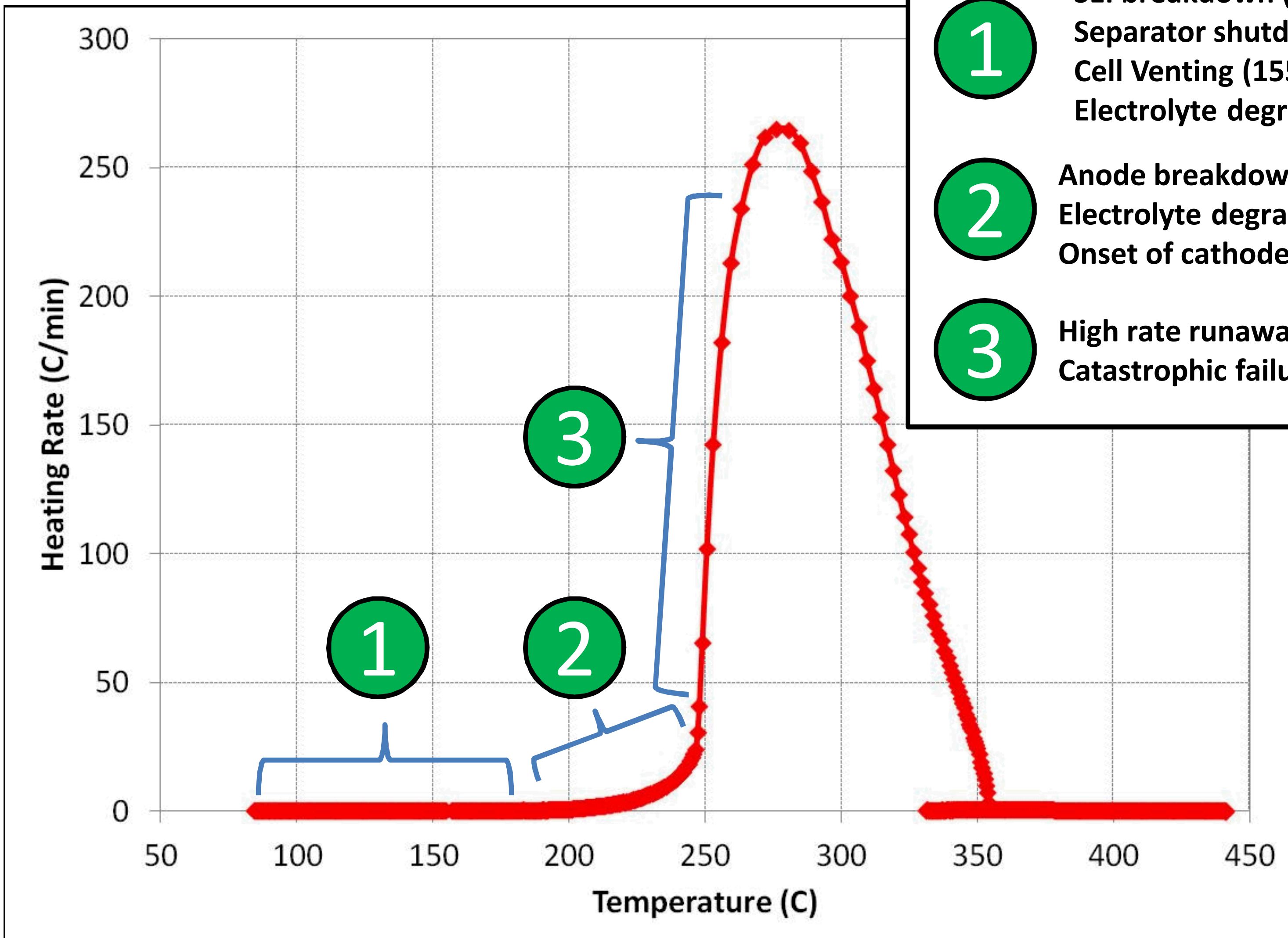
# Battery Safety R&D at Sandia

# Battery Safety R&D Programs

- **DOE**
  - **Coated cathodes:**
    - *$AlF_3$-coated NMC*
    - *Phosphate-coated NMC*
    - *ALD alumina-coated NMC*
  - **Evaluation of additives:**
    - *Overcharge shuttles*
    - *Nonflammable phosphazenes/phosphates*
  - **Next generation active materials:**
    - *$xLiMnO_3 \bullet (1-x)LiMO_2$*
    - *$LiNi_{0.5}Mn_{1.5}O_4$*
  - **Si-composite anodes**
  - **Thermally stable electrolyte salts**
  - **Ionic liquid electrolyte development**

- **SNL LDRD**
  - **Nonflammable electrolyte development**
  - **Thermally stable separator development**

# Anatomy of Catastrophic Failure

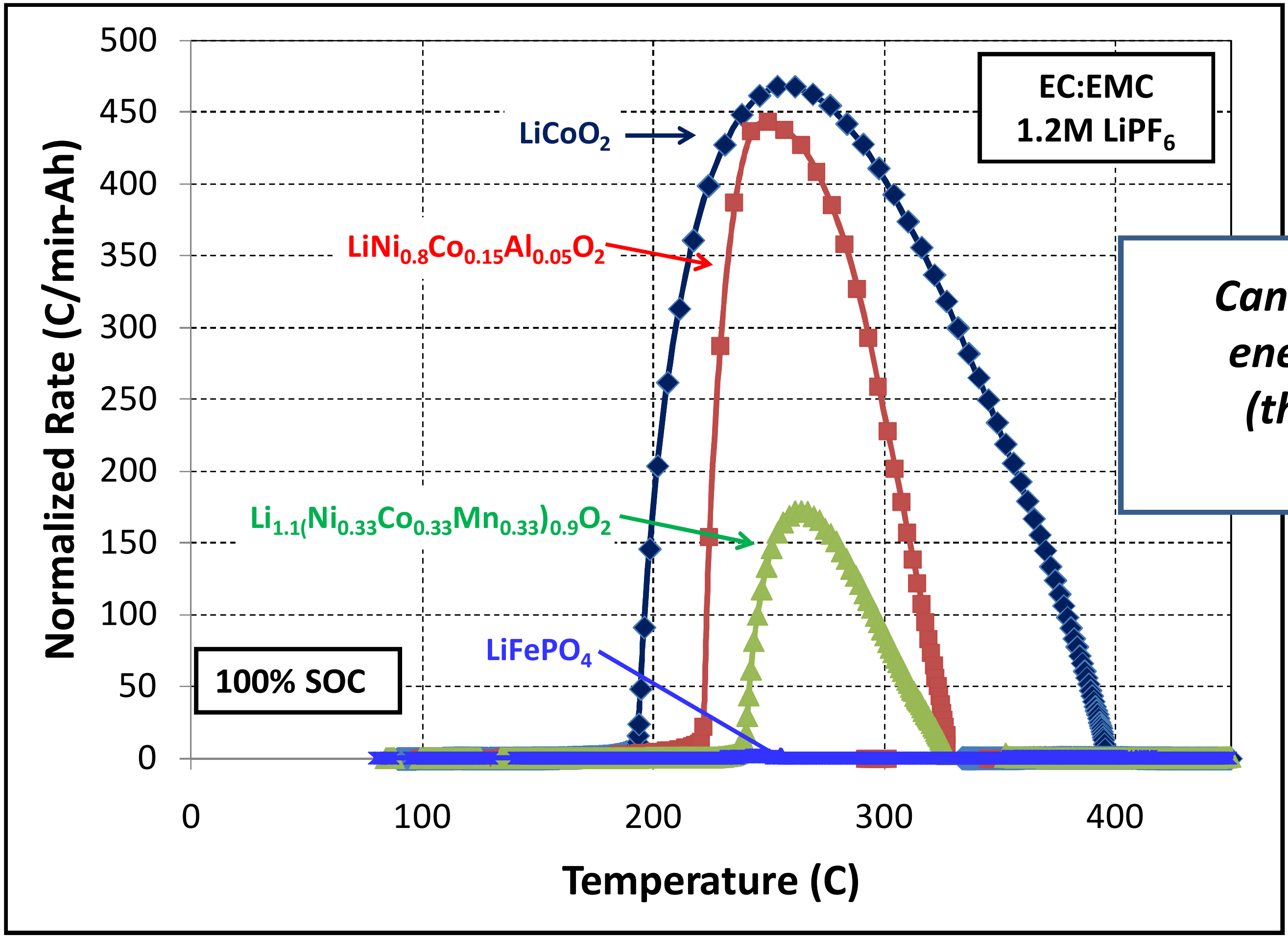



1 SEI breakdown (70-90 C)
Separator shutdown
Cell Venting (155-165 C)
Electrolyte degradation

2 Anode breakdown
Electrolyte degradation
Onset of cathode decomposition

3 High rate runaway
Catastrophic failure

# 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)?**

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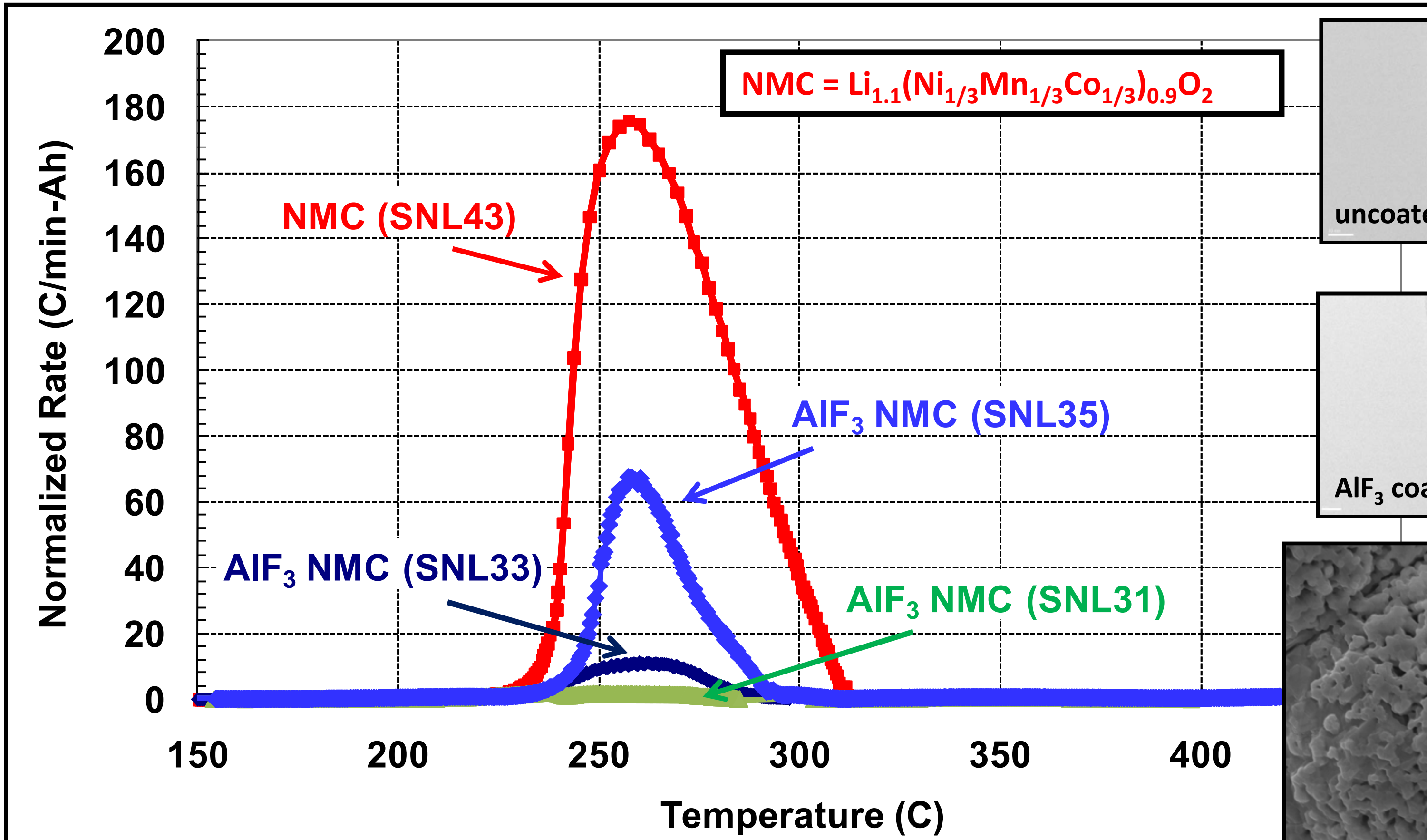
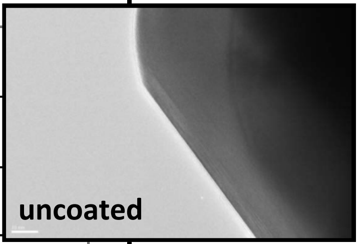
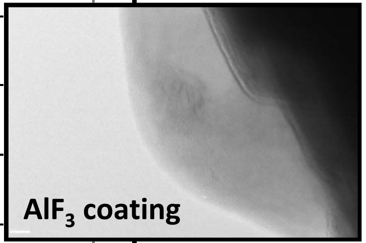
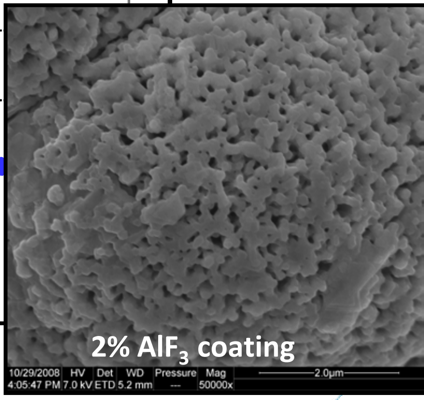
# Coated Cathodes – $AlF_3$ coated NMC



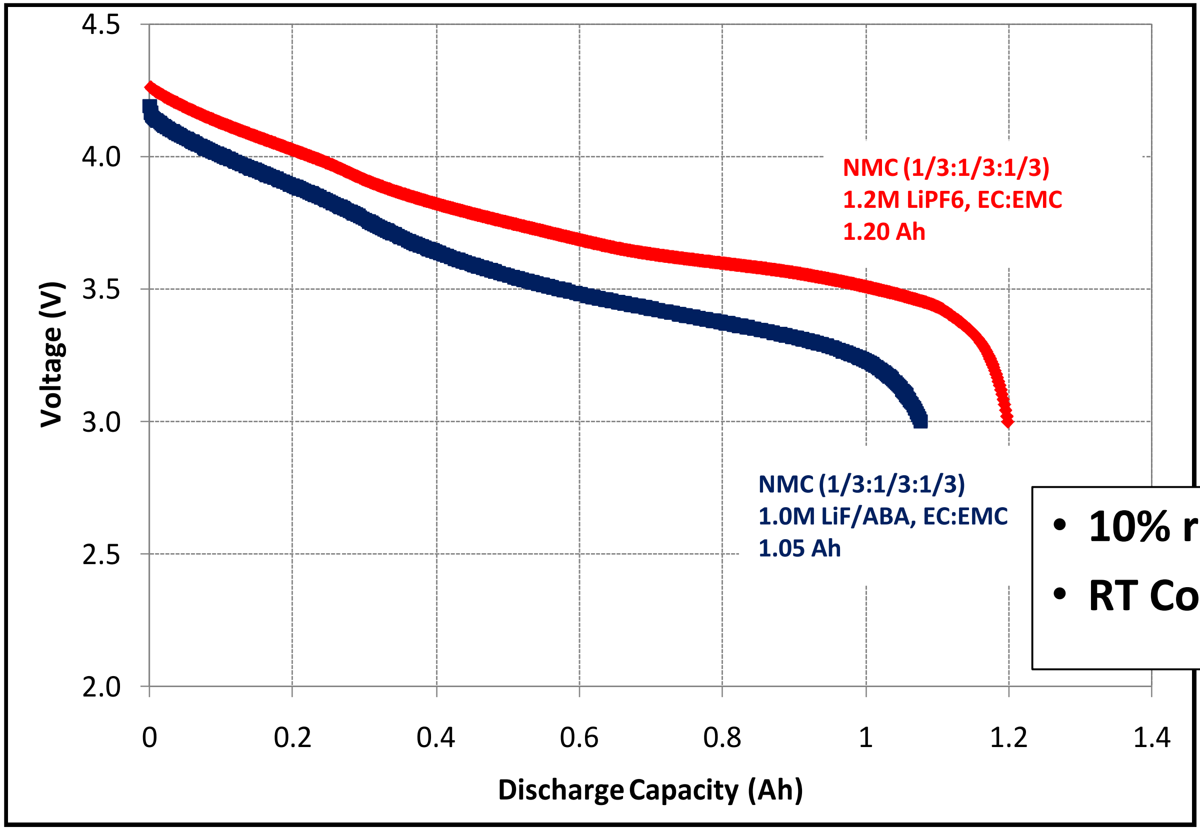

- ***Increased stabilization significantly improves the thermal response during cell runaway***
- ***Variability likely due to the material heterogeneity***

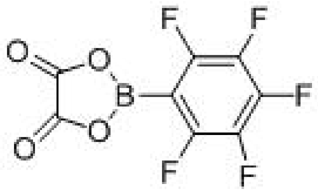
# Electrolytes to Improve Cathode Stability

***Objective: Develop ABAs to use with LiF (or non-$PF_6$ salts)***

***→ Reduce harmful decomposition from $PF_6^-$***

***→ Passivate the runaway reactions at the cathode***



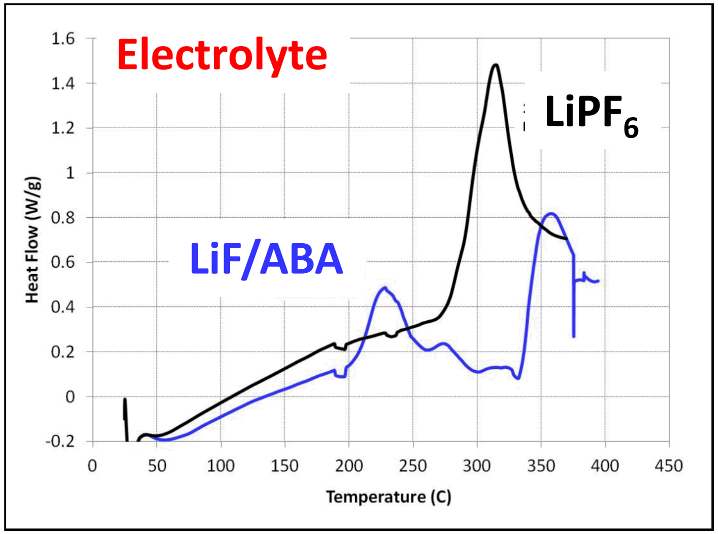

**Perfluorophenyloxaltoborate**

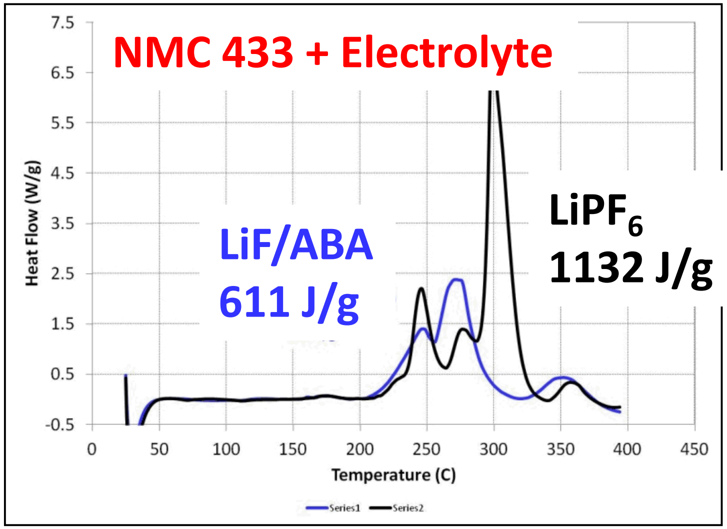
- **10% reduction in total capacity (cell)**
- **RT Conductivity = 2 mS/cm**

**~10% reduction in total capacity at C/5 with LiF/ABA compared to $LiPF_6$ in EC:EMC (3:7)**

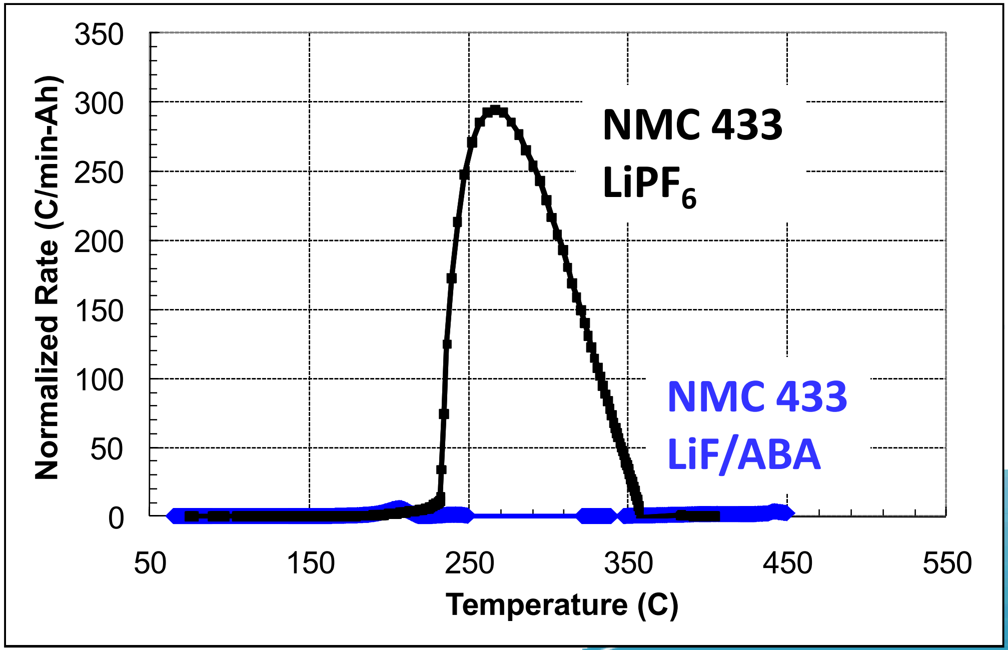
# Electrolytes to Improve Cathode Stability

DSC (Materials)



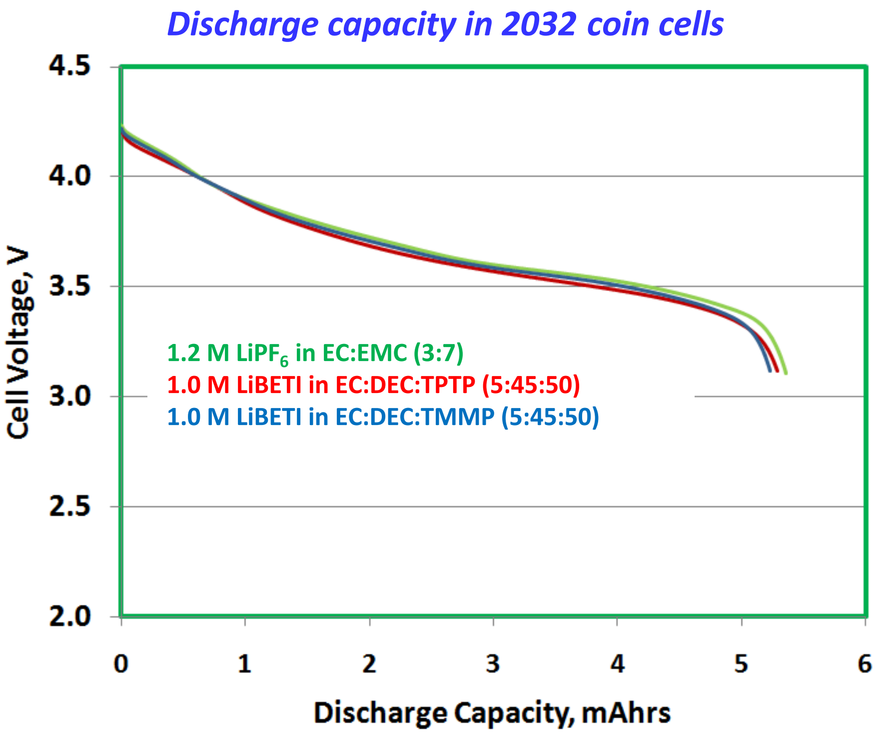

ARC (Cells)

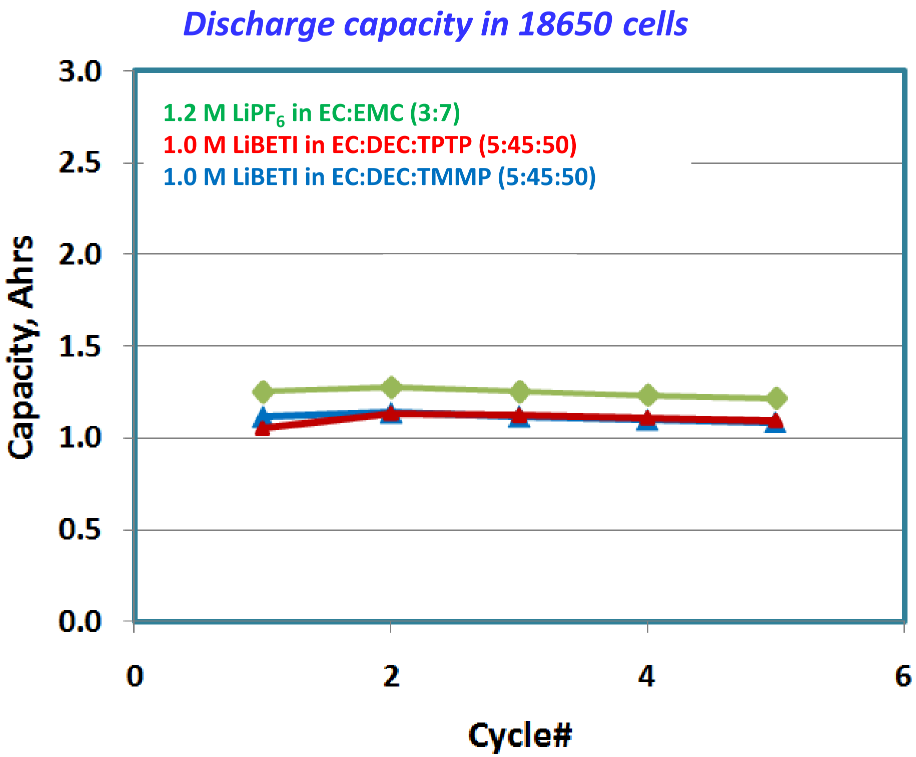



- 50% reduction in total specific heat output of NMC 433 with LiF/ABA electrolyte
- Significant reduction in cathode runaway in ARC measurements
- Good correlation between materials and cell measurements

# Nonflammable Electrolytes - Performance

*Performance of NMC cells with HFE electrolytes*




*< 10% diminished capacity of the LiBETI/HFE electrolyte cell compared to the $LiPF_6$/EC:EMC cell*

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

G. Nagasubramanian, C. J. Orendorff, J. Power Sources (2011)

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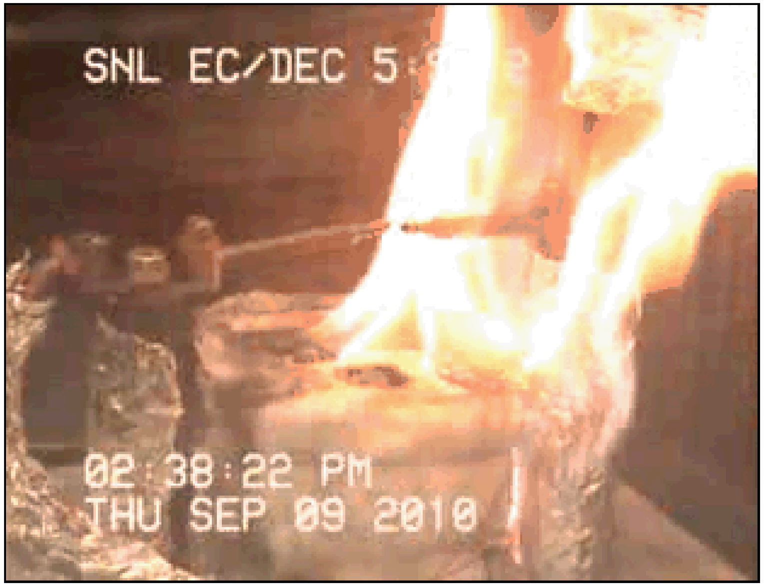
# Nonflammable Electrolytes – Ignition Testing

***Electrolyte sealed in 18650 cans and heated until vent***




..\..\Movies\EC_DEC_5_95_Vent_burn.mpg

***Ignition of EC:DEC electrolyte***


..\..\Movies\nonevent_vent.mpg

***No ignition of the 50% TPTP HFE electrolyte***

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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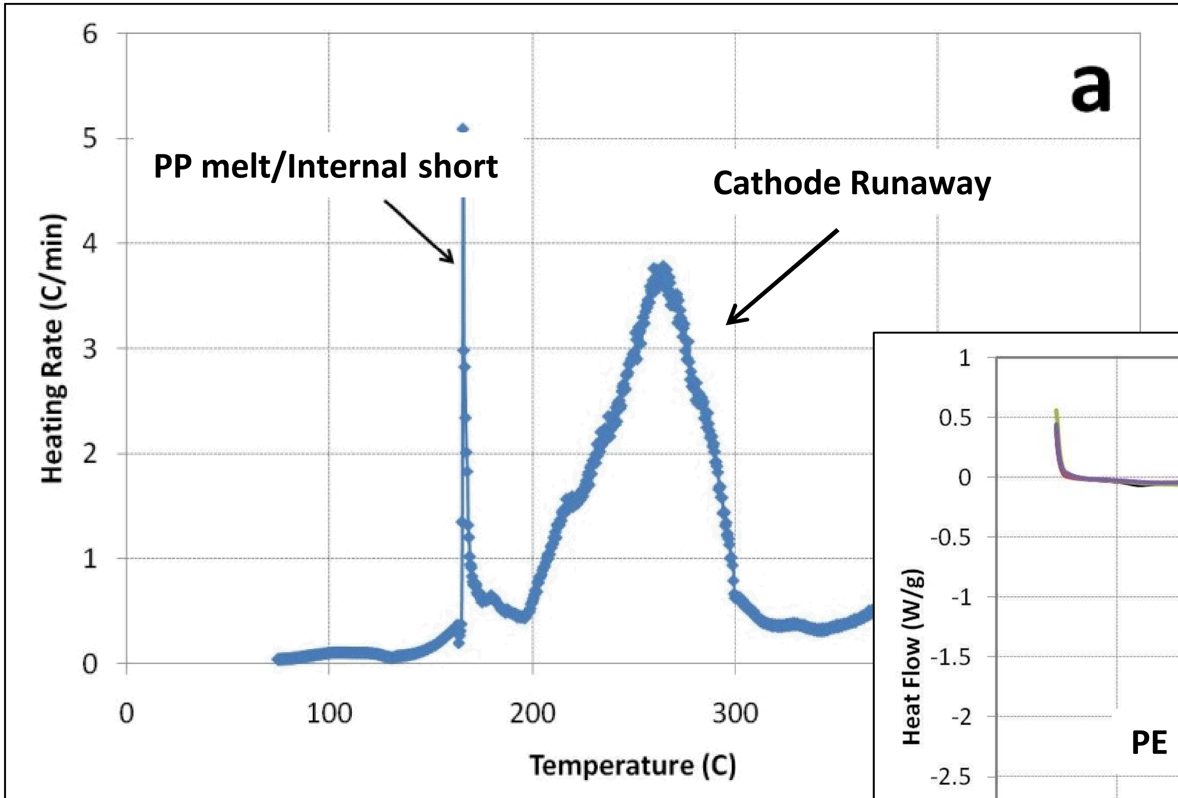
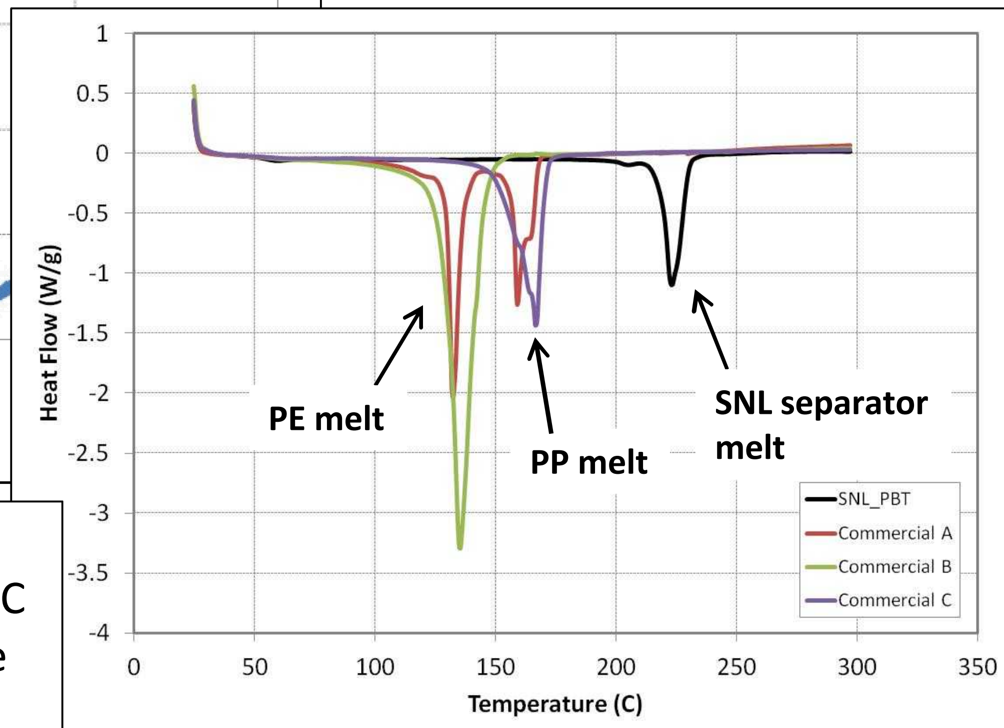
# Advanced Separator Materials

***Closing the gap between separator phase transition and cathode runaway temperature***

## Cell ARC



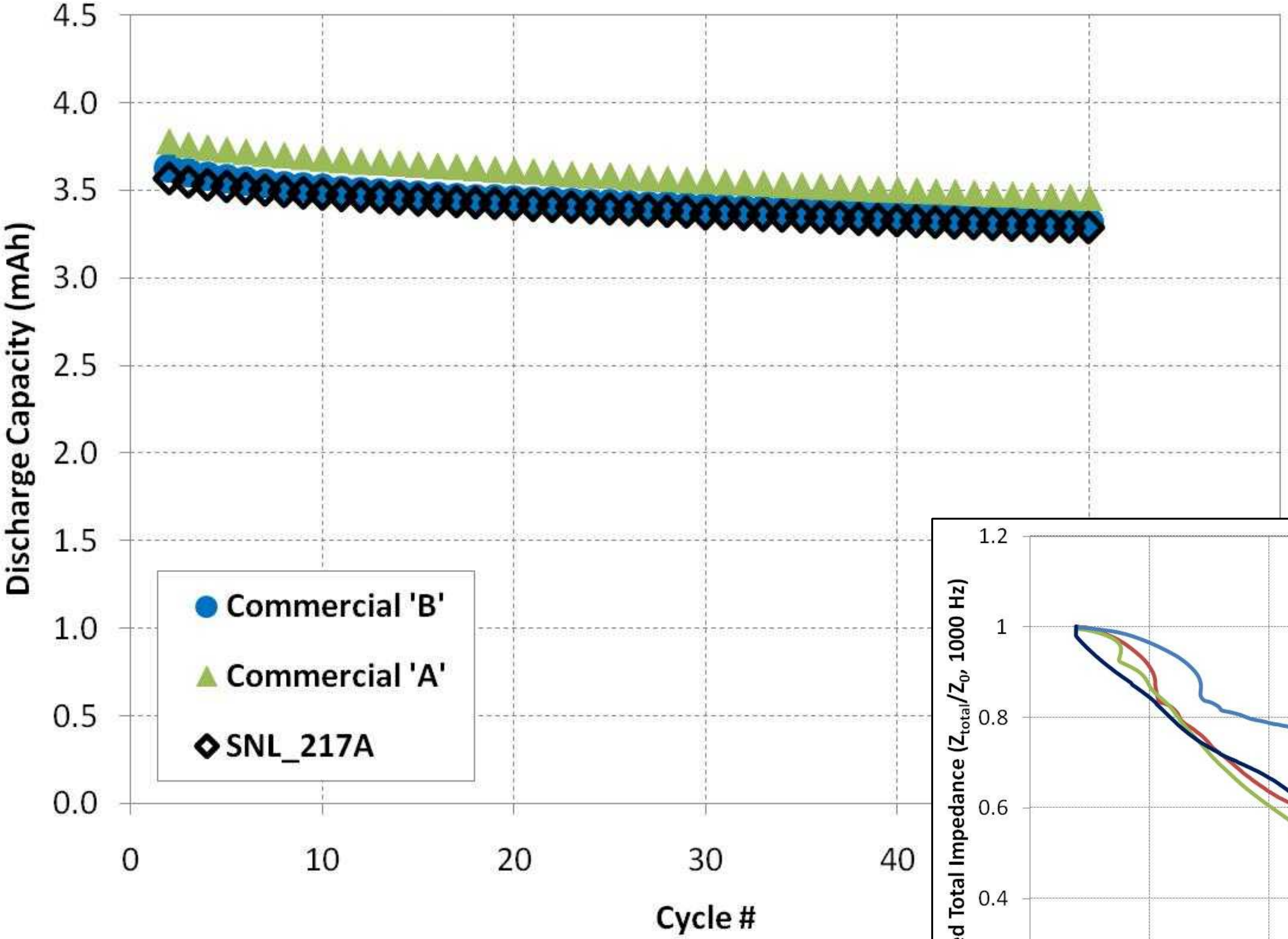

## Separator DSC



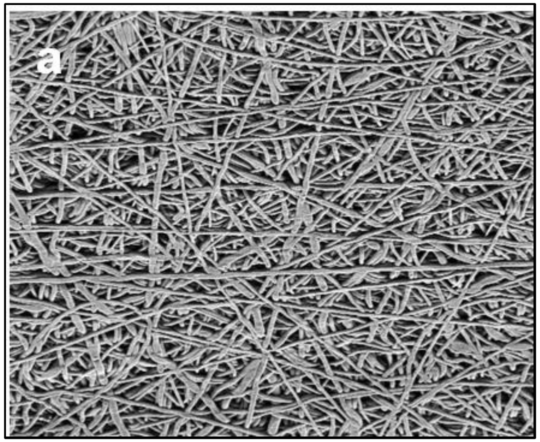

- PE and PP melt between 135 and 160 °C
- Cathode runaway between 190 and 240 °C
- Should target higher melting temperature separators to improve cell stability

# Advanced Separator Materials

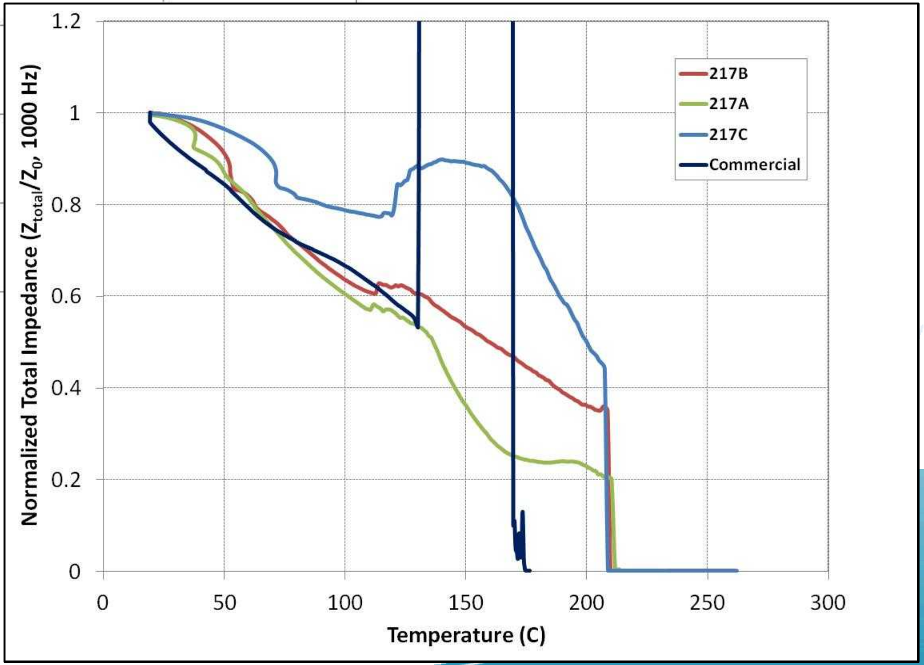
**Discharge capacity (C/5)**




**SEM**




**Separator Impedance**




- ***Comparable performance to commercial separators (C/5)***
- ***Improved thermal stability over PE/PP separators***