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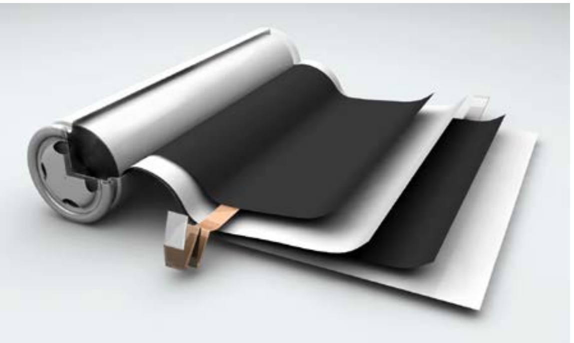

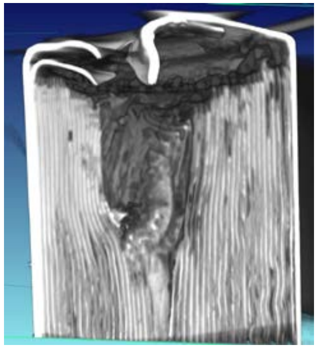

ES036

Abuse Tolerance Improvements

Christopher J. Orendorff, Kyle R. Fenton, Ganesan Nagasubramanian, Josh Lamb, and Travis M. Anderson

Sandia National Laboratories

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2014 Energy Storage Annual Merit Review

Washington, D. C. 6/17/2014

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Overview

Timeline

- Start Date: Oct. 2013
- End date: Oct. 2014
- Percent complete: >75%

Budget

- FY14 Funding: $750K
  - Abuse Evaluation/Prototyping - $550K
  - Development of abuse-tolerant components - $200K
- FY13 Funding: $1.0M
- FY12 Funding: $1.0M
- FY11 Funding: $1.35M

Barriers

- Barriers addressed
  - Develop intrinsically abuse-tolerant lithium-ion cells and batteries
  - Issues related to cell safety are represent significant challenges to scaling up lithium-ion for transportation applications
  - Obtain access to latest promising materials from developers and sufficient quantities of materials to determine reproducibility of results

Partners

- ANL, INL, NREL, JPL, ORNL, CU-Boulder, Case Western University
- XG Sciences, Physical Sciences Inc.

Relevance and Objectives

Developing inherently safe lithium-ion cell chemistries and systems

1. **Evaluate Abuse Tolerance Improvements**
   - Improve abuse tolerance in lithium-ion cells
   - Develop strategies to reduce the negative effects of an energetic thermal runaway
   - Identify and develop advanced materials or combination of materials that will minimize the sources of cell degradation during abuse events, leading to enhanced safety
   - Build and test full size cells to demonstrate improved abuse tolerance
2. **Abuse Resilient Components**
   - Design and develop strategies to mitigate the severity of thermal runaway in lithium-ion cells
3. **Cell Fabrication**
   - Build and test full cells to demonstrate improved abuse tolerance
   - Work with other Labs to standardize electrode formulations
   - Deliver cells and electrodes to ABR Partners to support materials development programs

Milestones

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Demonstrate improved abuse-tolerant cells, and report to DOE and the battery community

Obj.	Milestone	Status
1	Si/C: Prep and characterization of XG Sciences Si/C electrodes	
1	Si/C: Evaluate initial performance of XG Si/C 18650 cells	
1	Si/C: Initial calorimetry studies to determine thermal runaway response of XG Si/C	
1	Si/C: Evaluation of the thermal runaway response of other Si/C anodes (ANL)	Q3/Q4
1	Si/C: Abuse testing of Si/C cells	Q4
1	PSI: Evaluate thermal runaway response of $LiMPO_4$-coated NMC in cells	
1	ALD: Evaluate coatings on NMC, optimize coatings for safety performance	
1	ALD: Evaluate thermal runaway response of ALD-coated NMC in cells	Q3/Q4
1	C.W. FRION: Evaluate the flammability of FRION electrolytes	
2	SNL ABA: Synthesis of Gen 2 ABA (ABA-2)	
2	SNL ABA: Initial cell evaluation/calorimetry of ABA-1 and ABA-2	Q3
2	SNL ABA: Delivery of final ABA-2 to ANL MERF	Q4
2	SNL ABA: Complete abuse testing and calorimetry of ABA-2 in cells	Q4
2	SNL IL: Initial performance and calorimetry measurements of IL-3 in cells	Q3
3	Cell Fab: Resolve cell build failure issue for cylindrical cells	
3	Cell Fab: Build and deliver cells for the development programs	

Milestone Complete

Approach

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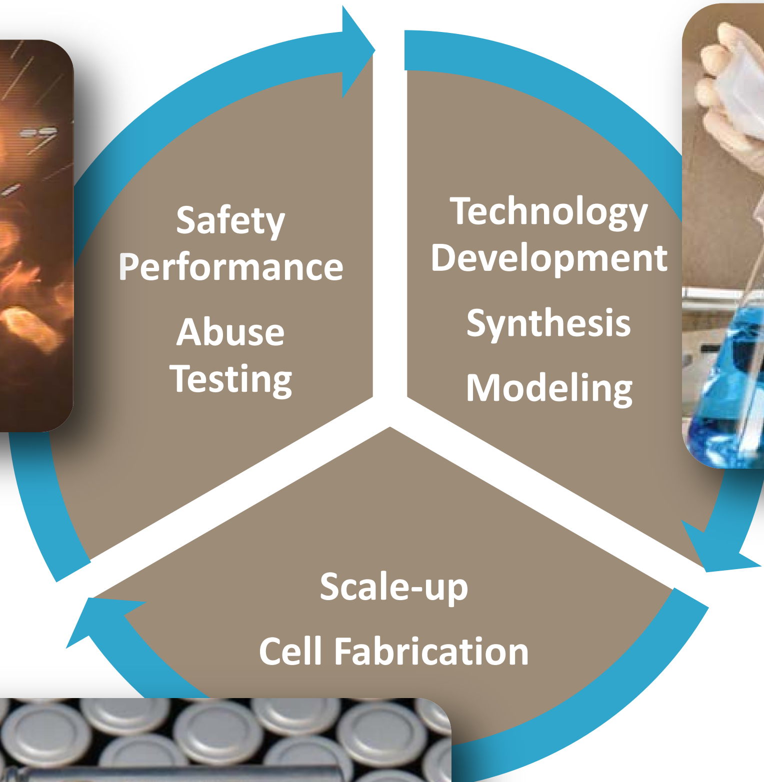

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Technical Accomplishments/ Progress/Results

Abuse Tolerance Improvements:

- **Si/C anode characterization (XG Sciences):**
  - Preliminary demonstration of performance in 1.2 Ah18650 cells
  - Evaluation of abuse response and thermal runaway characterization
  - Need to better understand gas generation and electrolyte reactivity at the Si/C electrode

- **Metal Phosphate-Coated Cathodes (PSI):**
  - Completed calorimetry measurements
  - Initial electrochemical performance demonstration

- **ALD Al_2O_3-Coated Cathodes (CU-Boulder/NREL):**
  - Optimization of coatings of positive electrodes and demonstration of electrochemical performance
  - Delivered ALD coatings on 18650 electrodes

- **FRION electrolyte (Case Western, LBNL)**
  - Completed initial cell vent flammability tests (CVFT) to determine utility as a flame retardant

Technical Accomplishments/ Progress/Results (continued)

Cell Fabrication/Electrode Processing:

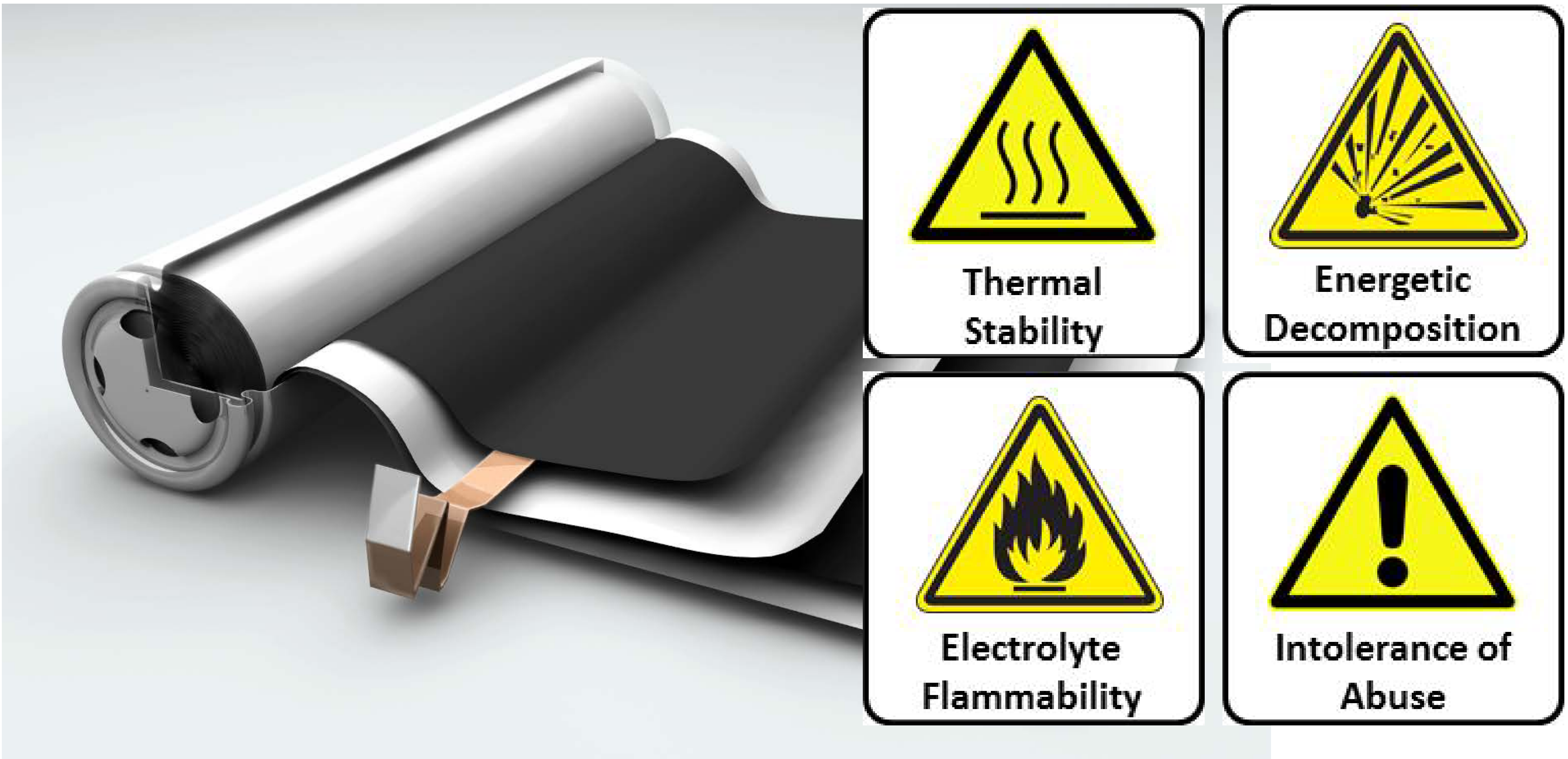
- **Cell builds to support ABR for FY14 (Toda NMC523 positive electrode, CP A10 graphite negative electrode)**
  - XG Sciences Si/C anode
  - SNL ABA Electrolyte
  - SNL Ionic Liquid Electrolyte
  - Physical Sciences Inc. $LiMPO_4$-coated NMC
  - Al_2O_3-coated NMC/ALD
  - Case Western FRION development (BATT)

Abuse Resilient Components

- **LiF/ABA Electrolytes**
  - Optimization of LiF/ABA electrolyte performance and demonstration in 1.1 Ah 18650 cells
  - Synthesis of LiF/ABA-2 with improved voltage stability (comparable to LiPF6)
  - Initial calorimetry completed on cells showing improved thermal runaway response compared to $LiPF_6$-based electrolytes

- **Ionic Liquid Electrolytes**
  - 18650 cell build with IL electrolytes and initial electrochemical performance complete

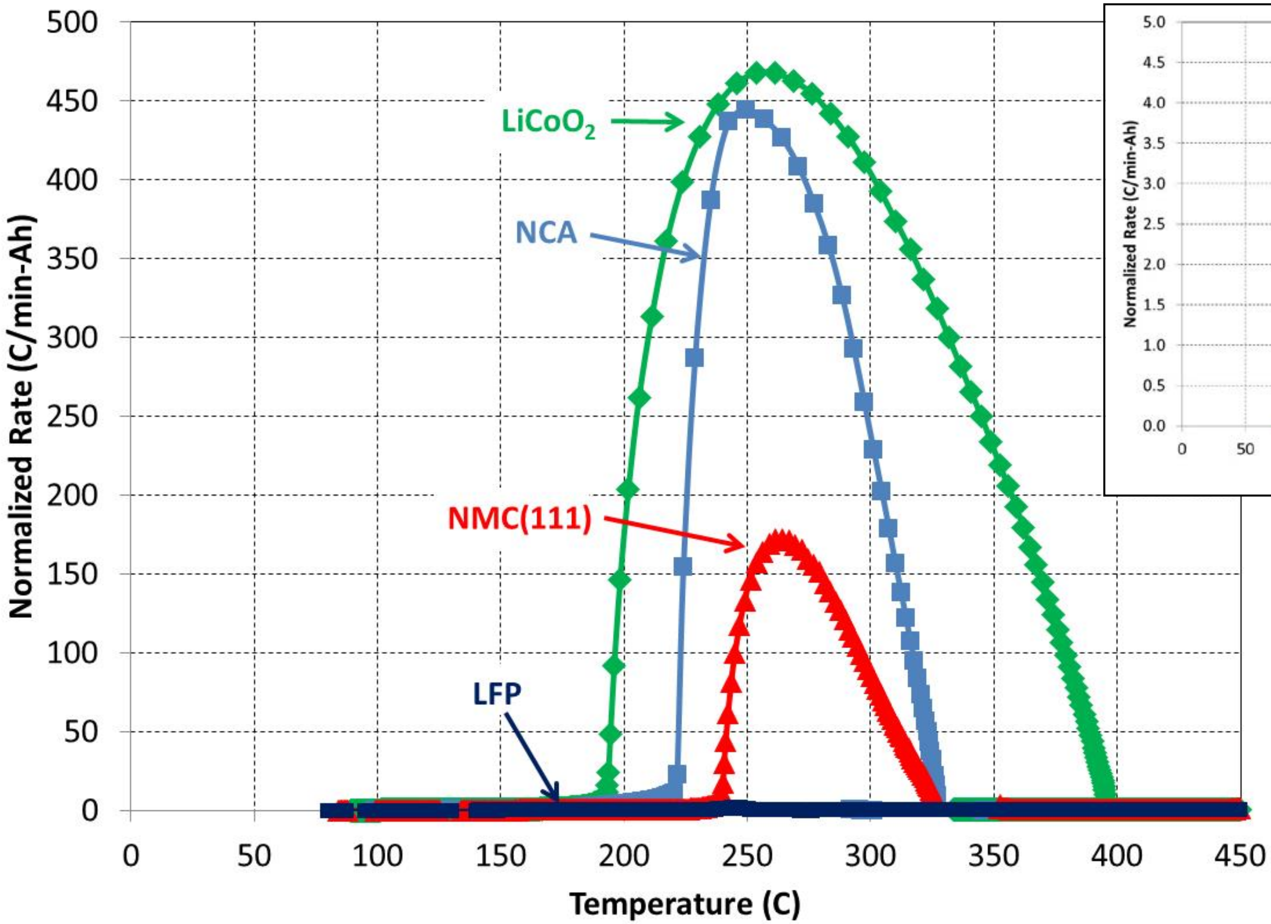
Challenges with Inherent Cell Safety

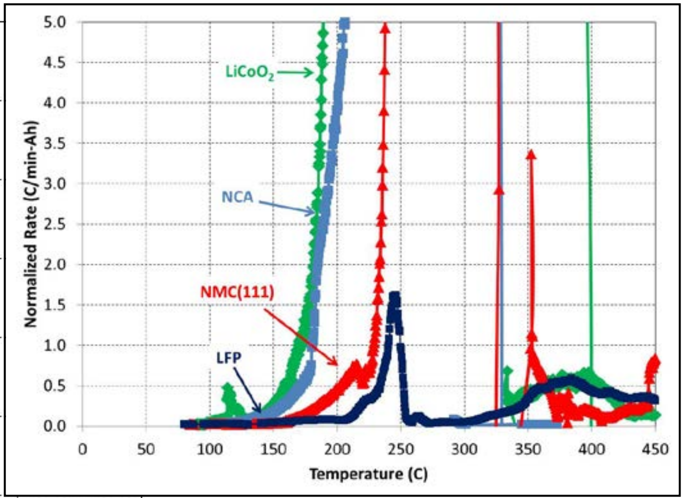


Need to address these issues at the cell materials level in order to field the most inherently safe energy storage products

Calorimetry of Lithium-ion Cells

Understanding the Thermal Runaway Response of Materials in Cells





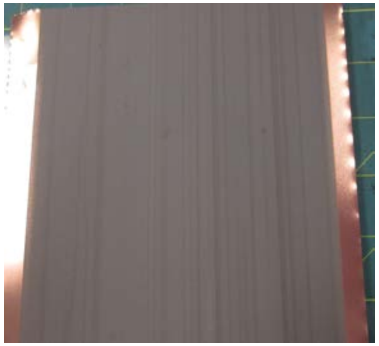
Cathode Runaway	
Cathode	$\Delta H_{runaway}$ (kJ/Ah)
$LiCoO_2$	15.9
NCA	9.8
NMC111	8.3
LFP	2.4

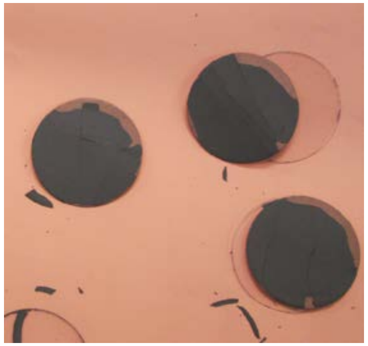
Can high energy cathodes behave like LFP during thermal runaway? Where do high capacity Si/C anodes fit on this plot?

Si/C Anode Abuse Tolerance

Understanding Safety Issues with Si Materials in Lithium-ion Cells

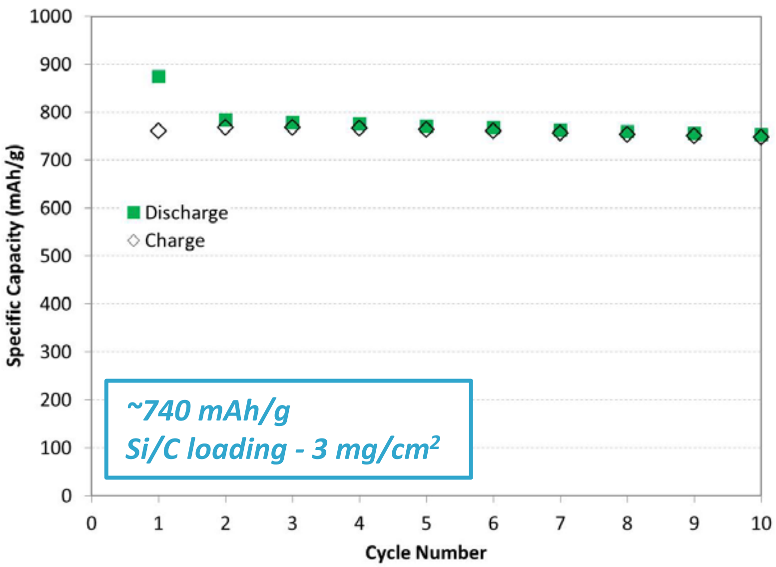
Electrode Processing Issues



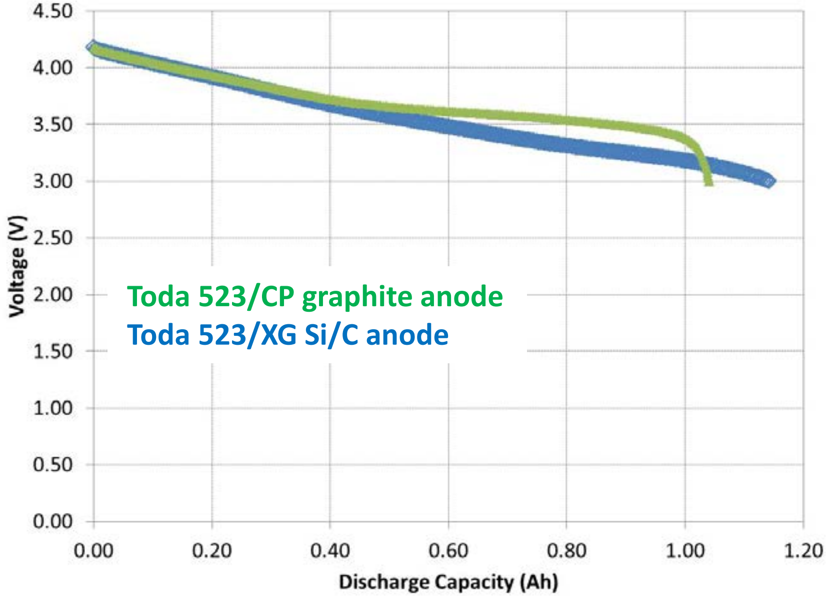


Slurry heterogeneity

Cracking > 4 mg/cm²



18650 Cell

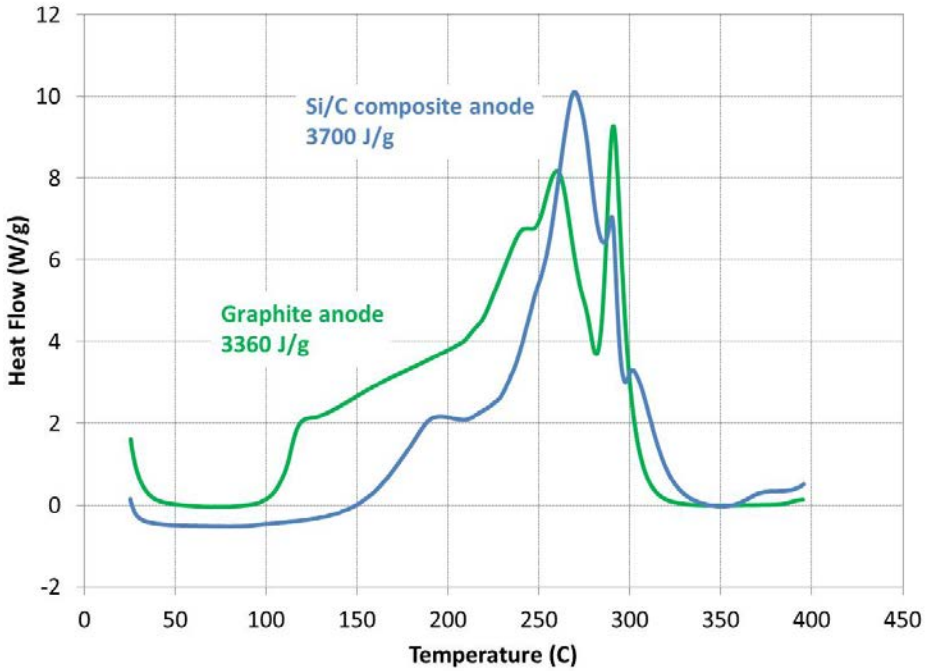


- **Cell parameters:**
  - **1.2 M $LiPF_6$ in EC:EMC (3:7)**
  - **No additives**
  - **N:P = 1.3**
- **~10% more capacity in the Si/C cell compared to the graphite anode cell**

Note: initial experiments done with EC. Subsequent experiments will be done to evaluate Si/C electrodes with FEC

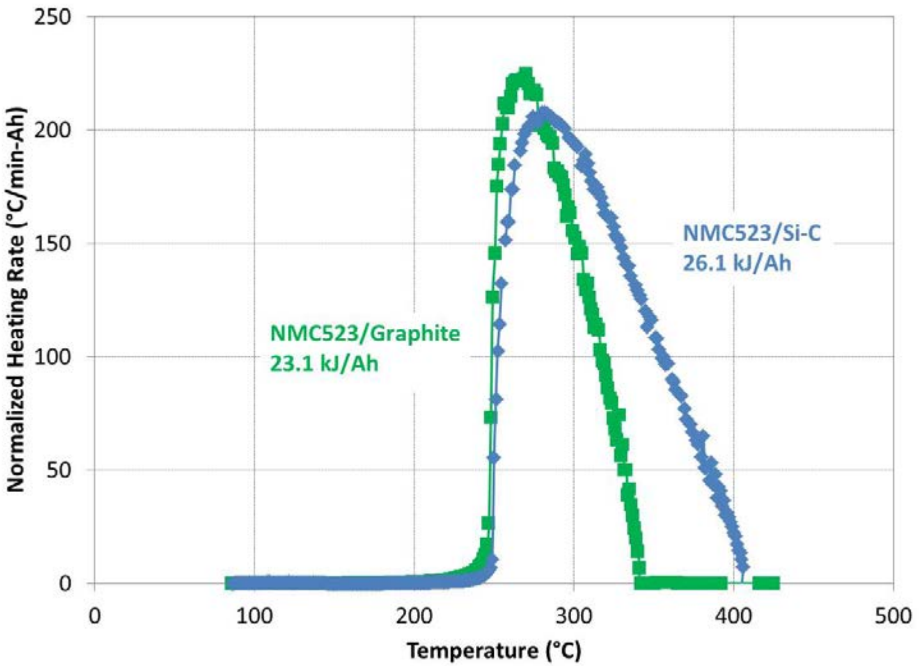
Si/C Anode Abuse Tolerance

Calorimetry on Si/C Materials



~10% increase in heat generation over graphite

Calorimetry on Si/C in 18650 Cells

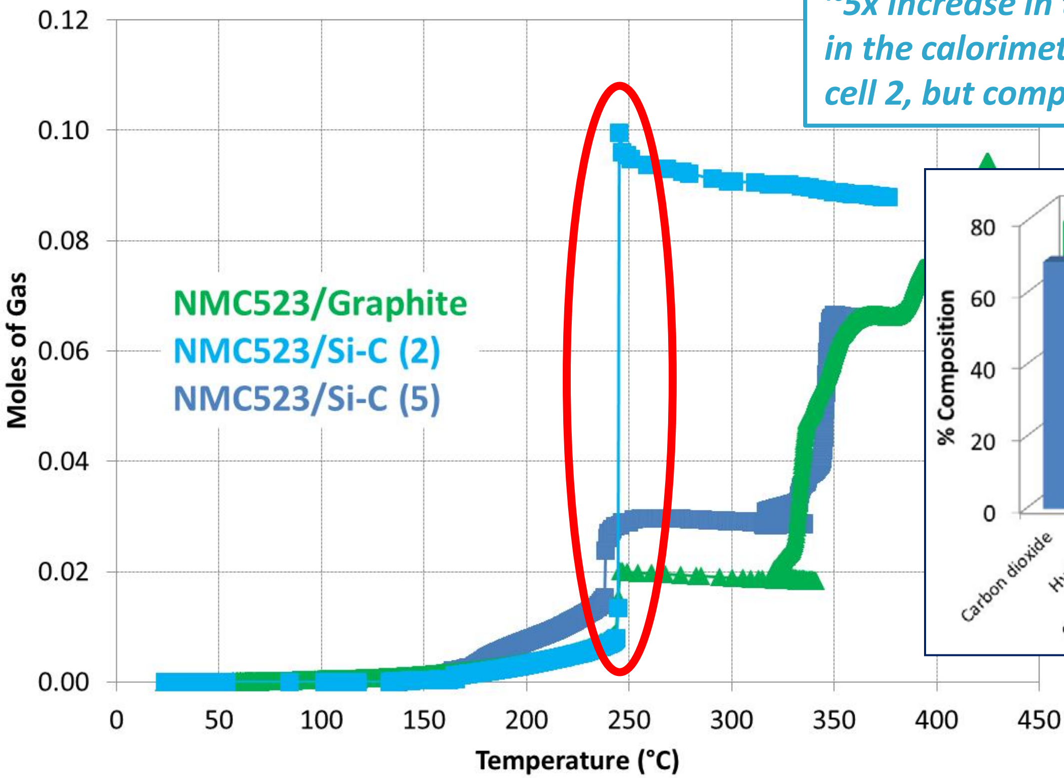


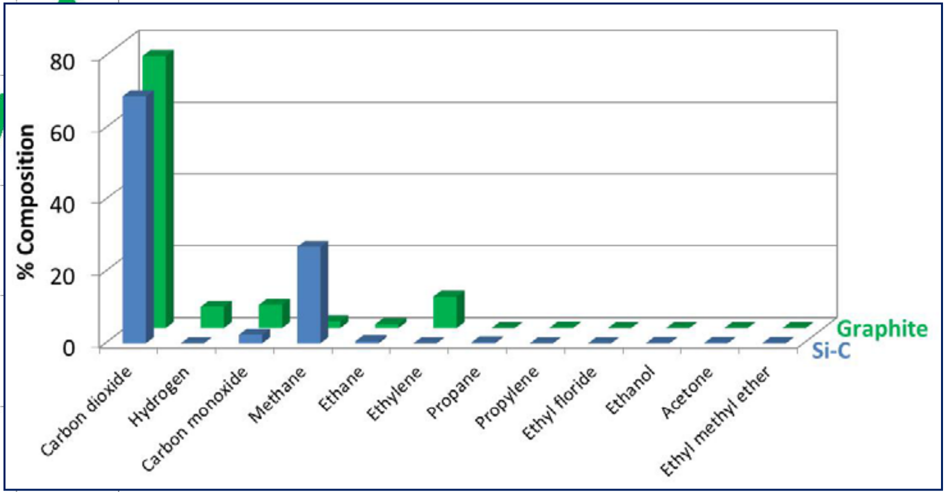
~10% increase in heat generation in cells

Thermal runaway enthalpy of Si/C-NMC cells is ~10% greater than Graphite-NMC cells

Si/C Anode Abuse Tolerance

~5x increase in the amount of gas generated in the calorimeter during thermal runaway of cell 2, but comparable gas generation for cell 5



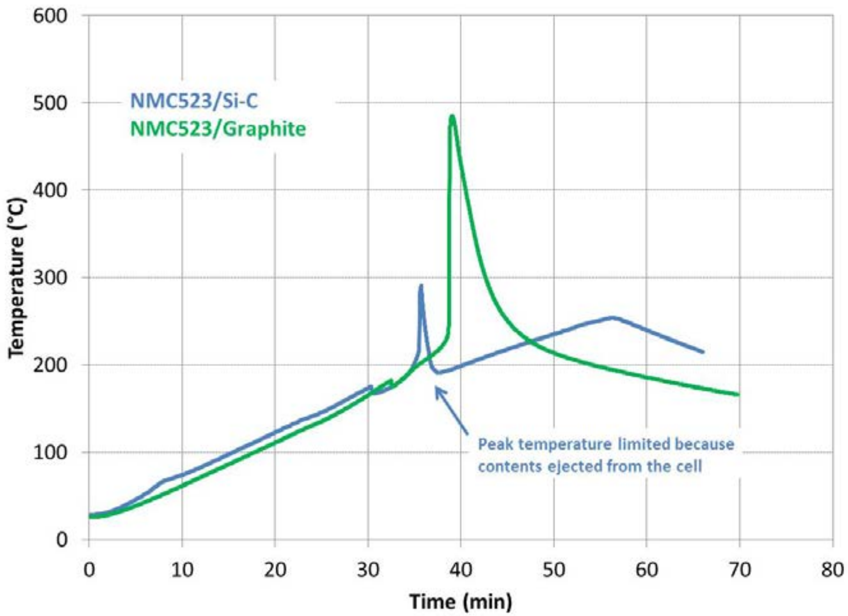


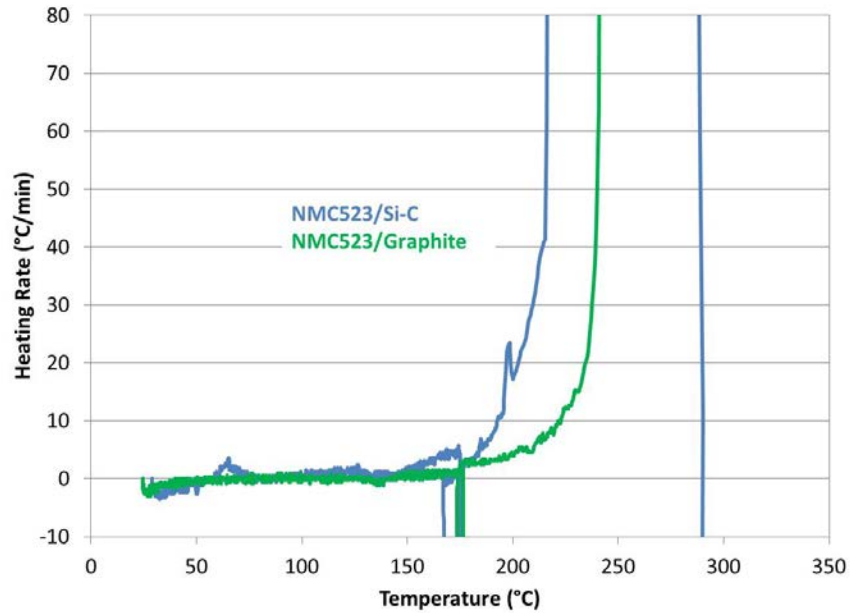
Significantly more methane and less hydrogen, carbon monoxide and ethylene produces in the Si-C cell compared to the graphite cell

Difference in gas generation attributed to the differences in surface reactivity and surface products generated at the anode/electrolyte interface

Si/C Anode Abuse Tolerance

Thermal Abuse Testing



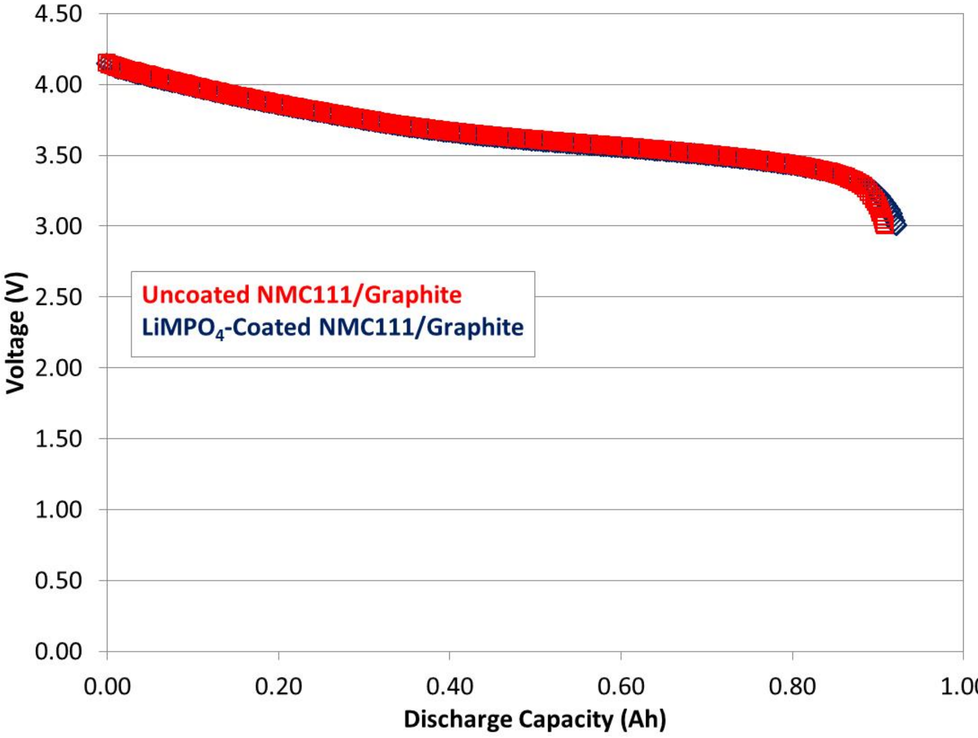


Comparable performance between the Si-C and Graphite cells, but self-ignition observed with the Si-C cell

$LiMPO_4$-Coated Cathodes (PSI)

- $LiMPO_4$ (M-Fe, Co, or Ni) coatings developed by Physical Sciences Inc. (PSI) designed to improve cycle life/cell performance
- Delivered 2 kg LiMPO4-coated NMC111 (Toda) (FY13)
- 18650 cells with $LiMPO_4$-coated NMC show comparable capacity to cells with uncoated NMC
- Cell parameters:
  - 1.2 M $LiPF_6$ in EC:EMC (3:7) (no additives)
  - N:P = 1:3
  - NMC111 (Toda), Conoco Phillips Graphite

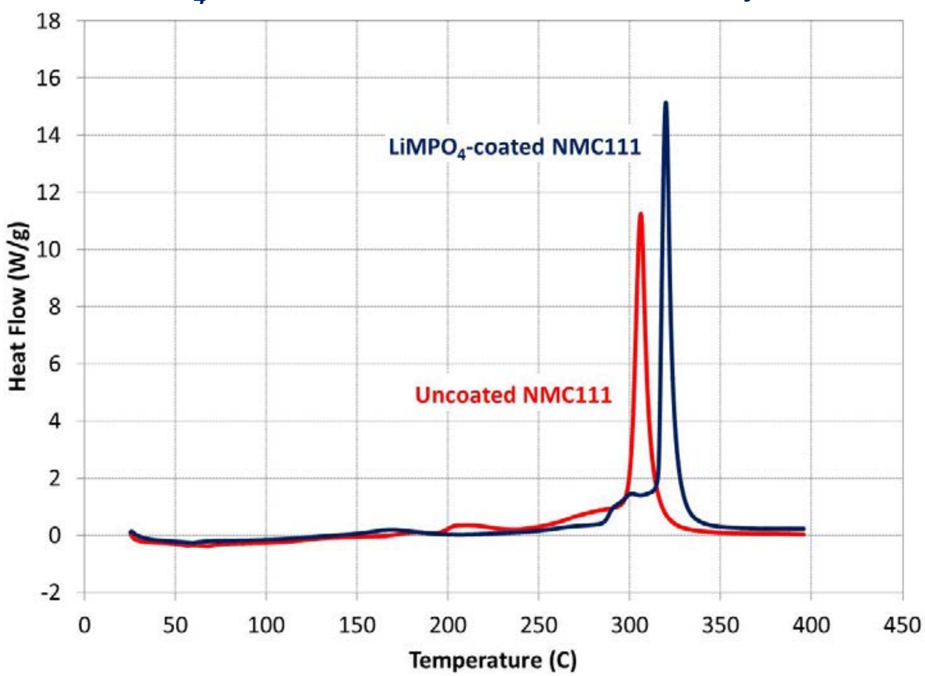
18650 Cell Performance



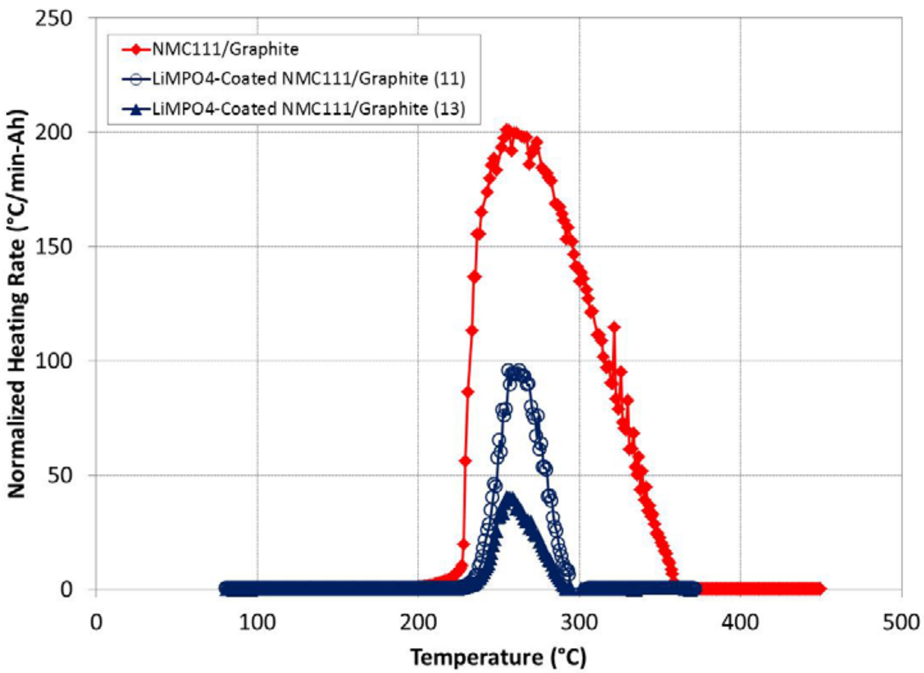
No change in initial cell capacity between the uncoated NMC and $LiMPO_4$-coated NMC cells

$LiMPO_4$-Coated Cathodes (PSI)

$LiMPO_4$-Coated NMC Materials Calorimetry



18650 Cell Calorimetry

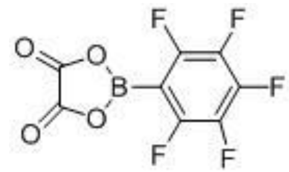


- **$LiMPO_4$ coating increases the decomposition temperature in DSC by ~20°C (kinetic barrier to degradation)**
- **Peak heating rates (kinetics of the runaway reaction) are significantly diminished (2-4x) during thermal runaway in 18650 cells, consistent with DSC results**

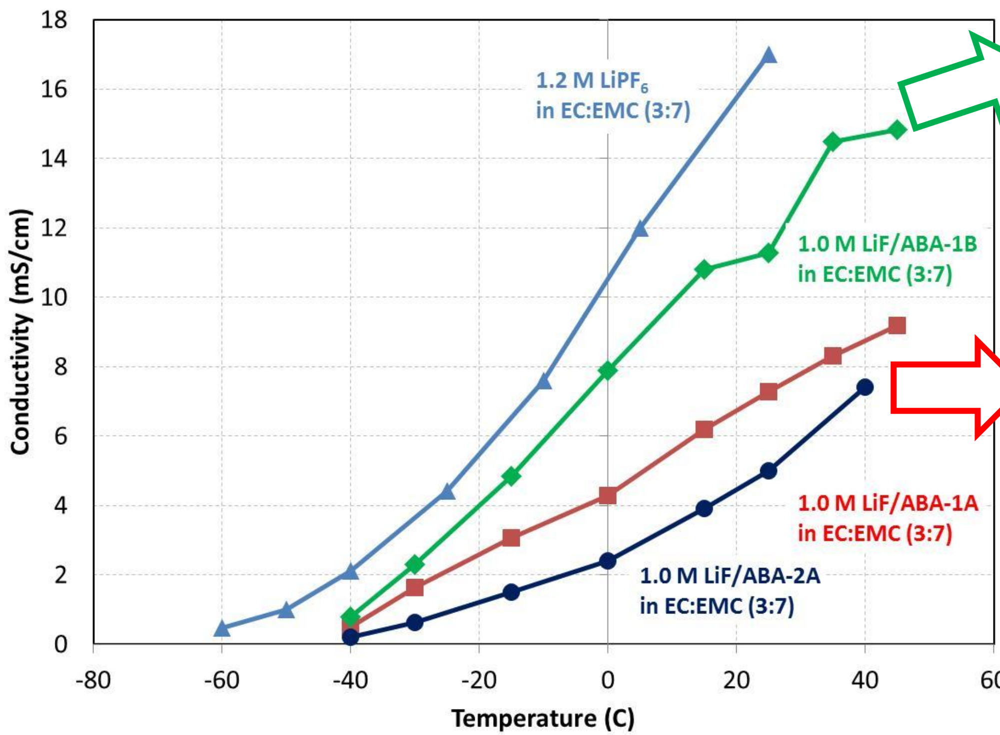
Significant improvement in thermal runaway response in $LiMPO_4$-coated NMC cells over uncoated NMC cells

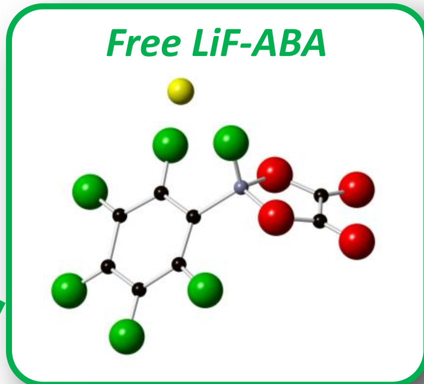
Abuse Resilient Components

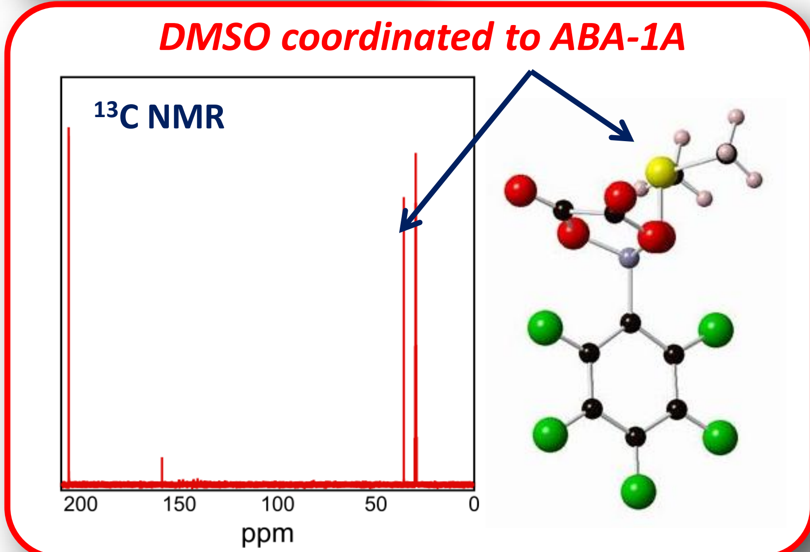
Electrolytes based on LiF and anion binding agents (ABAs)



Perfluorophenyloxaltoborate (ABA -1)





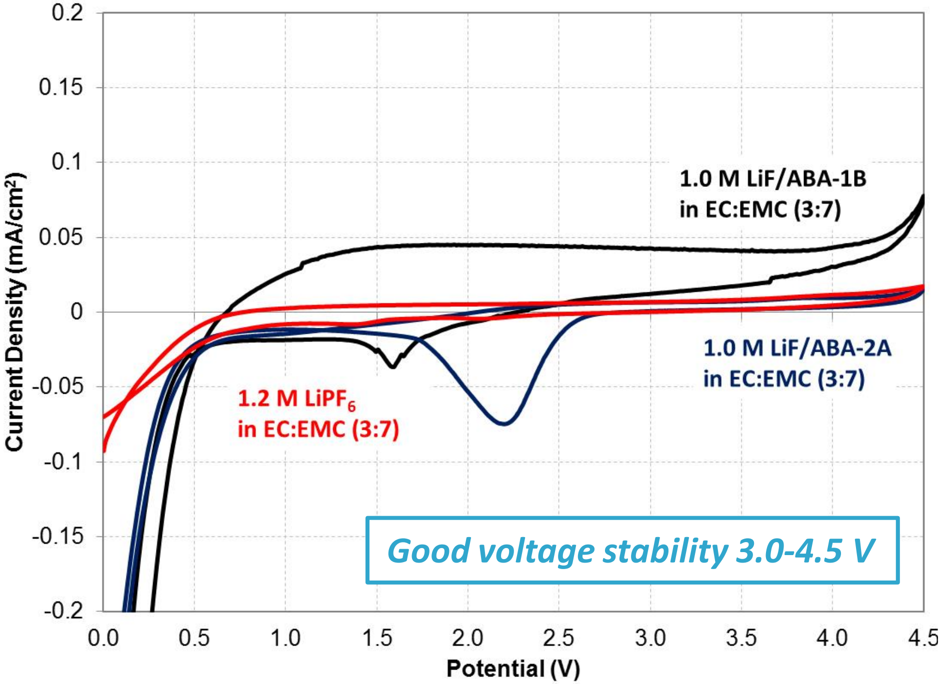


Improved performance of new ABA-based electrolytes

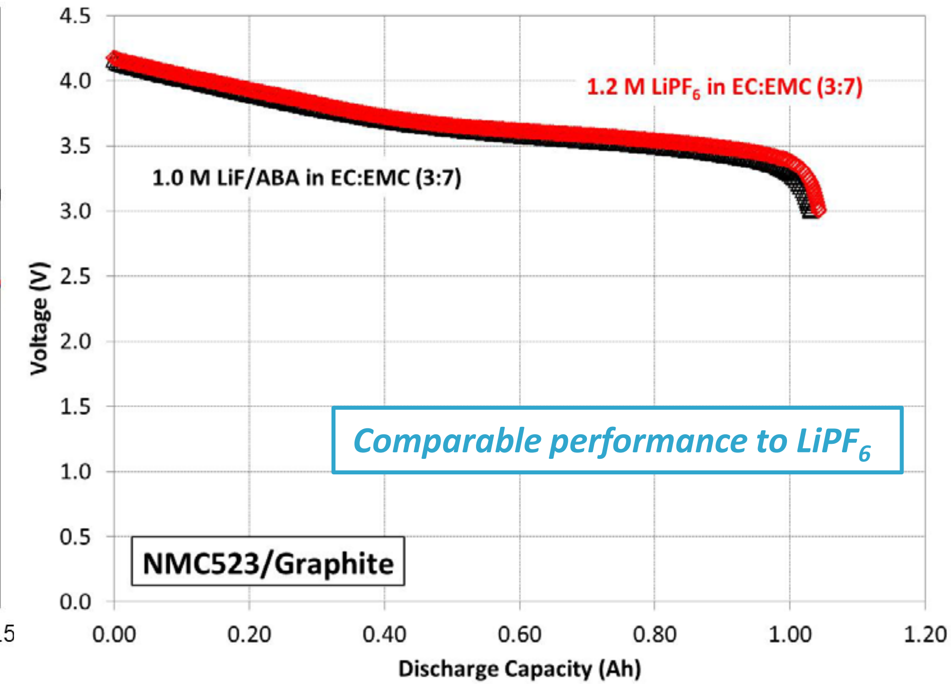
Abuse-Resilient Components

LiF/ABA Electrochemical Performance

Voltammetry of Liquid Electrolytes



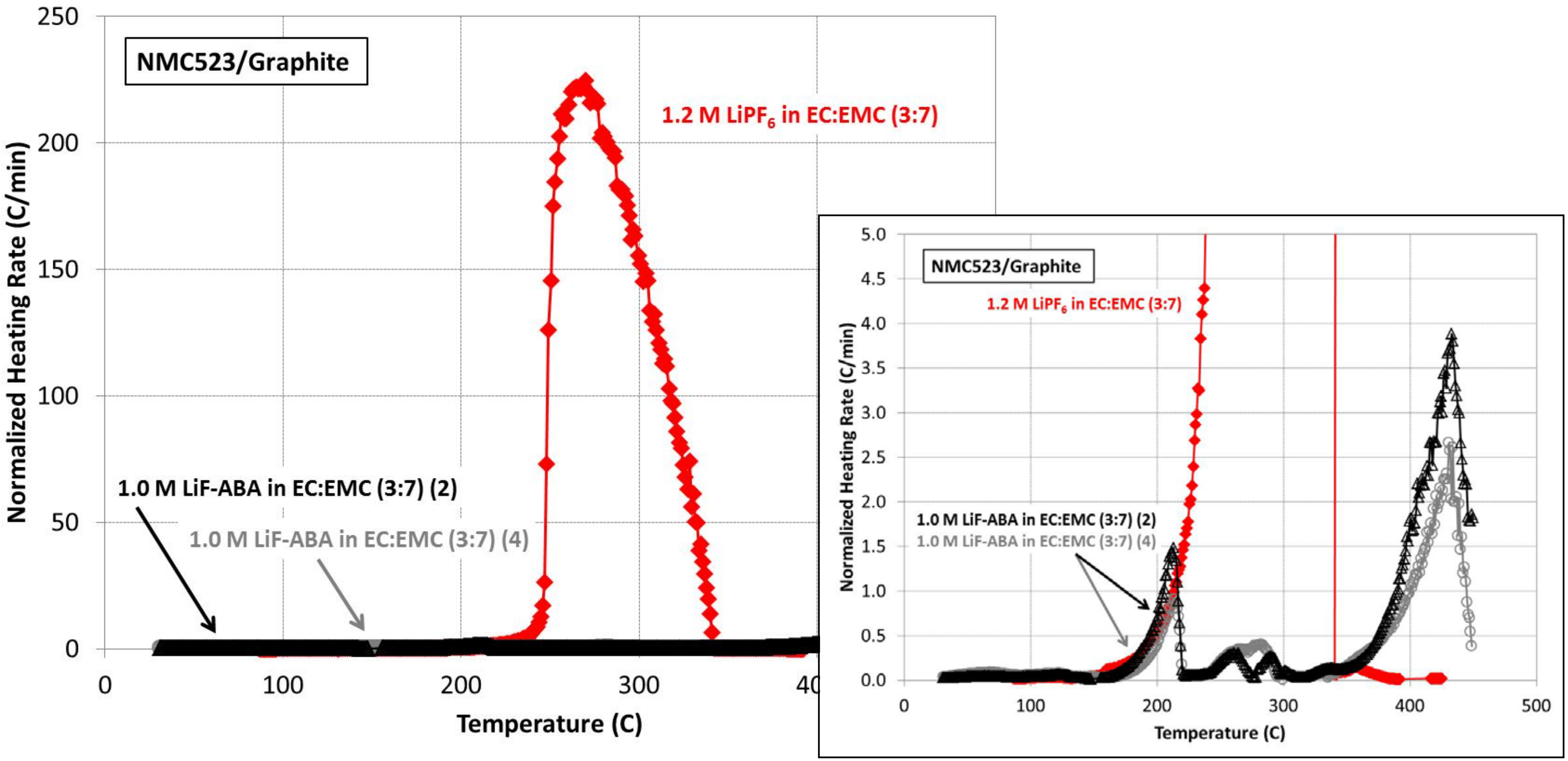
18650 Cell Performance



ABA-2A voltage stability comparable to $LiPF_6$ at 4.5 V
LiF/ABA electrochemical performance comparable to $LiPF_6$ during 18650 cell formation

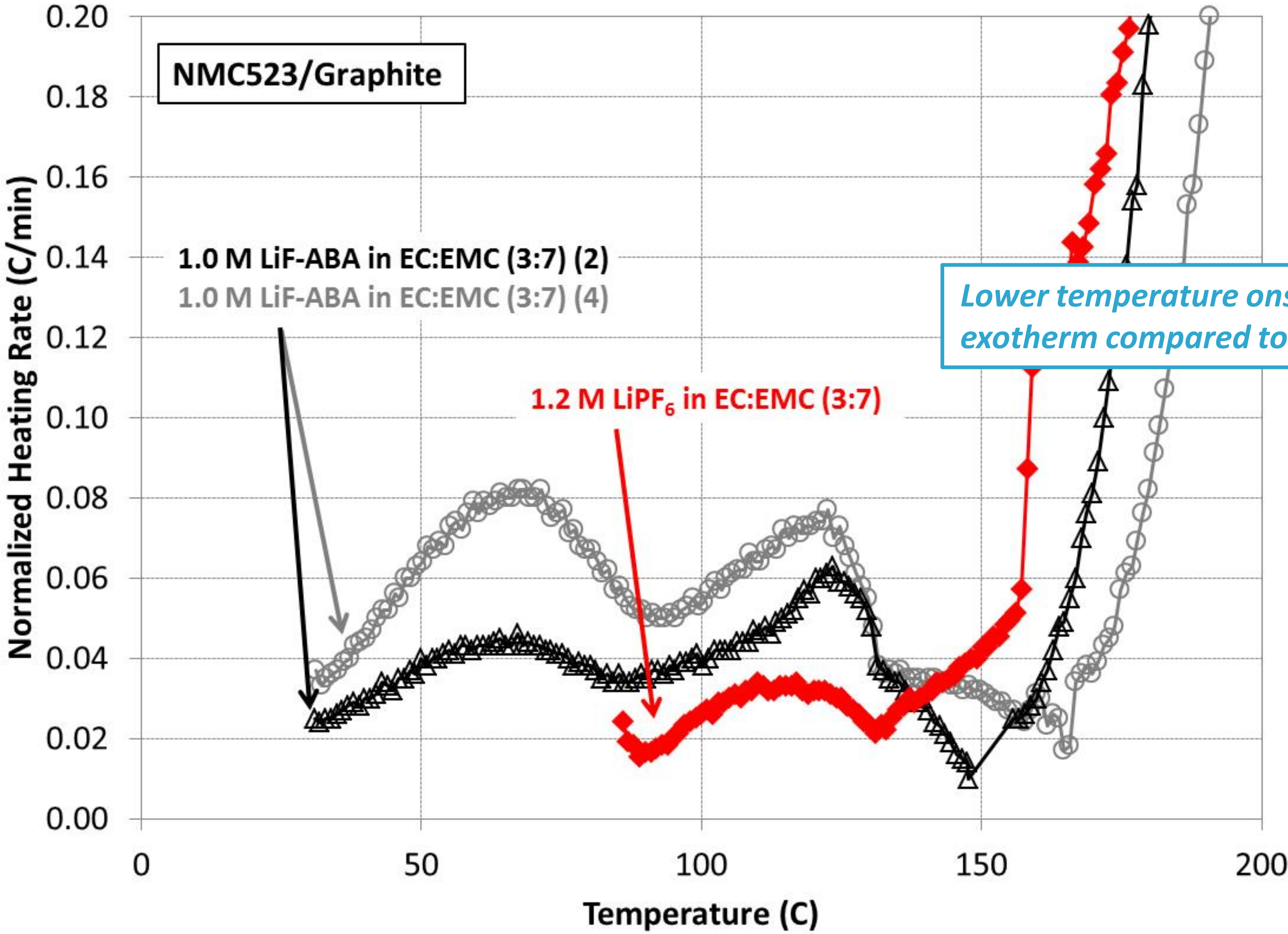
Abuse-Resilient Components

LiF/ABA Impact on Cell Thermal Runaway Response



High rate cathode thermal runaway is almost completely eliminated with LiF/ABA electrolytes

Abuse-Resilient Components



Lower temperature onset for the low rate exotherm compared to cells with $LiPF_6$ electrolyte

Need to evaluate differences between LiF/ABA and $LiPF_6$ cells at lower temperature

Collaboration and Coordination with Other Institutions

- **Si/C anode materials**
  - XG Sciences
  - ANL
- **Coated materials**
  - Physical Sciences Inc. (metal phosphates)
  - CU-Boulder and NREL (alumina ALD)
- **FRION Electrolyte Development**
  - Case Western Reserve Univ.
  - LBNL
- **SNL ABA**
  - Binrad Industries
- **Electrode Processing**
  - ANL
  - ORNL

Proposed Future Work

- Abuse tolerance of advanced materials (other Si-composite anodes, $LiNi_{0.5}Mn_{1.5}O_4$, $xLiMnO_3 \bullet (1-x)LiMO_2$)
- Complete Si/C anode characterization in cells and quantitative analysis of vent gas products
- Finalize safety performance measurements on ABA followed by scale-up at MERF (ANL)
- 18650 cell building, calorimetry, flammability, and abuse testing of cells with IL-cosolvent components to improve electrolyte resiliency to ignition
- Modeling notable improvements observed for these new materials to better understand the mechanisms that lead to improved abuse tolerance

Summary

- Fielding the most inherently safe chemistries and designs can help address the challenges in scaling up lithium-ion
- Materials choices can be made to improve the inherent safety of lithium-ion cells
- Si/C anodes contribute a larger fraction of their heat output during thermal at higher temperature (coinciding with the cathode runaway) compared to graphite
- Si/C anode/electrolyte reactivity during thermal runaway to produce gas needs to be understood
- Si/C tolerance to thermal abuse is not significantly different to graphite in NMC cells, but needs to be evaluated in larger capacity cells
- $LiMPO_4$-coated NMC shows good electrochemical performance and improved stability during thermal runawaY
- FRION-containing electrolytes at 0.5% (wt) do not inhibit ignition/flammability, but should be evaluated at greater concentrations in order to maximize impact
- ABA electrolytes have been optimized to give electrochemical performance comparable to $LiPF_6$ electrolytes in 18650 cells
- ABA electrolytes show a significant improvement in thermal runaway response of NMC cells; almost eliminating the high rate runaway reaction in some cases

Acknowledgements

- Dave Howell (DOE)
- Peter Faguy, OVT team (DOE)
- Rob Privette (XG Sciences)
- Christopher Lang (PSI)
- Ram Nagubandi (Binrad)
- Steven George (CU-Boulder)
- Jon Travis (CU-Boulder)
- Rob Tenent (NREL)
- Andy Jansen (ANL)
- Bryant Polzin (ANL)
- David Wood (ORNL)
- Greg Krumdick (ANL)
- Tom Wunsch
- Mani Nagasubramanian
- Travis Anderson
- Harry Pratt
- Leigh Anna Steele
- Bill Averill
- Pete Roth
- Josh Lamb
- Jill Langendorf
- Lorie Davis
- Scott Spangler

TECHNICAL BACK-UP SLIDES

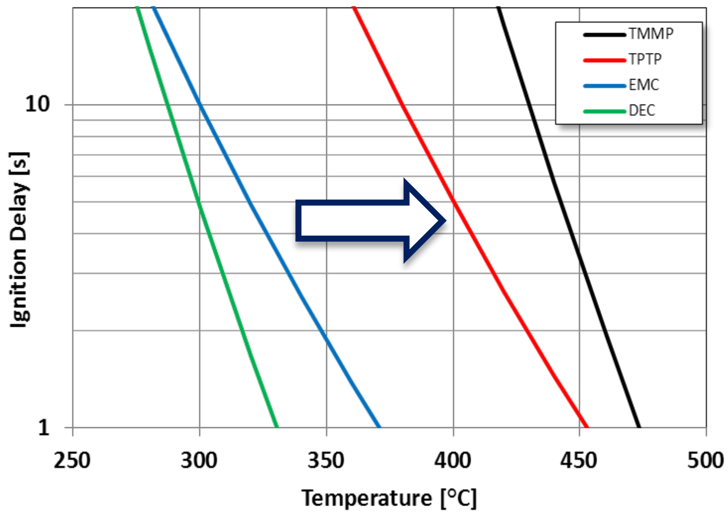
Electrolyte Flammability

- ***Tools for measuring electrolyte flammability***
  - *Conventional bulk liquid fuel flammability measurements do not accurately reflect flammability representative of a battery failure*
  - *Autoignition measurements at elevated pressures may not be relevant to battery electrolyte fuels*

Cell Vent Flammability Test (CVFT)

Electrolyte	Ignition (Y/N)	ΔTime (vent-ignition) (s)	Burn time (s)
EC:DEC (5:95 v%)	Y	1	63
EC:EMC (3:7 wt%)	Y	3	12
50% HFE-1	N	NA	NA
50% HFE-2	N	NA	NA

Autoignition in air



Tools can be applied to OVT programs to evaluate electrolyte flammability performance

FRION Electrolyte Development

Flame Retardant Ion (FRION) Electrolytes

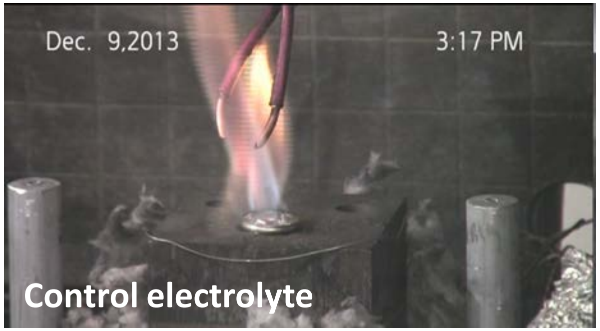
- Designed to inhibit electrolyte flammability from the BATT program

Cell Vent Flammability Testing (CVFT) FRION-containing electrolytes:

- 1.0 M $LiPF_6$ in EC:DEC (1:2) + 1% VC + 0.5% FRION (FRION)
- 1.0 M $LiPF_6$ in EC:DEC + 1% VC (Control)
- 5 g electrolyte sealed in an 18650 can and heated to vent
- Vented directly into a spark ignition source

Results:

- All cells vent at ~200 C
- All electrolytes ignite and burn with variable degrees sustained fire/reignition



Additional electrolytes of increased FRION concentration considered for future testing and analysis