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A Materials Approach To Abuse Tolerance In Lithium Ion Batteries

FreedomCAR & Fuel Partnership

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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NNSA National Nuclear Security Administration

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Consequences of Cell Failure

Field Failure

- **Manufacturing defects**
  - Separator damage
  - Foreign particles
    - **Internal shorts**

Abuse Failure

- **Mechanical**
  - Crush
  - Nail penetration
- **Electrical**
  - Short circuit
  - Overcharge
  - Overdischarge
- **Thermal**
  - Thermal ramp
  - Simulated fire

SNC-Lavalin Gulf Contractors Safety Alert, June 2008

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

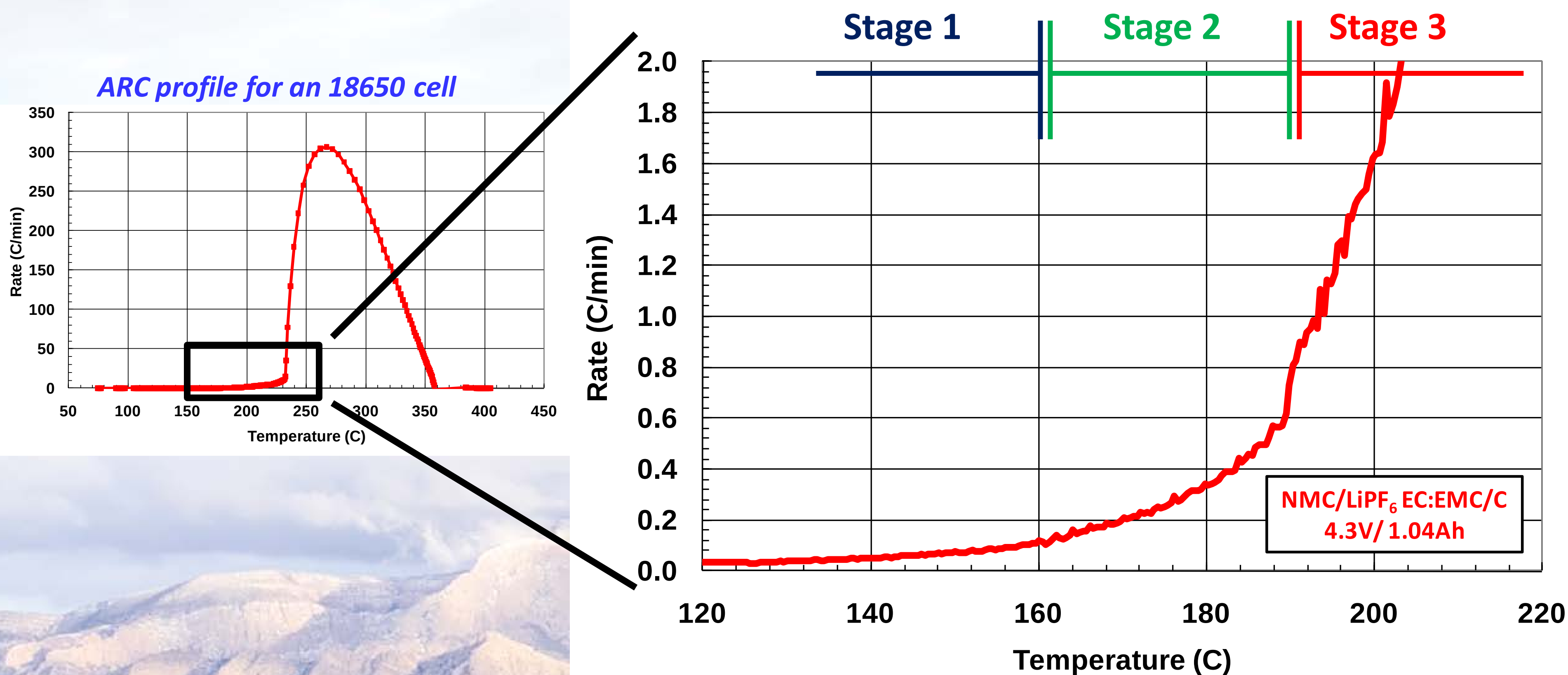
Critical Safety Concerns

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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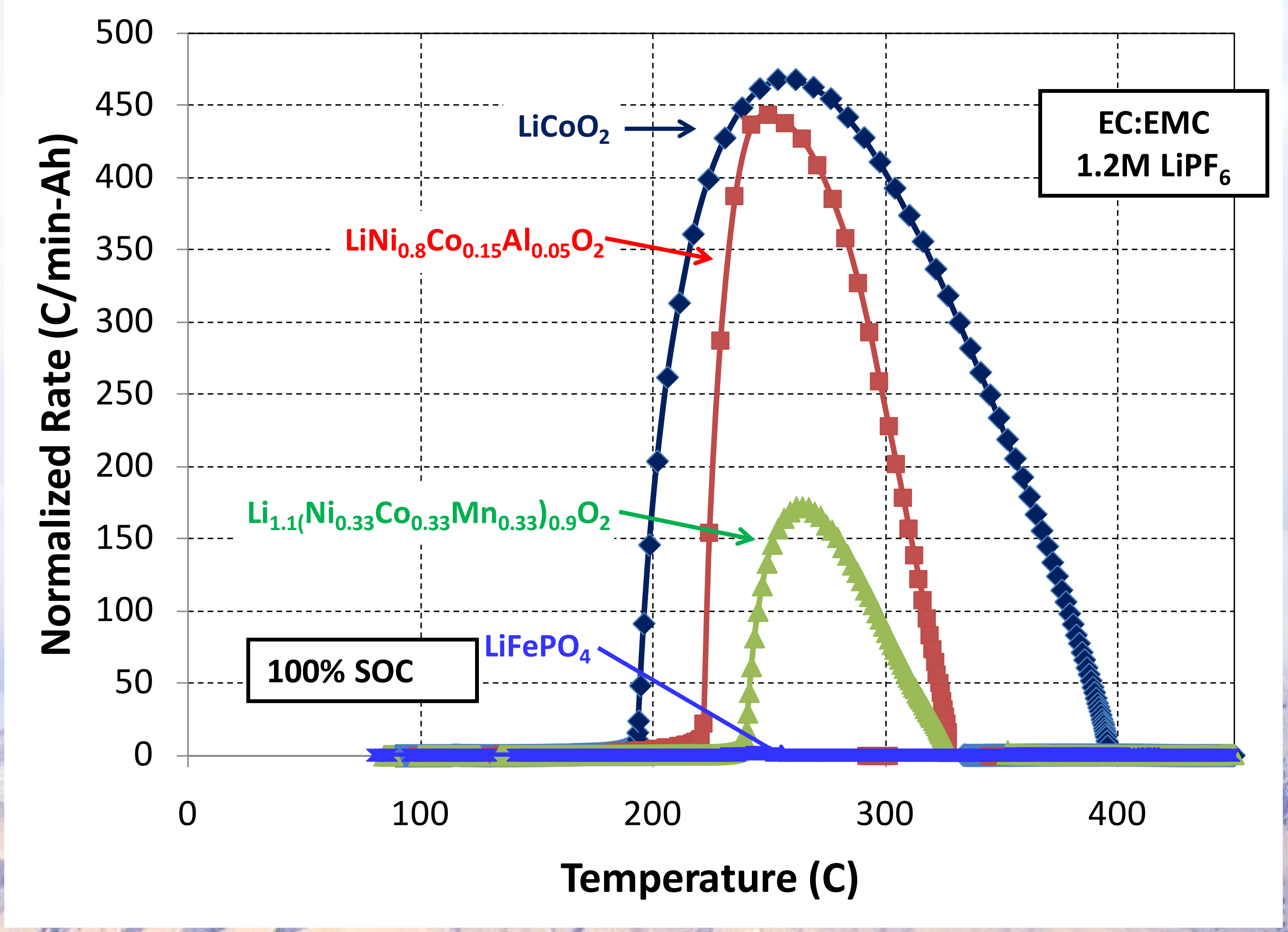
Thermal Runaway & Cathode Chemistry

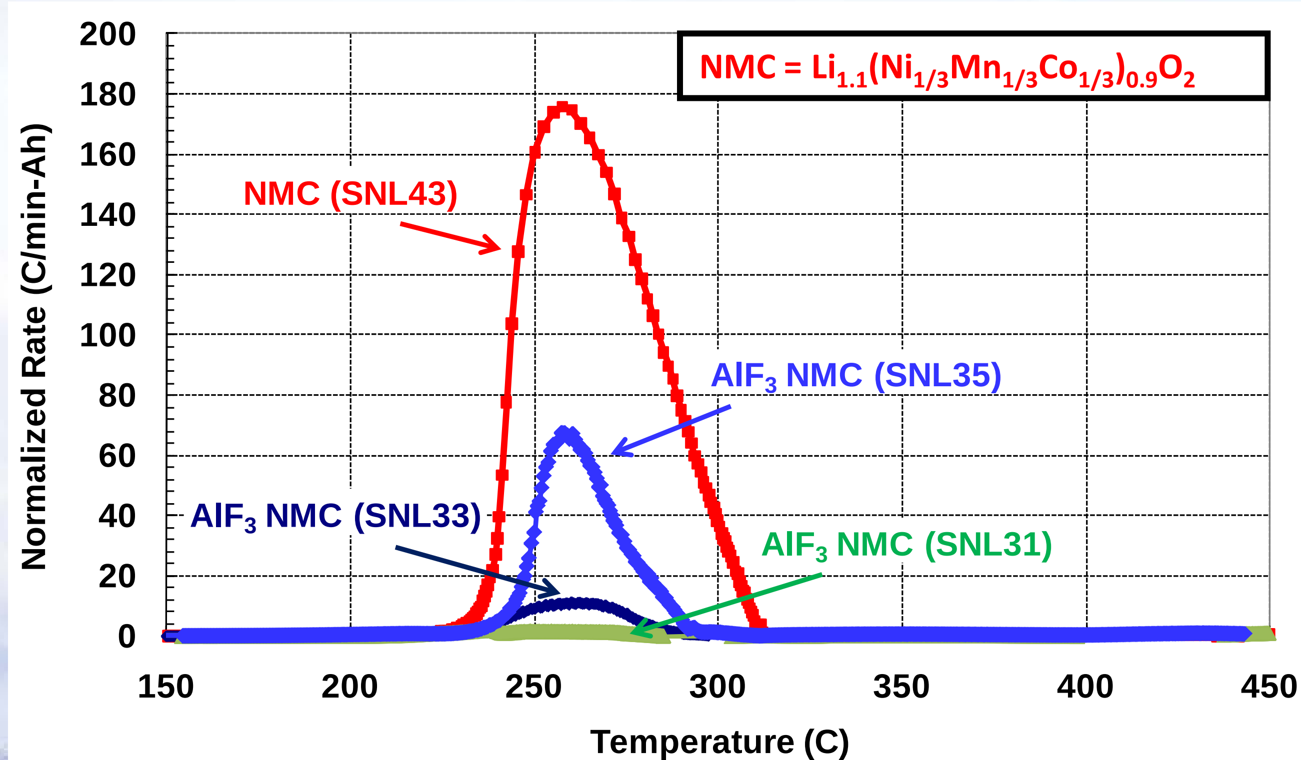
Accelerating Rate Calorimetry (ARC)

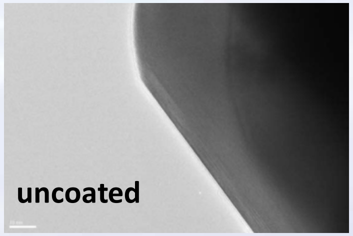


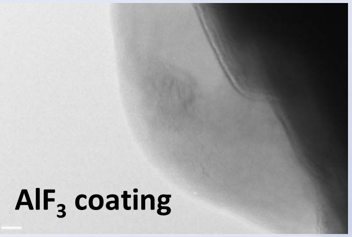
Can a high energy cathode cell behave thermally like an $LiFePO_4$ cell?

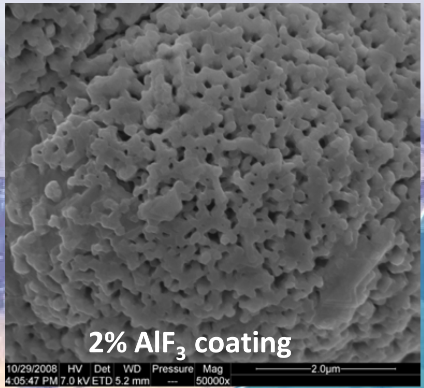
AlF_3-coated NMC Cathodes (w/ ANL)

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





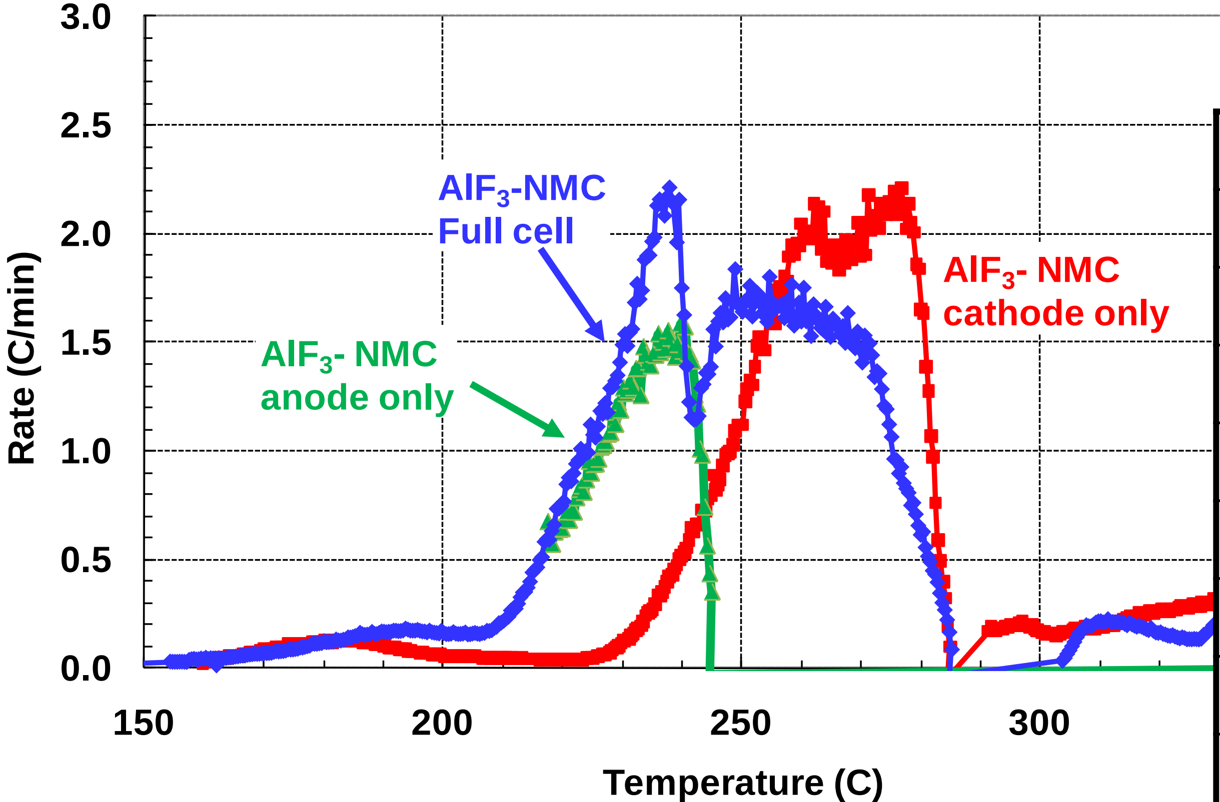




- ***AlF_3-coating improves the thermal stability of NMC materials by 20 °C; onset of decomposition ~260 °C (ANL)***
- ***Increased stabilization significantly improves the thermal response during cell runaway***
- ***Variability likely due to the material heterogeneity***

Electrode Contributions to Runaway

Anode and cathode contributions to runaway for AlF_3-coated NMC 18650 cells by ARC

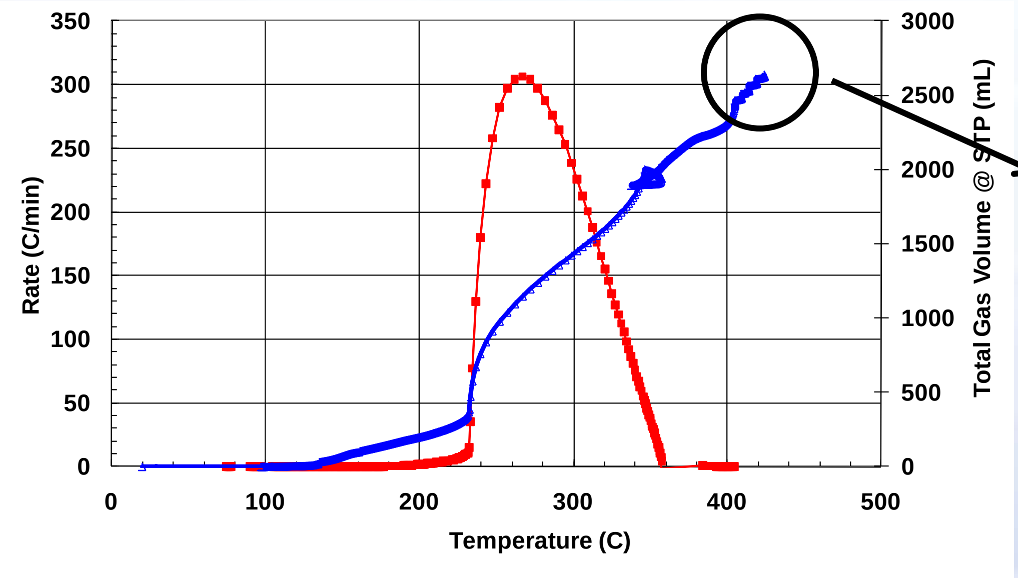


Estimated runaway enthalpy		
Cell	ΔH (kJ)	ΔH/Ah (kJ/Ah)
NMC_43	20.6	23.5
NMC_44	21.7	25.3
AlF3_31	17.5	26.3
AlF3_33	18.8	29.6
AlF3_35	19.6	29.0
AlF3_32c	10.9	16.9
AlF3_32a	13.2	20.3

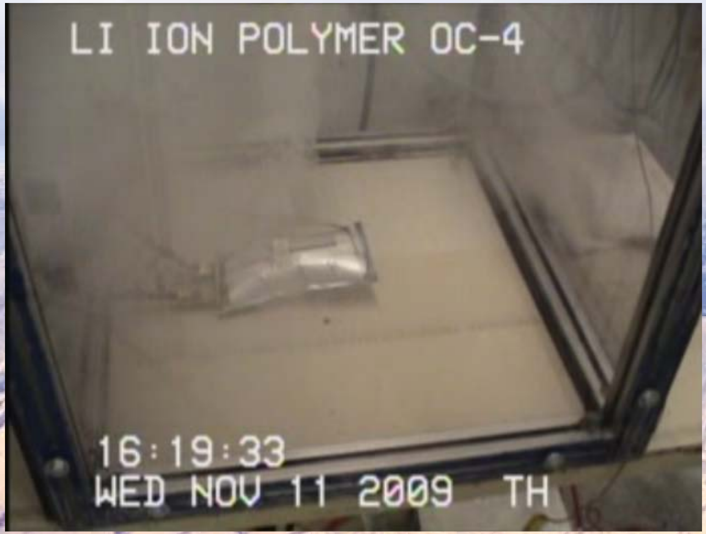
Good agreement between individual electrode ARC experiments and full 18650 cells
Total enthalpy is comparable for the coated and uncoated NMC (Gen3) cells
Inert coatings reduce the reaction rates, but the total heat output remains unchanged

Abuse Tolerant Inactive Materials (LDRD)

Electrolyte decomposition, gas evolution, and flammability



- ***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)

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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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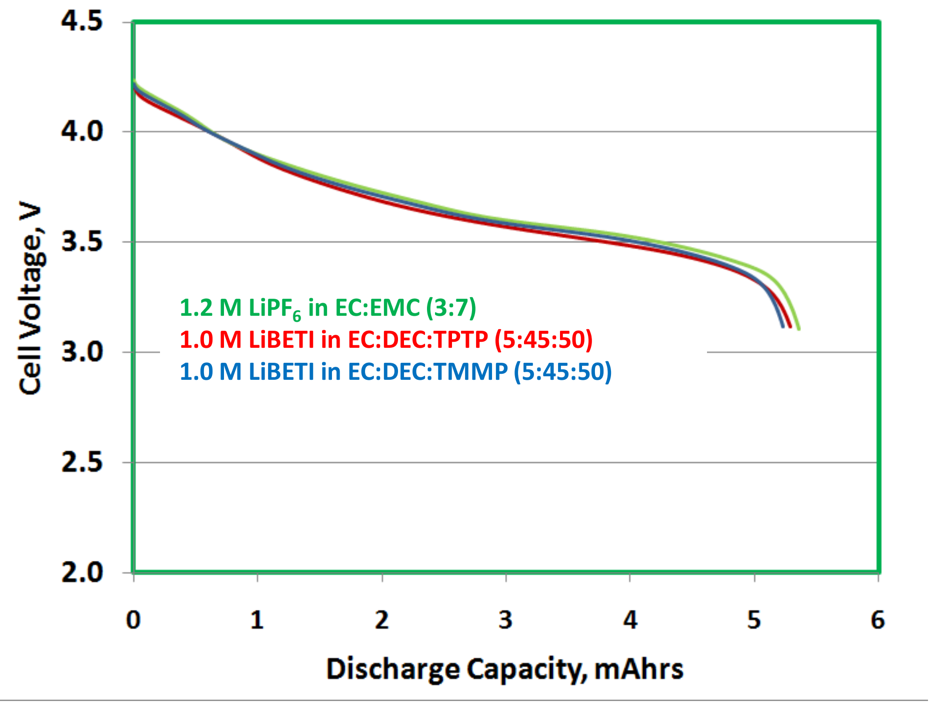
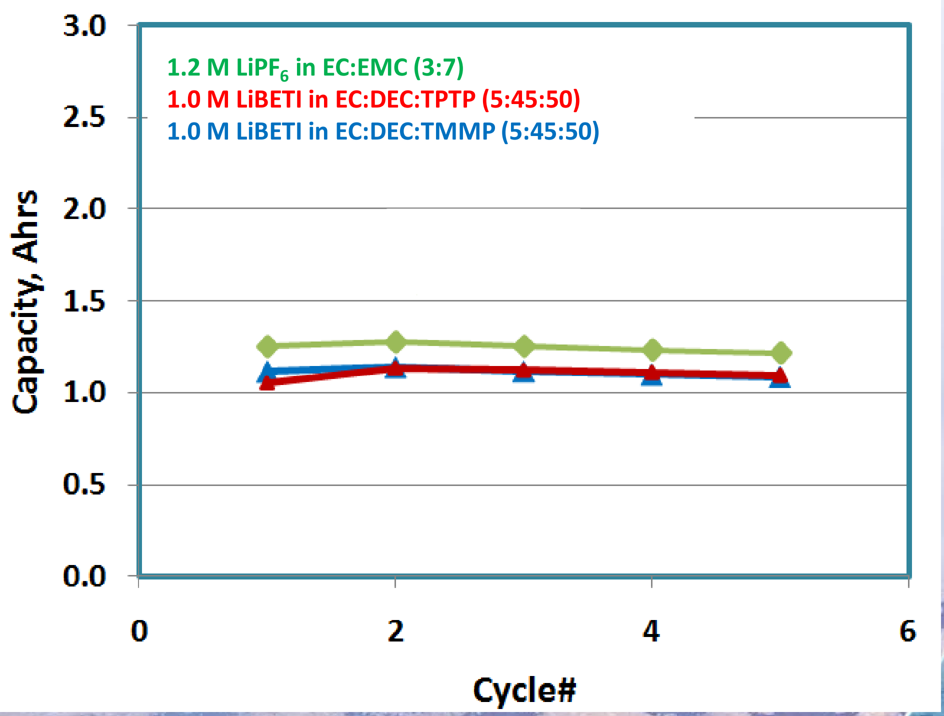
Cell Performance of HFE electrolytes

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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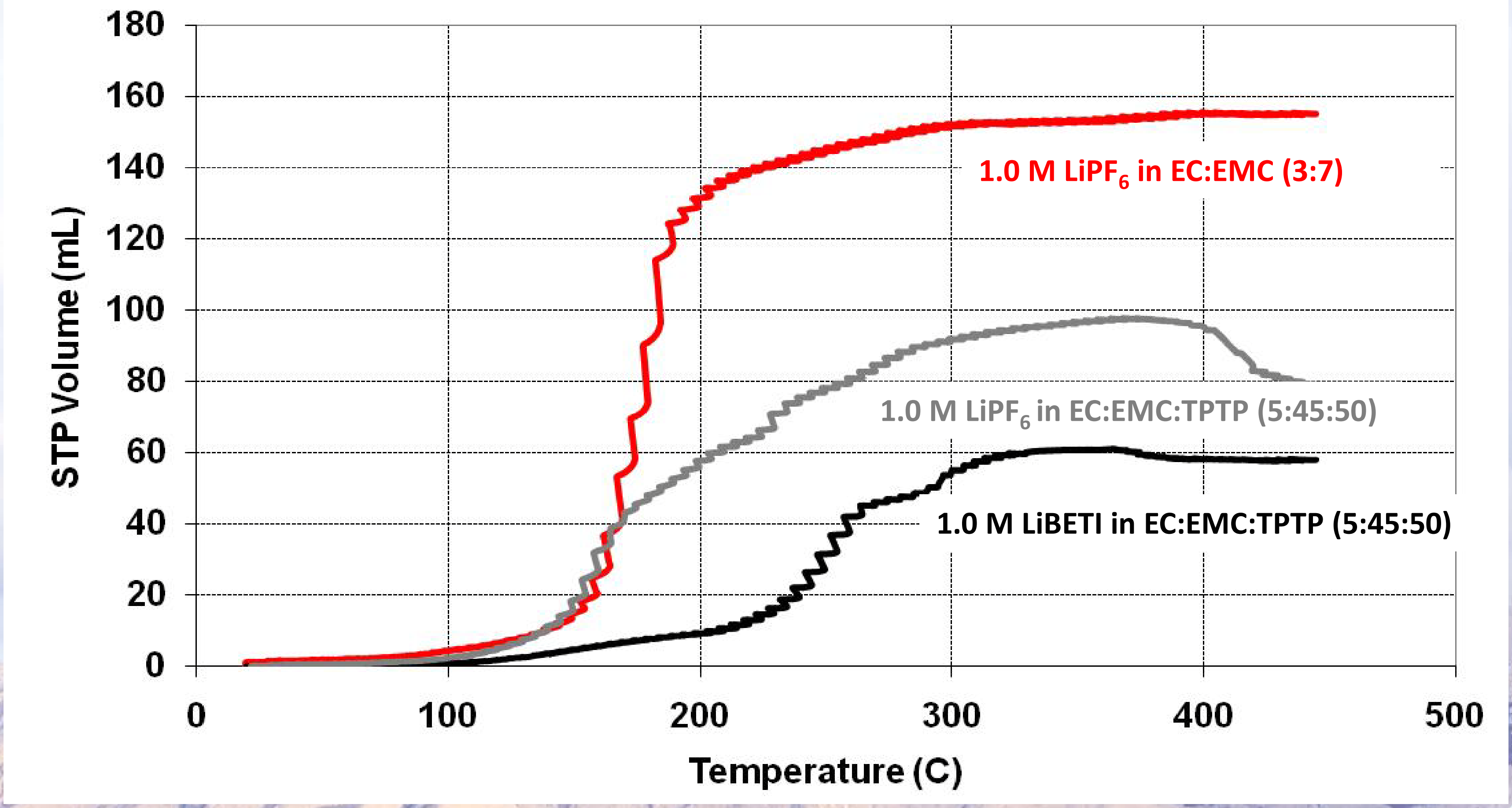
Reduced Gas Generation and Improved Thermal Stability

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



40-60% reduced gas generation (@ 300 ^{o}C)
Improved thermal stability

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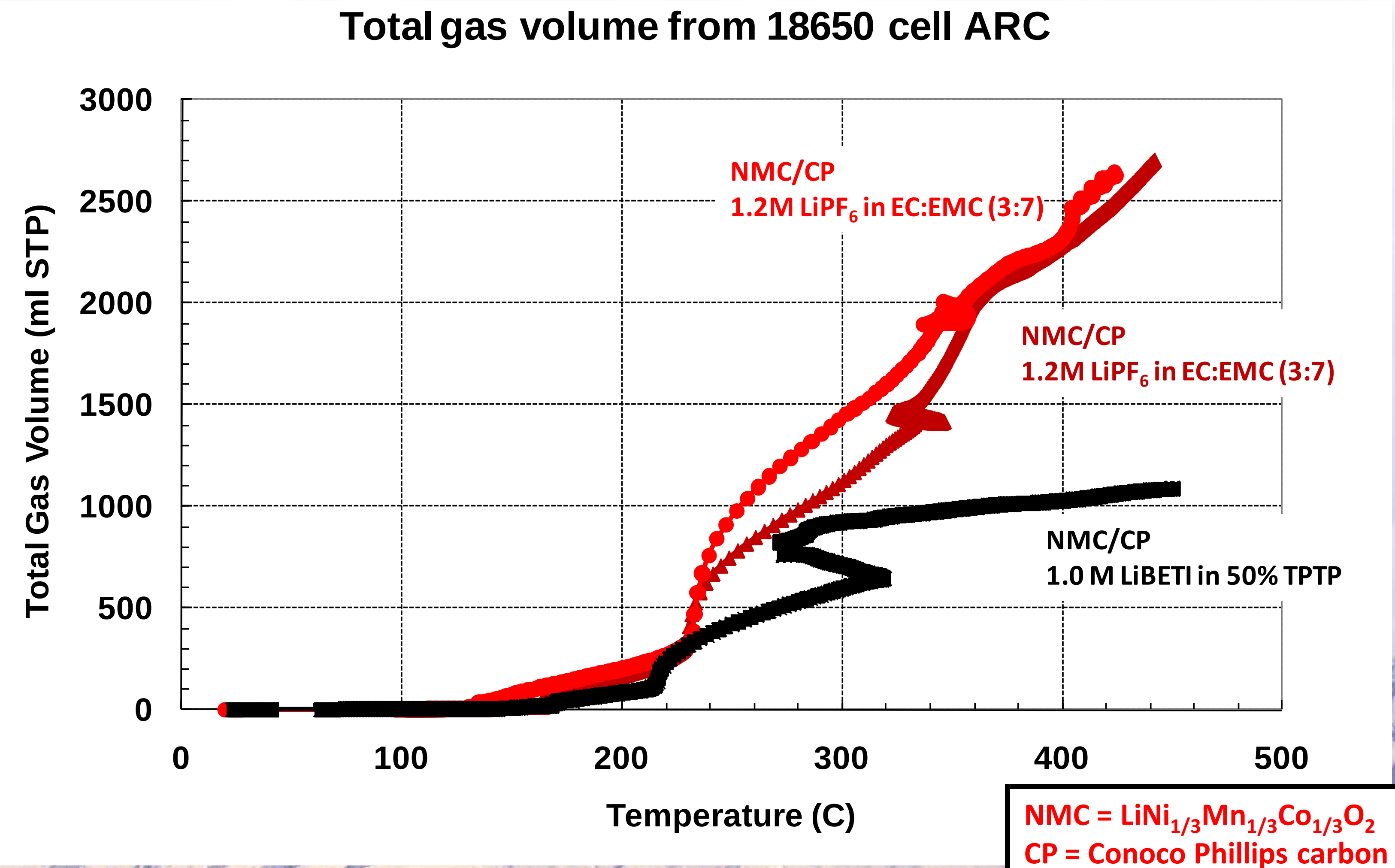
Reduced Gas Evolution in 18650 Cells



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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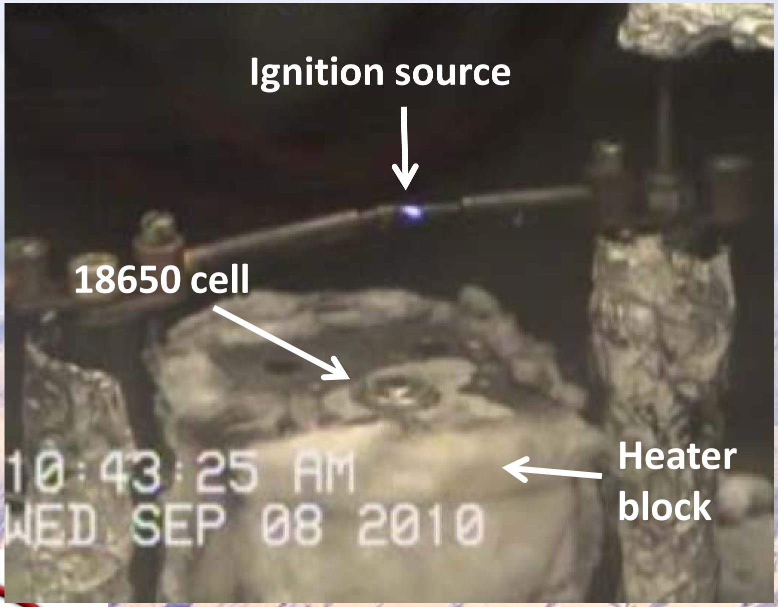
Electrolyte Flammability Test

- 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



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Flammability Testing

Electrolyte sealed in 18650 cans and heated until vent

Ignition of EC:DEC electrolyte

No ignition of the 50% TMMP HFE electrolyte

Electrolyte Flammability Results

Electrolyte Solvent	*Ignition*	*Δt (vent-ignition)*	*Burn time (s)*
EC:DEC (5:95)	Yes	< 1	36
EC:DEC (5:95)	Yes	1	63
EC:EMC (3:7)	Yes	5	6
EC:DEC:EMC:TMMP (5:35:30:30)	Yes	3	14
EC:DEC:EMC:TMMP (5:35:30:30)	No	NA	NA
EC:DEC:EMC:TMMP (5:35:30:30)	Yes	1	27
EC:DEC:EMC:TMMP (5:35:30:30)	No	NA	NA
EC:DEC:TPTP (5:45:50)	No	NA	NA
EC:DEC:TPTP (5:45:50)	No	NA	NA
EC:DEC:TPTP (5:45:50)	No	NA	NA
EC:DEC:TPTP (5:45:50)	No	NA	NA
EC:DEC:TMMP (5:45:50)	No	NA	NA
EC:DEC:TMMP (5:45:50)	No	NA	NA
EC:DEC:TMMP (5:45:50)	No	NA	NA

- ***More linear carbonate → more flammable solvent***
- ***At 50% HFE, electrolytes are non-flammable under cell venting conditions***
- ***At 30% HFE, electrolytes represent a flammability hazard***
- ***Need to perform a systematic study of %HFE and flammability from 5-50%***

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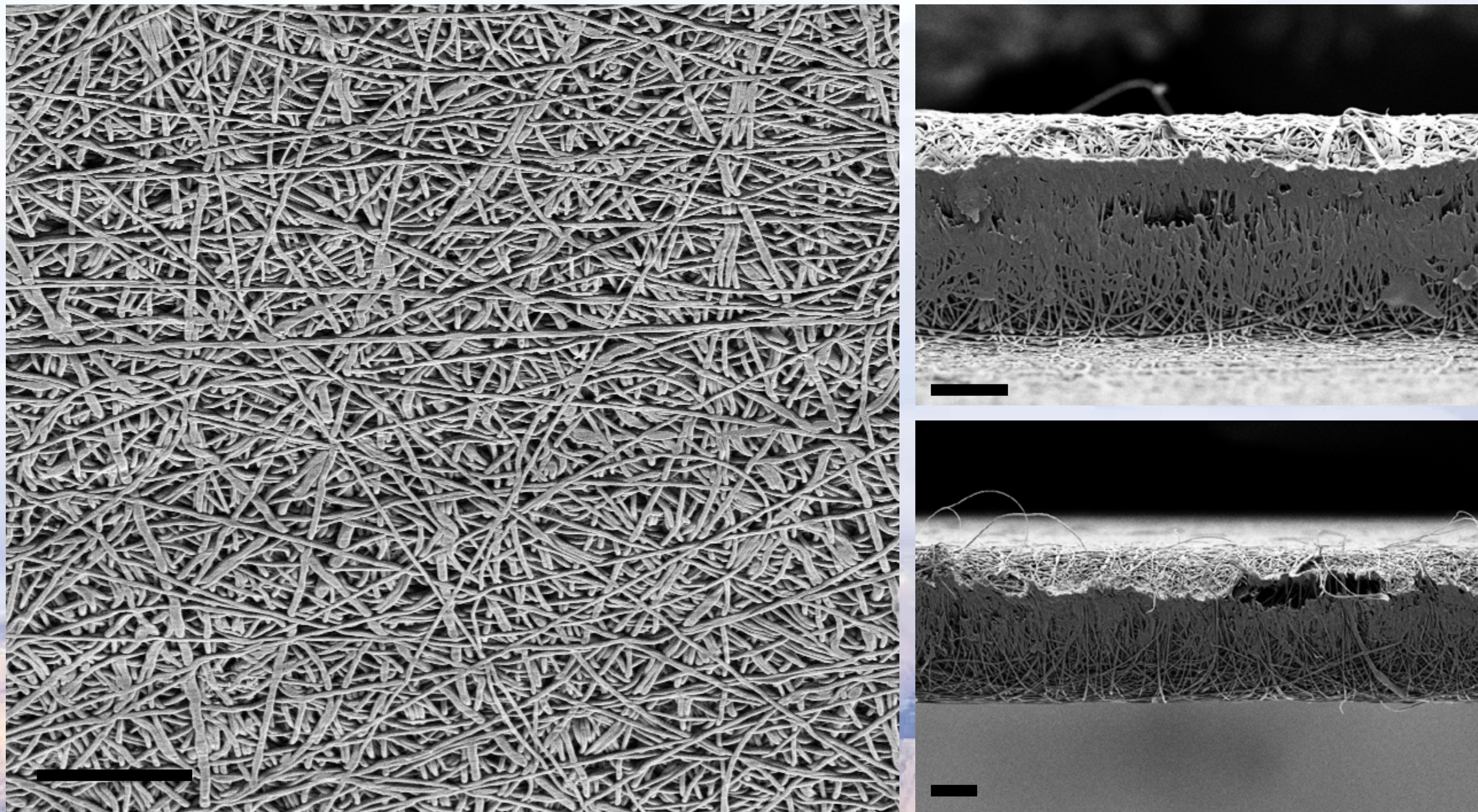
Non-shutdown Separators

SEM images of SNL developed separators based on terephthalate fibers



Scale bars represent 20 µm

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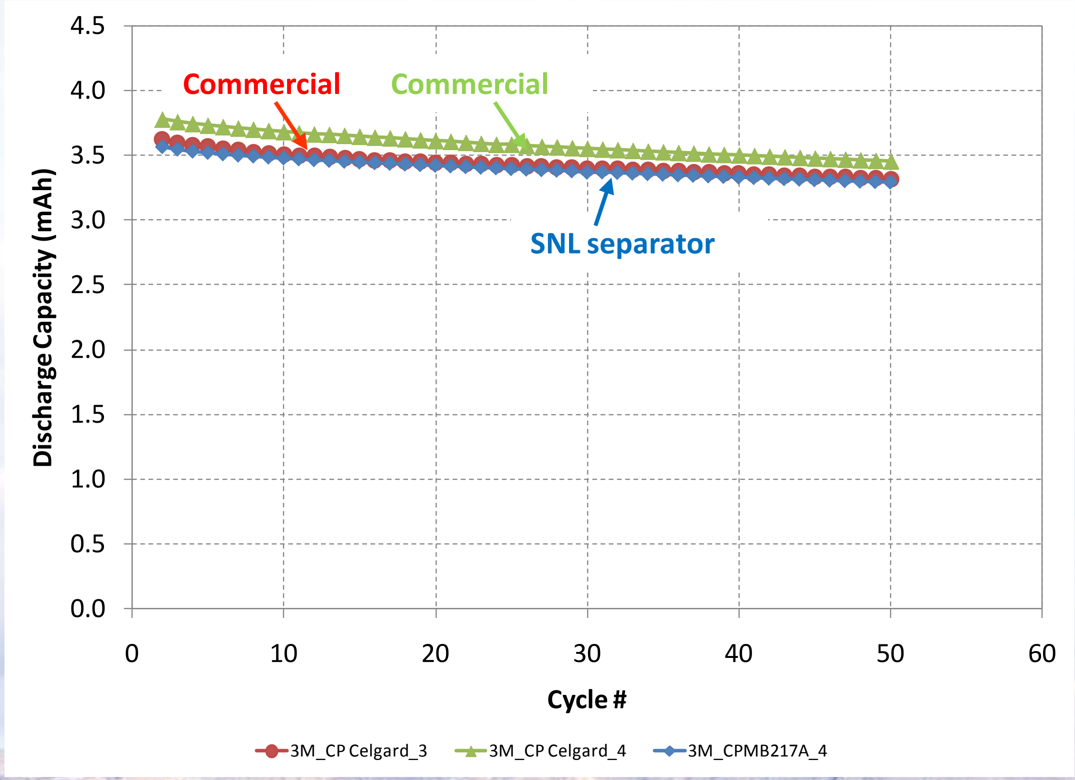
Performance of SNL Separators

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



Separator	(μm)	Gurley # (s/100 mL)
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 at C/10 rate in 2032 cells

Rate capability and long term cycling stability work are currently underway

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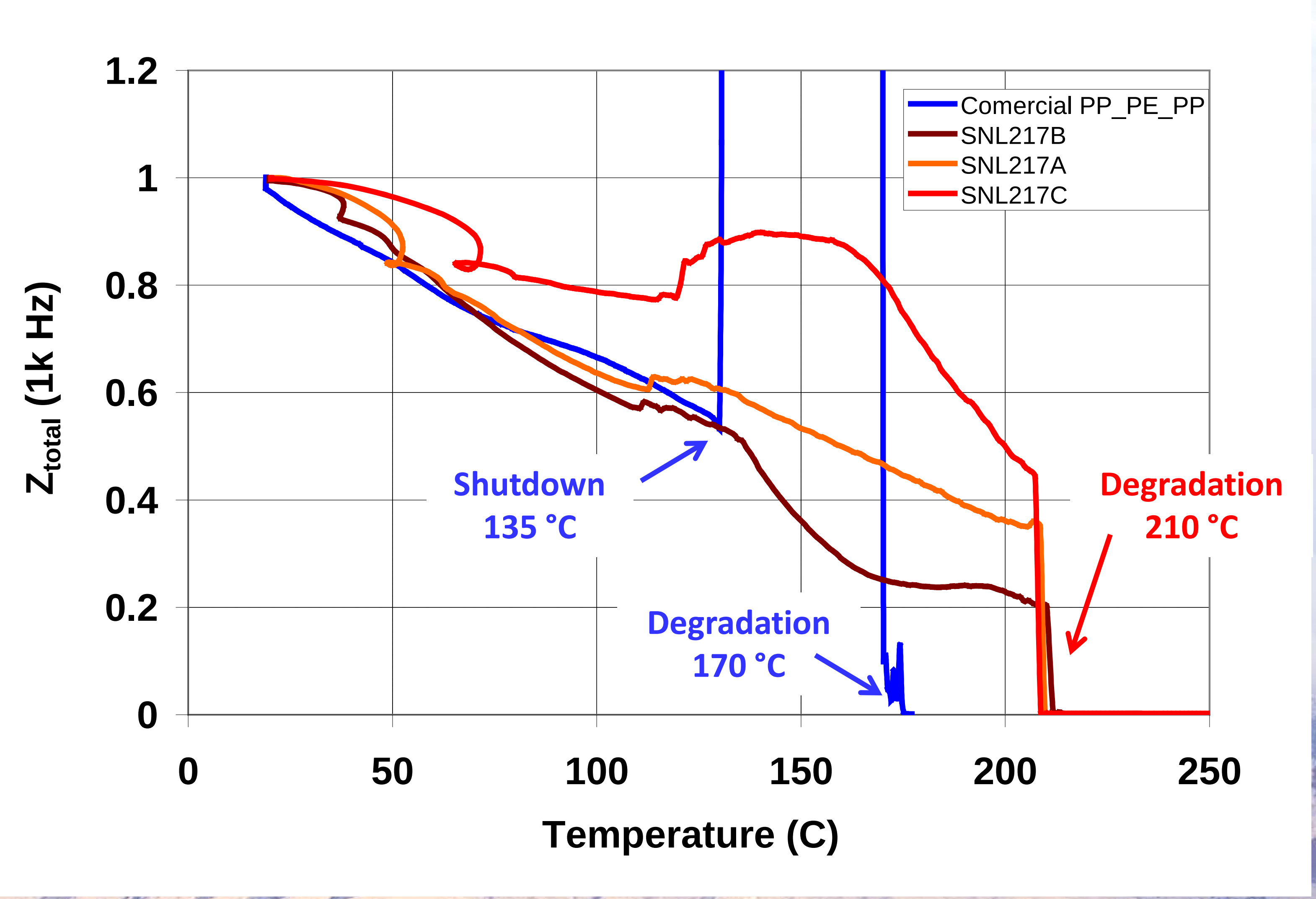
Thermal Integrity of Separators



SNL separators show thermal stability to 210 °C

Summary

- AlF_3-coated cathode materials can significantly improve the thermal response of cells during runaway by reducing the heating rate
  – Additional coatings evaluation in progress including Al_2O_3 and $M_x(PO_4)_y$
- Lithium sulfonimide salts (TFSI and BETI) show improved thermal stability over lithium hexafluorophosphate salts
- Sulfonimide/HFE electrolytes generate significantly less gas volume products upon thermal abuse
- Large co-solvent volume fractions of HFE can reduce the flammability of lithium-ion electrolytes during a cell vent
- Terephthalate-based separators show improved thermal stability with comparable performance to commercial polyolefin separators (up to 70 cycles)

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