SAND2011-0429C

Mitigating Critical Safety Concerns in Lithium-ion Batteries

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Advanced Automotive Battery Conference
Pasadena, CA January 25, 2011

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Consequences of Cell Failure

- ***Field Failure***
  - **Manufacturing defects**
    - Separator damage, foreign debris
    - Can develop into an internal short circuit
- ***Abuse Failure***
  - **Mechanical**
    - Crush
    - Nail penetration
  - **Electrical**
    - Short circuit
    - Overcharge
    - Overdischarge
  - **Thermal**
    - Thermal ramp
    - Simulated fire

SNC-Lavalin Gulf Contractors Safety Alert, June 2008

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Impact of Scale

Larger batteries in larger quantities:

- ***The numbers of cells used potential in the automotive industry (EVs and PHEVs) is 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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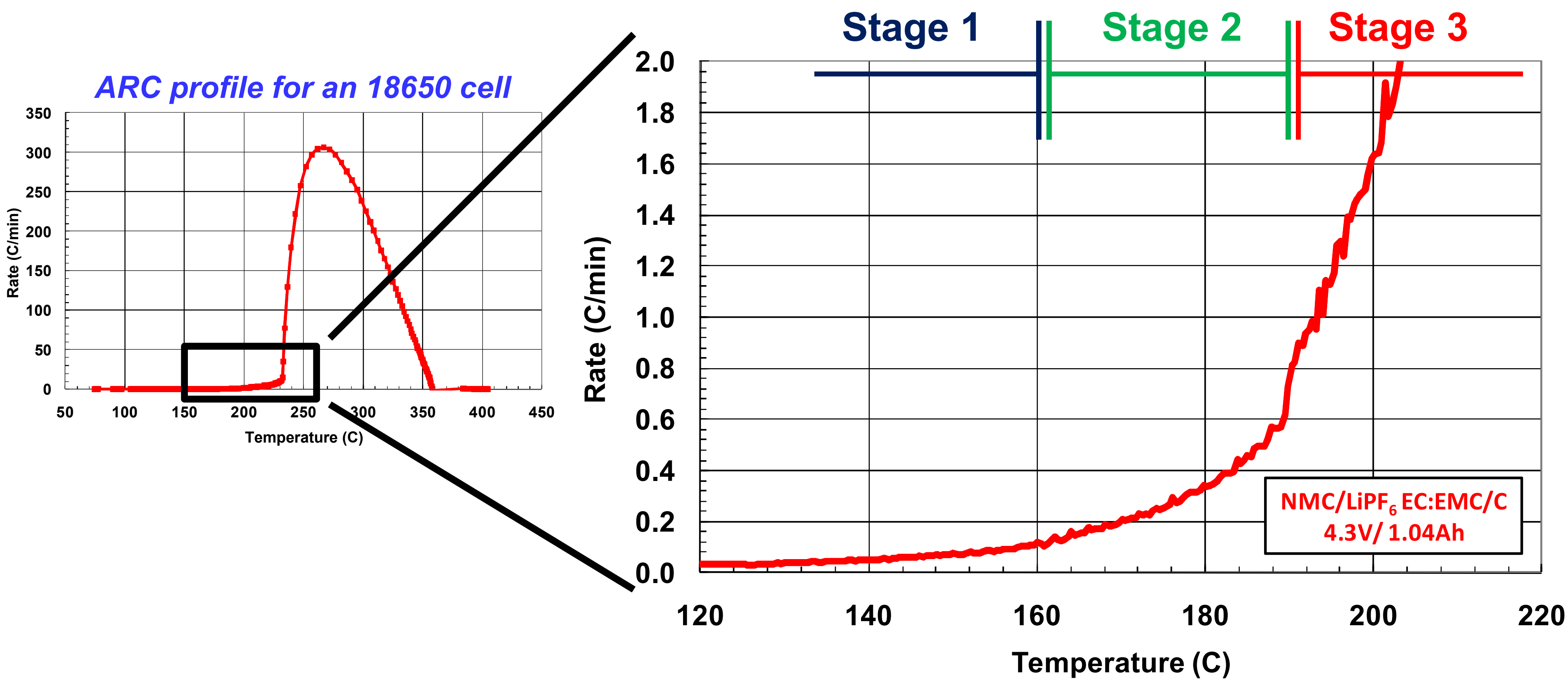
Critical Safety Concerns

Limitations toward developing inherently safe lithium-ion cell chemistries

- ***Energetic thermal runaway of active materials***
  - Exothermic materials decomposition, gas evolution, electrolyte combustion
  - Can be mitigated through new materials, coatings, additives
- ***Electrolyte degradation, gas generation & flammability***
  - Overpressure and cell venting is accompanied by an electrolyte spray which is highly flammable
  - Can be improved with electrolyte choices with minimal impact on performance
  - Need to ensure flammability testing accurately captures this active failure event
- ***Separator failure & internal short circuits***
  - Incomplete separator shutdown can lead to catastrophic failure at <135 C
  - Shutdown separators can show instabilities at high stand-off voltages (relevant to EV- and PHEV-scale modules and packs)
  - Need to examine the role of non-shutdown separators

Thermal Runaway in Lithium-ion Cells

Stages of Thermal Runaway



Stage 1: < 160°C – Onset (SEI layer breakdown, electrolyte degradation, etc.)

Stage 2: 160°C - 190°C – Acceleration (cell vent, accelerated anode and electrolyte degradation, onset of cathode decomposition)

Stage 3: > 190°C – Runaway (full cell materials degradation, energetic release and uncontrolled rapid disassembly)

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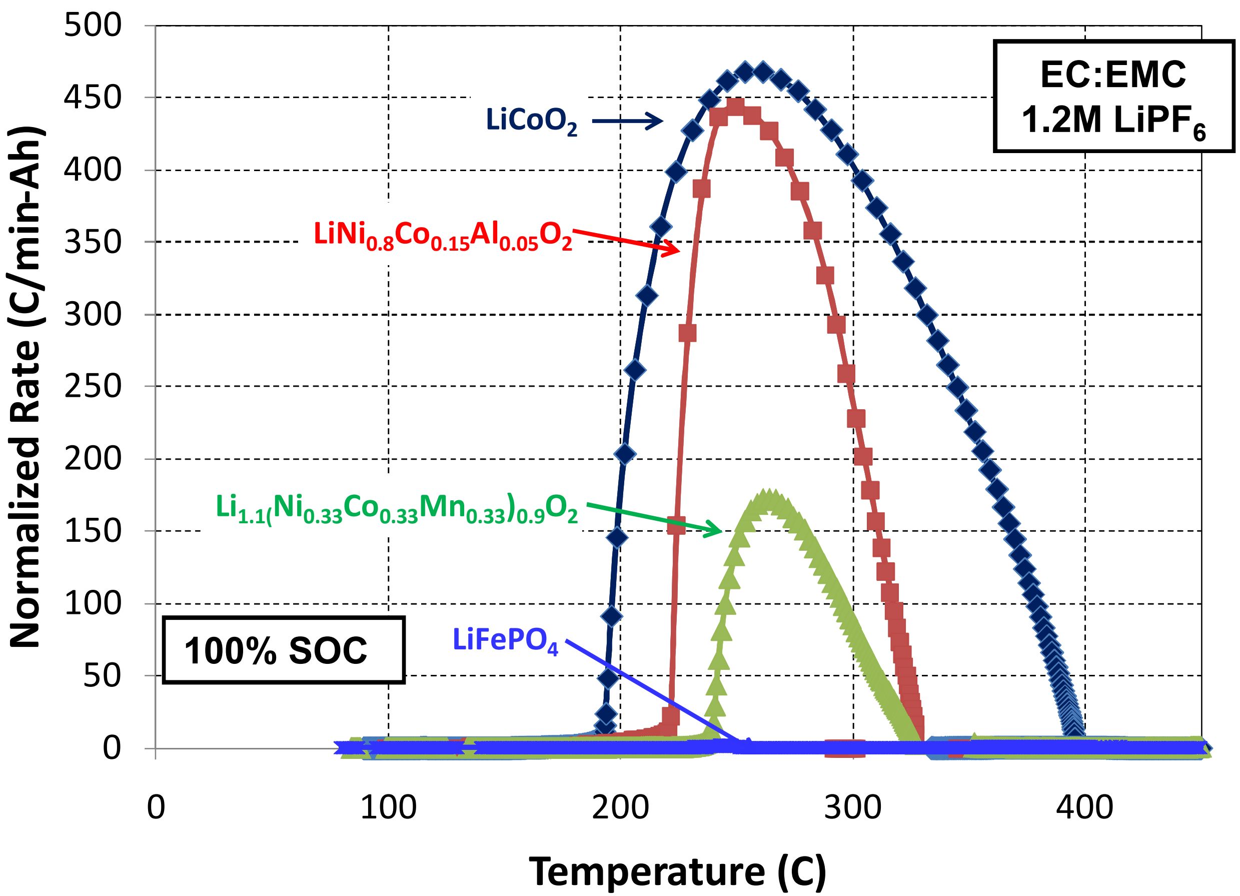
Thermal Runaway & Cathode Chemistry

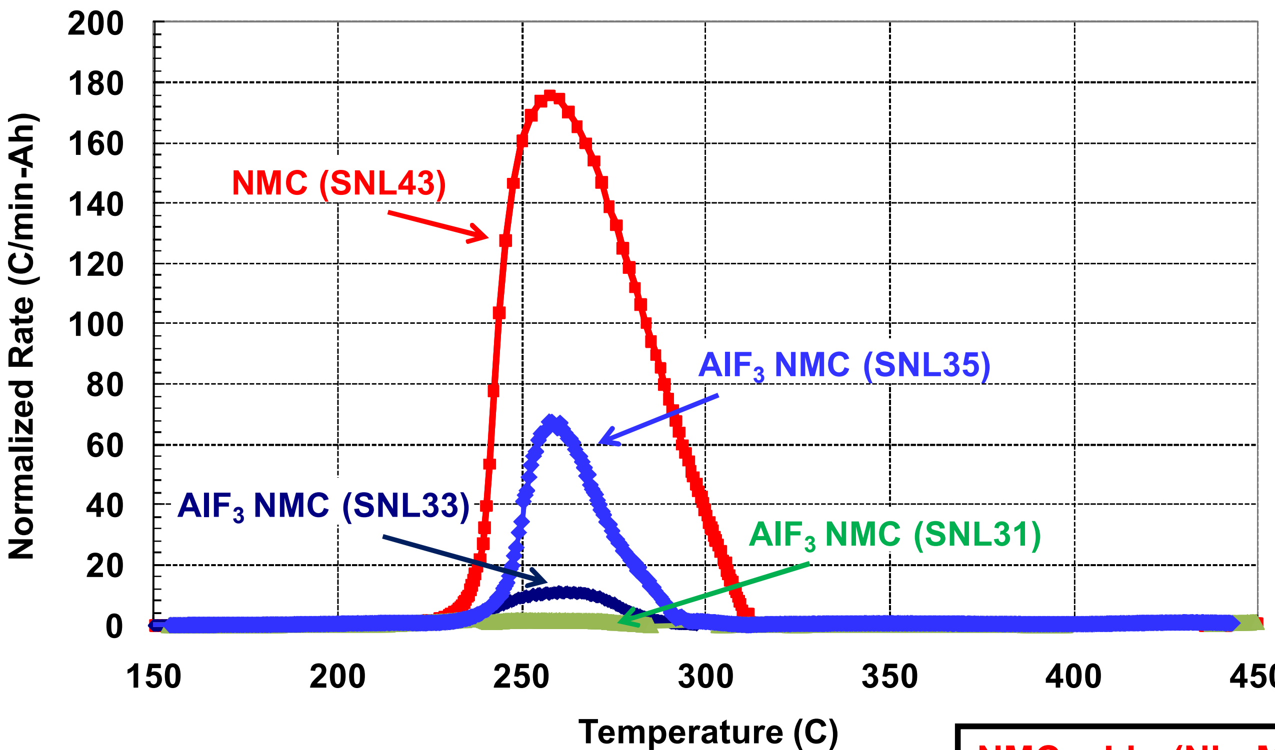
Accelerating Rate Calorimetry (ARC)



- Increased thermal runaway temperature and reduced peak heating rate for full cells
- Decreased cathode reactions associated with decreasing oxygen release

AlF_3-coated NMC Cathodes

Thermal response of AlF_3-coated NMC in 18650 cells by ARC



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

- ***AlF_3-coating improves the thermal stability of NMC materials by 20 °C – onset of decomposition ~260 °C (ANL)***
- ***Increased stabilization significantly improves the thermal response during cell runaway***

in collaboration with ANL

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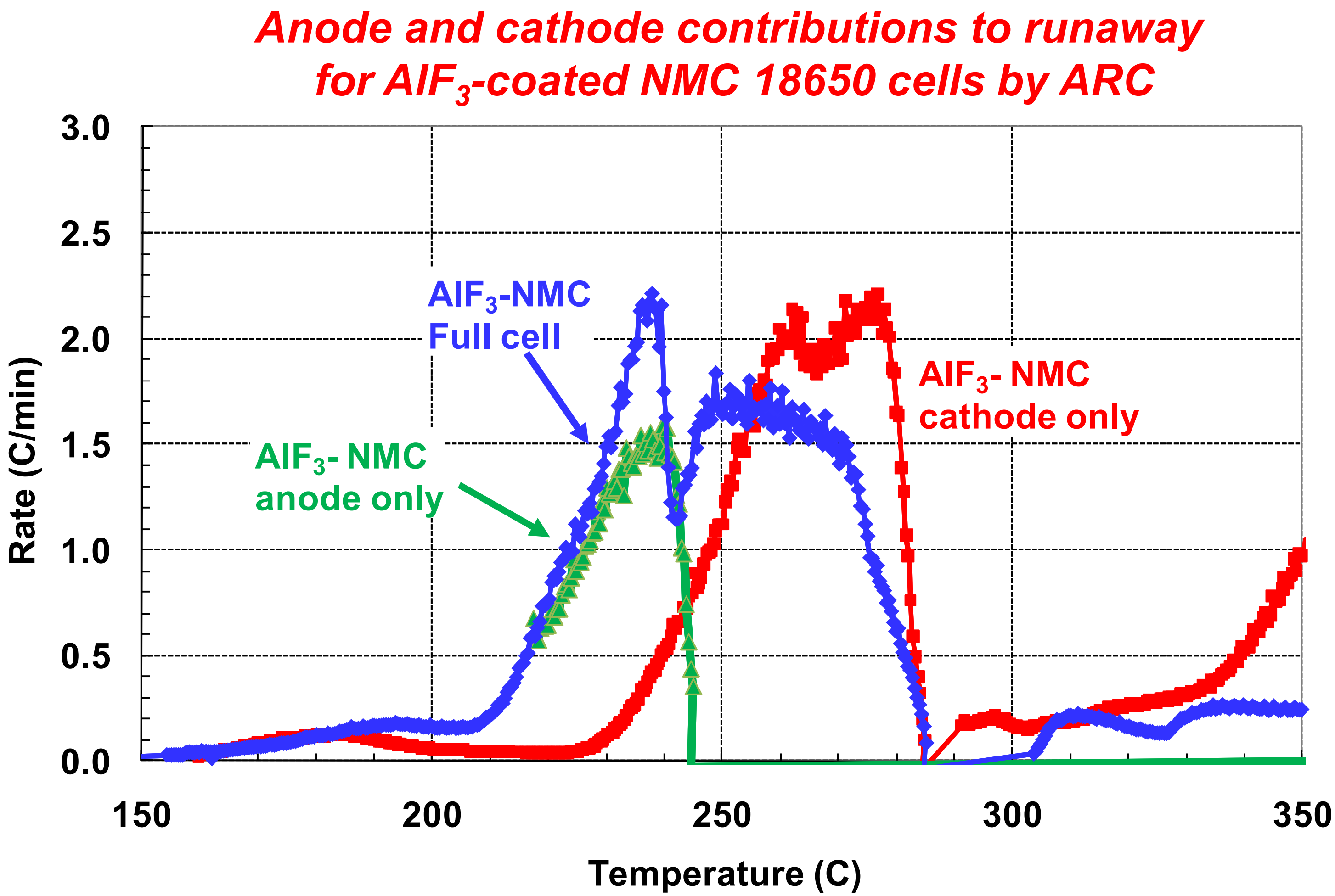
Electrode Contributions to Runaway



Good agreement between individual electrode ARC experiments and the full 18650 cell

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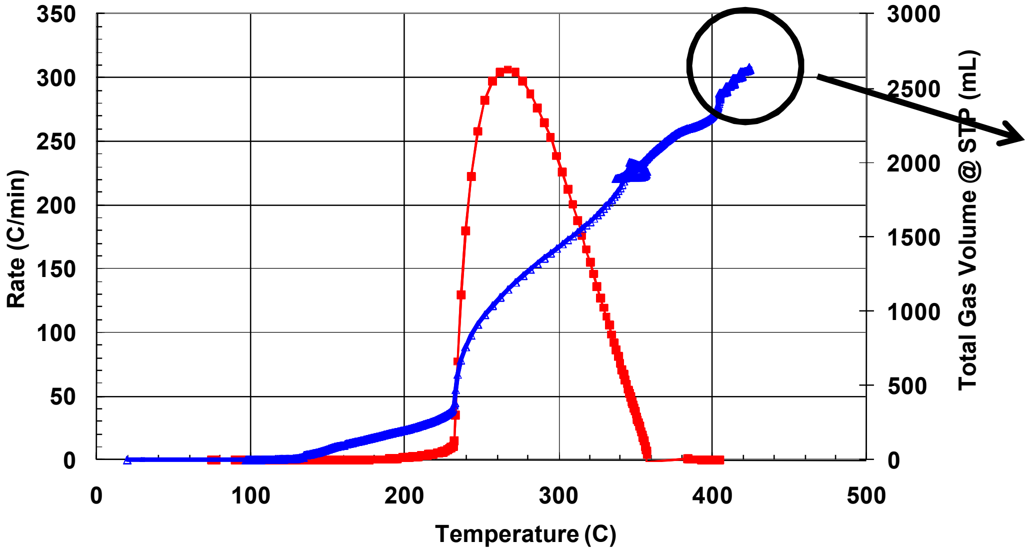
Electrolyte Degradation & Flammability

Decomposition and gas evolution

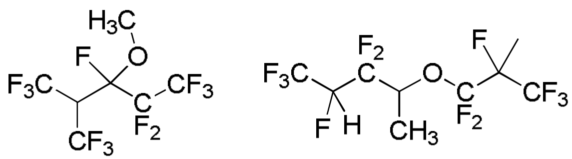


- *Large gas volume - 2.5 L for 18650 cell*
- *Cell vent → solvent aerosol spray (flammable)*
- *Cell vent → spreading particulates (inhalable)*

Electrolyte Safety Improvements

- Improve thermal stability
  - ↓ ΔH^{o}_{r} combustion electrolyte
  - ↑ Lithium salt decomposition temperature
- Reduce gas degradation products
  - Minimize the pressure rise in a cell
  - Reduce the aerosol spray of flammable electrolyte
  - Reduce the spread of particulates (some of which are health hazards)
- Flammability
  - Flame retardants
  - Additives
  - High flash-point solvents

Hydroflouroethers (HFEs):



TMMP **TPTP**

Lithium Sulfonimide Salts:

$LiN(CF_3SO_2)$ (LiTFSI)
$LiN(C_2F_5SO_2)$ (LiBETI)

Data is the following slides is for 1.0 M LiBETI in EC:DEC:TPTP (5:45:50) or 1.0 M LiBETI in EC:DEC:TMMP (5:45:50)

Naoi, K. et al. J. Electrochem. Soc. 157, A190-A195, 2010
Naoi, K. et al. J. Electrochem. Soc. 156, A272-A276, 2009

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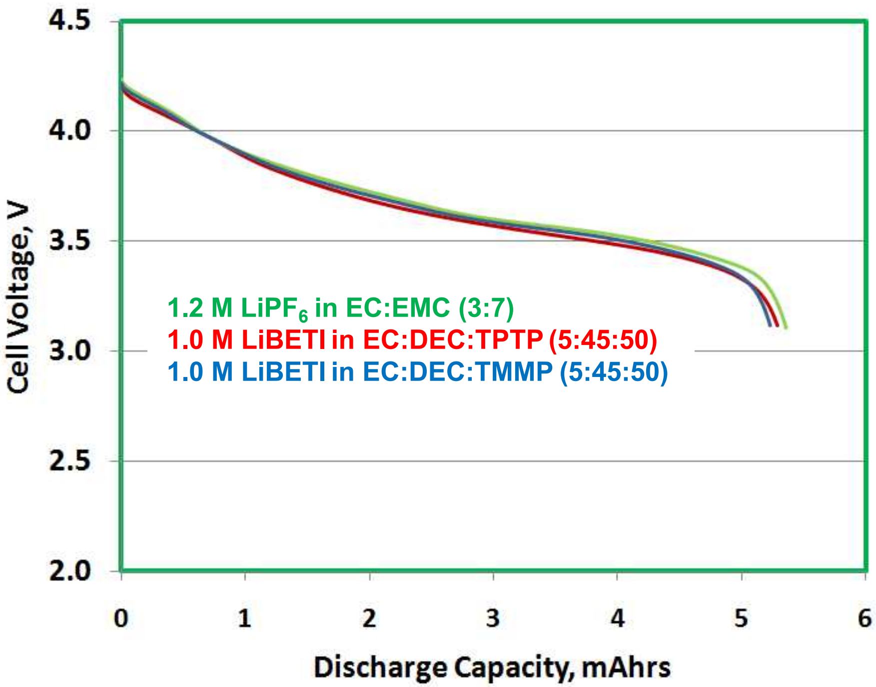
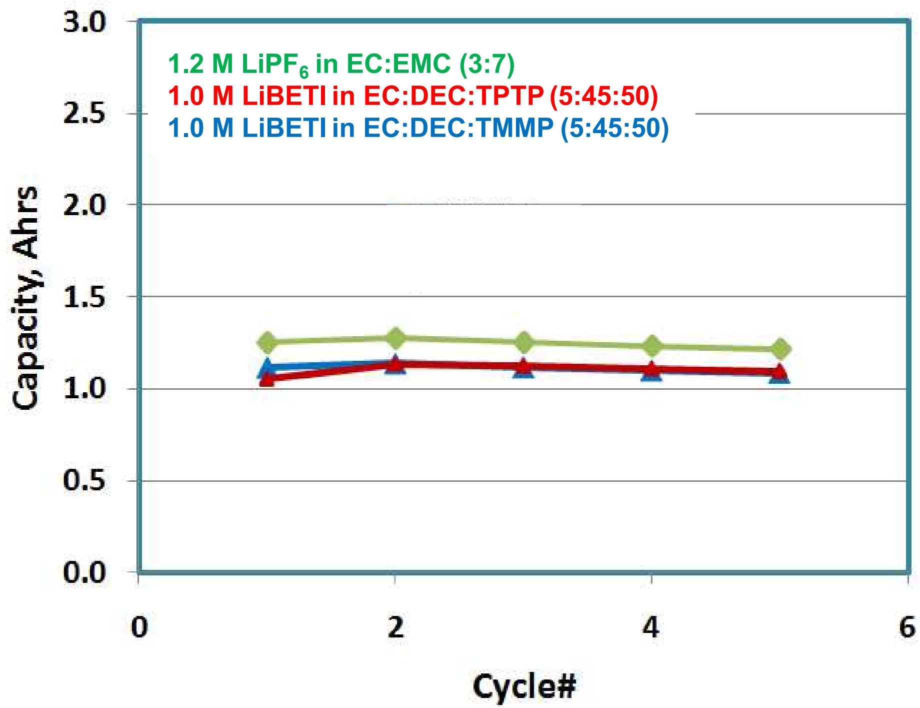
Cell Performance of HFE electrolytes

Performance of NMC cells with HFE electrolytes

Discharge capacity in 2032 coin cells



Discharge capacity in 18650 cells



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

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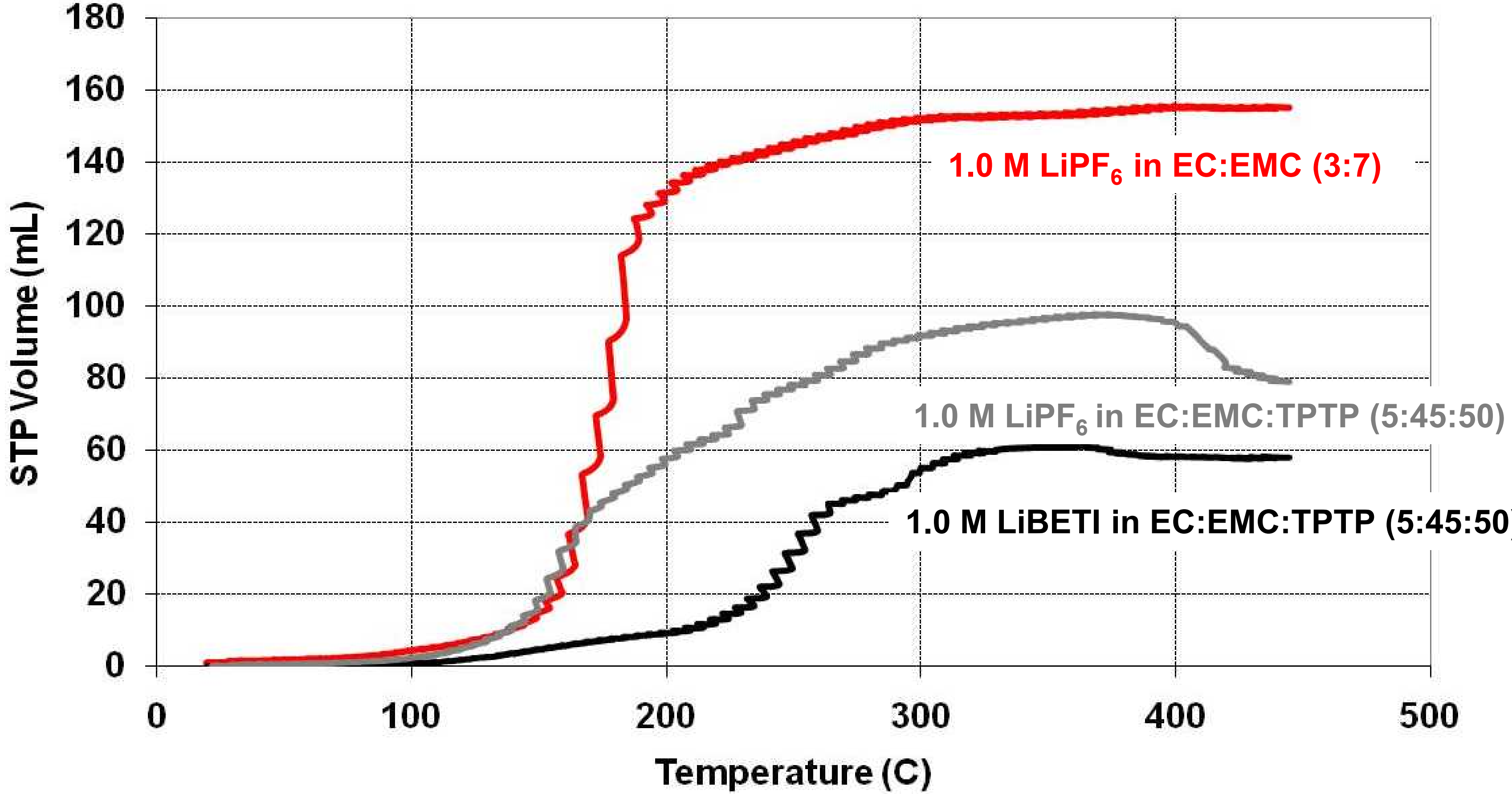
Reduced Gas Generation and Improved Thermal Stability

ARC bomb experiments to determine gas volume (0.5 g samples)



40-60% reduced gas generation (@ 300 °C)
Improved thermal stability

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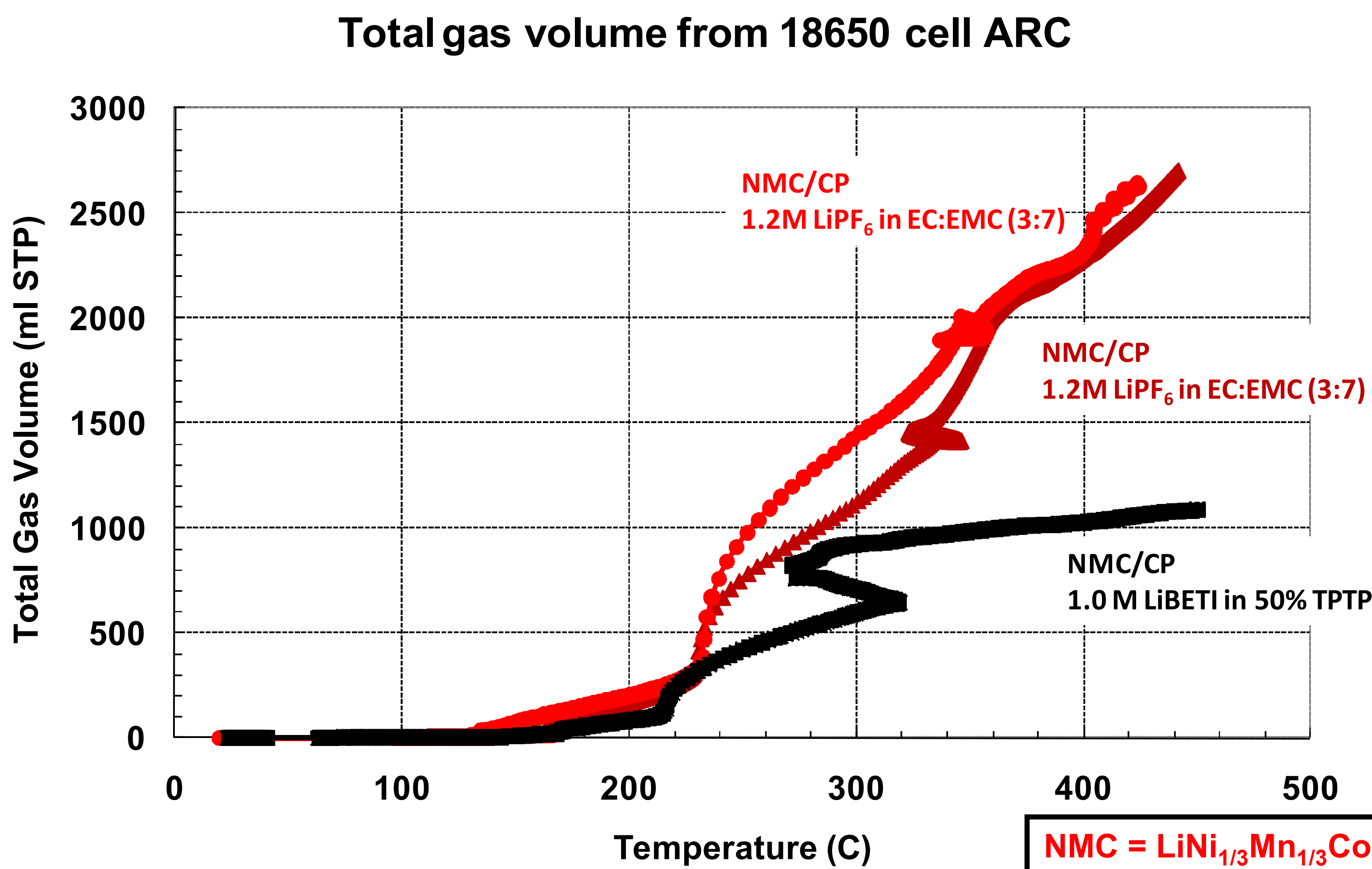
Reduced Gas Evolution in 18650 Cells



NMC = $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
CP = Conoco Phillips carbon

60% reduction in gas generation in 18650 cells
Consistent with results for electrolyte alone

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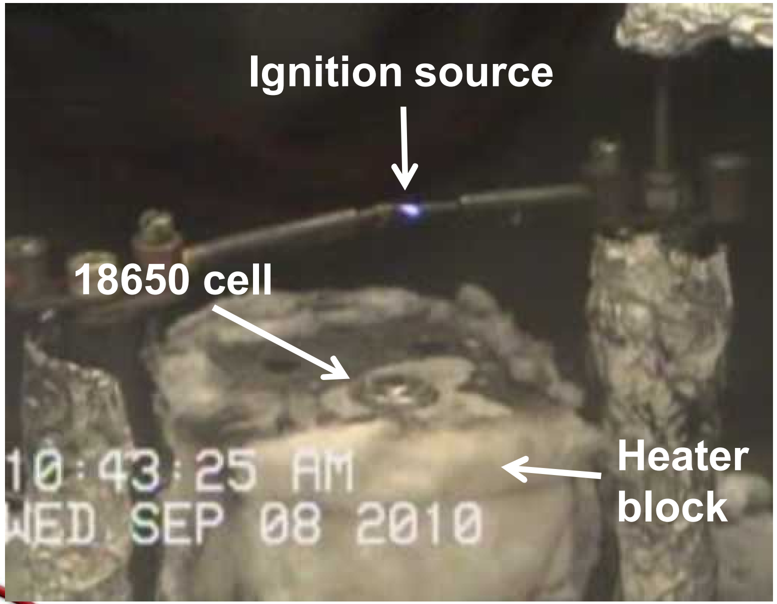
Electrolyte Flammability Test

- Traditional flammability experiments do not accurately capture the flammability hazard of a venting cell (pressure increase, solvent aerosol spray, etc.)
  - **Wick test/ignition test**
  - **Cotton ball fire**

Flammability Test Setup



Flammability Testing

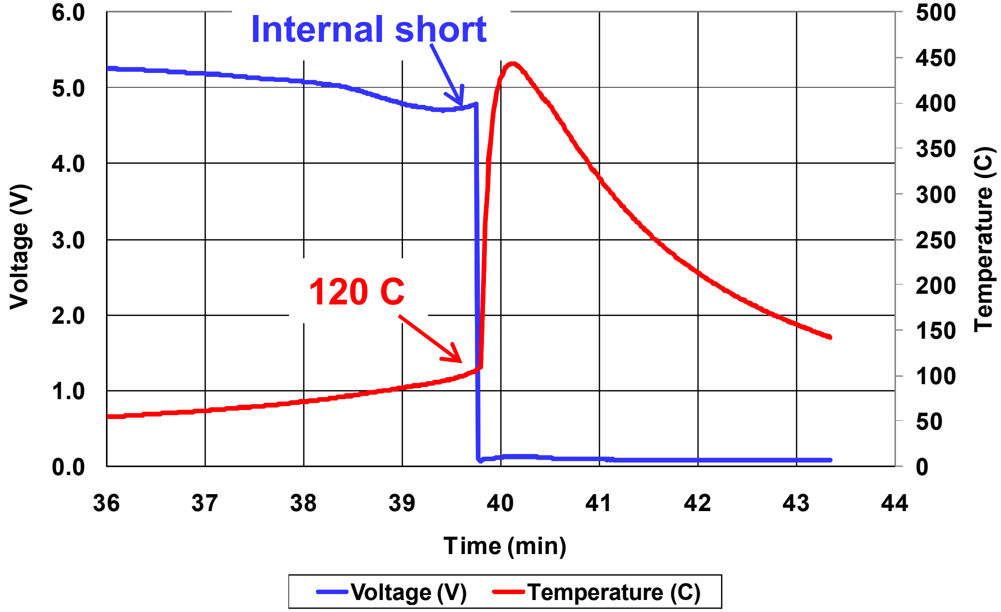
Electrolyte sealed in 18650 cans and heated until vent

Ignition of EC:DEC electrolyte

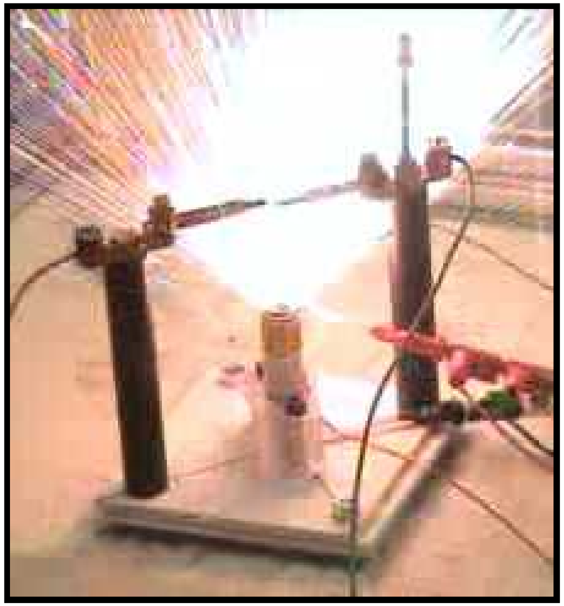
No ignition of the 50% TPTP HFE electrolyte

Separator Failure & Internal Short

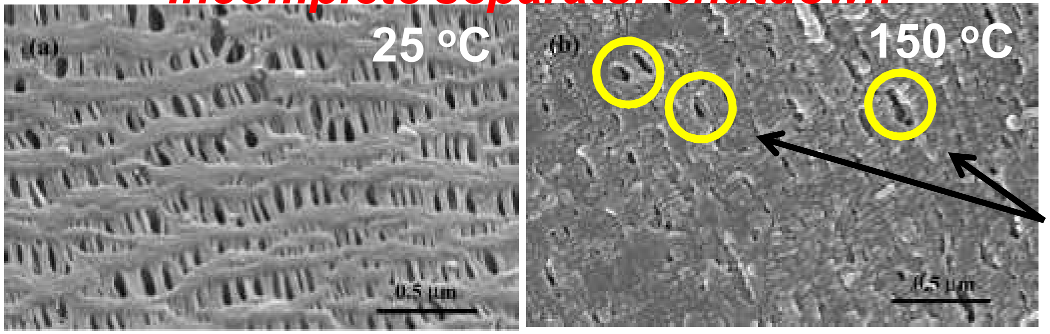
Separator Failure on Overcharge Abuse



Internal short leads to energetic runaway



Incomplete separator shutdown



Incomplete shutdown – increases local current density & heating

D. P. Abraham et al. *J. Power Sources*, 161 (2006), 648-657

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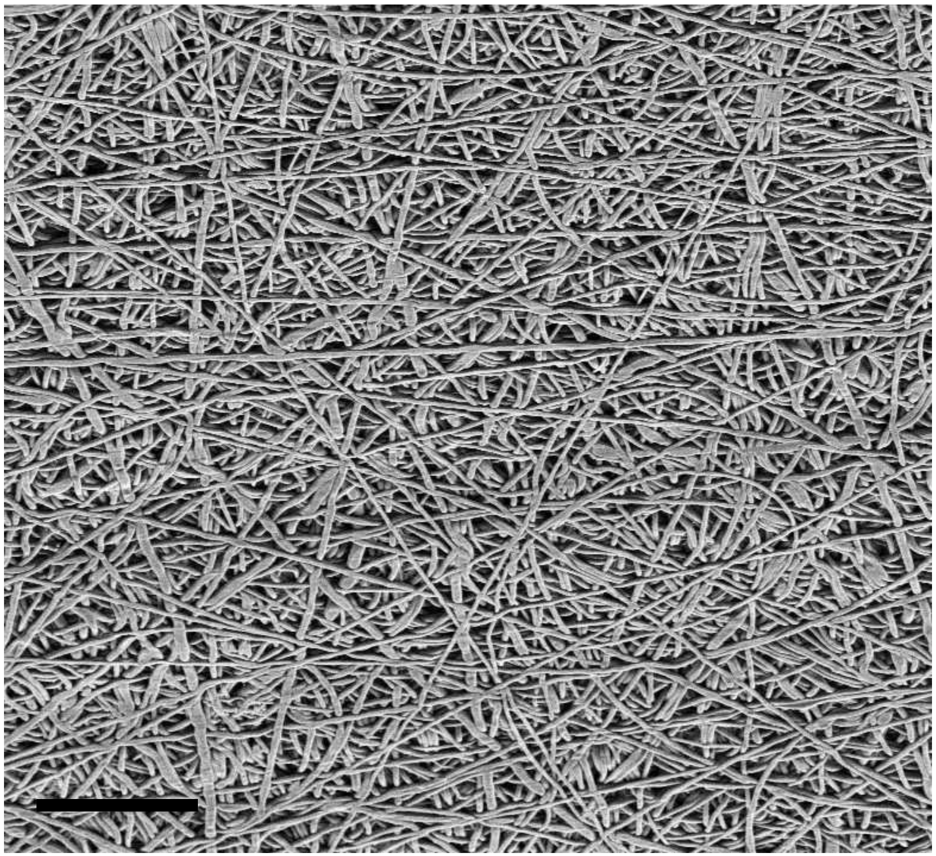
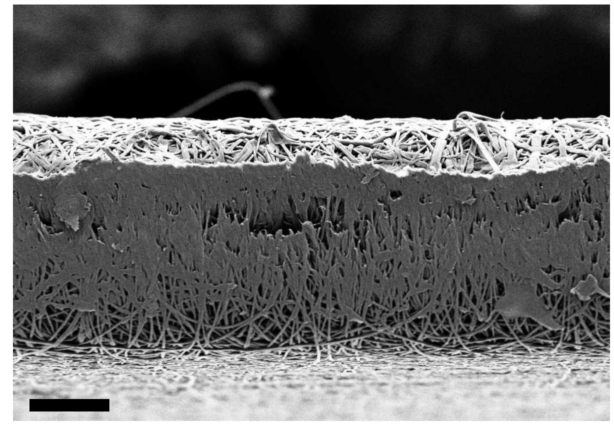
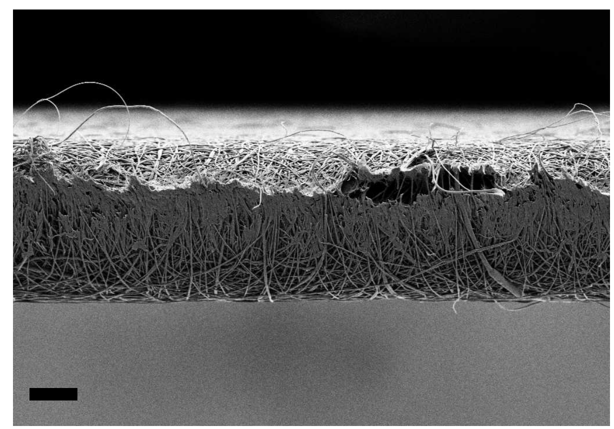
Non-shutdown Separators

SEM images of SNL developed separators based on terephthalate fibers



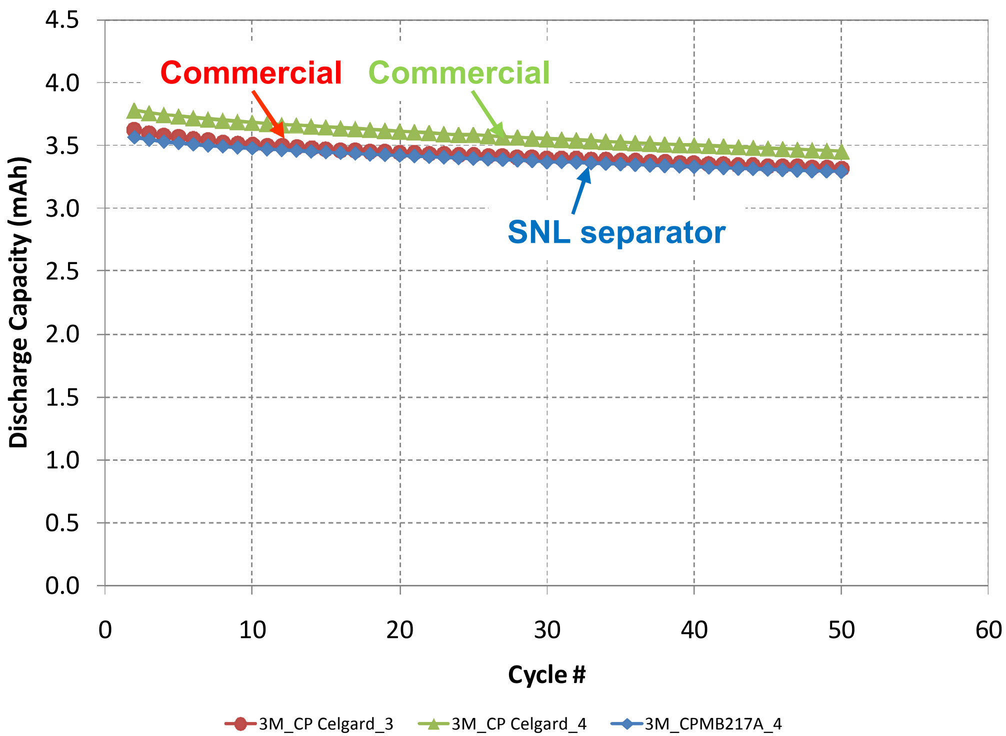




Scale bars represent 20 µm

Performance of SNL Separators

Discharge capacity of SNL NMC/CP cells with commercial and SNL separators



Separator	(μm)	Gurley # (100 mL/s)
Celgard 2325	25	570± 4
Tonen 25MMS	25	637± 10
Tonen 20MMS	20	524 ± 9
Separion®	20	23 ± 0.5
Porous Power HPX1	20	27 ± 4
SNL_217A	55	8 ± 1

Prototype performance comparable to commercially available separators

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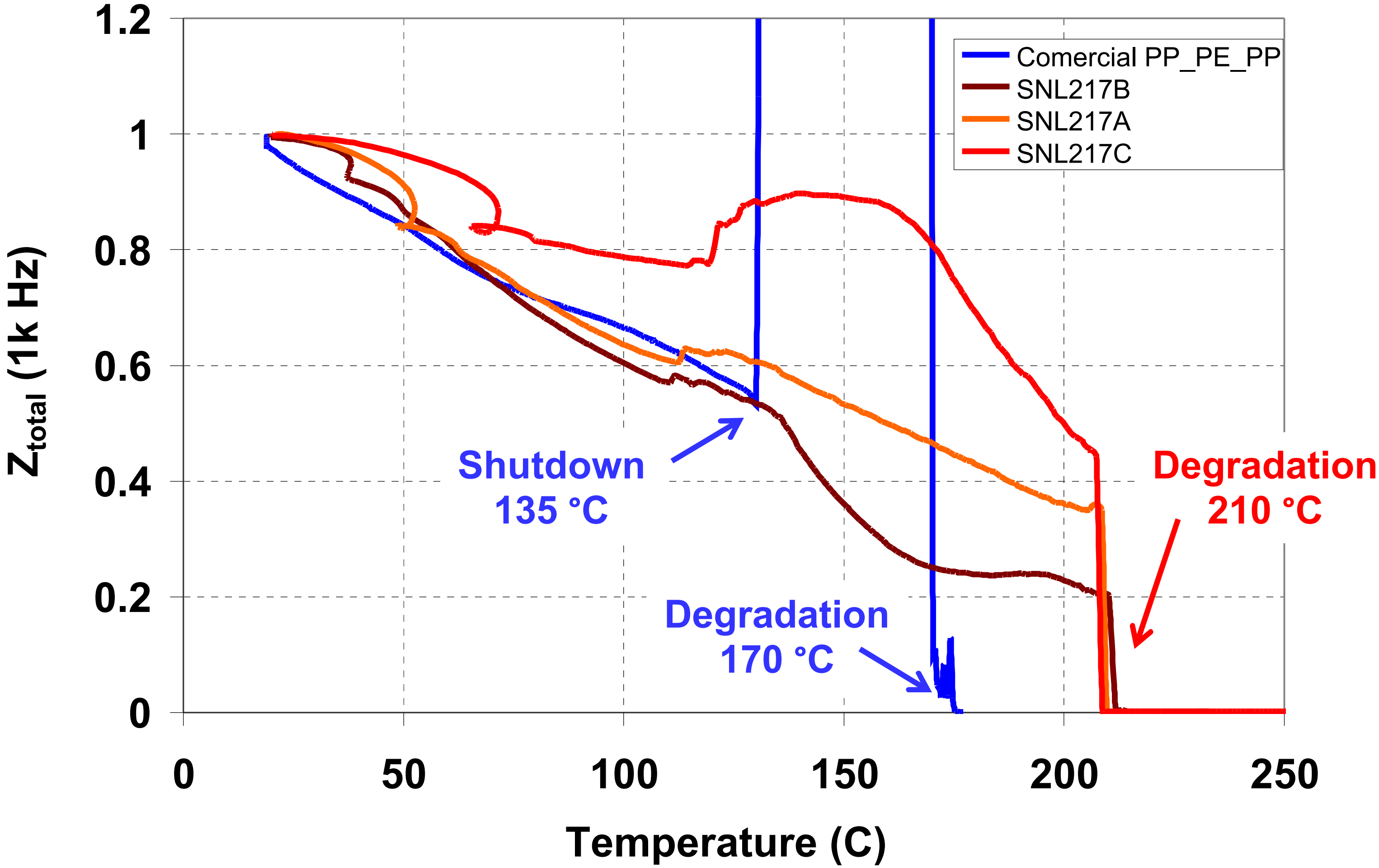
Thermal Integrity of Separators



SNL separators show thermal stability to 210 C

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Summary

- Potential safety issues associated with lithium-ion chemistries are going to scale with the size of the battery/application and numbers of cells
- Materials choices and improvements can have a significant impact on the abuse response and thermal behavior of lithium-ion cells
- Cathode materials and inert cathode coatings can decrease the reaction kinetics and enthalpy during a runaway event
- Electrolytes can have a significant impact on the total energy released during a runaway and can be tailored to produce less gas upon degradation and to be less flammable upon ignition
- Flammability testing actual cells/cell systems is a more relevant measure of the flammability hazard of lithium-ion electrolytes
- Separators materials choices can be made to give more thermally stable separators with improved abuse tolerance

Acknowledgements

- Tom Wunsch
- Dave Howell (DOE)
- Hank Westrich (SNL, LDRD)
- Pete Roth
- Ganesan Nagasubramanian
- Bill Averill
- Tim Lambert
- Jill Langendorf
- Lorie Davis
- Mike Russell
- Dave Johnson
- Denise Bencoe
- Carlos Chavez