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A Materials Approach To Abuse Tolerant Lithium-ion Cells

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Cost of Battery Failure for the Emerging Transportation Market?

- ***Field incidents will likely be very different than for consumer electronics***
- ***Costs are independent of failure mechanism***
- ***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

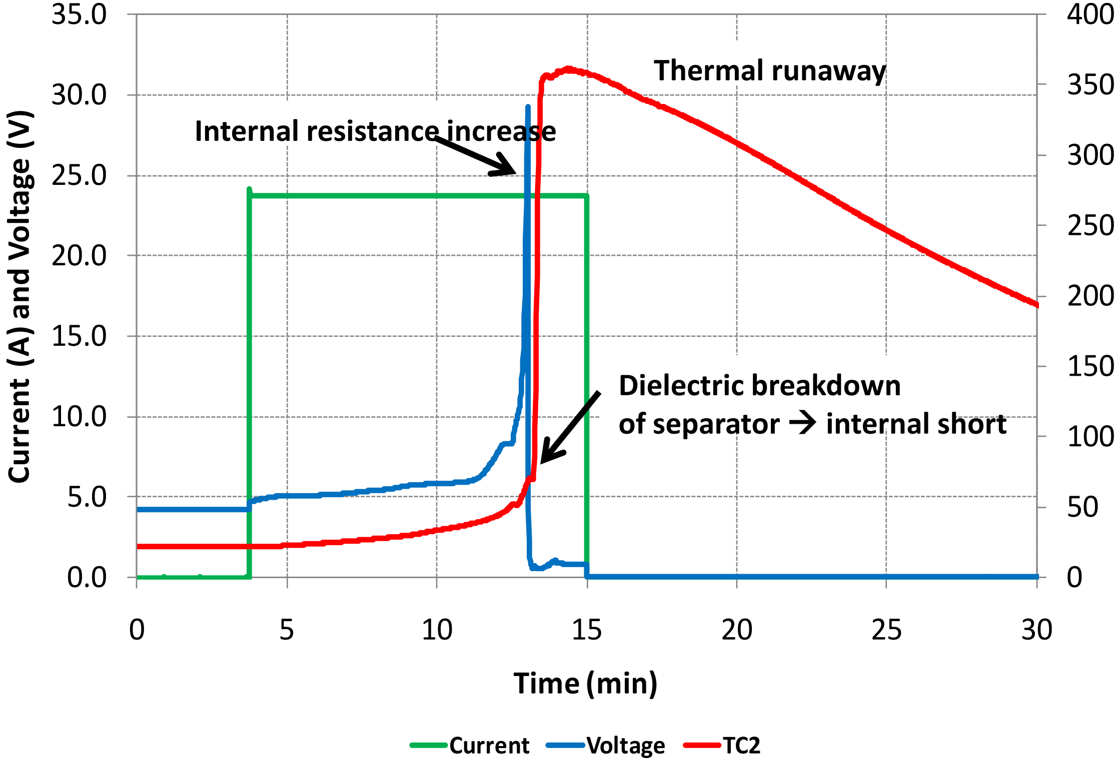
Larger batteries in larger quantities:

- ***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)***

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

12 Ah (~50 Wh) Pouch Cell Overcharge Abuse



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Internal temperature limited due to ejection of cell contents

500 Wh battery failure….5000 Wh battery 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
- ***Electrolyte degradation/gas generation and impact on cell runaway***
  - Overpressure and cell venting is accompanied by an electrolyte spray and solvent vapor which is highly flammable
- ***Internal short circuits***
  - Defects can develop into internal shorts over time and are a challenge to predict, reproduce in a laboratory, and mitigate
- ***Separator instabilities for high voltage systems***
  - Thermal instabilities in separators can lead to shorting and cell failure
- ***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

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Effects of Electrolyte - Cathode Runaway

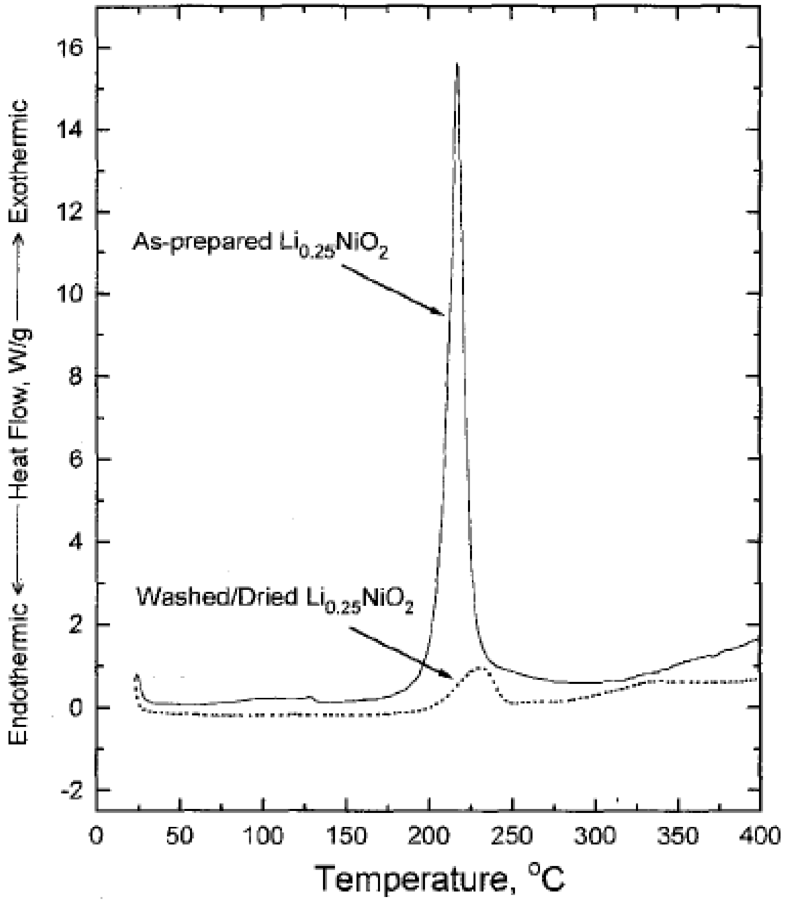


Fig. 2. DSC curves comparing $Li_{0.25}NiO_2$ with and without a washing/vacuum-drying procedure to remove electrolyte.

Oxygen liberation:

$$Li_{1-x}NiO_2 \rightarrow (2-x)Li_{(1-x)/(2-x)}Ni_{1/(2-y)}O + (x/2)\ O_2$$

$$Li_xCoO_2 \rightarrow xLiCoO_2 + (1-x)/3\ Co_3O_4 + (1-x)/3\ O_2$$

Solvent combustion:

$$C_3H_4O_3 + 5/2\ O_2 \rightarrow 3\ CO_2 + 2\ H_2O$$

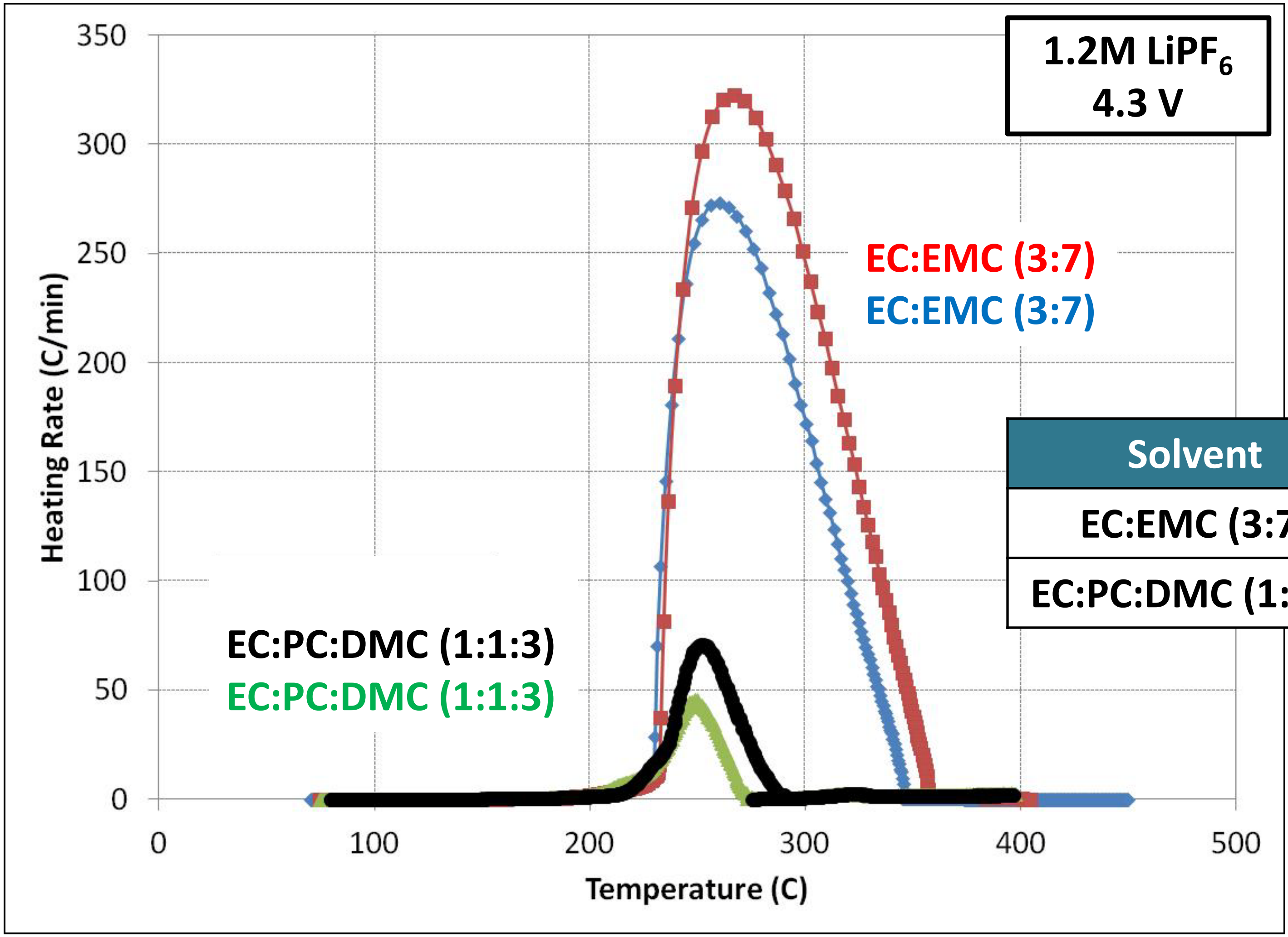
$$\Delta H_c^\circ = 1070\ kJ/mol$$

$$C_5H_{10}O_3 + 6\ O_2 \rightarrow 5\ CO_2 + 5\ H_2O$$

$$\Delta H_c^\circ = 2700\ kJ/mol$$

Z. Zhang et al. Journal of Power Sources 70 (1998) 16-20
J. K. Cho et al. J. Chem. Eng. Data, 16 (1971) 87-90
D. D. MacNeil et al. J. Electrochem. Soc. 148 (2001) A1205-A1210
J. R. Dahn et al. Solid State Ionics 69 (1994) 265-270

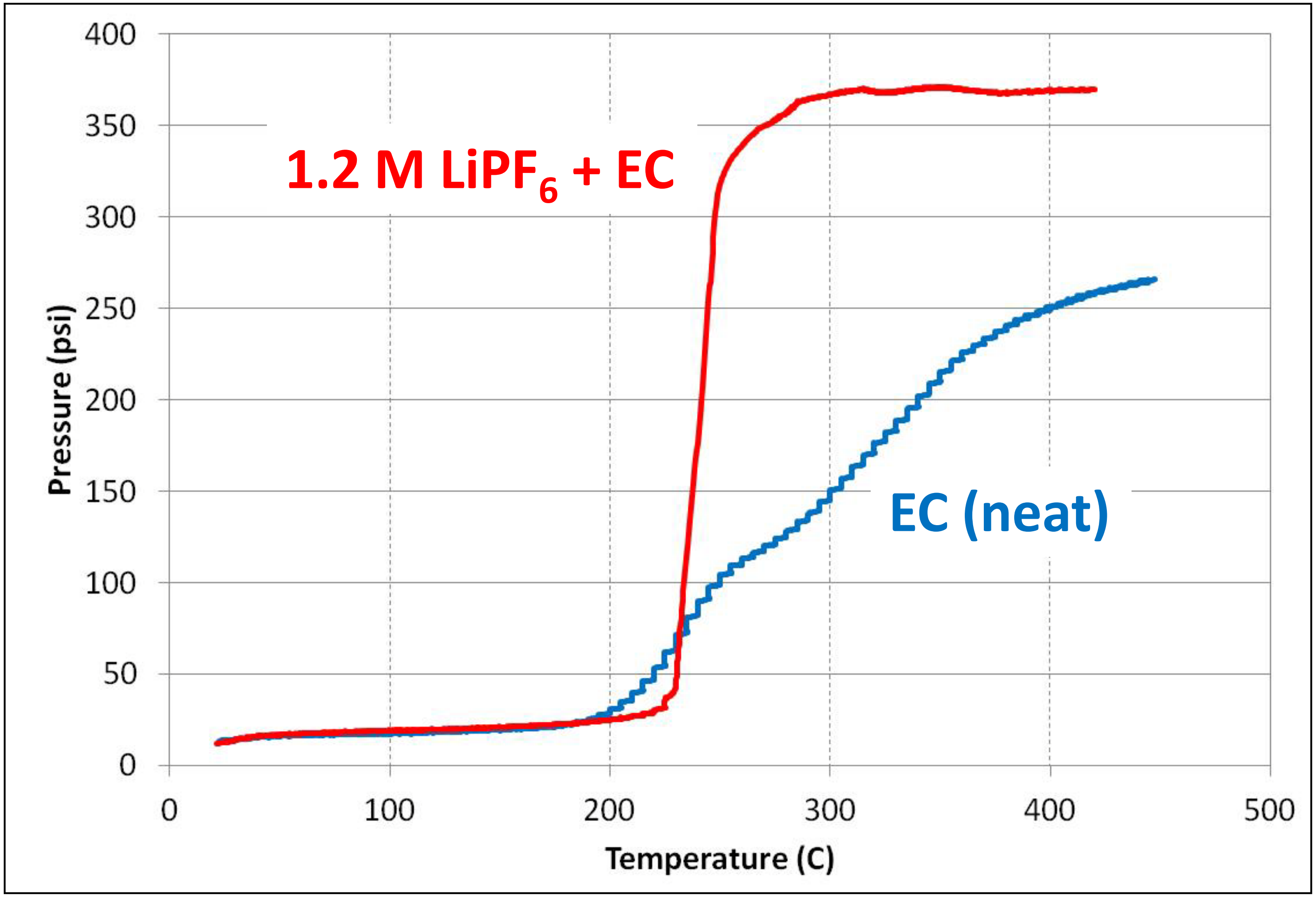
Effects of Electrolyte – Solvent Choice



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

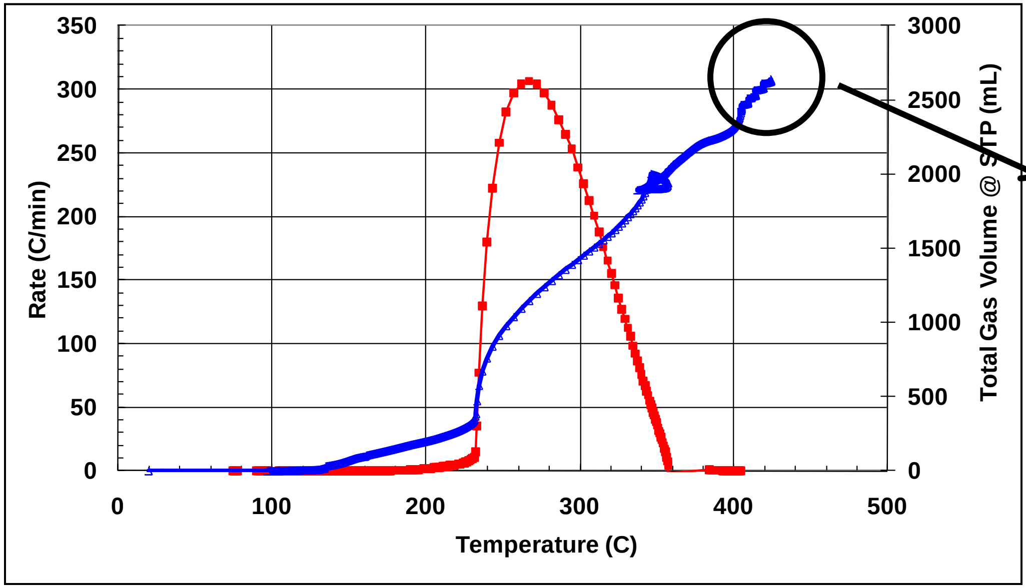
Solvent choice can affect the cell runaway reactions (independent of cathode)

Effects of Electrolyte – Decomposition

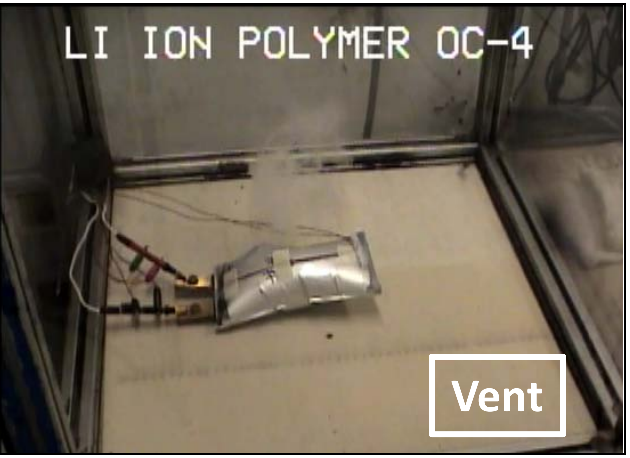


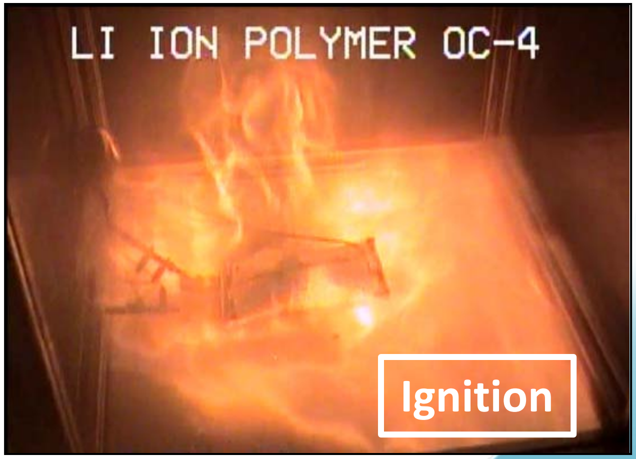
$LiPF_6$ catalyzes electrolyte solvent decomposition at elevated temperature

Effects of Electrolyte - Flammability



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





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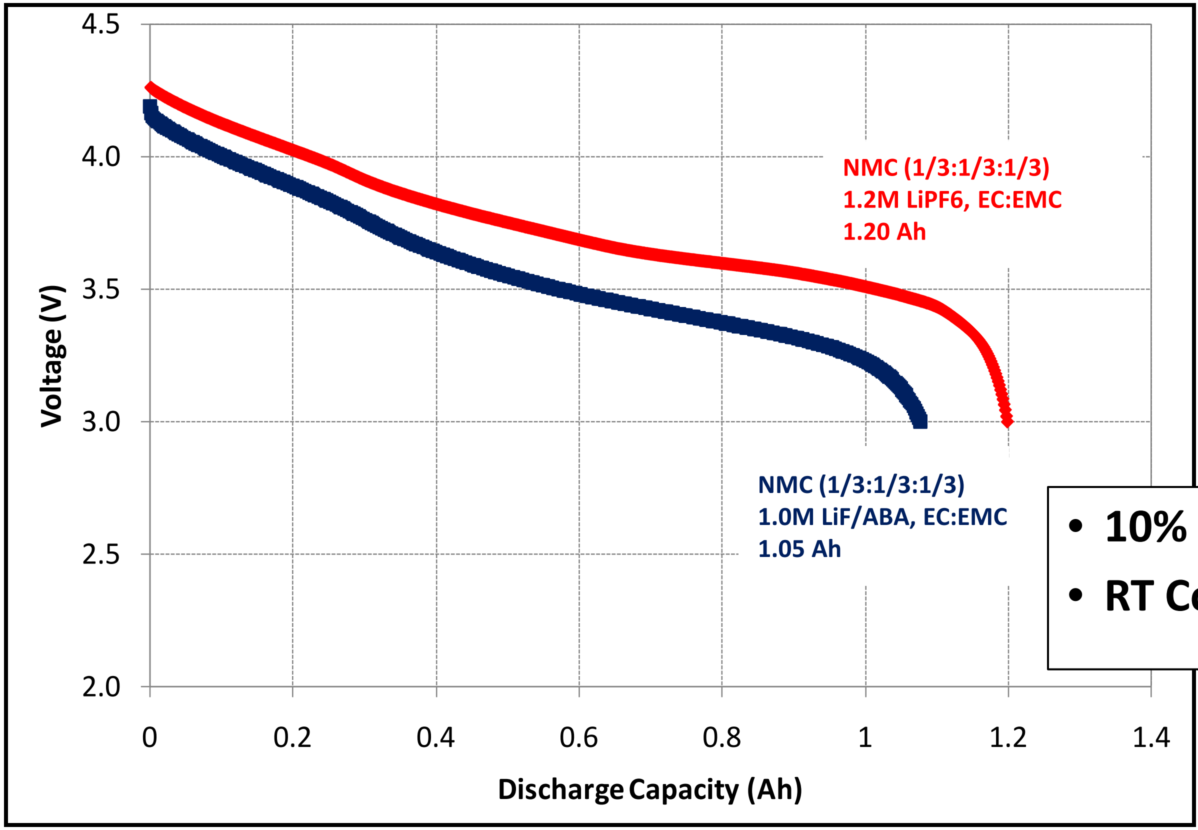
Cell venting leads to exposures of solvent vapor which is highly flammable!

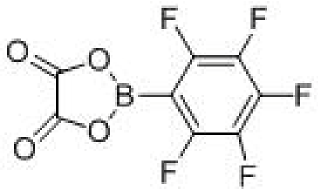
ABA Electrolyte Development

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

→ Reduce gas decomposition products

→ Passivate the runaway reactions at the cathode



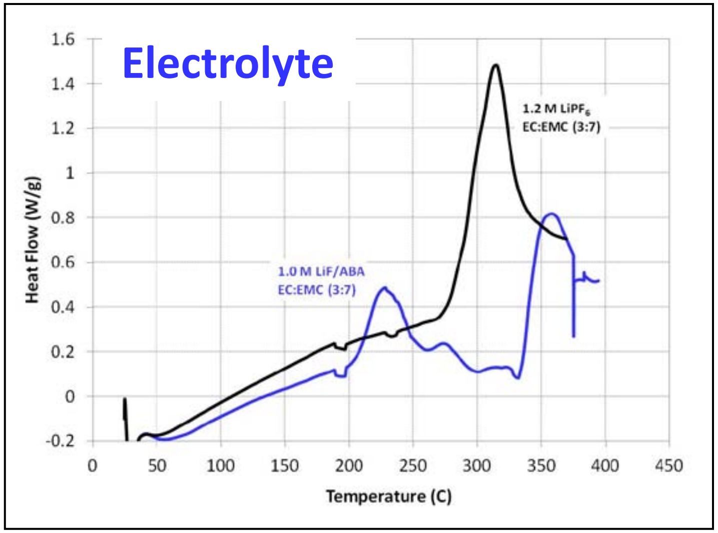


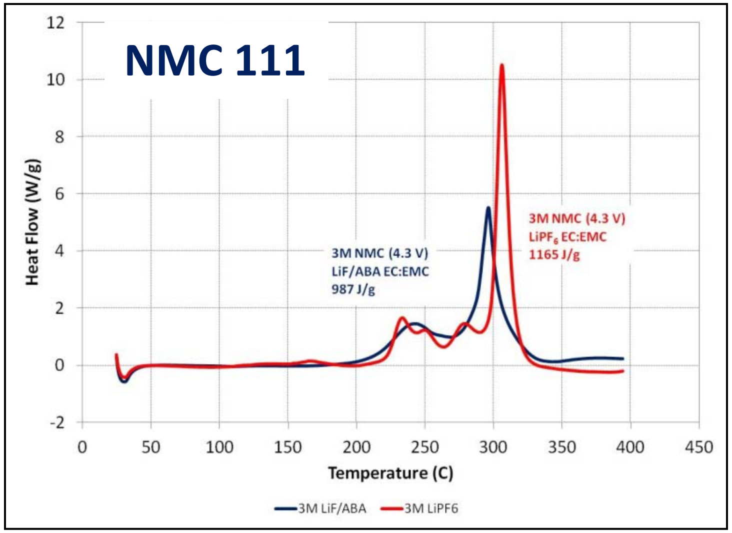
Perfluorophenyloxaltoborate

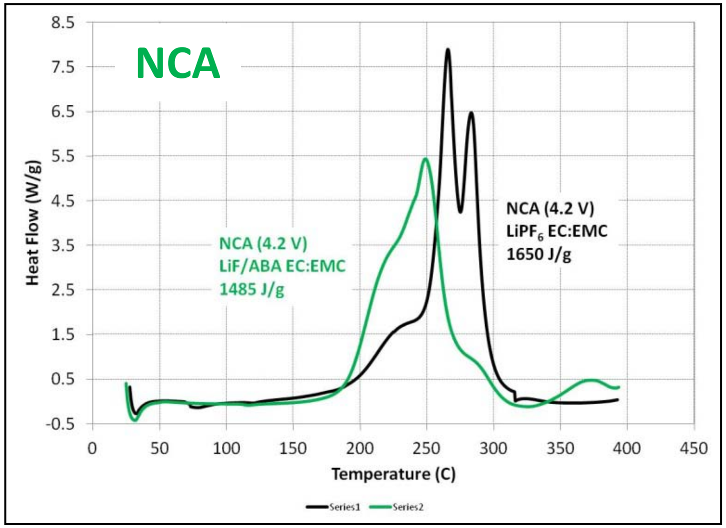
- **10% reduction in total capacity (cell)**
- **RT Conductivity = 2 mS/cm**

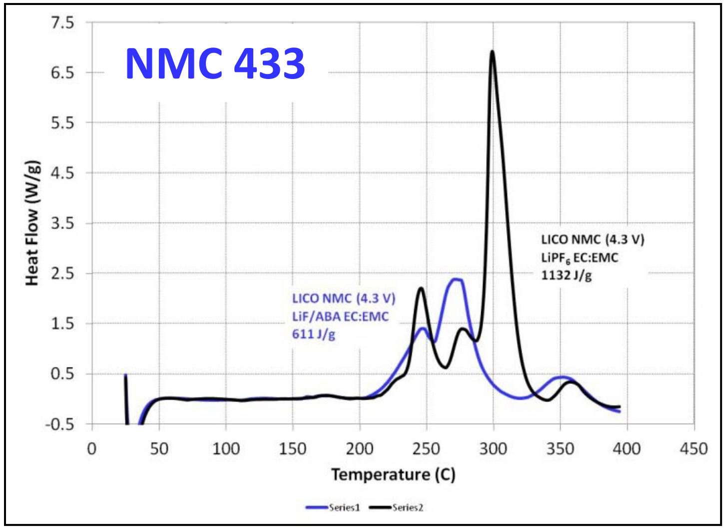
Collaboration with Binrad Industries and X. Q. Yang at BNL on ABA development work

ABA Electrolyte Development



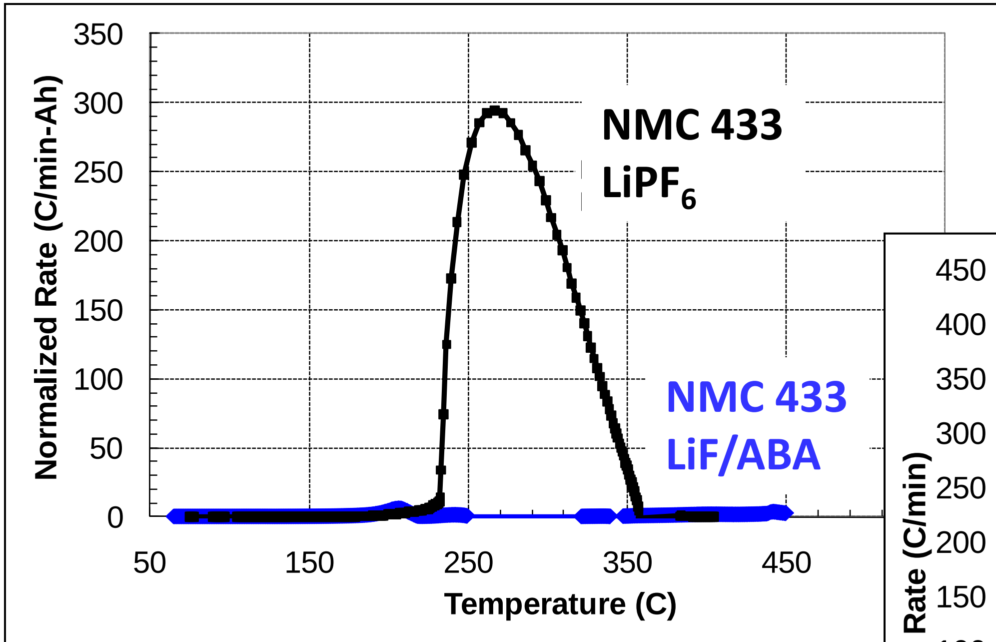


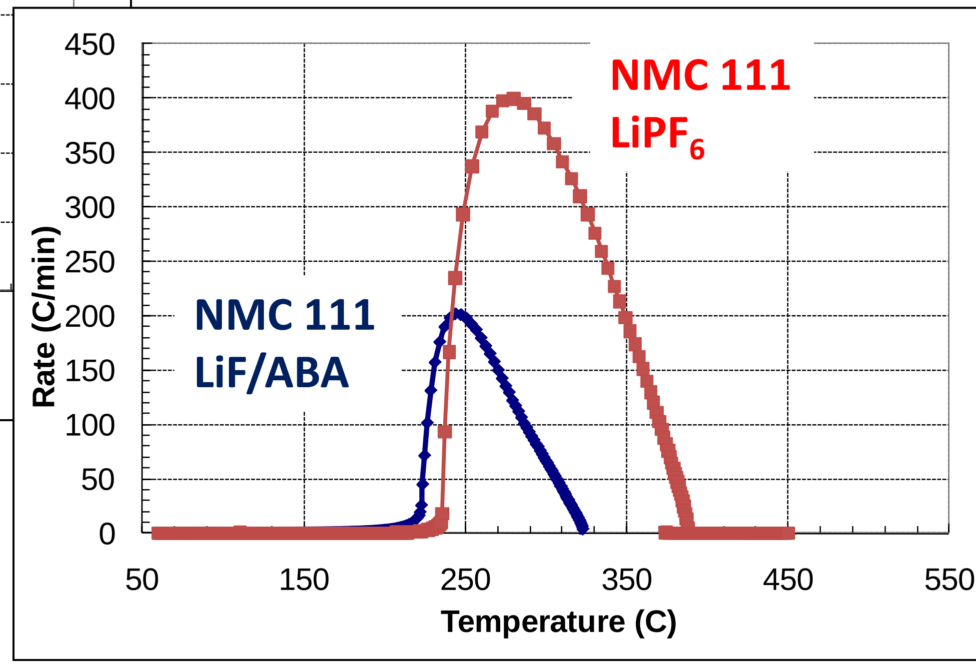




50% reduction in total specific heat output of NMC 433 with LiF/ABA electrolyte

ABA Electrolyte Development





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

Improvements in Electrolyte Safety

- **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)

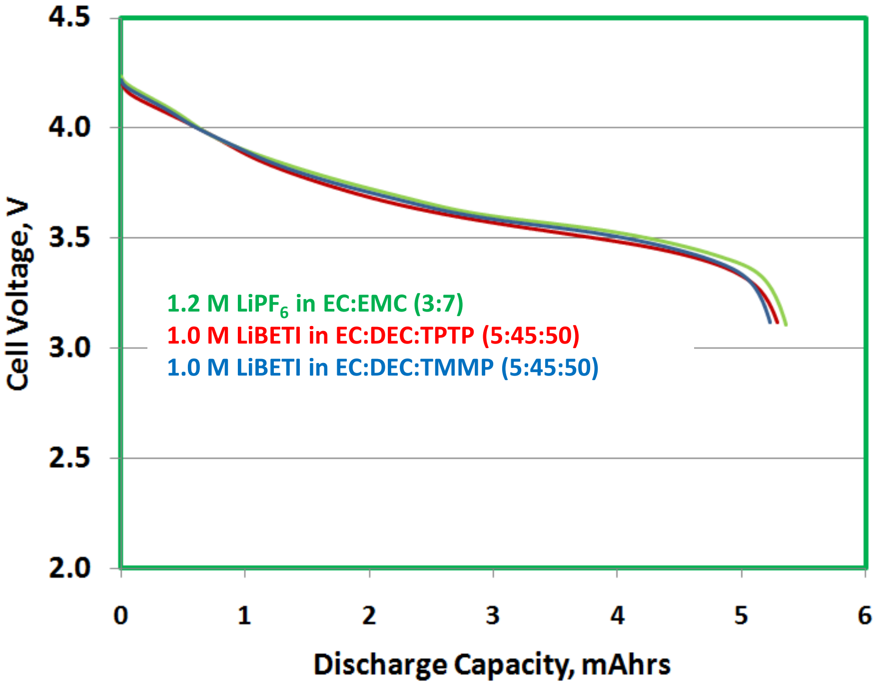
Data is the following slides is for 1.0 M LiBETI in EC:DEC:TPTP (5:45:50) or 1.0 M LiBETI in EC:DEC:TMMP (5:45:50)

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

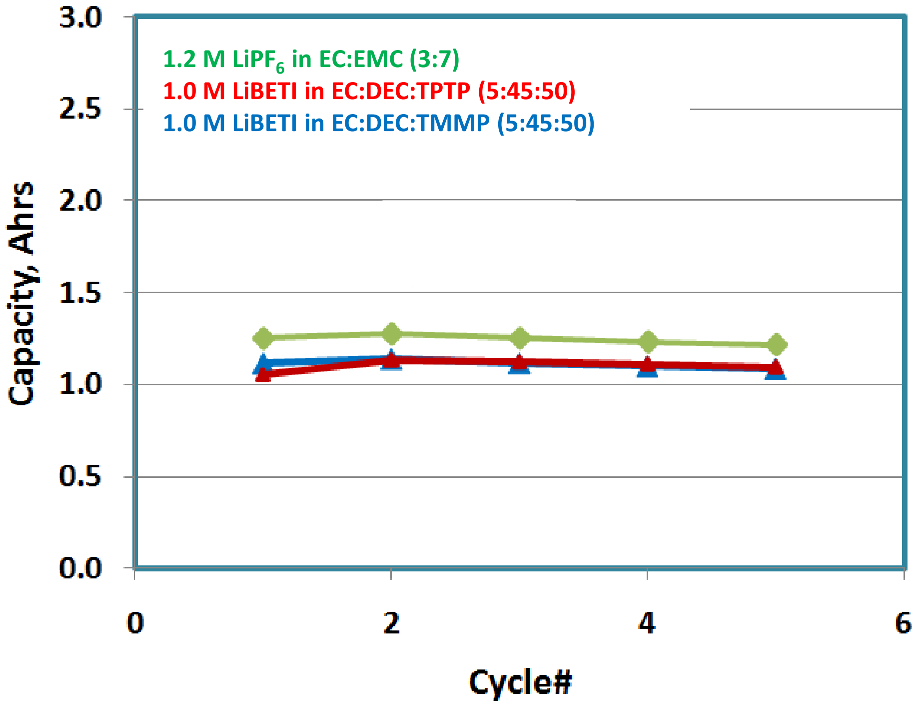
Cell Performance of HFE electrolytes

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

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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

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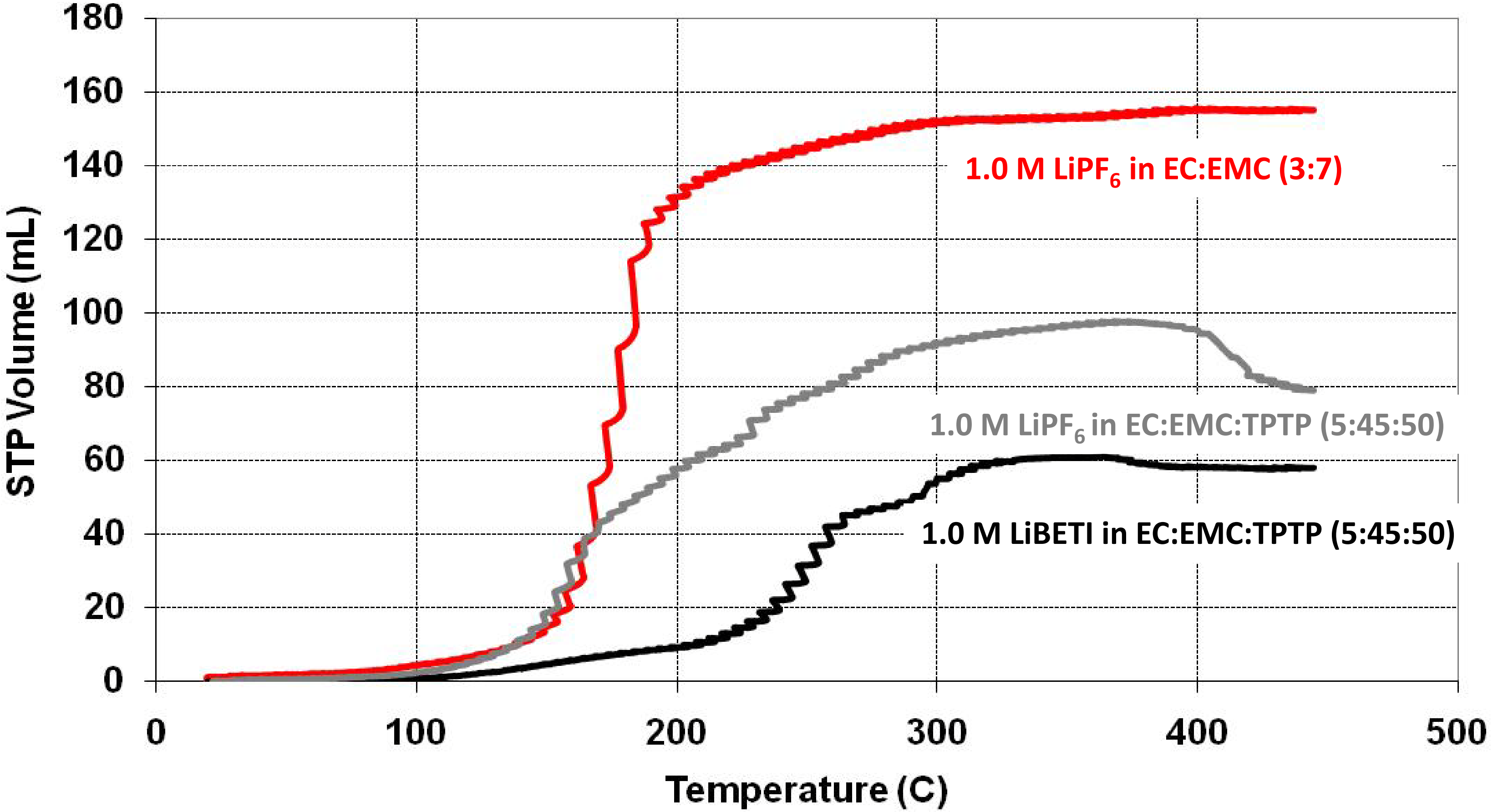
Reduced Gas Generation and Improved Thermal Stability

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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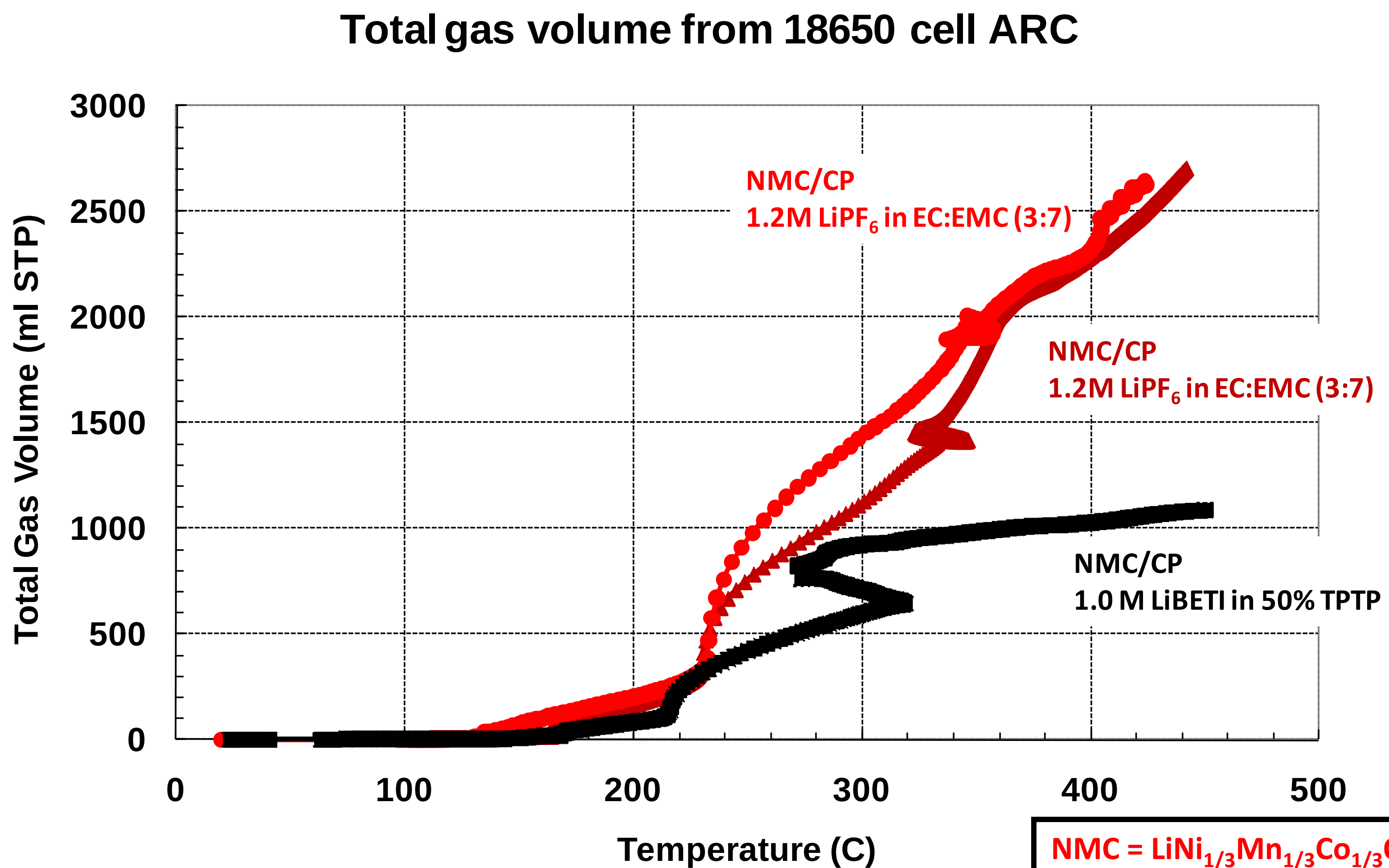
Reduced Gas Evolution in 18650 Cells



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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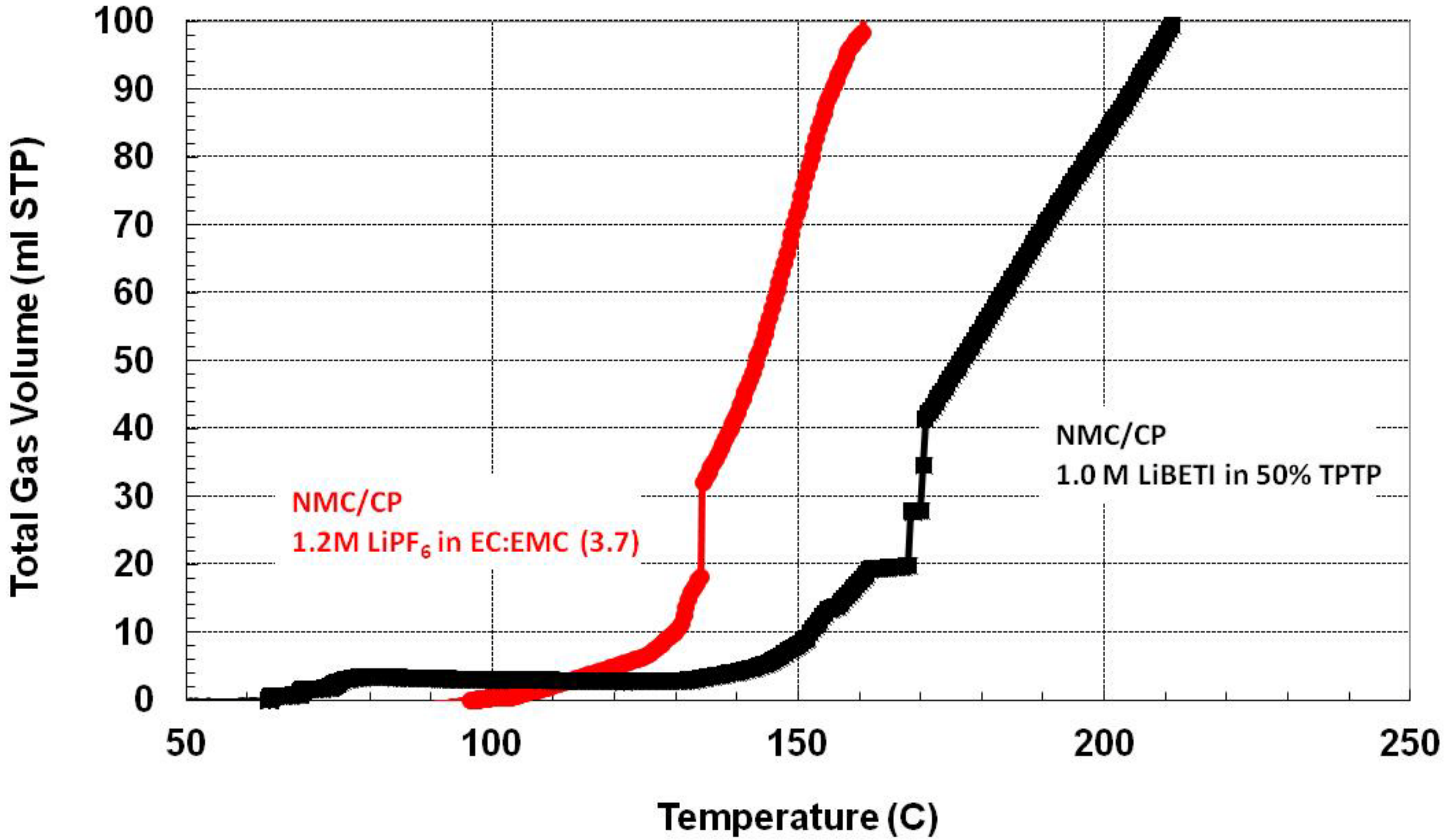
Cell Vent Temperature



Vent temperature of the sulfonimide/HFE cell is 35-40 °C higher than the PF_6/carbonate cell

Flammability 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

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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Summary

- **Fielding the most inherently safe chemistries and designs can help address the challenges in scaling up lithium-ion**
- **Choices in electrolyte salt and solvent can impact the combustion enthalpy, gas generation and flammability of the electrolyte to make cell safety significantly better or worse**
- **ABA-based electrolytes can significantly passivate the cathode runaway reaction at the material- and cell-scale**
- **Effect of ABA passivation is dependent on the cathode you choose**
- **Hydrofluoroether (HFE) co-solvents in lithium-ion cells show diminished performance (~10%) but also show reduced volume of gas decomposition product and are nonflammable in a venting cell**

Acknowledgements

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