Evaluation of Abuse Tolerance Improvements

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Overview

Timeline

- Project start date: Oct. 2007
- Project end date: Oct. 2014
- Percent complete: <60%

Barriers

- Barriers addressed
  - Develop intrinsically abuse tolerant Li-ion cells and batteries
  - Obtain access to latest promising materials from developers & sufficient quantities of materials to determine reproducibility of results

Budget

- Total project funding $2.4M (FY10 and FY11)
  - 100% DOE share
- Funding received in FY10: $1.1M
- Funding for FY11: $1.3M

Partners

- **ANL –** AlF_3-NMC, Al_2O_3-NCA
- **BNL/Binrad Industries –** ABA electrolytes
- **INL/Univ. Hawaii –** Aged cell evaluation
- **PSI –** $M_3(PO_4)_x$-NMC

Relevance of Critical Safety Issues

Developing 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 over the lifetime of a cell***
  - The effect of cell age (calendar and cycle life age) on abuse tolerance is largely unknown
  - Evaluate the changes in thermal behavior and abuse response of cells through the aging process and at end-of-life

Objectives/Milestones

- ***Objectives***
  - Identify degradation mechanisms of gas and heat-producing reactions in lithium-ion rechargeable cells
  - Identify and develop advanced materials or combination of materials that will minimize the sources of cell degradation during abuse events, leading toward improving inherent cell safety
  - Build and test full size cells to demonstrate improved abuse tolerance

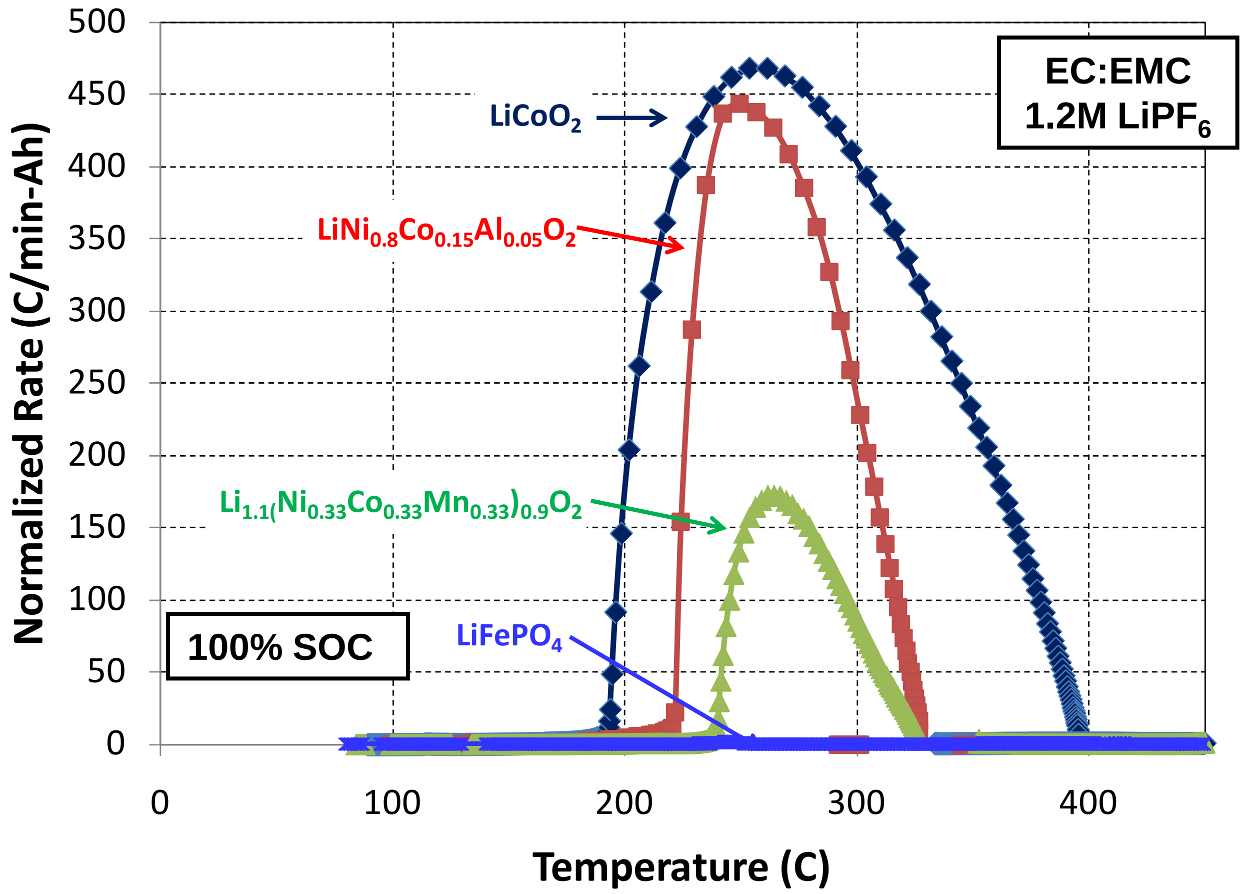
- ***Milestones***
  - Demonstrate improved abuse tolerant cells and report to DOE and the battery community (publications, presentations, conference proceedings, etc.)

Technical Accomplishments and Progress

- Upgrade accelerating rate calorimeter hardware and software from CSI (early 80s) to THT (2010)
- Completed evaluation of AlF_3-coated NMC cathodes in full 18650 cells built in the Sandia prototyping facility. Results shows a significant improvement in peak heating rates during thermal runaway, albeit with some variability between cells
- Work in progress to evaluate other coated materials in FY11 using accelerating rate calorimetry including Al_2O_3-coated NCA and $M_3(PO_4)_x$-coated NMC
- Continued development of LiF/anion binding agent (ABA)-based electrolyte, targeting a more abuse tolerant, thermally stable electrolyte system
- Results show a significant improvements in cell enthalpies during runaway reactions using LiF/ABA electrolytes along with a 40% reduction in total gas generation. Decreasing reaction enthalpy may be a result of reducing the electrolyte decomposition and oxidation during runaway
- Initiated work to evaluate the effect of calendar and cycle age of cells on their thermal response and to study how cell age effects cell-to-cell variations in electrochemical performance under normal use and abuse tolerance
- Routine production of 18650 cell prototypes to support the ABR program abuse tolerance work. Current SNL prototypes are 1.2 Ah NMC/graphite cells.

Thermal Runaway & Cathode Chemistry

Accelerating Rate Calorimetry (ARC)



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

AlF_3-coated NMC Cathodes (w/ ANL)

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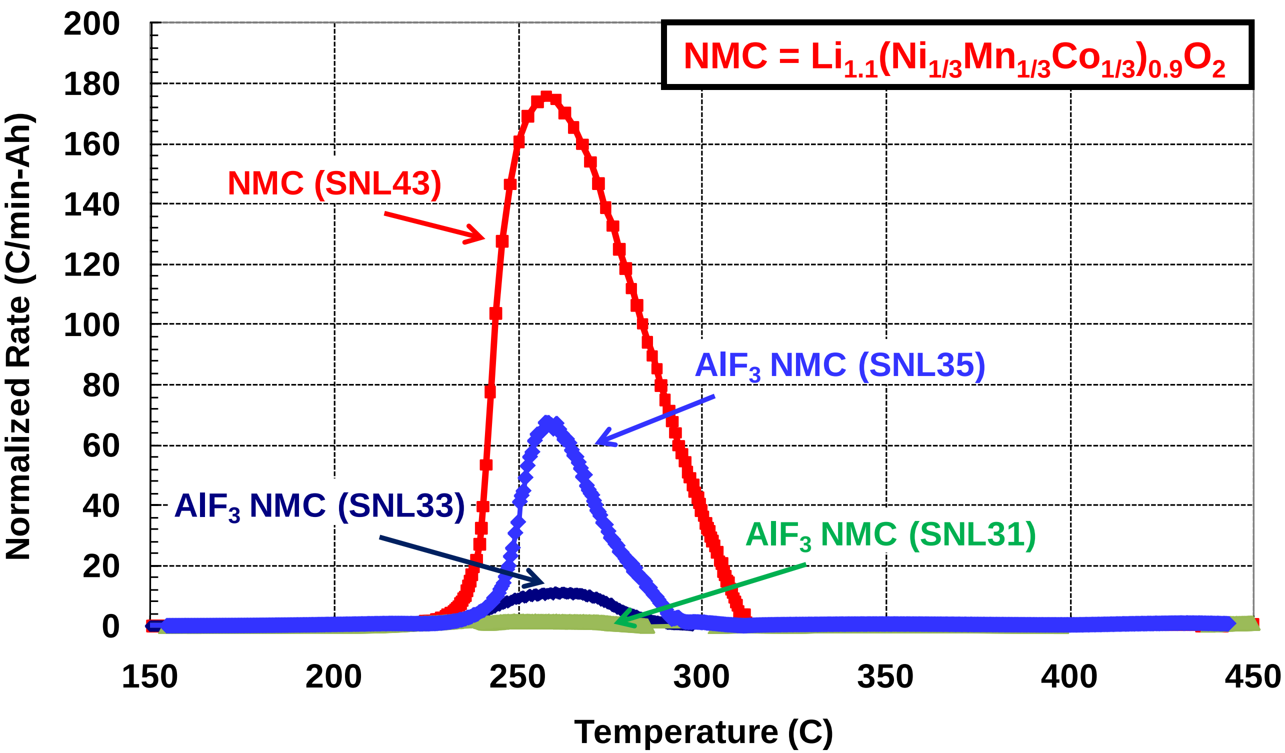
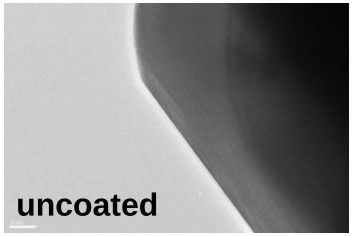
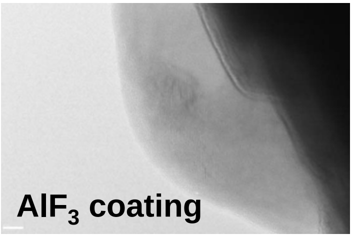
Thermal response of AlF_3-coated NMC in 18650 cells by ARC



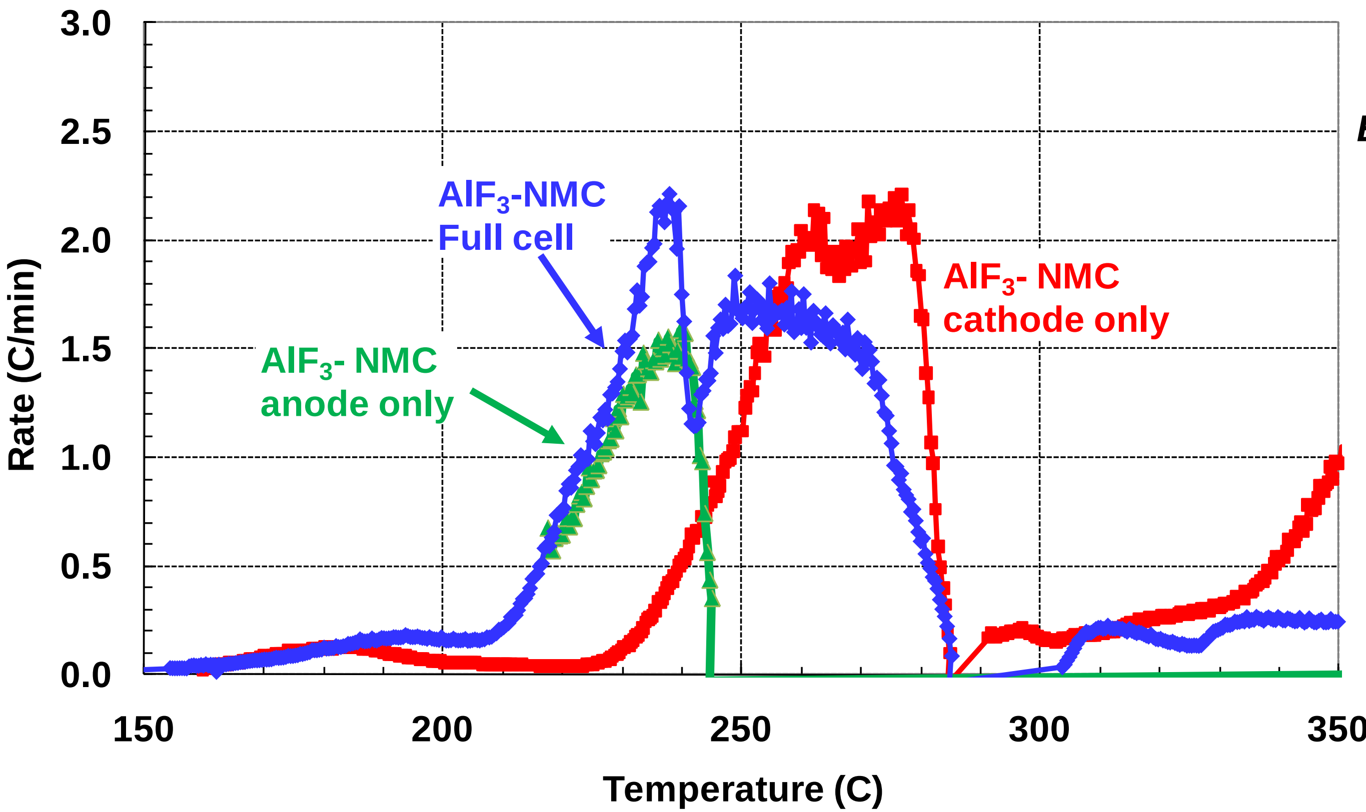




- *AlF_3-coating improves the thermal stability of NMC materials by 20 ^oC; onset of decomposition ~260 ^oC (ANL)*
- *Increased stabilization significantly improves the thermal response during cell runaway*
- *Variability likely due to the material heterogeneity*

Electrode Contributions to Runaway

Anode and cathode contributions to ARC runaway profiles



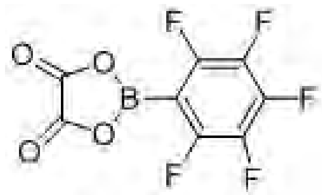
Estimated runaway enthalpy

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

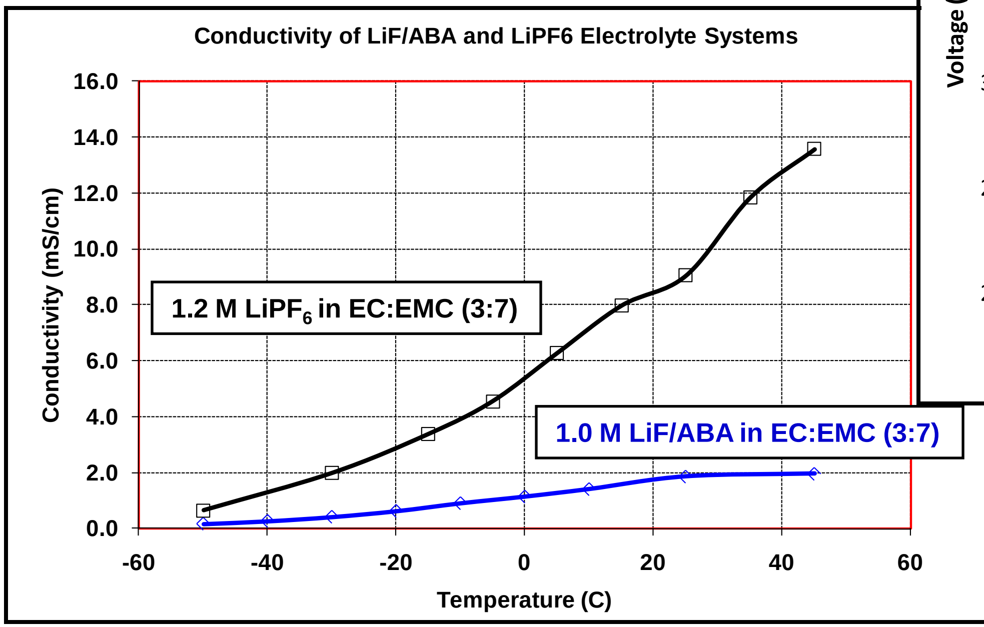
Good agreement between individual electrode ARC experiments and full 18650 cells
Total enthalpy is comparable for the coated and uncoated NMC (Gen3) cells
Inert coatings reduce the reaction rates, but the total heat output remains unchanged

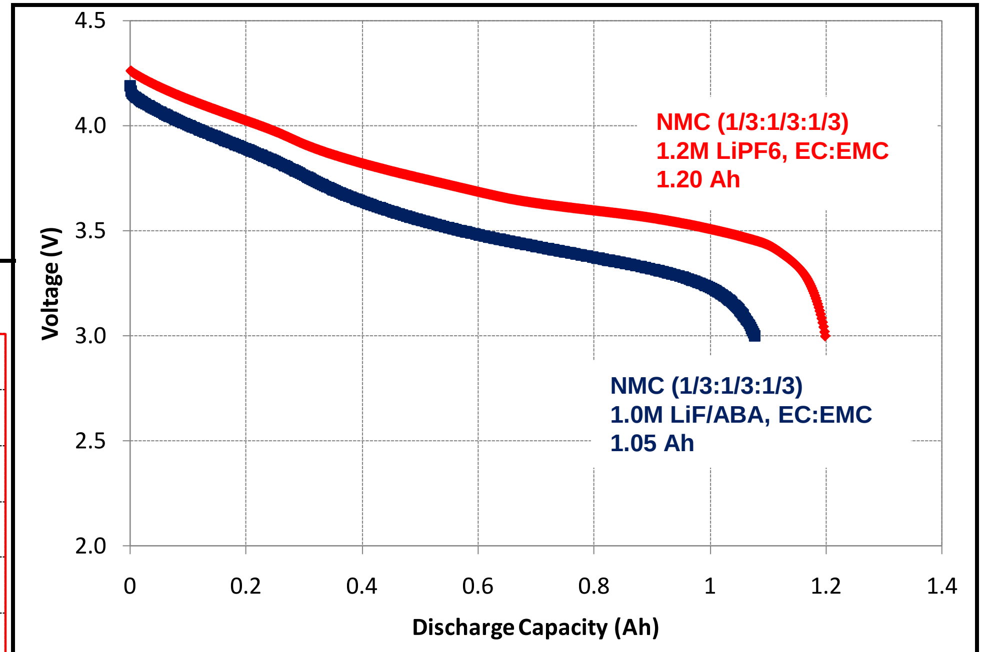
LiF/ABA Electrolyte

Objective: Develop thermally stable electrolytes with reduced gas generation



Perfluorophenyloxaltoborate





Developed in collaboration with Binrad Industries
Analogous to the PFPBO developed at BNL (Yang)
Collaboration with BNL on ABA development work

- **4x poorer conductivity than 1.2 M $LiPF_6$**
- **15-20% capacity reduction in initial cell builds**
- **Could improve with ABA purification *or* use as an additive x**

LiF/ABA Electrolyte - ARC

ARC and gas volume of LiF/ABA NMC cells

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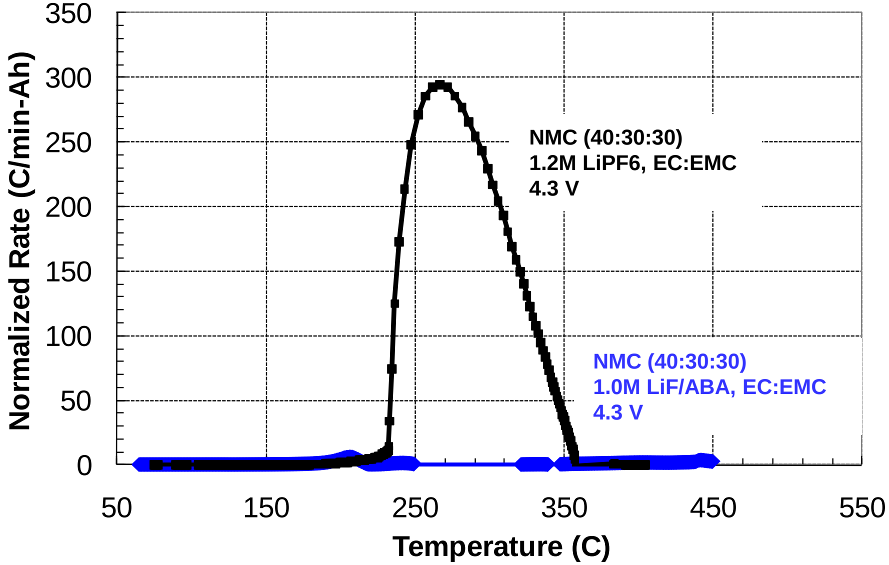

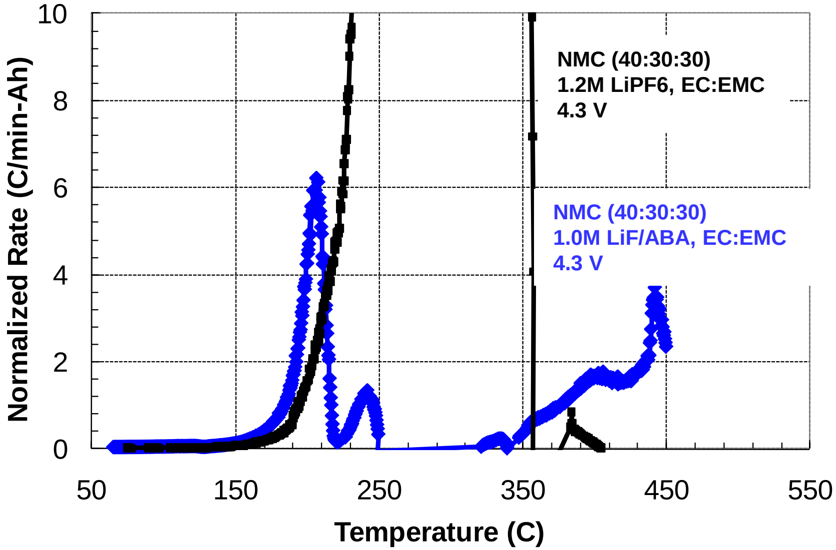

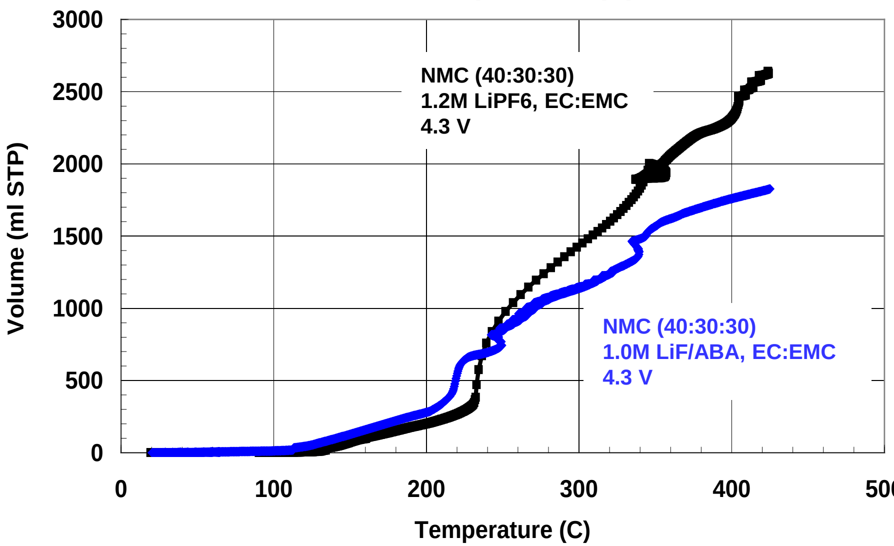

- *Reduced onset temperature with LiF/ABA compared to $LiPF_6$*
- *No high rate cathode runaway*
- *40% reduction in total gas volume compared to $LiPF_6$*

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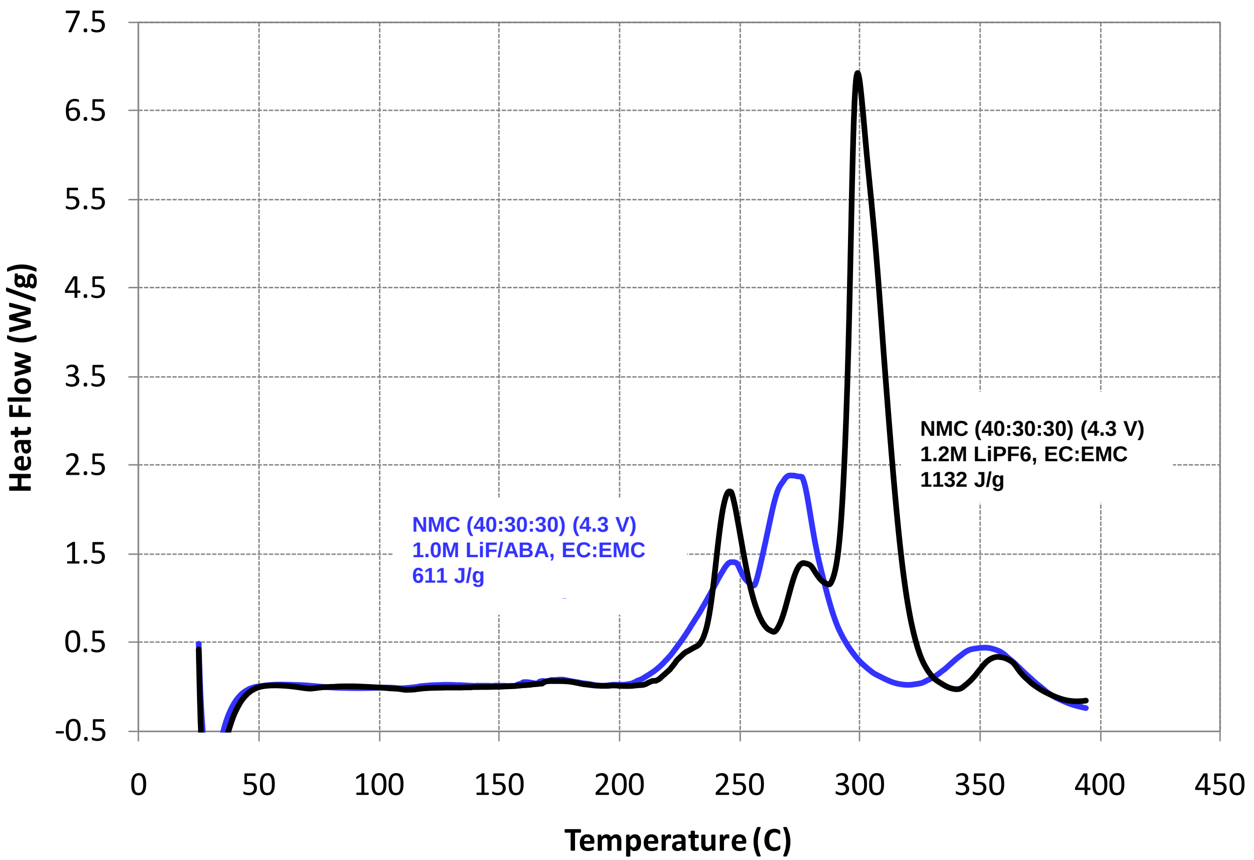
LiF/ABA Electrolyte - DSC

NMC Cathode DSC in LiF/ABA and $LiPF_6$ electrolytes



Significant reduction in cathode enthalpy in LiF/ABA compared to that in $LiPF_6$
Consistent with observations made for cell ARC of total reduction heat output
Experiments underway to determine mechanism for thermal behavior

Cell Age Effects on Thermal Runaway

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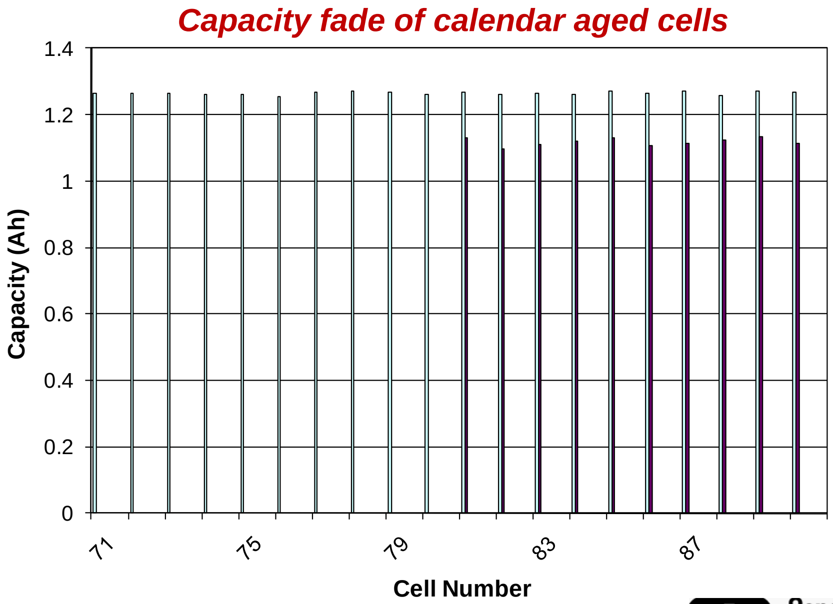
- ## *Objectives*
  - Determine the effect of cell age on thermal profile (ARC)
  - Investigate how thermal profiles vary from cell-to-cell and if variations change with cell age (implications in system thermal modeling)
  - Determine how cell-to-cell variations in performance change with cell age (implications in system performance over time)
  - Study the differences in cell thermal response between calendar and cycle life aged cells

- ## *Status to date*
  - Performance data of fresh cells (Sanyo SA cells) (INL)
  - ARC testing in progress for 10 fresh cells (SNL)
  - 10 cells calendar aged at 60°C for 2 months (~30% power fade)



Collaboration with Jeff Belt (INL) and Bor Yann Liaw (Univ. Hawaii)

Cell Age Effects on Thermal Runaway

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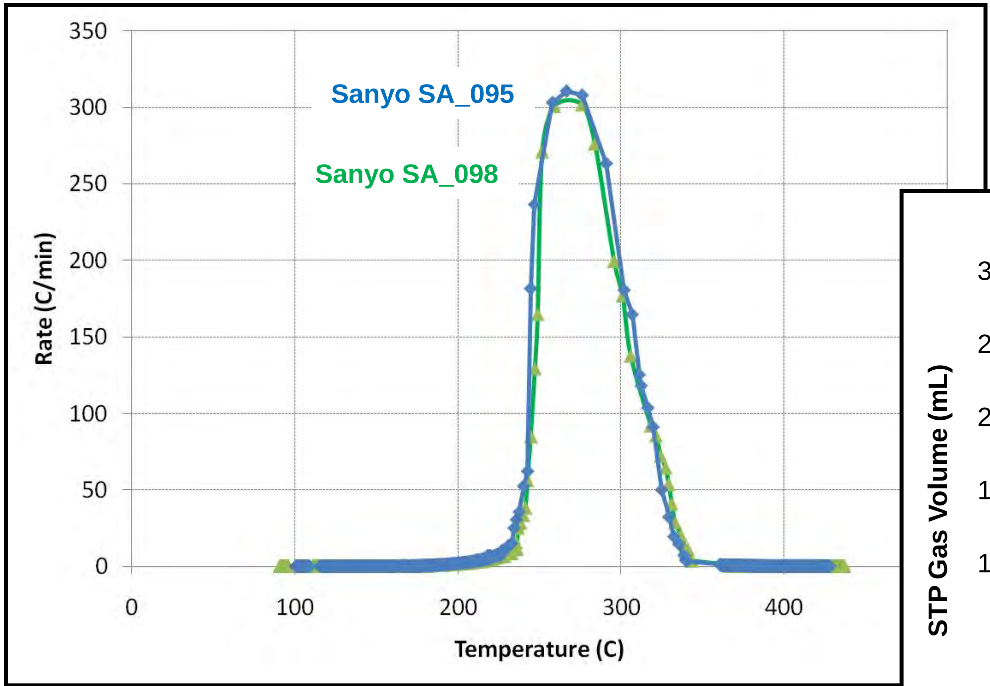
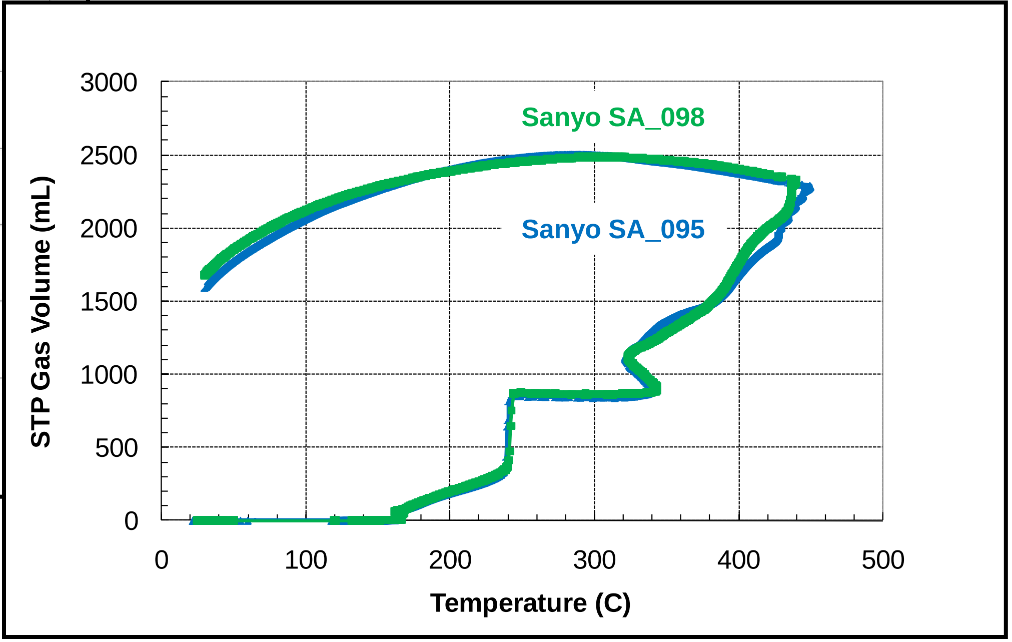
ARC experiments on fresh Sanyo SA cells (control population)





Good agreement in the thermal response & gas volume of initial cells
Continue measurement on calendar aged cells

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SNL Lithium-ion Cell Prototyping

- **Recent cell building activities to support ABR**
  - AlF_3-NMC ARC work in 18650 cells (ANL)
  - F-LiBOB additive work (ANL – finished end of FY10)
  - LiF/ABA electrolyte development
  - Coated electrodes provided to INL for initial electrolyte screening
- **Cell prototyping needs for FY11**
  - Non-flammable electrolyte cell performance/abuse tolerance (INL)
  - Electrolyte performance/flammability (JPL)
  - Al_2O_3-coated NCA development and ARC evaluation (ANL)
  - $M_3(PO_4)_x$-NMC cathode development (PSI)
- **Experience with coating $LiFePO_4$, NMC, $LiCoO_2$, $LiMn_2O_4$, and high voltage cathode chemistries and MCMB and Conoco Phillips (CP) G8 graphite**
- **Routinely producing 18650 cells (~1.2 Ah) to support EERE and SNL programs (3M BC-618 (NMC) and CP G8 baseline chemistry)**

SNL Lithium-ion Cell Prototyping

Baseline Performance of SNL-Built NMC Cells

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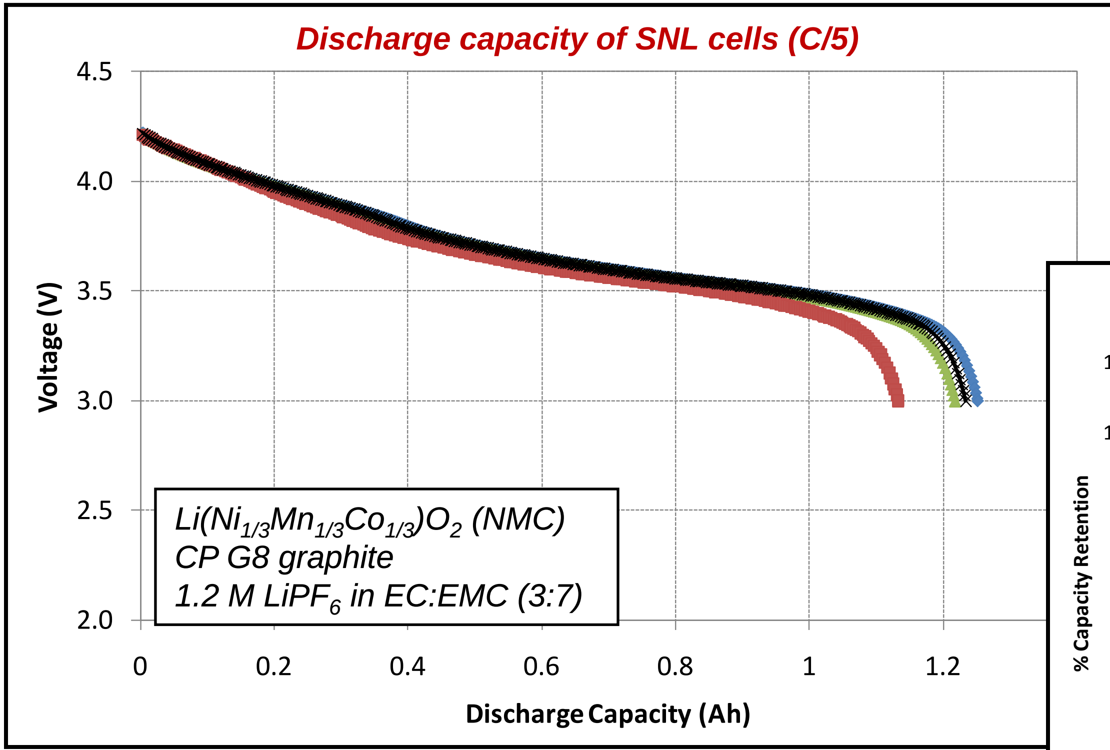
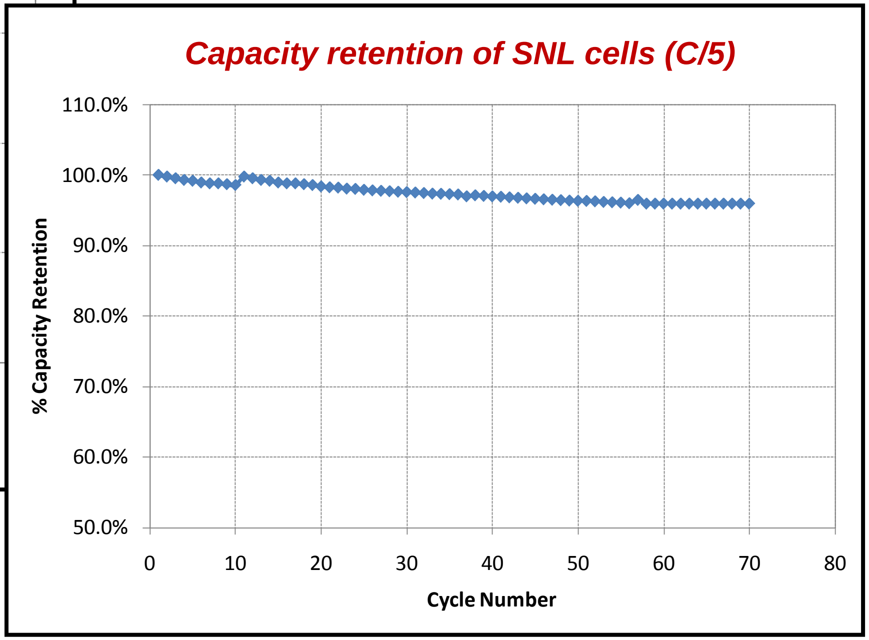
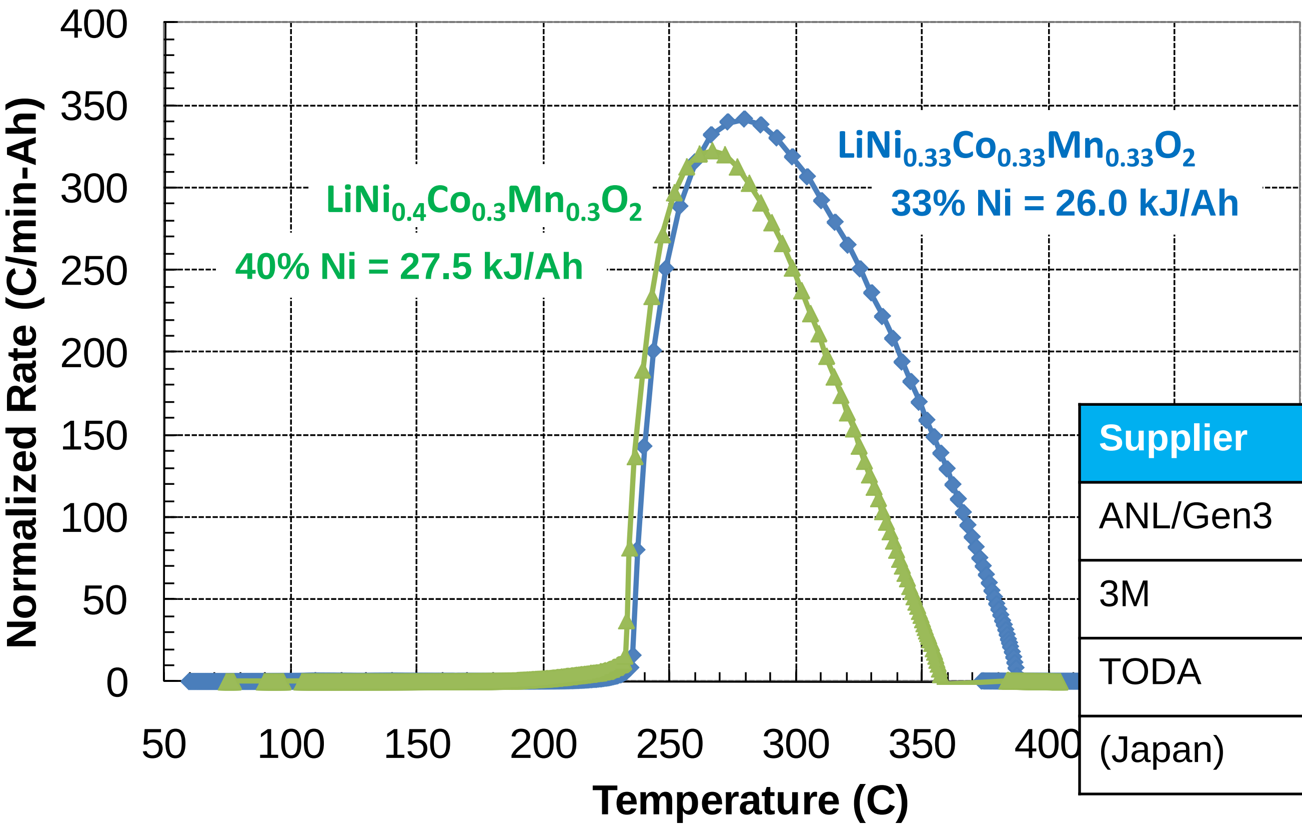




- *Routine production of 1.15-1.25 Ah cells (NMC/graphite)*
- *4% capacity fade observed at 70 cycles (C/5 C/D rate)*
- *Working with 3M to optimize coating the NMC cathode for 1.3 Ah design*

ARC Work on SNL-Built NMC Cells

Accelerating Rate Calorimetry of SNL-Built NMC Cells



Supplier	NMC stoichiometry
ANL/Gen3	$Li_{1.1}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{0.9}O_2$
3M	$Li_{1+x}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{1-x}O_2$
TODA	$Li_{1+x}(Ni_{0.5}Mn_{0.3}Co_{0.2})_{1-x}O_2$
(Japan)	$Li_{1+x}(Ni_{0.4}Mn_{0.3}Co_{0.3})_{1-x}O_2$

Comparable onset runaway temperatures and enthalpies for 33% & 40% Ni NMC cells
Future work will study other stoichiometries of NMC cathode cells

Collaboration and Coordination with Other Institutions

- **ANL** (VT program)
  - Studying coated cathode material abuse response in cells including AlF_3-coated NMC and Al_2O_3-coated NCA
  - Characterization the abuse response of high energy cathodes
  - Studying electrolyte additives in full cells
- **INL** (VT program)
  - Calendar and cycle life aging of cells to determine the effect of age of thermal response and abuse tolerance
  - Abuse tolerance and flammability testing of phosphazine-based electrolytes in cells
- **JPL** (VT program)
  - Flammability and performance evaluation of electrolytes in cells
- **Univ. Hawaii** (outside VT program)
  - Study how cell-to-cell variability in performance and thermal response changes with cell calendar and cycle age
- **BNL** (VT program)
  - Characterizing and developing electrolytes
- **Binrad Industries** (outside VT program)
  - Industrial partner to develop ABA electrolytes
- **Physical Sciences Inc.** (outside VT program)
  - Industrial partner providing $M_3(PO_4)_x$-coated NMC

Summary

- Materials choices can have a significant impact on improving abuse tolerance and the thermal response in full cell testing
- Coated cathode materials (AlF_3-NMC) reduce the total peak heating rate (and severity) during a runaway reaction while the total runaway enthalpy remains unchanged (consistent with observations made in DSC measurements)
- Good agreement between anode and cathode runaway profiles in ARC measurements
- ABA electrolytes show a significant reduction in runaway reactivity and reduced gas generation
- No high temperature (>300 C) electrolyte degradation observed in the DSC results for the LiF/ABA electrolyte compared to $LiPF_6$ resulting in a ~50% reduction in the energy released; consistent with ARC measurements of full cells
- Possible mechanism points to ABA decomposition passivates NMC surface or somehow limits the electrolyte decomposition
- Almost no cell-to-cell variability observed for fresh Sanyo SA cells measured by ARC (onset temperature, heating rates, runaway enthalpy)
- Measurements on fresh cells serve as the foundation for ARC measurements on calendar and cycle-life aged cells
- Routine production of 1.2 Ah cells in the SNL prototyping facility
- Cell building capabilities allow us to make performance and abuse response measurements of development or commercial materials in actual full-sized cells

Proposed Future Work (FY11 and FY12)

- **Abuse tolerance and ARC measurements on advanced active materials**
  - High capacity cathodes (ANL)
  - Silicon-based anode chemistries
  - Coated cathodes including Al_2O_3-NCA (ANL) and $M_3(PO_4)_x$-NMC (ANL, PSI)
- **Stability, flammability, reduced gas generation of electrolyte additives**
  - Flammability/performance evaluation of JPL electrolytes (K. Bugga/M. Smart, JPL)
  - Flammability/ARC of phosphazine electrolytes (K. Gering, INL)
- **Characterization of ABA electrolyte behavior**
  - DSC, XPS, and vibrational spectroscopy on ABA systems to determine mechanism for reduced cell enthalpy during runaway
- **Development of new ABA-based electrolytes**
  - Full cell studies and performance testing with ABA electrolyte additives (BNL)
  - New ABA chemistries and full cell testing (Binrad, BNL)
- **Aged cell abuse tolerance**
  - Complete ARC studies on control population and calendar aged cells (30% power fade) (INL)
  - Studying the effect of cycle-life age on the thermal performance and cell-to-cell variability (INL, Univ. Hawaii)
  - Abuse testing of calendar and cycle-life aged cells
  - Study the effect of cell age on different cell chemistries (anode, cathode and electrolyte) (INL, Univ. Hawaii)
- **Cell prototyping**
  - Continue cell building to support ABR materials development and abuse tolerance work
  - Study the effect of NMC composition from different commercial suppliers on cell runaway response

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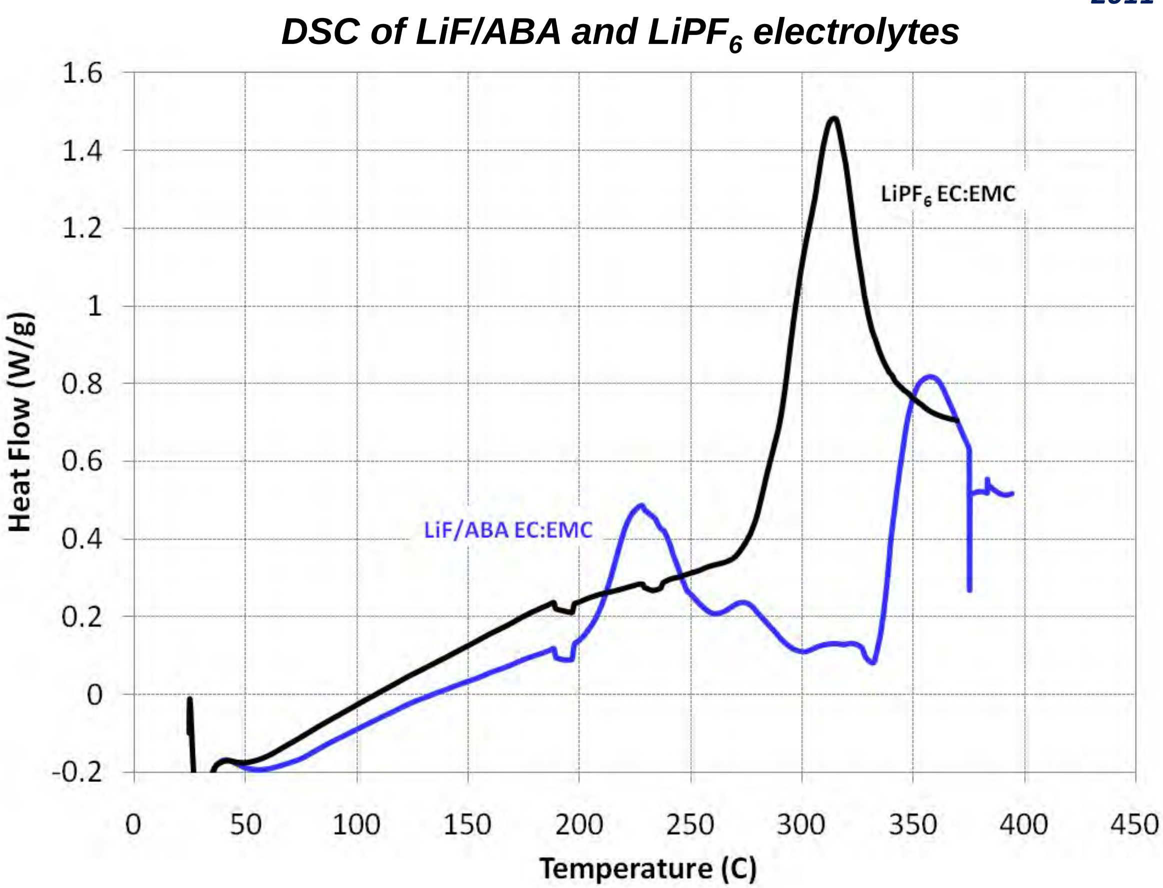
- Lorie Davis
- Mike Russell
- Dave Johnson
- Denise Bencoe

Technical Back-up Slides

LiF/ABA Electrolyte - DSC



ABA decomposition onset at 200 C, coincides with onset of cell runaway
No electrolyte decomposition >300 C for LiF/ABA EC:EMC
Significant reduction in total decomposition energy for LiF/ABA compared to $LiPF_6$

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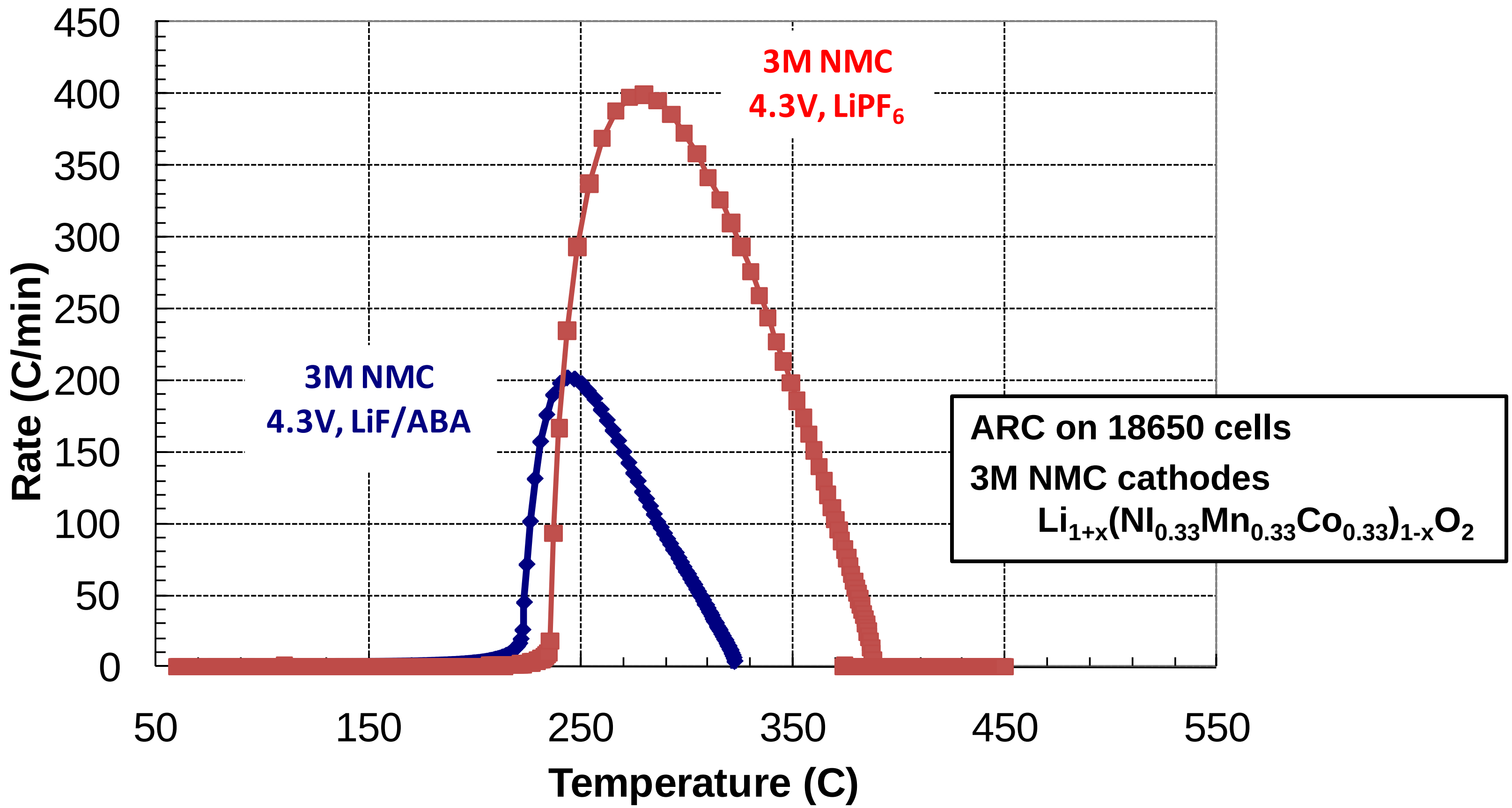
LiF/ABA Electrolyte in 3M NMC Cells



33% Ni NMC cells show a similar trend of decrease peak heating rate in LiF/ABA Electrolyte, but not as dramatic an effect as observed for the 40% NMC cells