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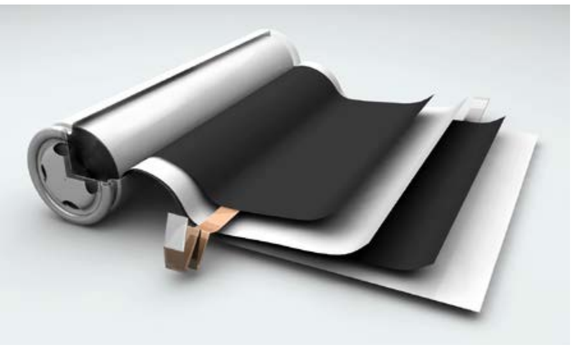
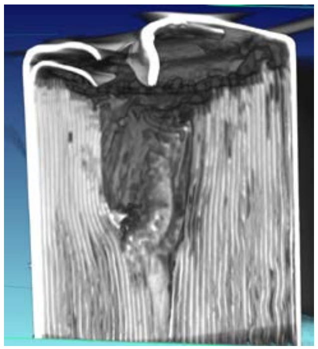

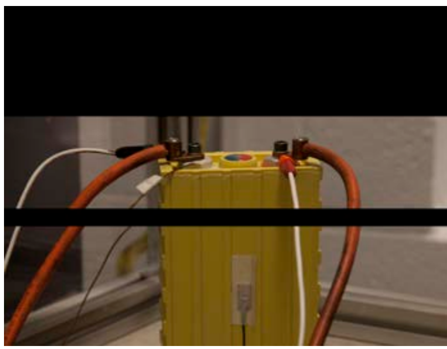

Abuse Tolerance Improvements

Christopher J. Orendorff

Technical Staff

ES036

2013 Energy Storage Annual Merit Review

Washington, D. C. 5/14/2013

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Overview

Timeline

- **Start Date: Oct. 2007**
- **End date: Oct. 2013**
- **Percent complete: >90%**

Budget

- **FY13 Funding: $1.0M**
  - Abuse Evaluation - $500K
  - Cell Prototyping - $300K
  - Electrolyte Development - $200K
- **FY12 Funding: $1.0M**
- **FY11 Funding: $1.35M**

Barriers

- **Barriers addressed**
  - Develop intrinsically abuse tolerant Li-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 & sufficient quantities of materials to determine reproducibility of results

Partners

- **ANL, INL, NREL, JPL, ORNL, CU-Boulder**
- **A123, Daikin America**

Relevance and Objectives

Developing inherently safe lithium-ion cell chemistries and systems

- **Evaluate Abuse Tolerance Improvements**
  - Improve overcharge 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
- **Electrolyte Development**
  - Identify degradation mechanisms of gas and heat-producing reactions in lithium-ion cells
  - Develop thermally stable electrolyte salts and solvents that improve lithium-ion safety
- **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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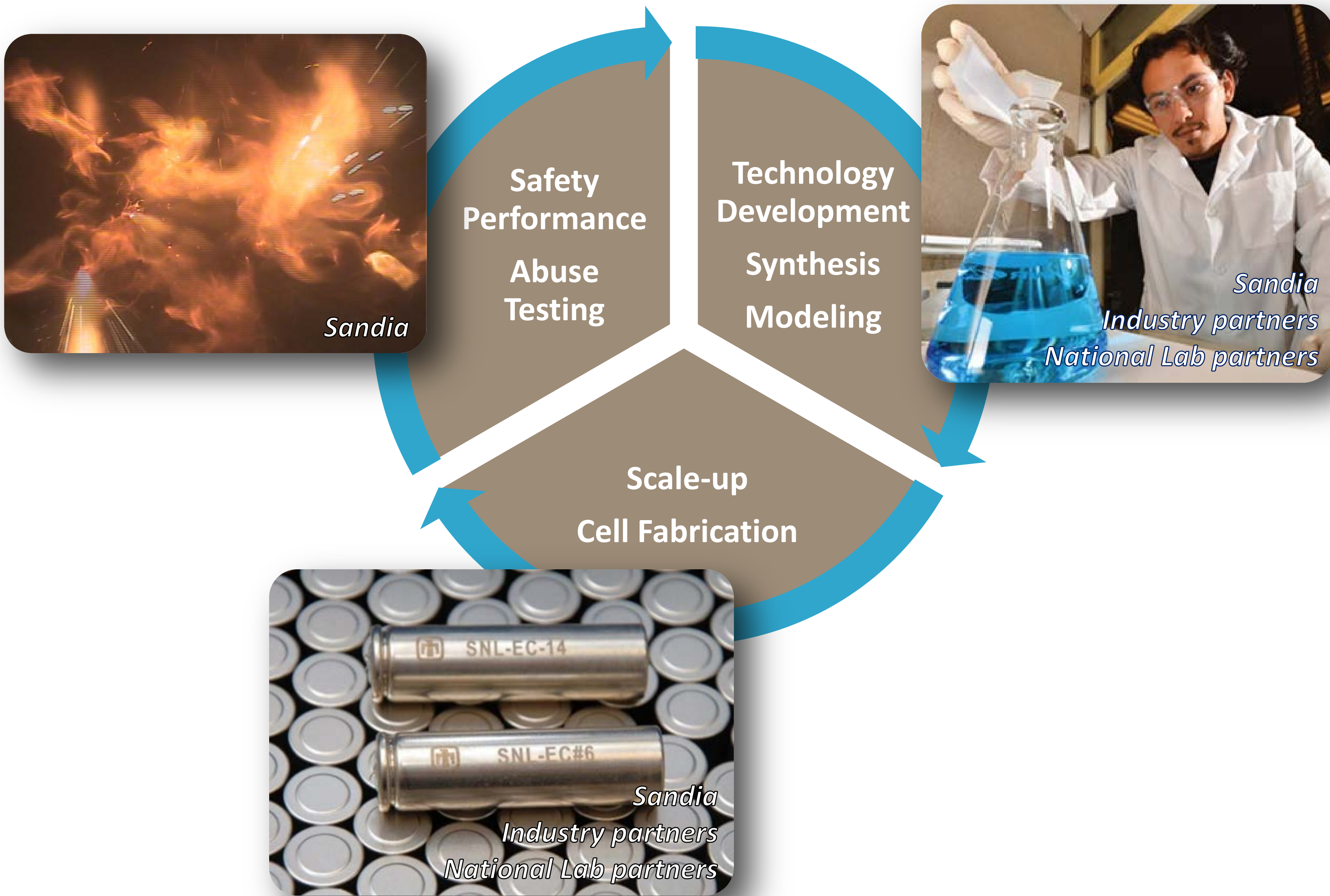
Demonstrate improved abuse tolerant cells and report to DOE and the battery community

Milestone	Status
RS2: Complete safety performance evaluation of RS2	
INL Ph: Flammability measurements on phosphazene electrolytes	
SNL ABA: Synthesis of lot -2 of ABA-1 (200g), electrochemical/coin cell characterization	
SNL ABA: Anode SEI stabilization/18650 cell building and abuse testing	Q3/Q4
SNL IL: Synthesis of candidate IL and determine electrochemical stability	
SNL IL: Electrolyte formulation/optimization	Q3
SNL IL: Abuse testing, flammability, and calorimetry measurements	Q4
PSI: Scale up and deliver 2 kg $LiMPO_4$-coated NMC	
PSI: Cell building, abuse testing, and calorimetry of LiMPO4-coated NMC	Q3/Q4
ALD: initial calorimetry measurements on ALD-coated NMC111	
ALD: evaluate coatings on NMC523, optimize coatings for safety performance	Q3
C.W. FRION: Deliver FRION additive to ANL ; ANL prepare electrolytes	
C.W. FRION: Cell building, abuse testing, flammability, and calorimetry measurements	Q3/Q4

Approach



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Safety
Performance
Abuse
Testing
Technology
Development
Synthesis
Modeling
Sandia
Industry partners
National Lab partners
Scale-up
Cell Fabrication
SNL-EC-14
SNL-EC#6
Sandia
Industry partners
National Lab partners

Technical Accomplishments/ Progress/Results

Abuse Tolerance Improvements:

- **RS2 Overcharge Shuttle (ANL):**
  - Overcharge abuse testing shows a significant improvement in abuse tolerance at 1C rate relative to cells without the shuttle
  - Demonstration of baseline performance retention post-test
- **Phosphazene Electrolyte (INL):**
  - Completed flammability measurement on the 3% phosphazene electrolytes. Results suggest that at 3%, PhIL-2 additive shows some improvement in flammability compared to the control electrolyte (EC:EMC (2:8)).
- **Metal Phosphate-Coated Cathodes (PSI):**
  - Delivered 2 kg of LiMPO4-coated NMC
  - Cell building and testing is in progress
- **ALD Al_2O_3-Coated Cathodes (NREL):**
  - Completed ALD coating on graphite/NMC111 couples
  - Results show that a 1 nm alumina coating on graphite improves the stability of the anode SEI
  - Alumina coatings on NMC that are ~0.5 nm thick have no measureable impact on the thermal stability of NMC

Technical Accomplishments/ Progress/Results (continued)

Cell Fabrication/Electrode Processing:

- **Cell builds to support ABR for FY13 (Toda NMC523 positive electrode, CP A10 graphite negative electrode)**
  - INL Phosphazene
  - 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)

- **Standardization of electrode formulation across the ABR Program**
  - Toda NMC523 positive electrode, CP A10 graphite negative electrode
  - NMC523 electrodes evaluated through the materials screening process at ANL

Thermally Stable Electrolyte Development

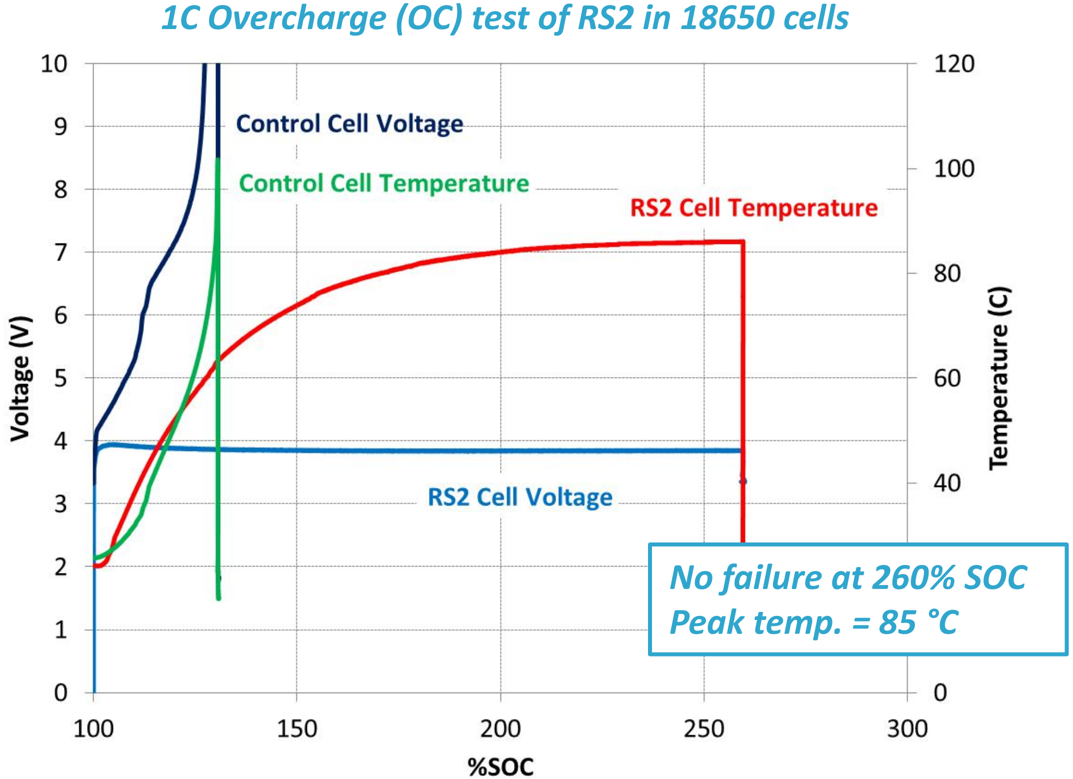
- **LiF/ABA Electrolytes**
  - Improved synthesis of LiF/ABA (scalable process)
  - Demonstrated improved anode performance and SEI formation with new LiF/ABA electrolytes

- **Ionic Liquid Electrolytes**
  - Synthesis of IL-3 with improved electrochemical stability over earlier candidates
  - Developed electrolyte formulations using IL-3 that show good performance up to 40% IL cosolvent

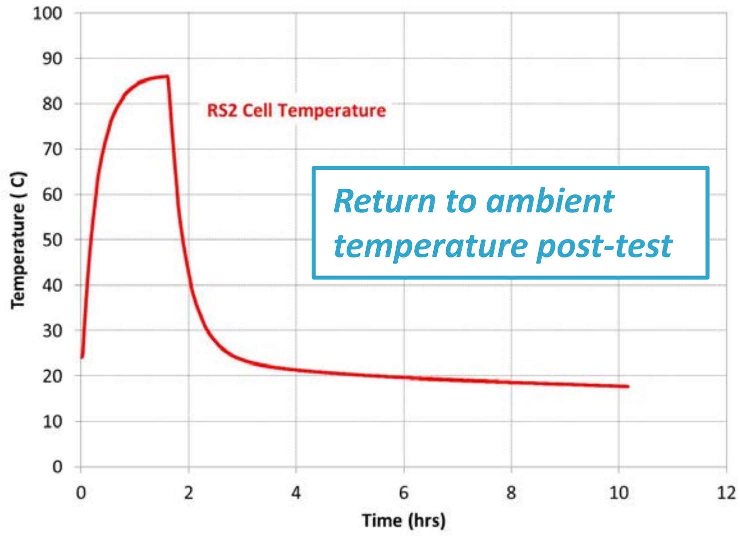
Challenges with Inherent Cell Safety

G. Nagasubramanian et al. J. Power Sources 196 (2011) 8604-8609
G. Nagasubramanian et al. (2013) http://dx.doi.org/10.1016/j.electacta.2012.09.065
Chen, Z. et al. Energy Environ. Sci. 4 (2011) 4023-4030
C. J. Orendorff et al. Adv. Energy Mater 3 (2013) 314-320

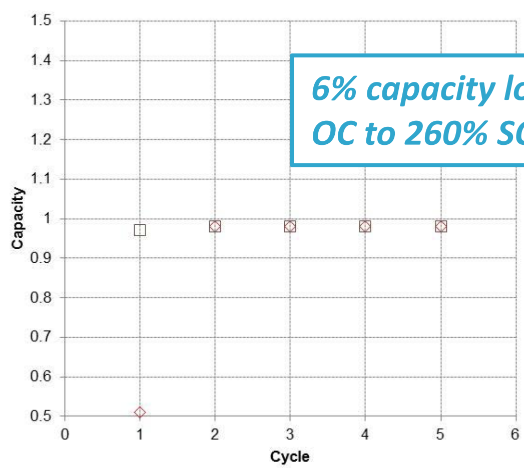
Improved Overcharge Abuse Tolerance



No failure at 260% SOC
Peak temp. = 85 °C



Return to ambient temperature post-test



6% capacity loss after OC to 260% SOC

Demonstrates not only improved abuse tolerance, but retention of functionality

Coatings to Mitigate Energetic Thermal Runaway

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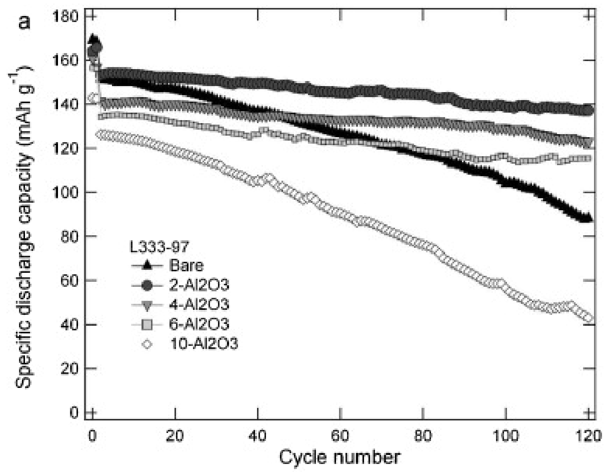
Coating parameters

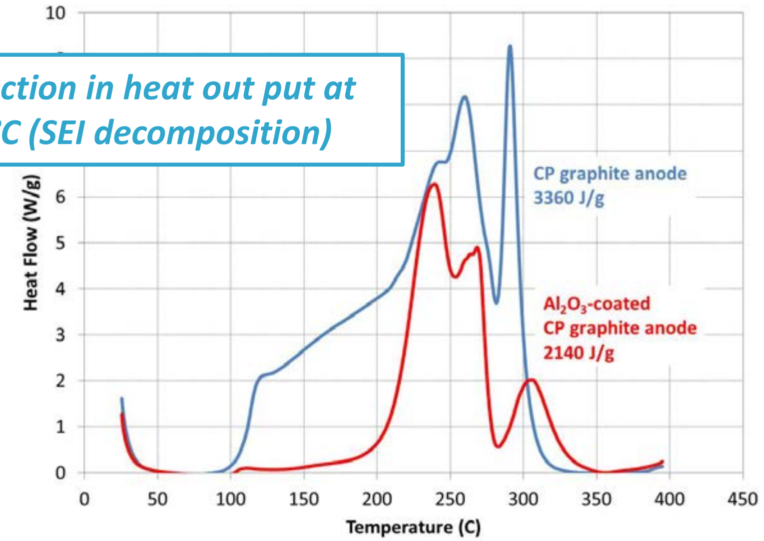
Electrode	# of ALD cycles	Al_2O_3 thickness (nm)
Graphite anode	**5**	**1**
NMC111	**2**	**0.4**



Riley, L. A. et al. J. Power Sources 196 (2011) 3317-3324

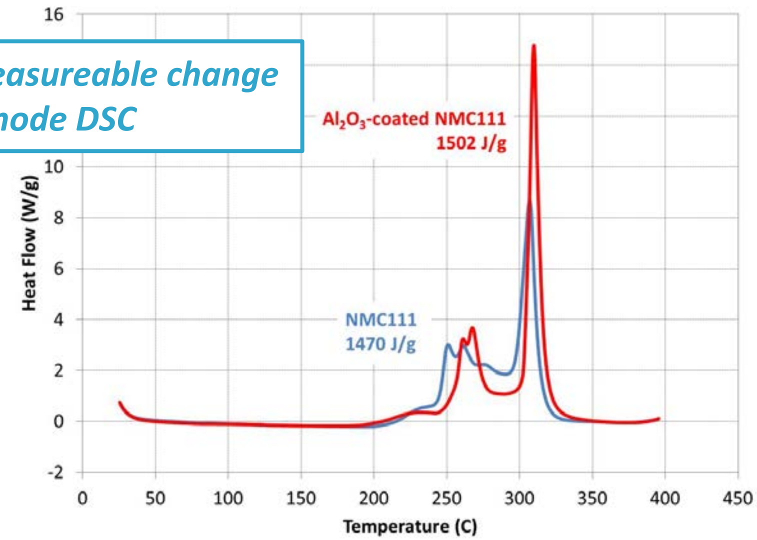
Coated anodes show notable improvements in thermal stability

Anode DSC



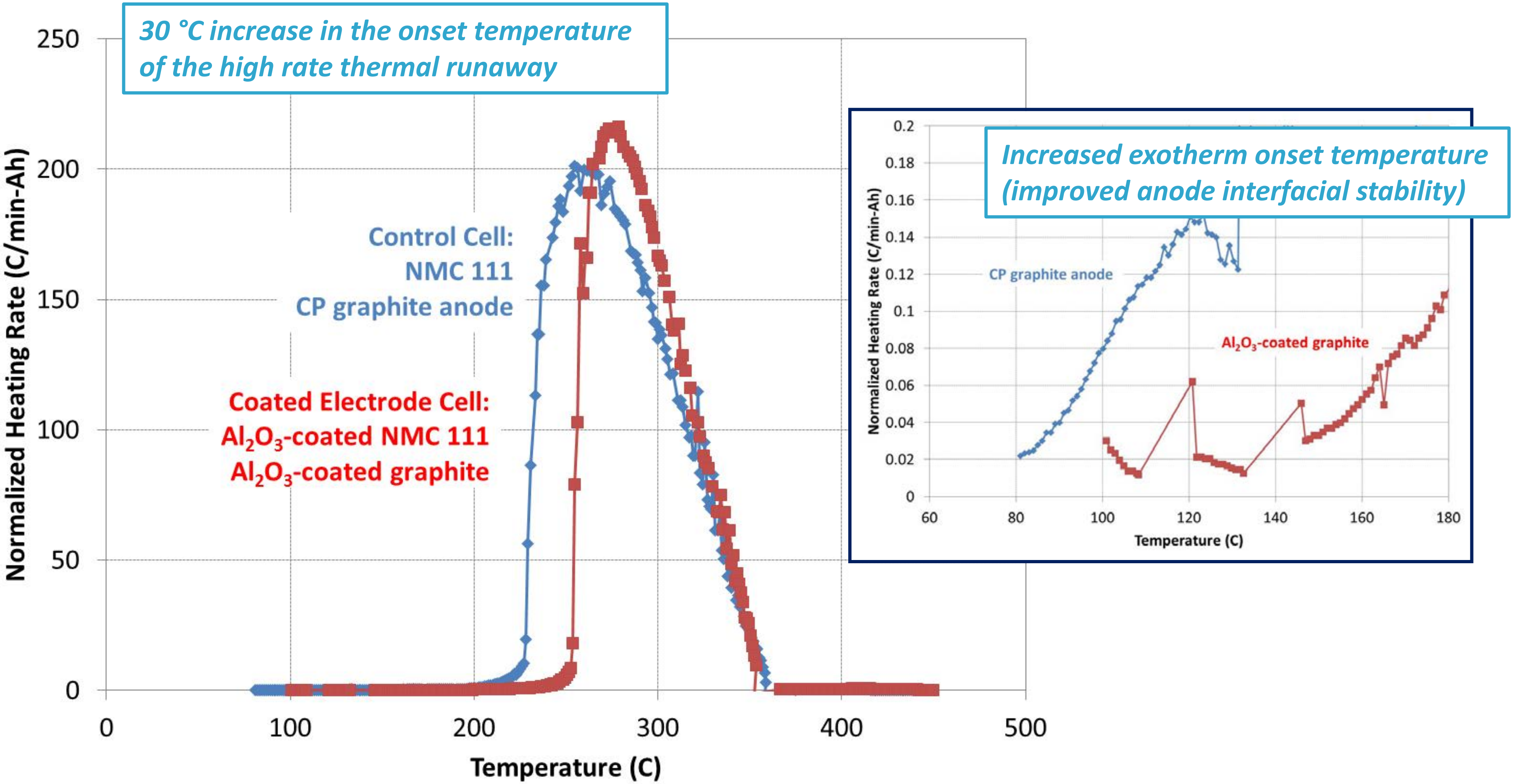
Reduction in heat out put at 100 °C (SEI decomposition)

Cathode DSC



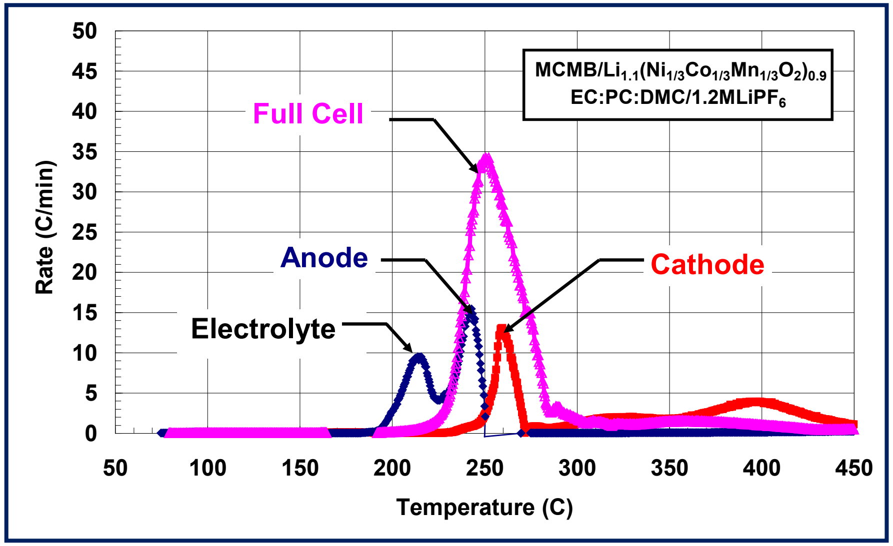
No measureable change in cathode DSC

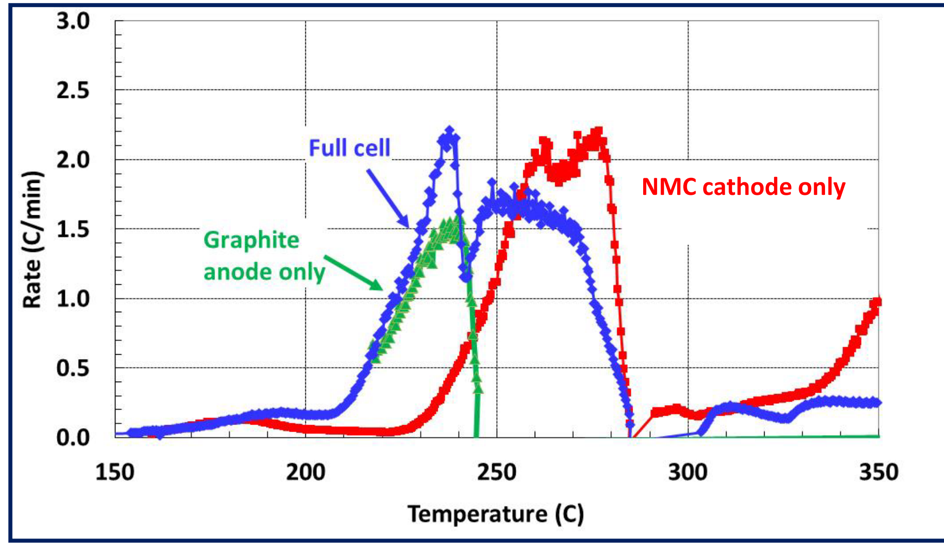
Alumina-ALD Coatings



Observed improved onset temperatures for both the low rate exotherm and the high rate runaway reactions, however, kinetics of the high rate reaction are unchanged

Positive and Negative Electrode Contributions to Thermal Runaway



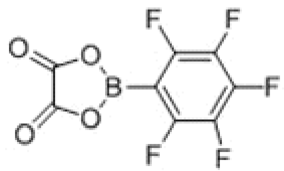


Graphite anodes contribute to both the onset of a cell exotherm at low temperature (< 100 °C) and initiation of the high rate runaway process in NMC cells

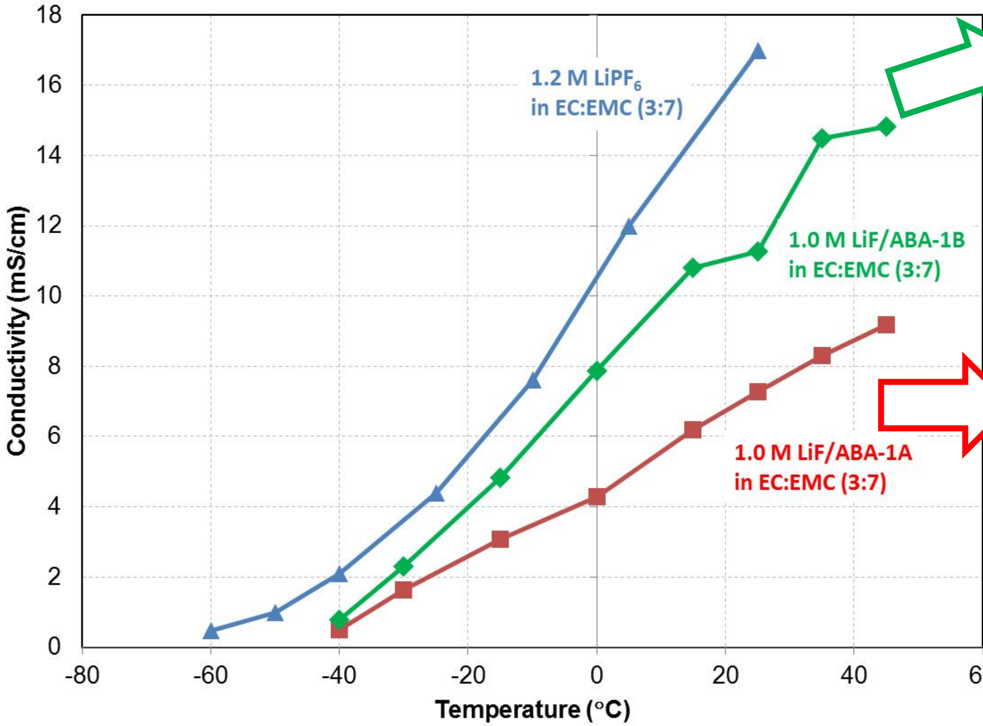
Increasing onset temperatures for both the low rate exotherm and high rate runaway in coated electrode cells suggests improved stability of the coated anode and a more stable SEI

Thermally Stable Electrolyte Salts

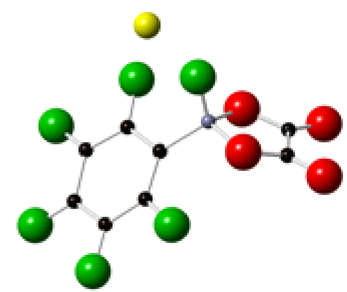
Electrolytes based on LiF and anion binding agents (ABAs)



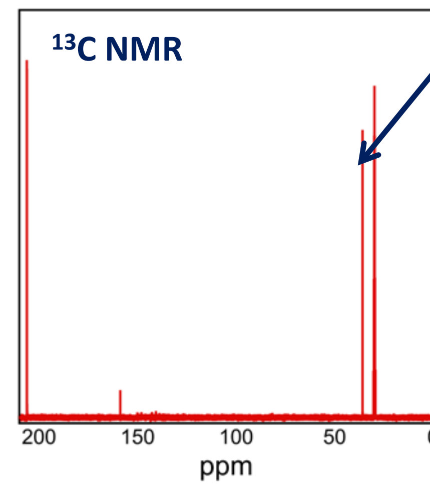
Perfluorophenyloxaltoborate (ABA-1)

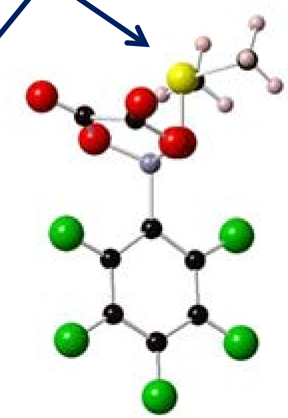


Free LiF-ABA



DMSO coordinated to ABA-1A

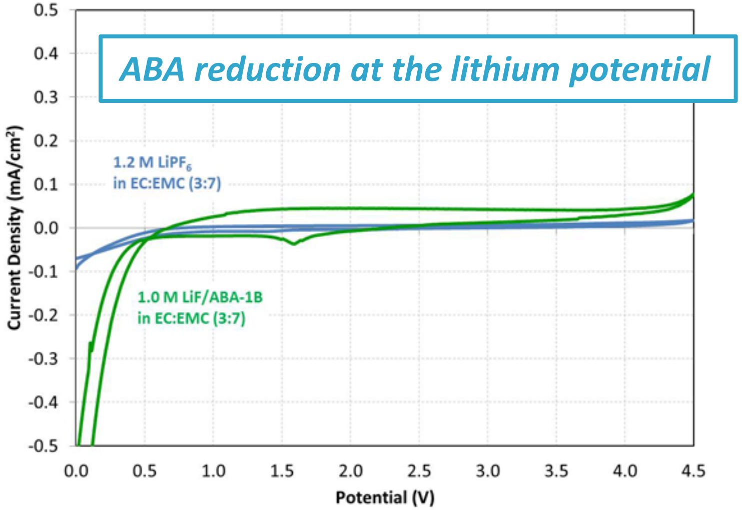


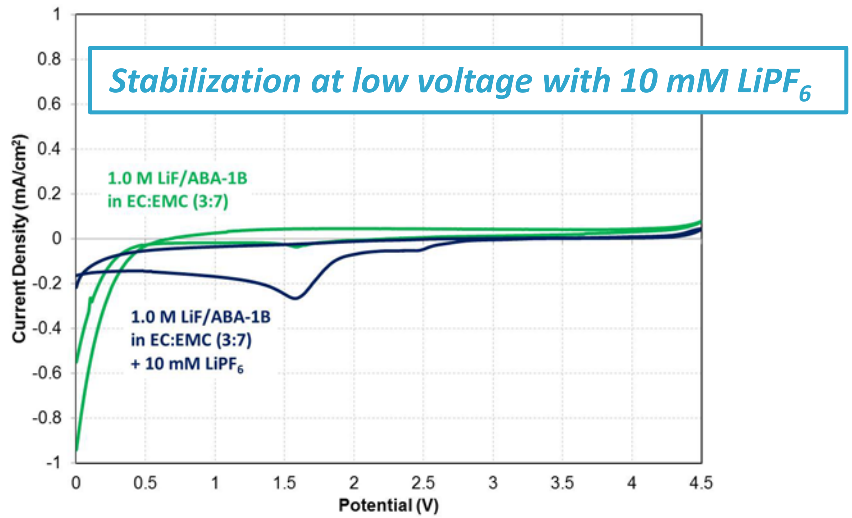


Improved performance of new ABA-based electrolytes

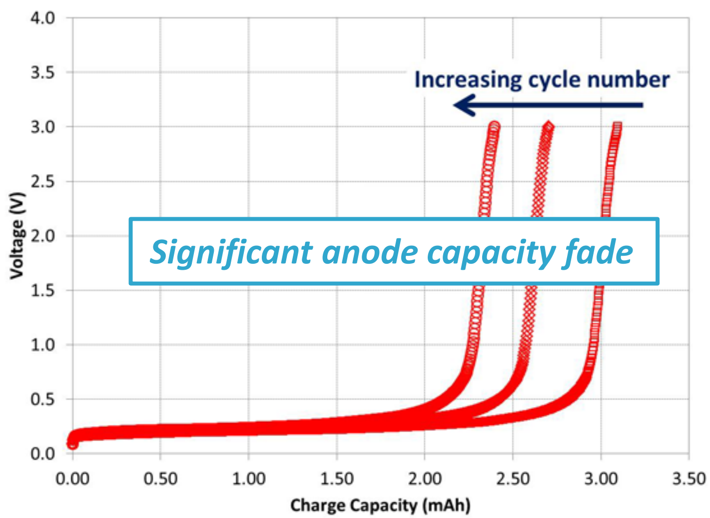
ABA Performance Improvements

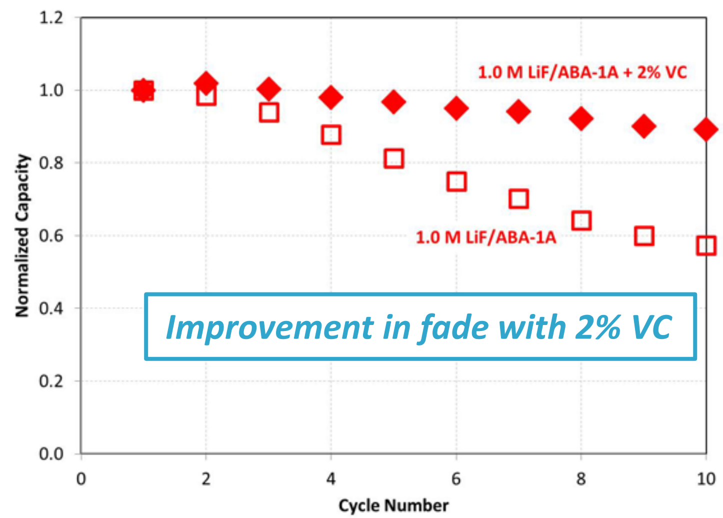
Electrochemical stability vs. lithium





Cell performance





Calorimetry of Cathodes + ABA

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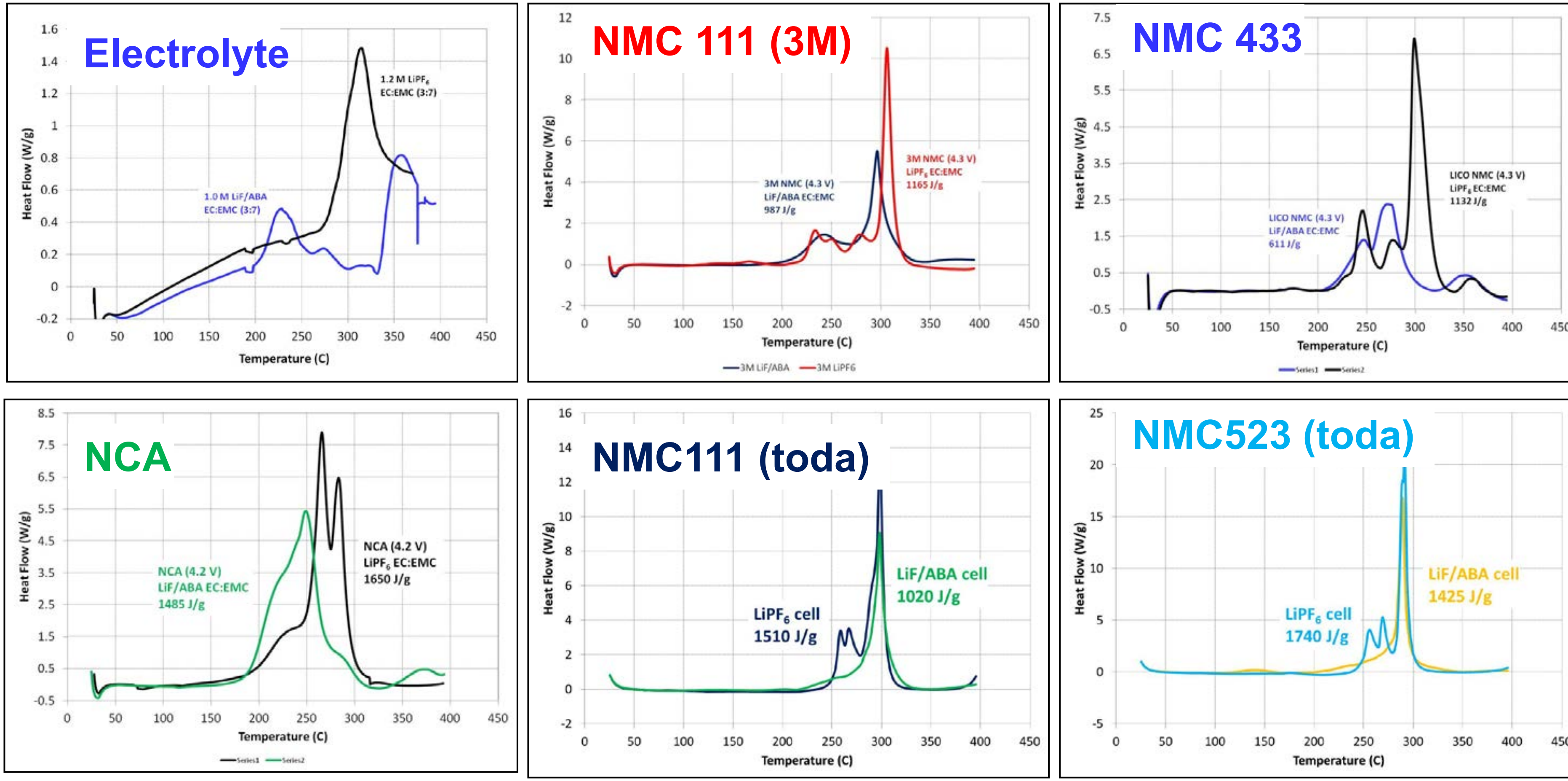


All cathodes show some reduction in specific heat generated with ABA electrolytes compared to $LiPF_6$

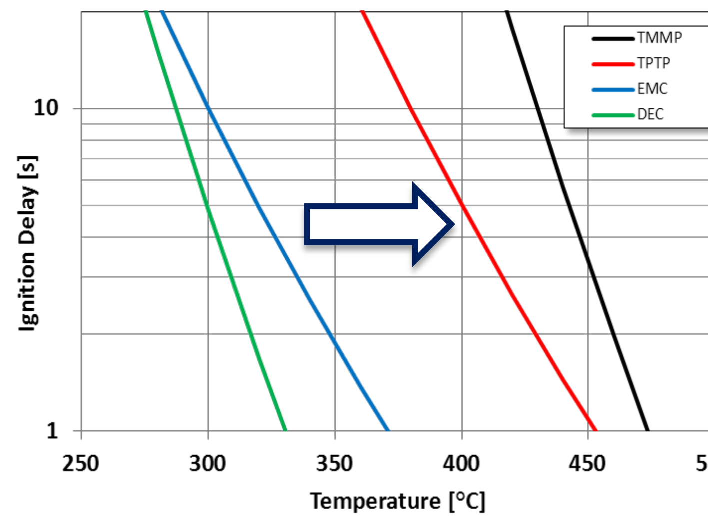
Electrolyte Flammability

- ***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*

Flammability of venting cells

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

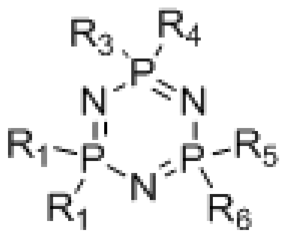
Autoignition in air



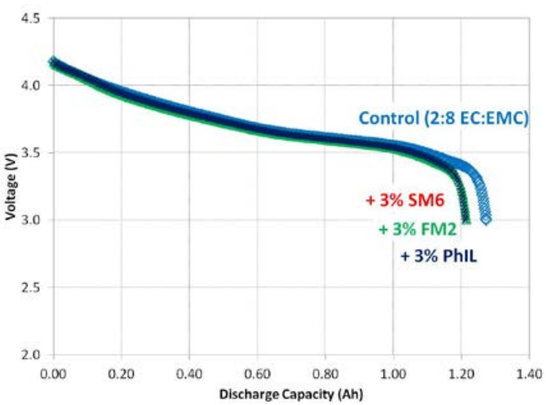
Tools can be applied to ABR electrolyte development efforts to determine flammability behavior of new electrolytes

Flammability tools developed under Sandia LDRD Program

INL Phosphazene Electrolyte



SM-6: ester substituted
FM-2: perfluorinated SM analogue
PhIL-2: ionic liquid analogue



From 2012 AMR

Flammability measurements:

Electrolyte	Ignition (Y/N)	ΔTime (vent-ignition) (s)	Burn time (s)	Vent temperature (C)
Baseline(1)	Y	20	90	211
Baseline(2)	Y	<1	138	213
SM-6(1)	Y	1	156	213
SM-6(2)	Y	1	284	213
FM-2(1)	Y	7	140	217
FM-2(2)	Y	<1	209	220
PhIL-2(1)	Y	12	8	215
PhIL-2(2)	Y	Vent not observed	12/17	215

Electrolytes with 3% PhIL ignite, but show a reduction in the total burn time

Ionic Liquid Electrolyte Development

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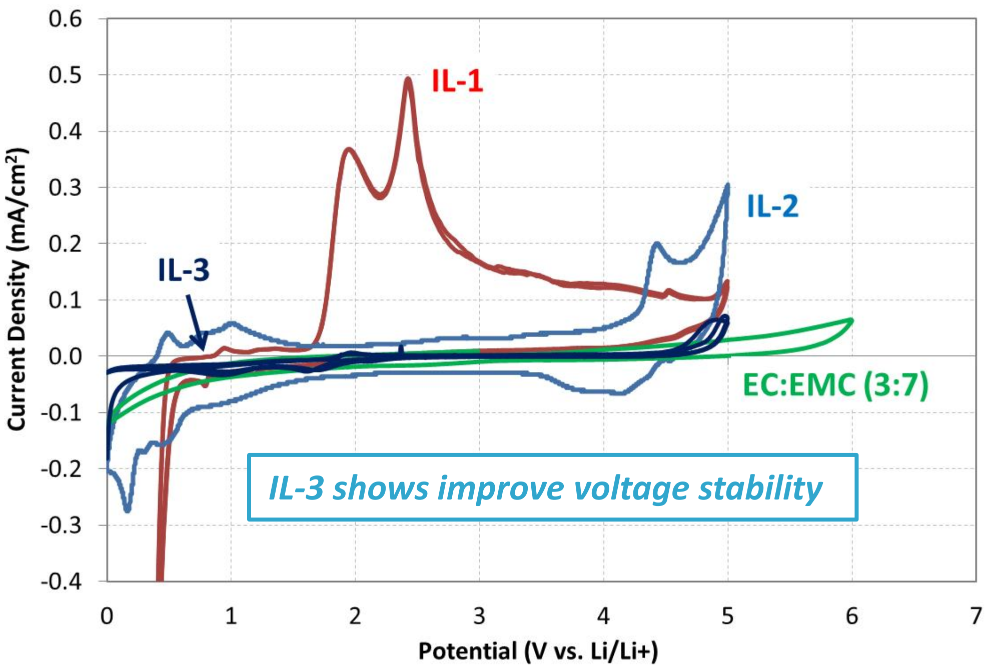
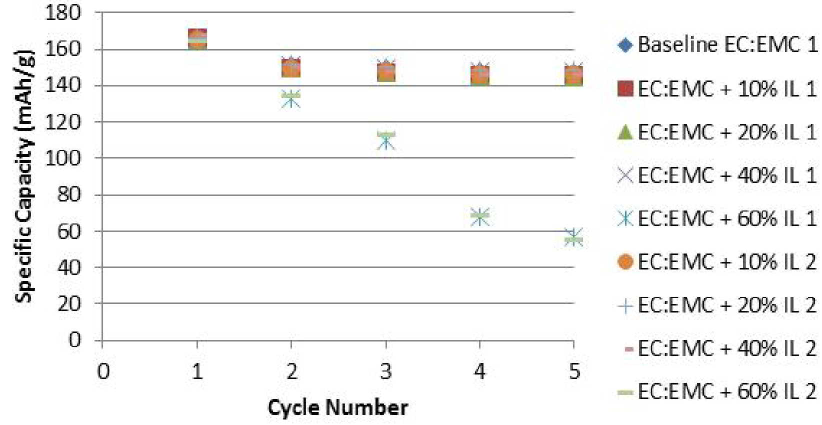
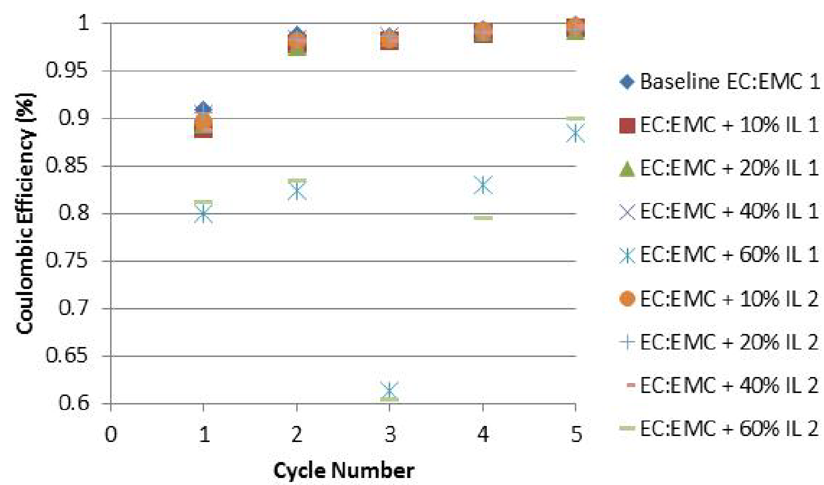
Electrochemical stability vs. lithium



Specific capacity



Coulombic efficiency



Good electrochemical performance of IL-3 18650 cell builds, performance testing, and abuse testing underway

No measureable change in initial performance up to 40% IL cosolvent

Collaboration and Coordination with Other Institutions

- **RS2 Overcharge Shuttle**
  - ANL (development, scale up)
  - A123 (cell fab.)
- **Coated materials**
  - Physical Sciences Inc. (metal phosphates)
  - CU-Boulder and NREL (alumina ALD)
- **Electrolyte Development**
  - INL (phosphazene development)
  - JPL (low temperature electrolytes)
- **Electrode Processing (ABR standardization effort)**
  - ANL
  - ORNL

Proposed Future Work

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- Abuse tolerance of advanced materials (Si-composite anodes, $LiNi_{0.5}Mn_{1.5}O_4$, $xLiMnO_3 \bullet (1-x)LiMO_2$)
- Cell evaluation of coated cathodes both precipitation coated materials ($M_x(PO_4)_y$-coated NMC 111 and Al_2O_3-coated $xLiMnO_3 \bullet (1-x)LiMO_2$) and ALD coated electrodes (Al_2O_3-coated NMC 111 and NMC 523)
- 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 cosolvents
- 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
- Overcharge shuttle additive (RS2) provides significant overcharge protection from catastrophic failure and also retention of functionality (minimal capacity loss)
- Preliminary results for alumina-coated electrodes show benefits to anode stability with ~1 nm coatings
- LiF/ABA electrochemical stability and performance issues related to SEI formation have been improved with new electrolyte formulations and improved ABAs
- INL PhIL-2 phosphazene additive shows an improvement in flammability performance even at 3% additive
- Development of electrochemically viable ionic liquid (IL)-based electrolytes that are high purity. Candidate electrolytes show no negative impact on initial electrochemical performance with up to 40% IL cosolvent

Acknowledgements

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