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Abuse Tolerance Improvements

ES036

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Overview

Timeline

- Start Date: Oct. 2007
- End date: Oct. 2014
- Percent complete: <70%

Budget

- FY12 Funding: $1.0M
    - Abuse Evaluation: $500K
    - Cell Prototyping: $300K
    - Electrolyte Development: $200k
- FY11 Funding: $1.35M
- FY10 Funding: $900K
- Funding for FY13: TBD

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, BNL
- A123, Binrad Industries

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Relevance and Objectives

Developing inherently safe lithium-ion cell chemistries and systems

- **Evaluate Abuse Tolerance Improvements**
  - Improve overcharge abuse tolerance in lithium-ion cells
  - 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
  - Develop experimental techniques to better understand, characterize and mitigate internal shorting field failures
- **Electrolyte Development**
  - Identify degradation mechanisms of gas and heat-producing reactions in lithium-ion cells
  - 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

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

Milestone	Status
RS2:Cell fab using RS2 shuttle (SNL & A123)	
RS2:Calorimetry measurements, balance, abuse measurements	
RS2: tested cells to ANL post test facility for analysis	Q4
INL Ph: phosphazene electrolytes receive & cells built (SNL)	
INL Ph: Initial ARC measurements on each electrolyte	
INL Ph: Flammability measurements on phosphazene electrolytes	Q3
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 electrolytes for Li-ion (2)	
SNL IL: Electrolyte formulation/optimization	Q3
PSI: coated M3(PO4)x on Toda NMC (111)/preliminary characterization	
PSI: Scale up and deliver 2 kg M3(PO4)x-coated NMC to SNL/cell building/abuse testing	Q3/Q4
NREL ALD: ALD coated 3 pairs of 18650 electrodes (CP A10 and Toda NMC 111)	
NREL ALD: SNL to build cells/calorimetry and abuse measurements	Q3

Approach

Technology Development
Materials Characterization
Modeling

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ABR Lab partners
Industry partners

Scale up
Cell Fabrication

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ABR Lab partners
Industry partners

Abuse Tolerance Characterization

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Technical Accomplishments/ Progress/Results

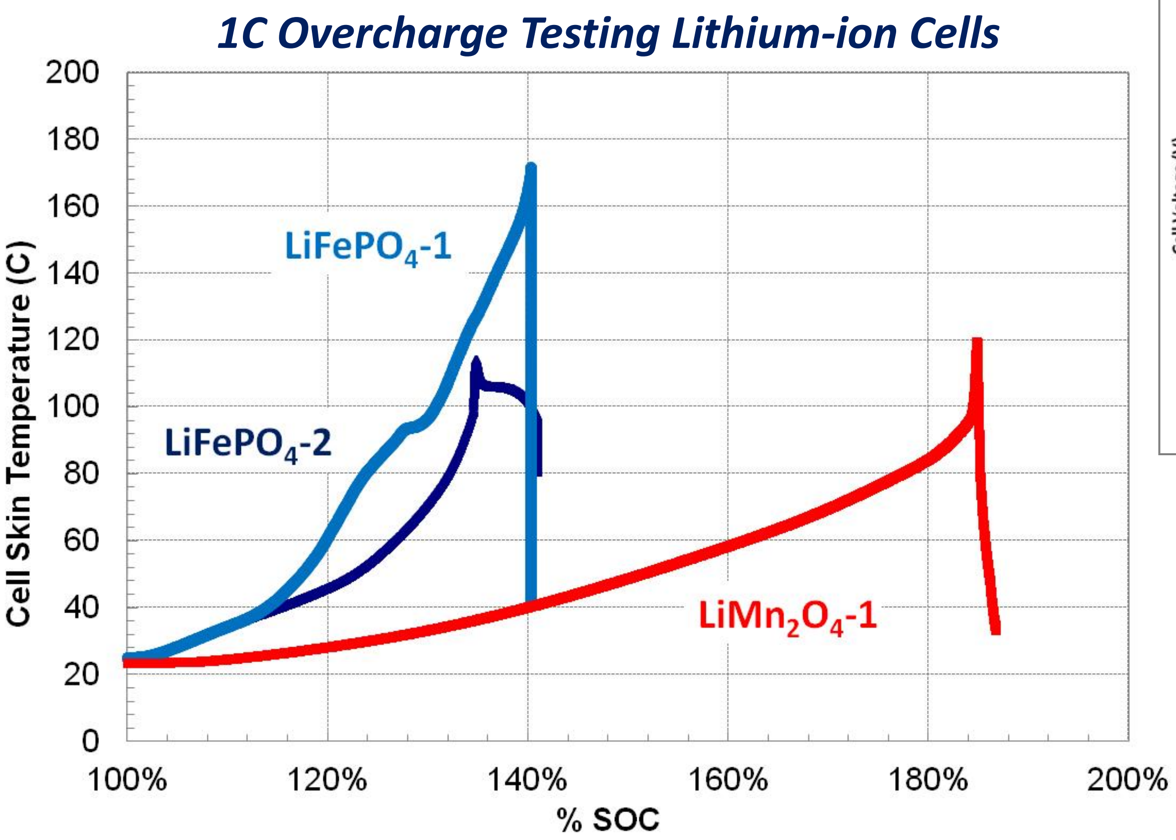
- **Abuse Tolerance Improvements:**
  - RS2 Overcharge Shuttle (ANL):
    - *Isothermal calorimetry measurements on LFP cells with the shuttle give quantitative heat output data during activation*
    - *Accelerating rate calorimetry shows no change in thermal stability in LFP cells with and without the shuttle*
    - *Cell cycling shows the functionality of the shuttle for cell balancing*
    - *Overcharge abuse testing shows a significant improvement in abuse tolerance at 1C rate relative to cells without the shuttle*
  - Phosphazene Electrolyte (INL):
    - *Preliminary accelerating rate calorimetry results show no significant difference in phosphazene cells compared to the control*
    - *Ignition/Flammability experiments are in progress*
  - Metal Phosphate-Coated Cathodes (PSI):
    - *Coatings prepared on Toda NMC111 show comparable performance to the uncoated cathode (specific capacity, fade, etc.)*
    - *DSC measurements show stabilization in the degradation temperature, consistent with observations made for AlF_3 and Al_2O_3 coated cathodes (ANL)*
    - *Cell measurements of performance and safety in Q3 FY12*
  - ALD Al_2O_3-Coated Cathodes (NREL):
    - *Electrodes ALD coated Q2*

Technical Accomplishments/ Progress/Results (continued)

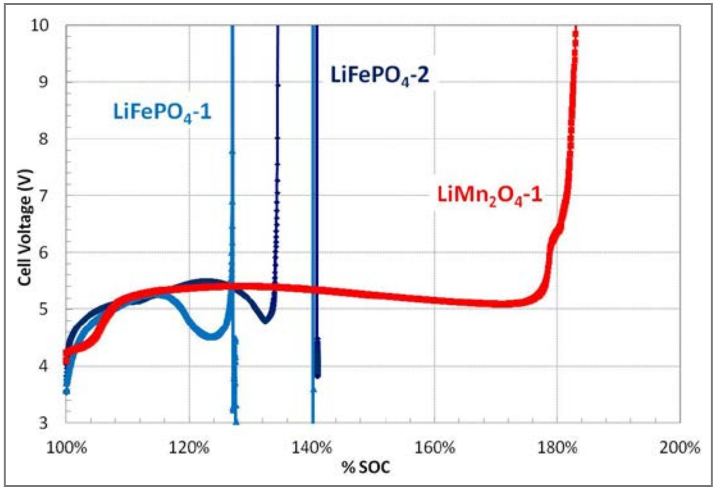
- **Cell Fabrication/Electrode Processing:**
  - Cell builds to support ABR for FY12 (Toda NMC111 positive electrode, CP A10 graphite negative electrode)
    - *ANL RS2 Overcharge Shuttle (Q1, SNL 20 cells/A123 36 cells)*
    - *INL Phosphazene (Q1, 32 cells)*
    - *JPL Electrolyte (Q3, 24 cells)*
    - *SNL ABA Electrolyte (Q3, 12 cells)*
    - *SNL Ionic Liquid Electrolyte (Q4 12 cells)*
    - *Physical Sciences Inc. $M_x(PO_4)_y$-coated NMC (Q3, 12 cells)*
    - *NREL Al_2O_3-coated NMC/ALD (Q3 6 cells, Q4 12 cells)*
  - Standardization of electrode formulation across the ABR Program
    - *Toda NMC523 positive electrode, CP A10 graphite negative electrode*
    - *Distribution of first NMC523 processed electrodes to ANL and ORNL*

- **Thermally Stable Electrolyte Development**
  - LiF/ABA Electrolytes
    - *Scale up of ABA1, synthesis of new ABA molecules (ABA2 and ABA3)*
    - *Electrolyte show reduced heat generation of both 111 and 523 NMC cathodes*
    - *ABAs do show some degradation at high voltage*
  - Ionic Liquid Electrolytes
    - *Synthesis of two candidate ILs*
    - *Improved low voltage stability of ionic liquid cations*

Overcharge Abuse Tolerance



E.P. Roth, DOE Annual Merit Review 2008



Cathode	x @ 100% SOC	Onset (SOC)
Li_xFePO_4	0	100%
$Li_xMn_2O_4$	0.1	110%
NCA	0.36	125%
NMC (111)	0.48	150%
Li_xCoO_2	0.5	160%

$LiFePO_4$ is inherently intolerant of overcharge because it is completely delithiated at 100%SOC

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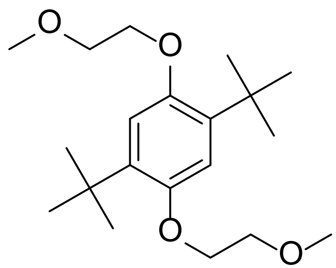
RS2 Overcharge Shuttle

Collaboration with ANL (Khalil Amine, Greg Krumdick) and A123 (Leslie Pinnell, Tony Gozdz)

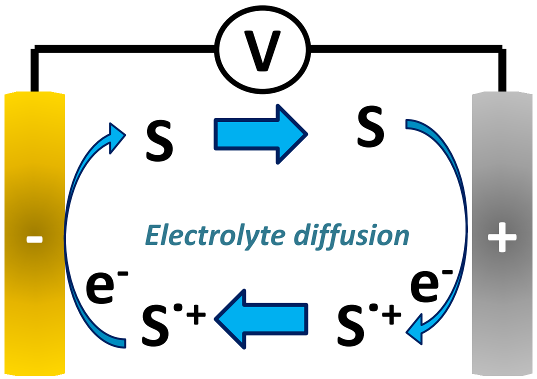
ANL RS2



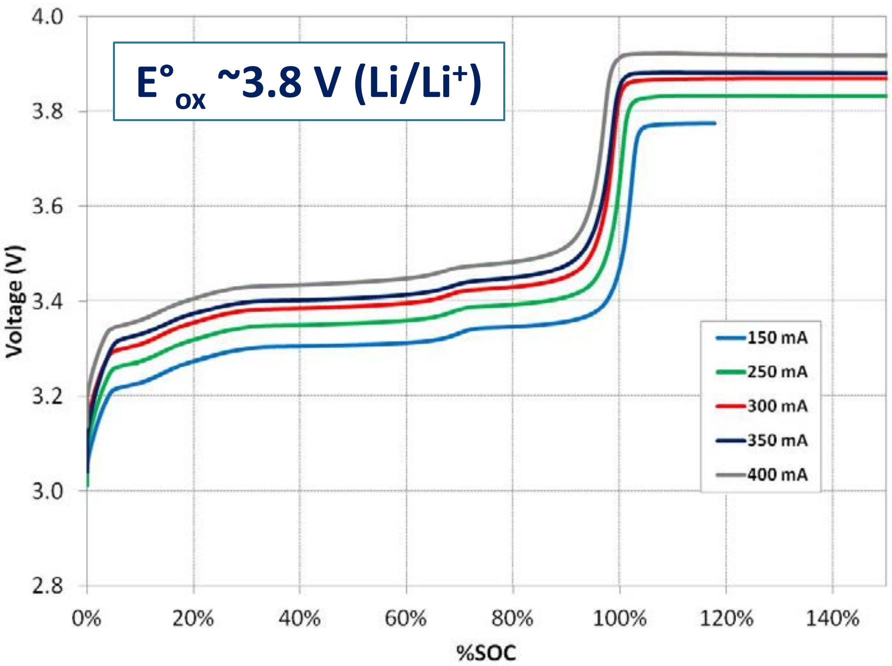
(1,4-Bis(2-methoxyethoxy)-2,5-di-*tert*-butylbenzene)

LFP 18650 Cells
1.2 M $LiPF_6$ in EC:EMC (3:7)
+ 0.2 M RS2

How the shuttle principle works:



18650 Cell Charging



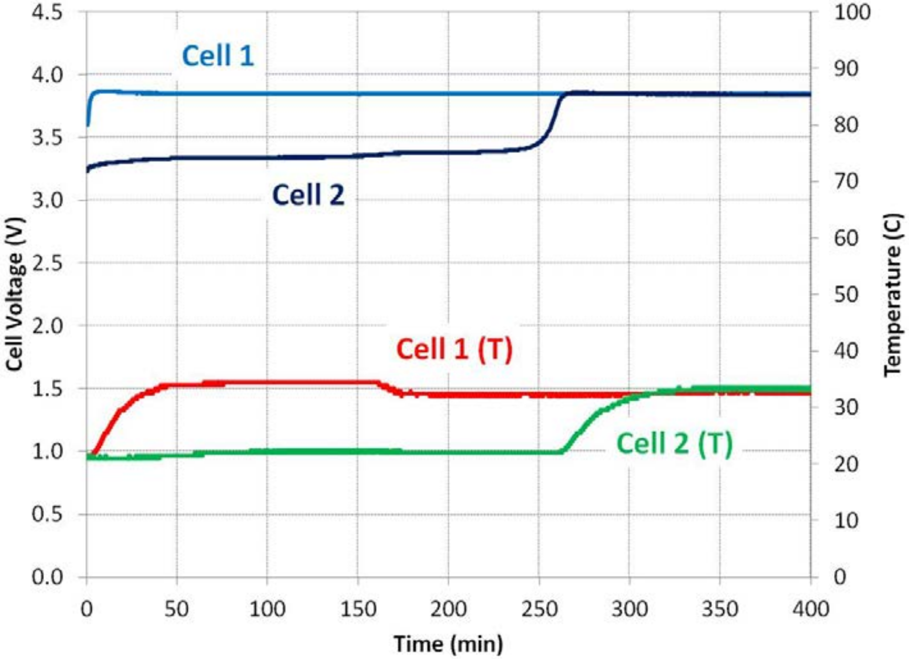
Does this actually work for cell balancing?
What is the heat output during shuttle activation?
Does this improve overcharge abuse tolerance?

RS2 Overcharge Shuttle – Cell Balancing

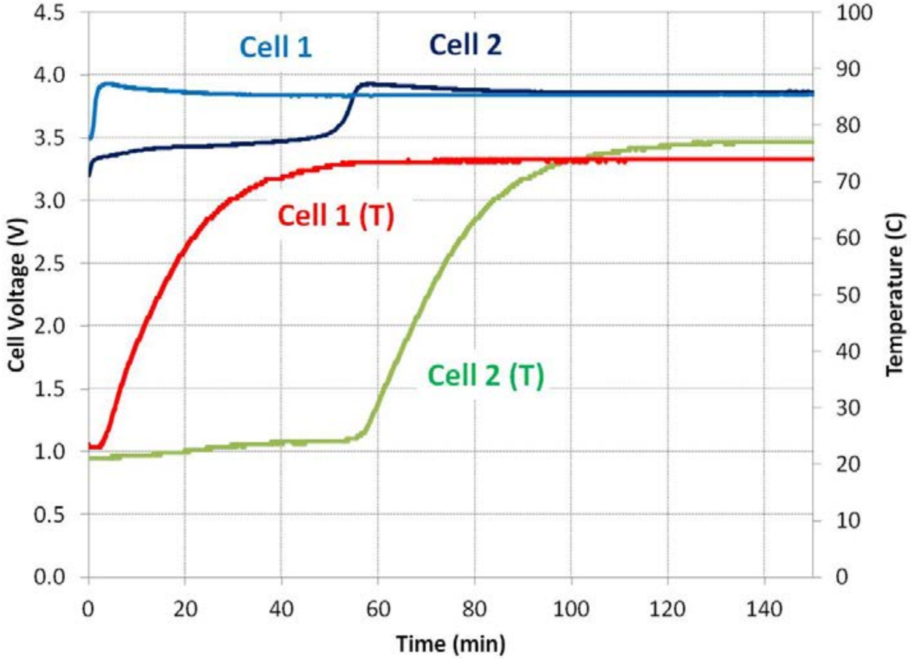
2 imbalanced cells in series

Cell 1, V_o = 3.60 V
Cell 2, V_o = 3.25 V

200 mA Charge (C/5)

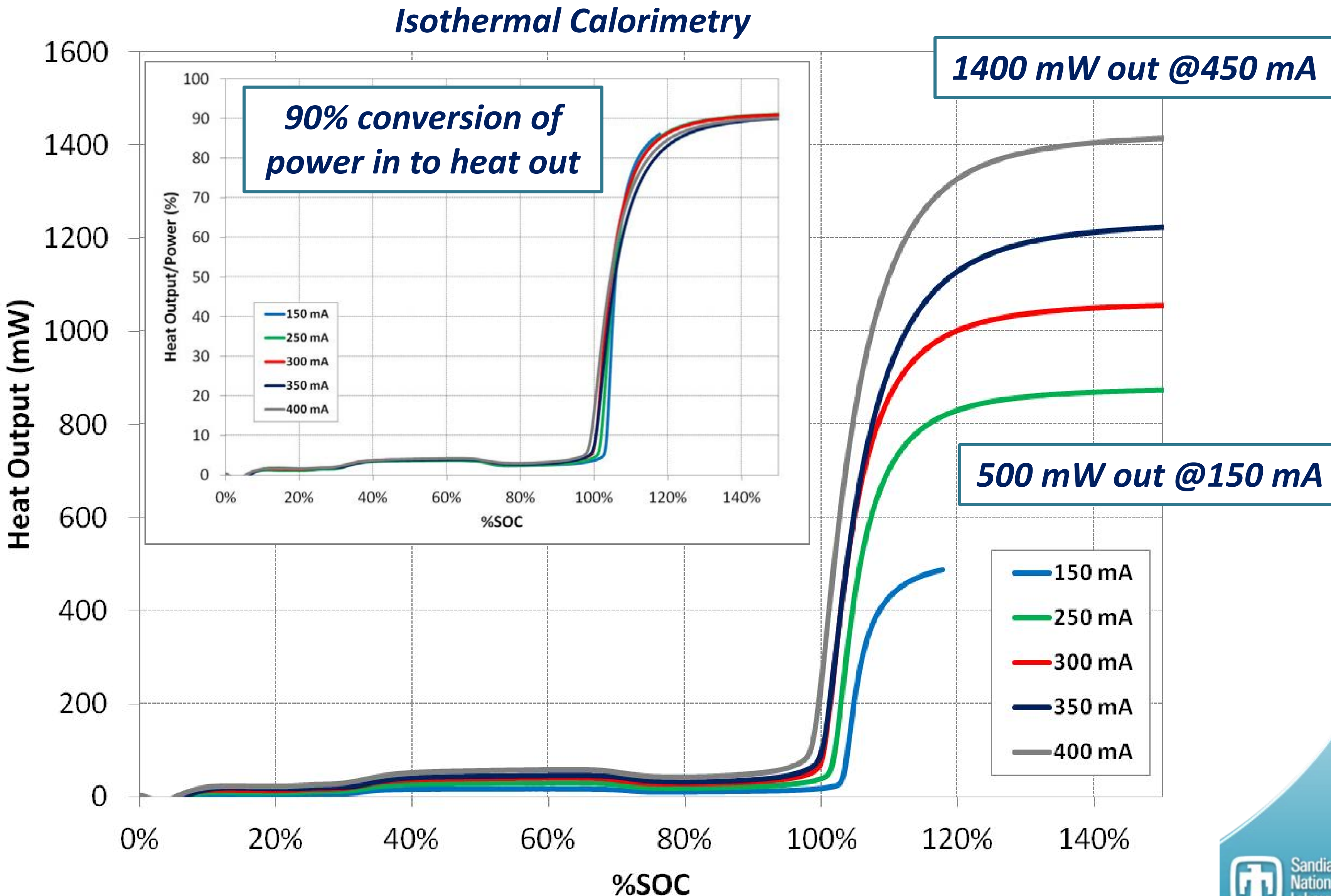


1 A Charge (1C)



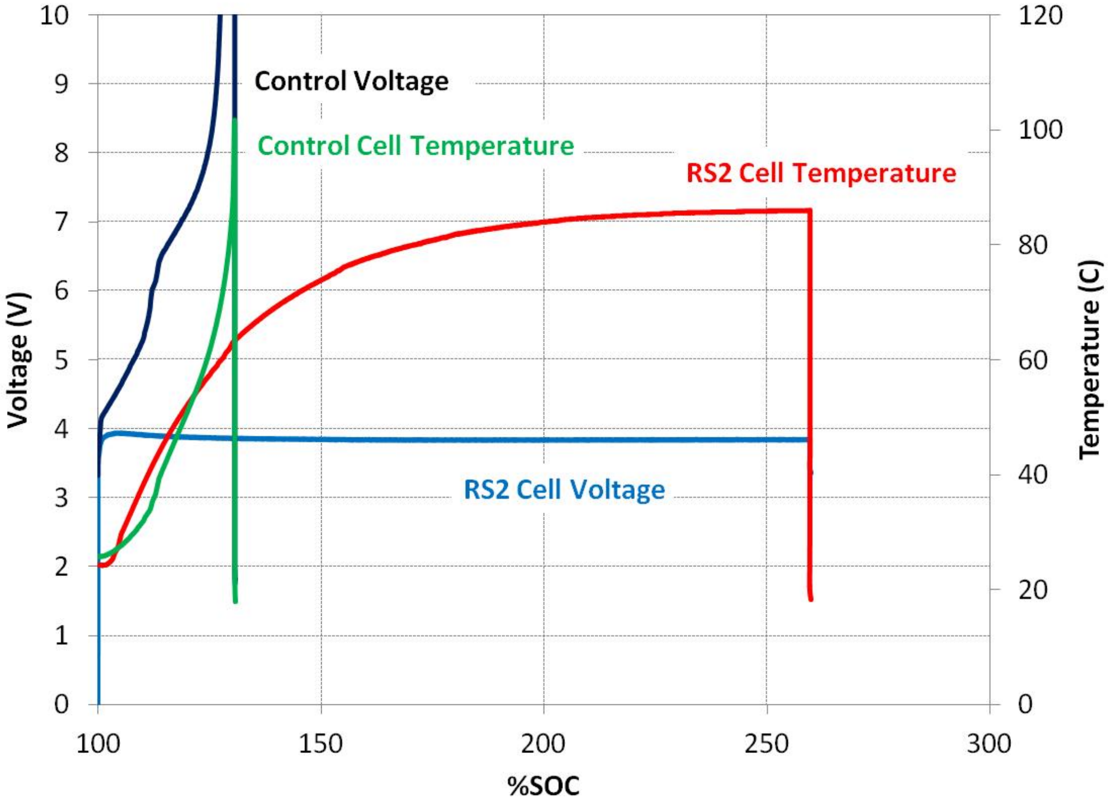
- ***Balanced in 4.5 hrs at 200 mA with a max. temperature of 32 °C***
- ***Balanced in 1.5 hrs at 1 A with a max. temperature of 85 °C***
- ***RS2 is very effective for cell balancing***

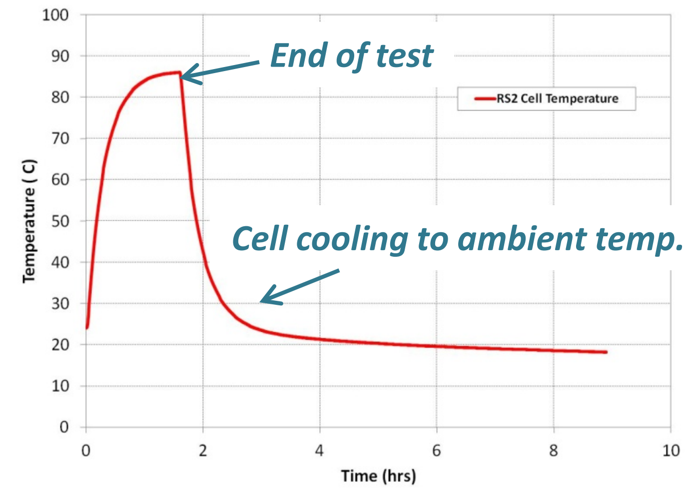
RS2 Overcharge Shuttle

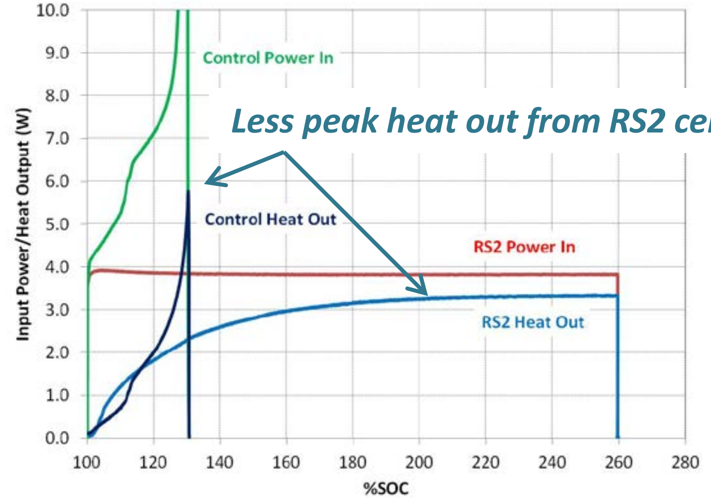


RS2 Overcharge Shuttle – Overcharge Abuse

1 A Constant Current (1C) Overcharge Abuse Test

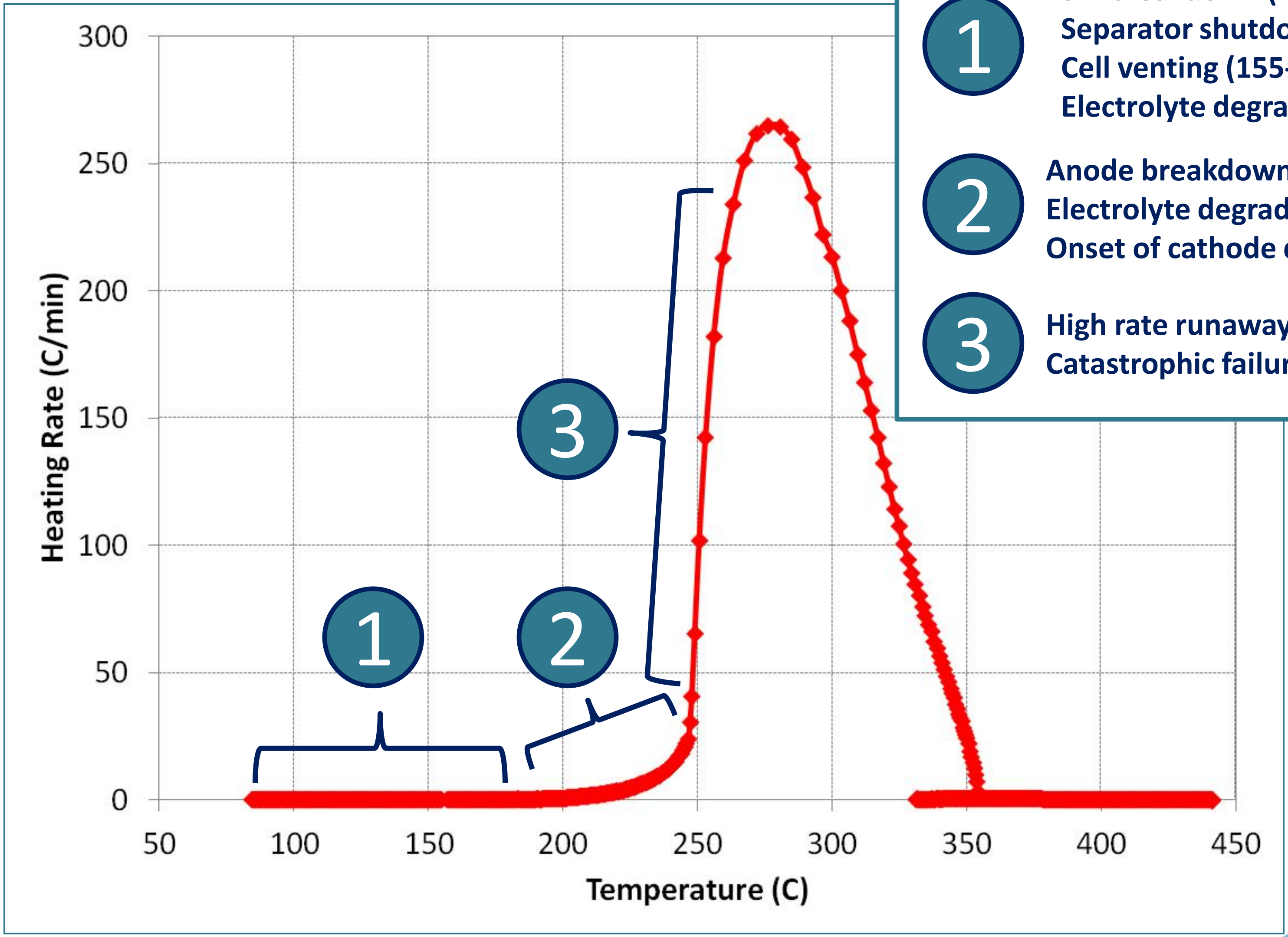






Control cell failure at 130%SOC
RS2 cell test stopped at 260%SOC with no failure event
RS2 cell temperature ~90 °C at 260%SOC

Stages of Lithium-ion Cell Runaway

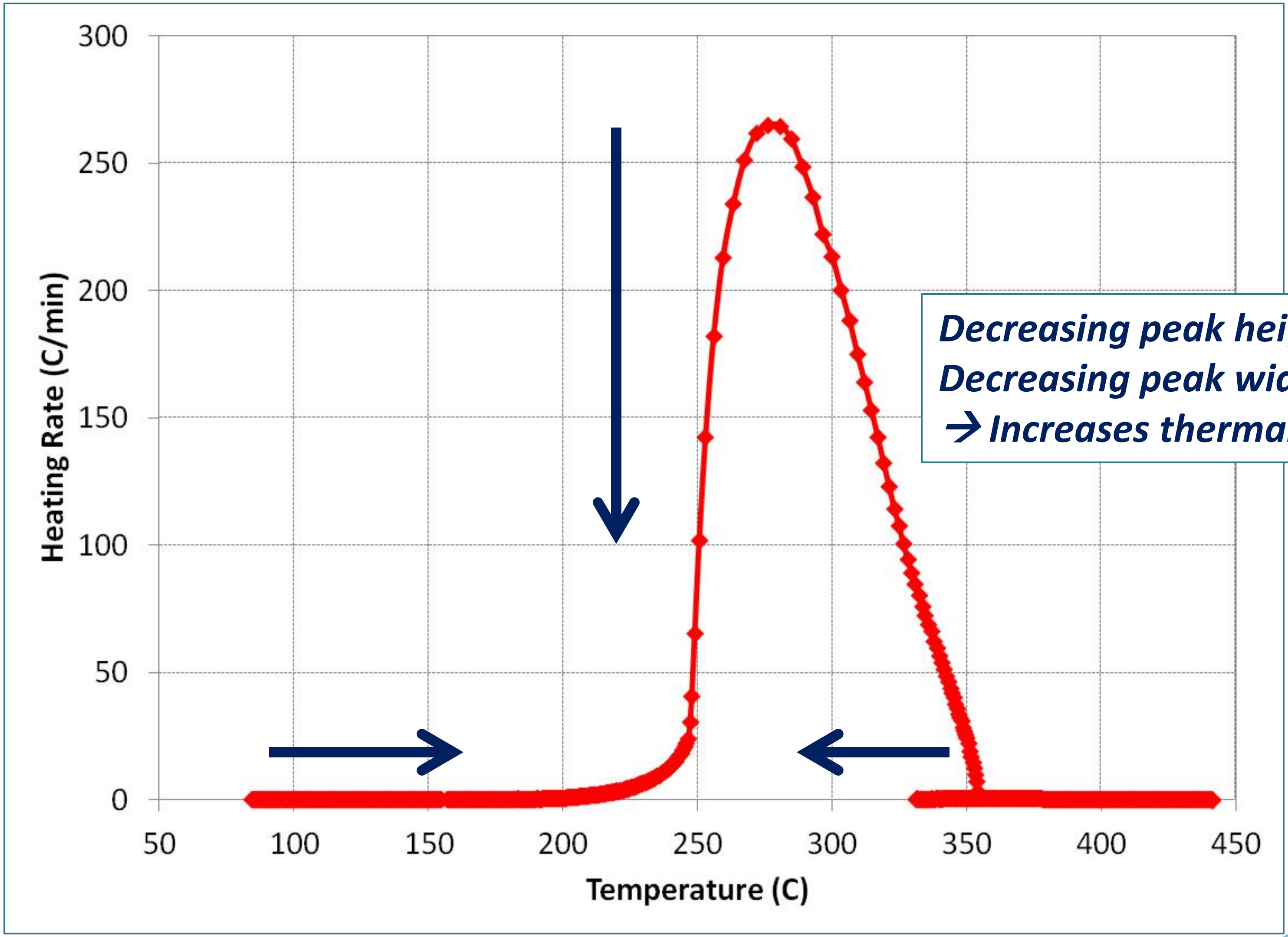


1
SEI breakdown (70-90 C)
Separator shutdown
Cell venting (155-165 C)
Electrolyte degradation

2
Anode breakdown
Electrolyte degradation
Onset of cathode decomposition

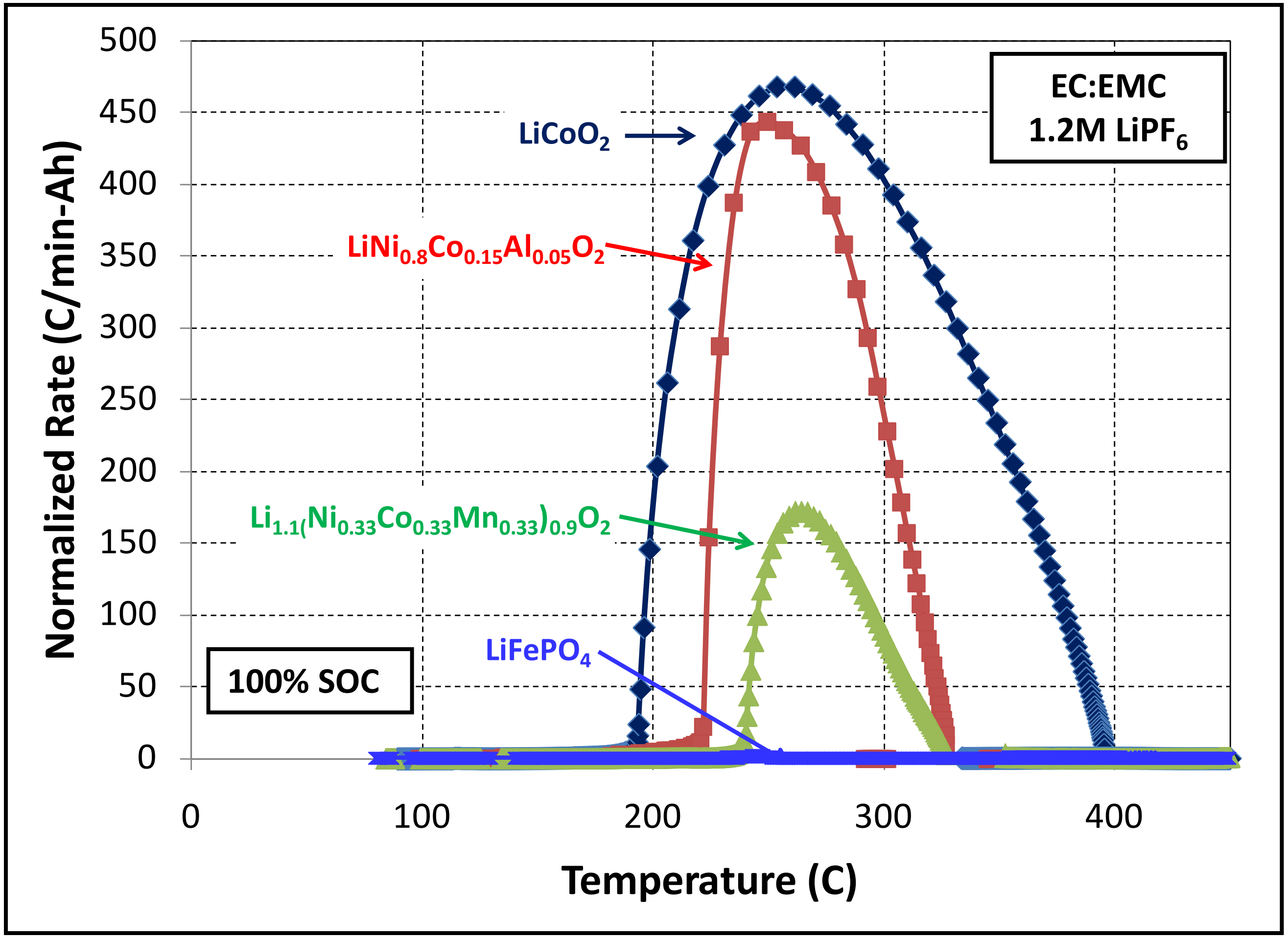
3
High rate runaway
Catastrophic failure

Stages of Lithium-ion Cell Runaway



Decreasing peak height
Decreasing peak width
→ Increases thermal stability

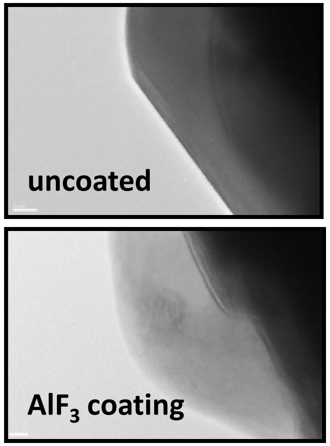
Accelerating Rate Calorimetry of Advanced Materials in Cells

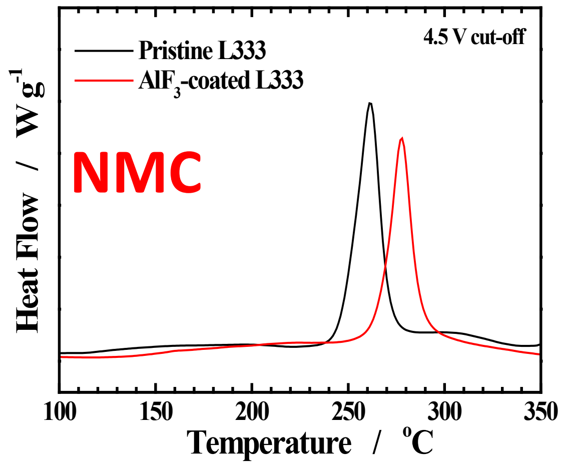


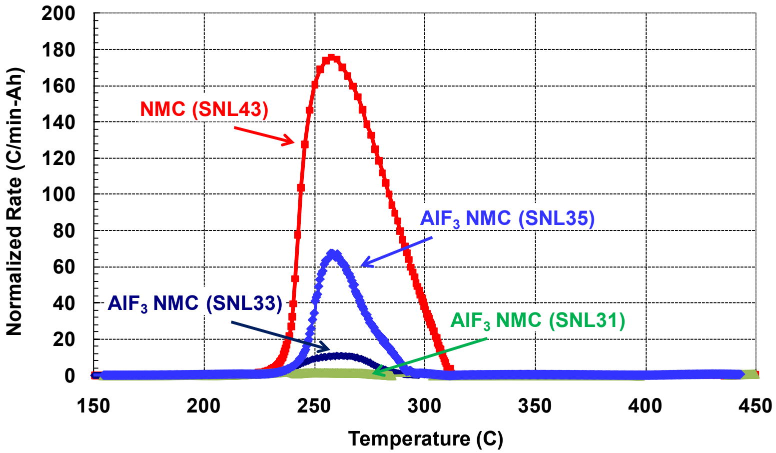
ARC response of high voltage and high capacity cathodes?
ARC response of cells with high capacity anodes (Si-composites)?

Coated Cathodes

AlF_3 Coating: Collaboration with ANL (Khalil Amine, Zonghai Chen)







Technology Development → Materials Characterization → Cell Evaluation

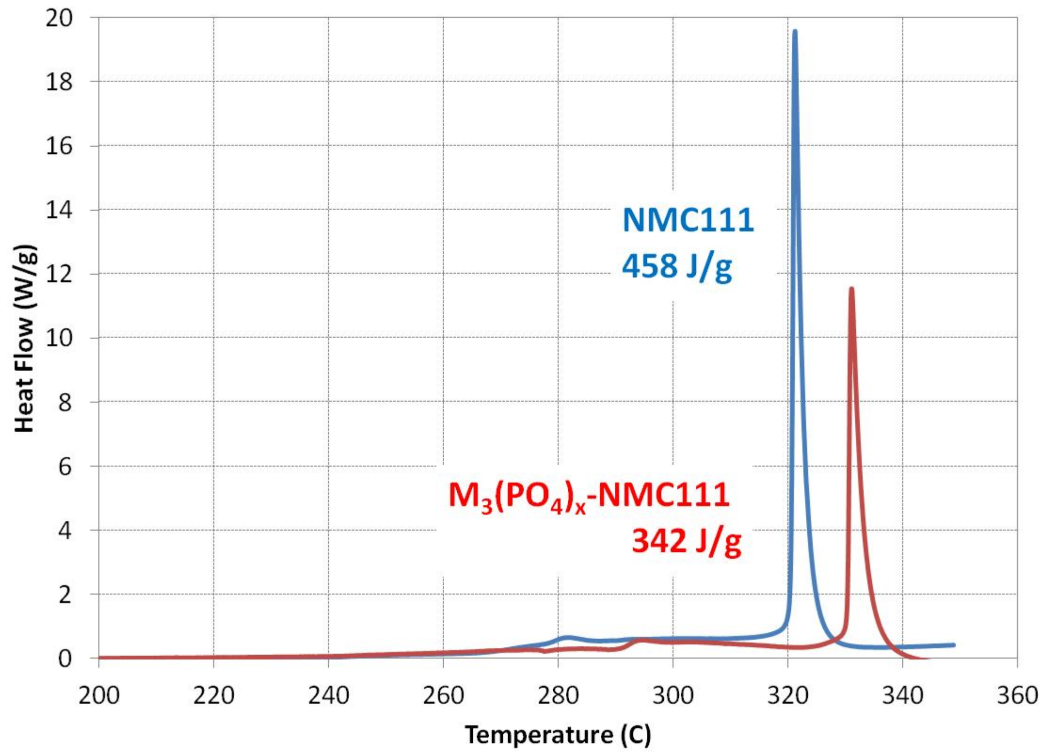
C.J. Orendorff, DOE Annual Merit Review 2011

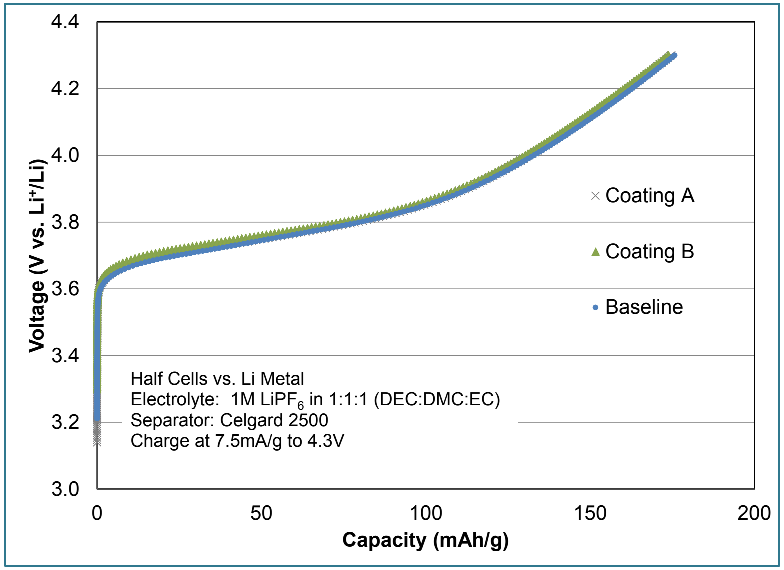
- **Continuation of coatings work:**
  - Improve coating homogeneity
  - Improve interfacial resistance/ionic conductivity
  - Coating advanced cathode materials
  - Demonstration of improved abuse response in cells
- **Solution co-precipitation particle coating (ANL, Physical Sciences)**
- **Atomic Layer Deposition (ALD) electrode coatings (NREL)**

Coated Cathodes – Metal Phosphate Coatings

Collaboration with Physical Sciences Inc. (Christopher Lang)

- ***Phosphate coating developed under 2008 NASA NRA***
- ***Improve ionic conductivity***
- ***Improve homogeneity of coating***
- ***Apply toward ABR materials***





Comparable capacity to uncoated NMC
Improved thermal stability of $M_x(PO_4)_y$-coated NMC
Scale up and cell measurements Q3 and Q4 FY12

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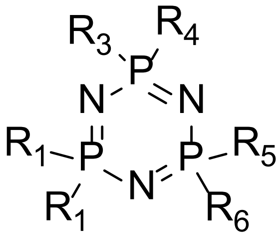
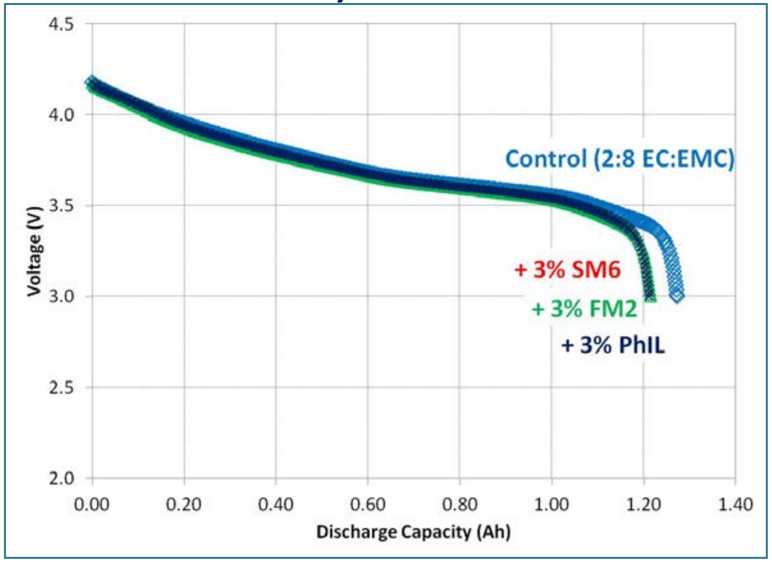
Phosphazene Electrolyte Characterization

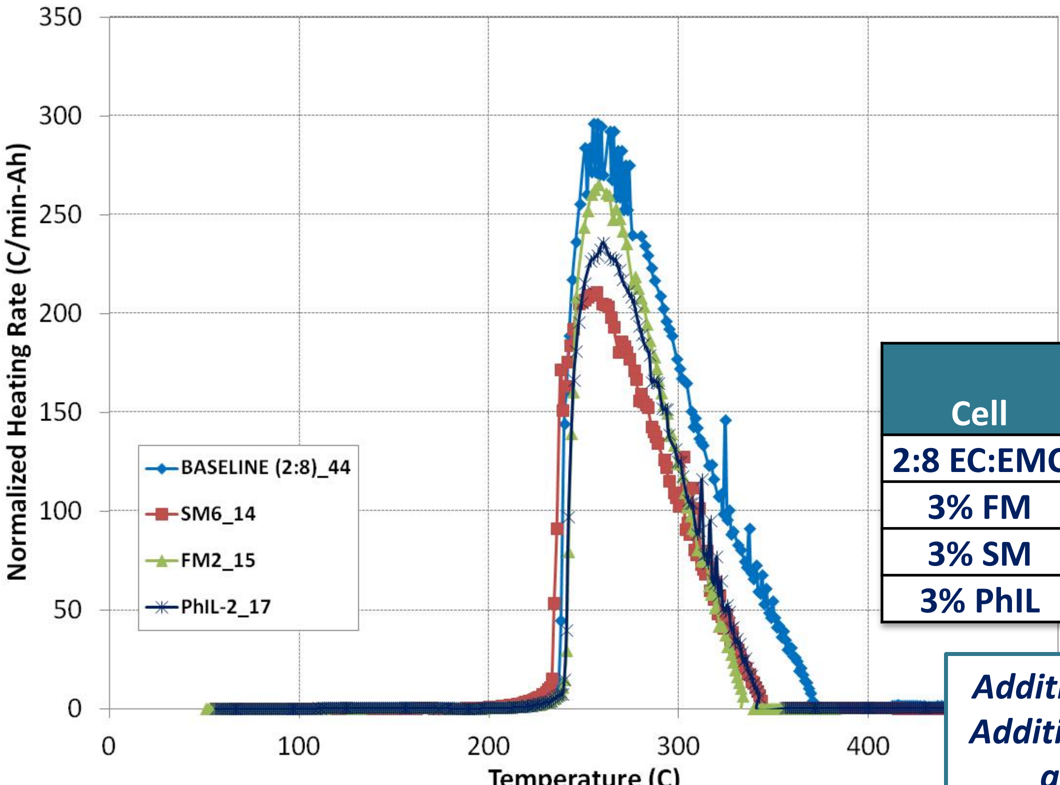
Collaboration with INL (Kevin Gering, Mason Harrup)



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

Toda NMC111/CP A10 18650 cells





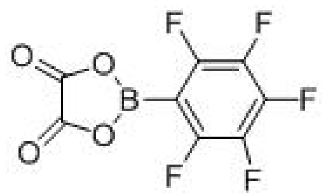
Cell	Enthalpy (kJ)	Normalized enthalpy (kJ/Ah)
2:8 EC:EMC	27.4	21.6
3% FM	24.9	20.6
3% SM	25.3	20.2
3% PhIL	25.4	20.9

Additive cells show slightly less capacity than the control
Additive cells show a reduction in the peak heating rates and total enthalpy of NMC cells during runaway
Flammability measurements scheduled for Q3 FY12

LiF/ABA Electrolyte Development

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

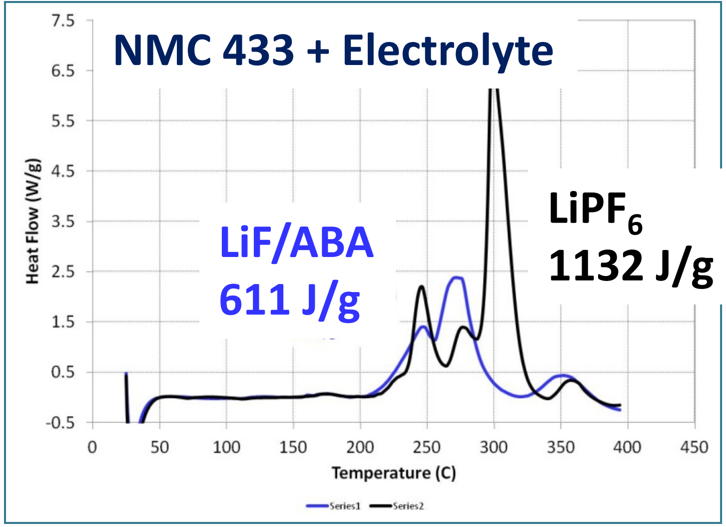
- ***→ Reduce harmful decomposition from PF_6^-***
- ***→ Passivate the runaway reactions at the cathode***



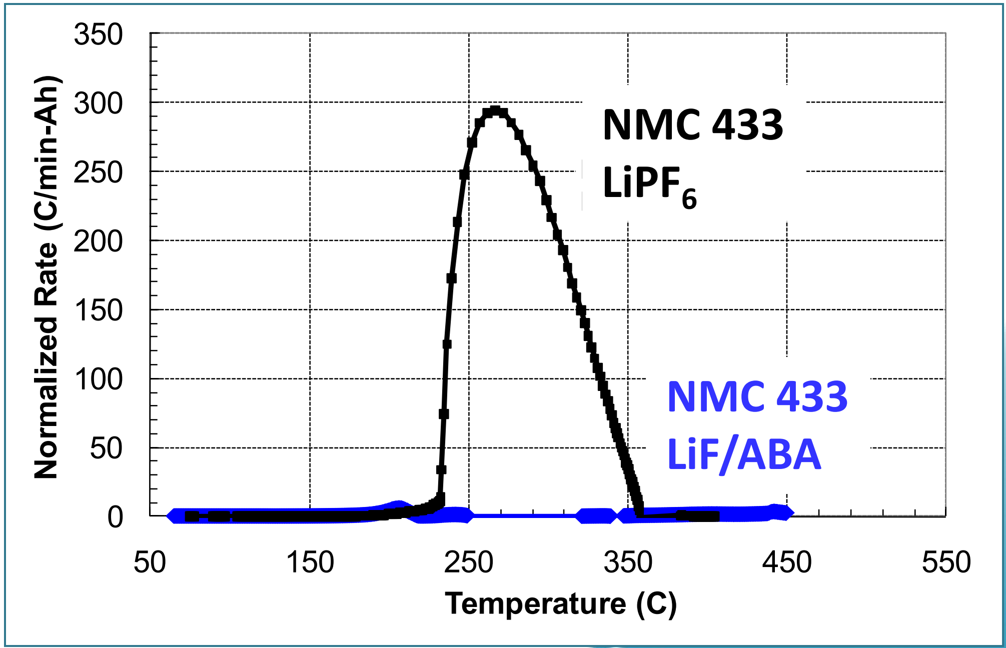
Perfluorophenyloxaltoborate

Drastic improvement in thermal stability of NMC 433 cathode and in 18650 cells

DSC (Material)

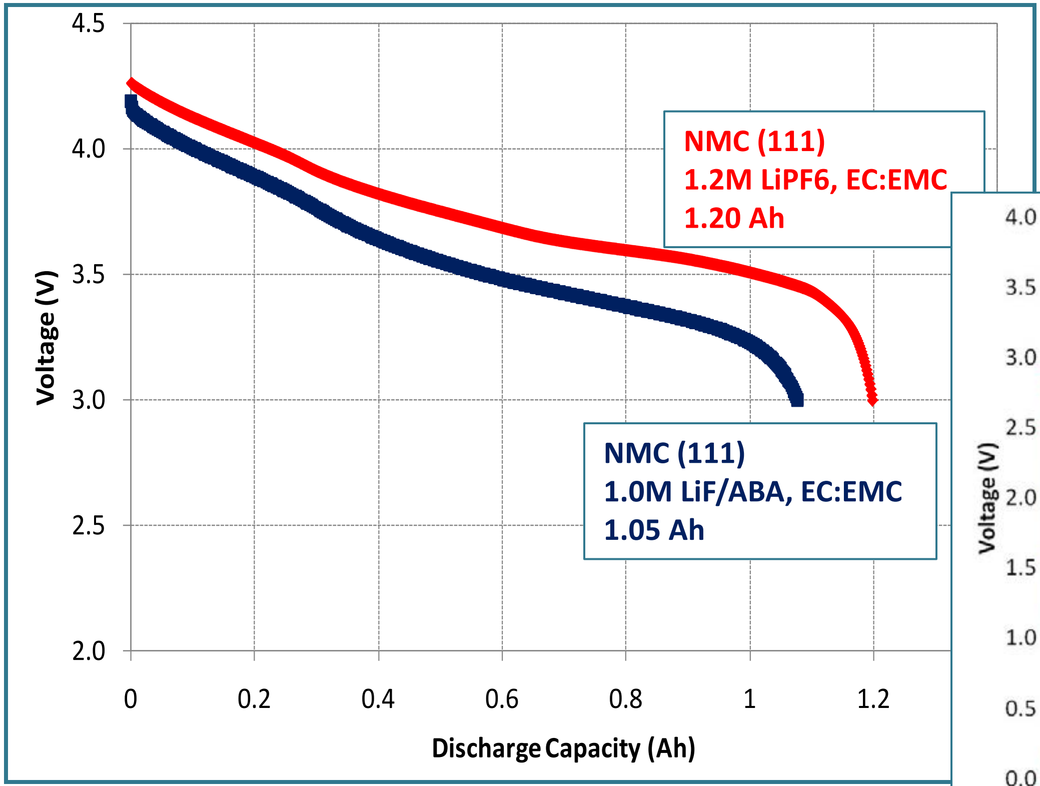


ARC (18650 cell)

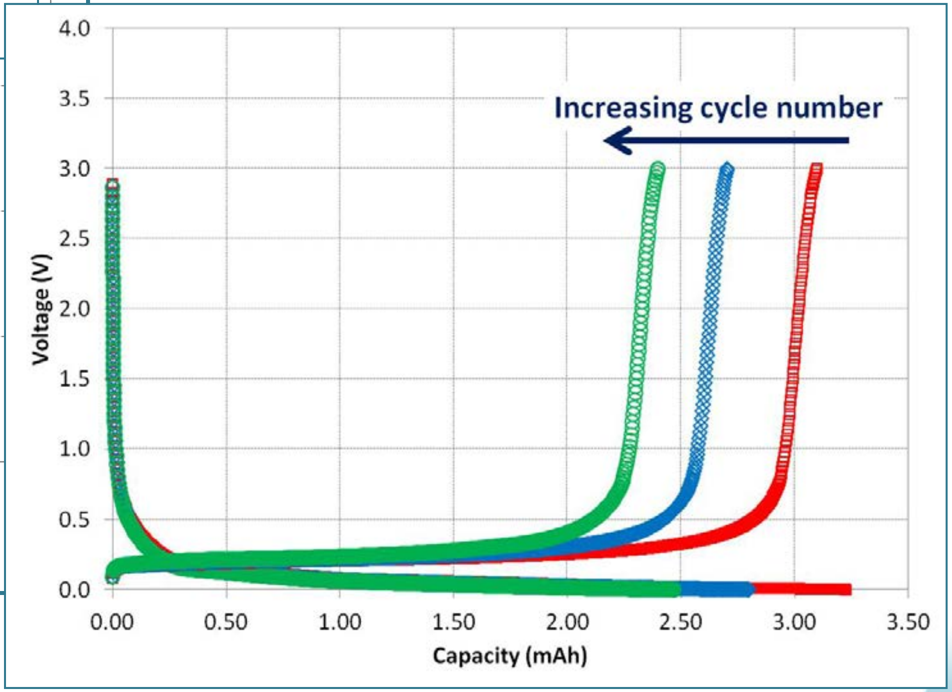


LiF/ABA Electrolyte Performance

18650 cell discharge capacity



Anode ½ cell (vs. Li) capacity fade



~10% capacity reduction compared to the $LiPF_6$ cell
Significant fade in anode capacity (SEI instability)
Work ongoing to improve SEI film formation using LiF/ABA (VC and $LiPF_6$ additives)

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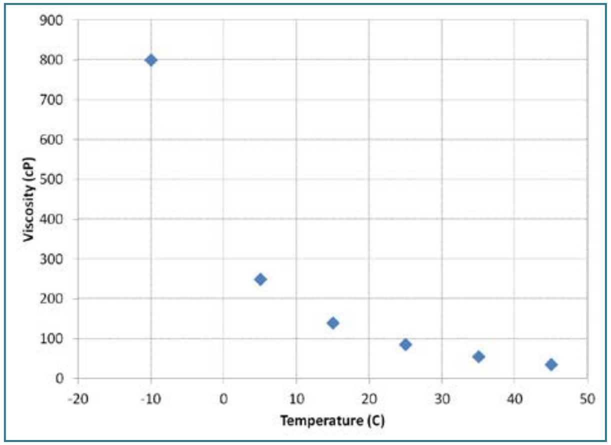
Ionic Liquid (IL) Electrolyte Development

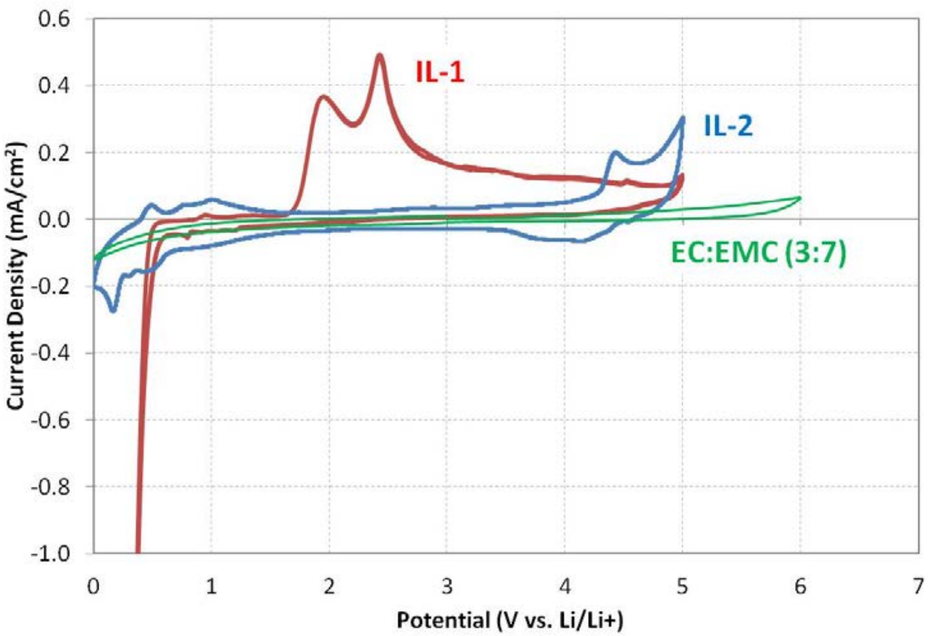
Objective: Develop non-carbonate based electrolyte solvents

- → ***Reduce the combustion enthalpy of the system***
- → ***Eliminate flammability of electrolyte***

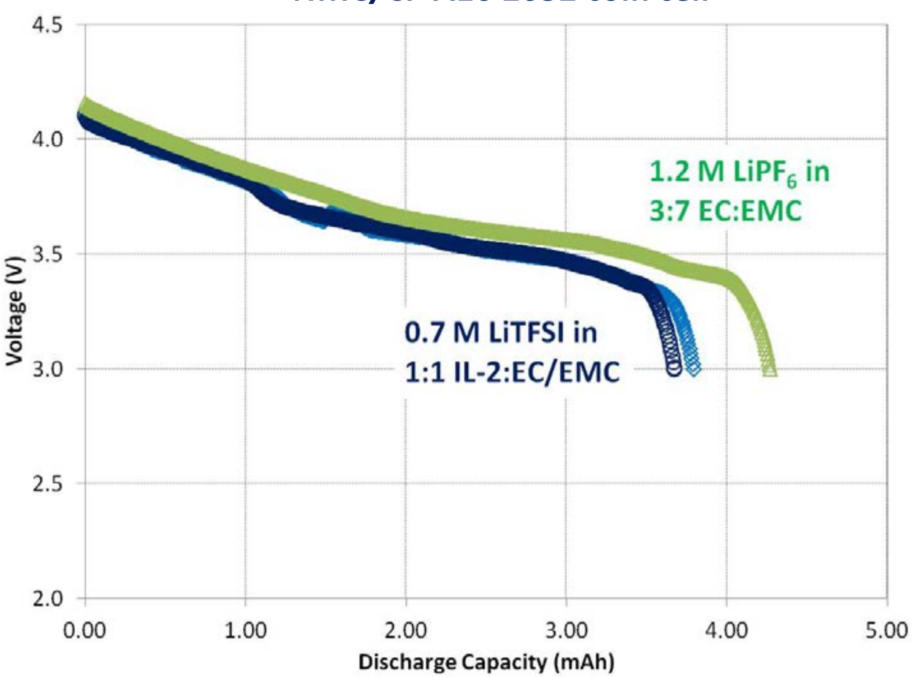
IL-2 Viscosity



Voltage stability of ILs vs. Li/Li^+



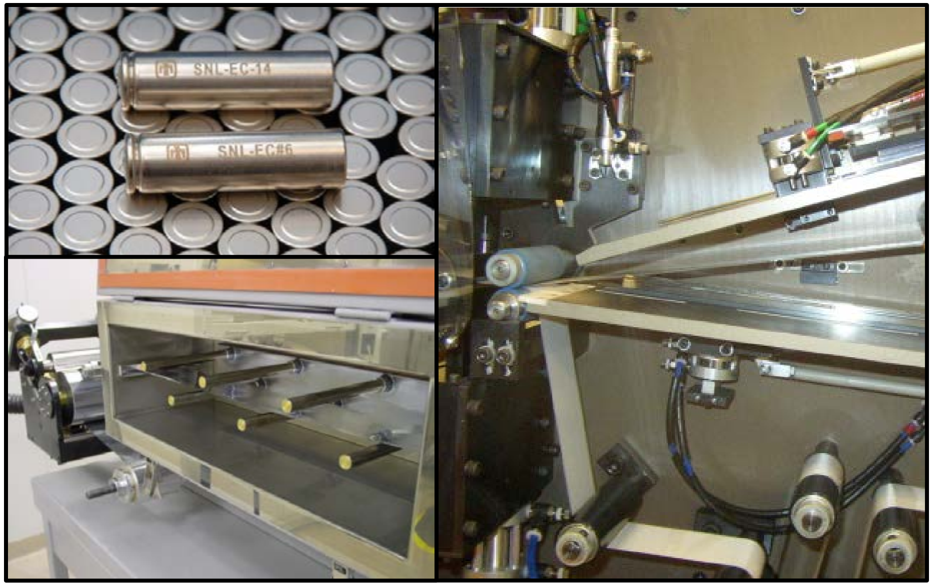
NMC/CP A10 2032 coin cell



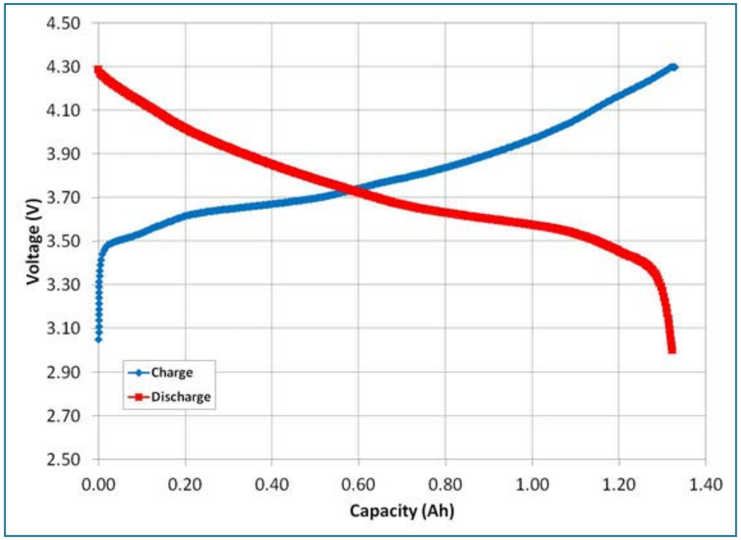
Improved low voltage stability of IL-2 over IL-1
Viscosity = 180 cP at 25 C
80% capacity compared to 1.2 M $LiPF_6$ in EC:EMC (3:7) at C/5

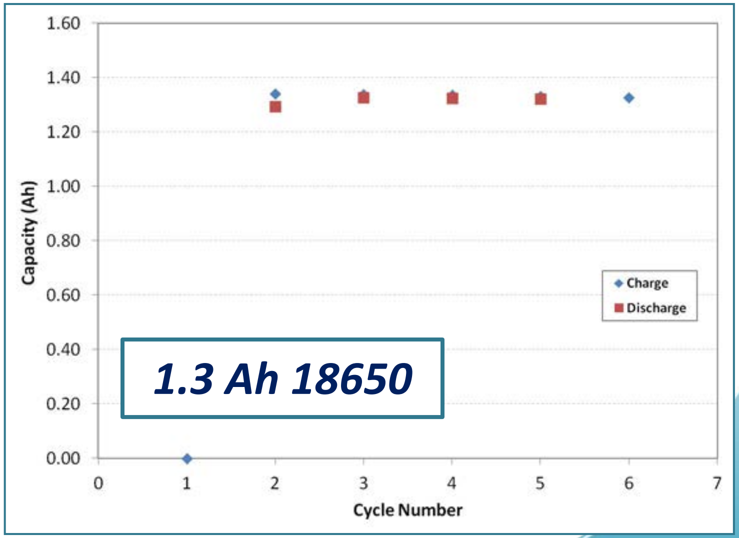
Cell Prototyping Facility

- **Cell Deliverables FY12**
  - LFP/CPA10
    - *ANL RS2 Shuttle (Q1, SNL 20 cells)*
  - Toda NMC 111/CP A10
    - *INL Phosphazine (Q1, 32 cells)*
    - *JPL Electrolyte (Q3, 24 cells)*
    - *SNL ABA Electrolyte (Q3, 12 cells)*
    - *SNL Ionic Liquid Electrolyte (Q4 12 cells)*
    - *PSI $M_x(PO_4)_y$-coated NMC (Q3, 12 cells)*
    - *NREL Al_2O_3-coated NMC/ALD (Q3 12 cells)*
  - NEI $LiNi_{0.5}Mn_{1.5}O_4$ (Q3-Q4)



Toda NMC(111)/CP A10 in 1.2 M $LiPF_6$ EC:EMC (3:7)





Electrode Formulation

- **Cathode Composition**
  - Toda NMC $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ – 94 wt%
  - Conductive Carbon (SAB) – 3 wt%
  - PVDF Binder
    (Kureha #1300) – 3 wt%

- **Cathode Electrode Properties**
  - Current collector – 17 mm carbon coated aluminum
  - Total electrode thickness ~ 180 mm (double sided coating for 18650)
  - Cathode coating thickness ~ 163 mm double / ~80 mm single
  - Compression – thickness reduction to ~80% of cast (~143 mm)
  - Porosity ~45%
  - Electrode Loading – 30 mg/cm^2 double

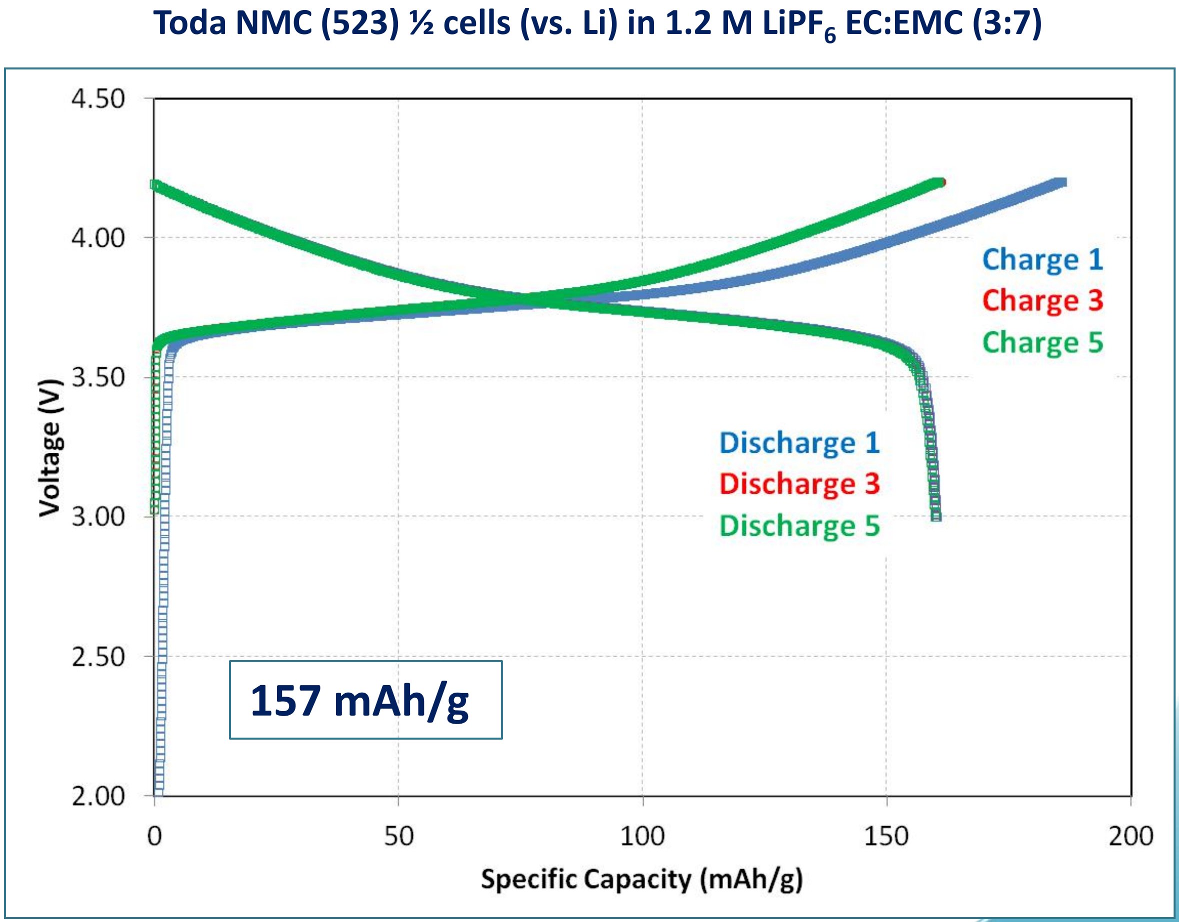
- **Anode Composition**
  - CP A10 (A12) – 92 wt%
  - Conductive Carbon (SAB) – 2 wt%
  - PVDF Binder
    (Kureha #9200) – 6 wt%

- **Anode Electrode Properties**
  - Current collector – 22 mm copper
  - Total electrode thickness ~ 180 mm (double sided coating for 18650)
  - Cathode coating thickness ~ 158 mm double / ~79 mm single
  - Compression – thickness reduction to ~80% of cast (~140 mm)
  - Porosity ~50%
  - Electrode Loading – 13 mg/cm^2 double / ~7 single

Electrode Processing Standardization

- **Higher energy electrochemical couple**
  - Toda NMC523
- **Cathode formulation**
  - 90% Toda NMC523
  - 5% Solvay 5130
  - 5% Denka carbon

Round robin testing between ANL, SNL, ORNL in Q3
Optimization of cathode and anode processing in Q3/Q4



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Collaboration and Coordination with Other Institutions

- **RS2 Overcharge Shuttle**
  - ANL (development, scale up)
  - A123 (cell fab.)
- **Coated-cathodes**
  - Physical Sciences Inc. (metal phosphates)
  - NREL (ALD coated electrodes)
  - ANL (previous AlF_3 work)
- **Electrolyte Development**
  - Binrad Industries (ABAs)
  - INL (phosphazene development)
  - JPL (nonflammable electrolytes)
- **Electrode Processing (ABR standardization effort)**
  - ANL
  - ORNL

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Proposed Future Work

- 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)
- Complete ARC and flammability measurements to support electrolyte thrust programs (INL phosphazene and JPL nonflammable electrolyte)
- Characterization of new ABA-based electrolyte materials and abuse studies on cells with ABA
- Optimization of ionic liquid design and electrolyte formulation
- 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) does provide significant overcharge protection and utility for cell balancing
- Heat generation from RS2 activation >C/5 will need to be addressed to maintain battery performance and life
- Preliminary results for $M_x(PO_4)_y$-coated NMC show promise for improving cathode thermal stability; ALD coated electrodes could show the same benefit
- Phosphazene additives show some modest improvement in thermal stability in NMC cells; flammability measurements will determine nonflammable properties in cells
- LiF/ABA electrolyte show significant improvements in thermal stability, however, voltage stability (>4.2 V) and SEI characteristics need to be improved

Acknowledgements

- Dave Howell
- Peter Faguy, OVT team
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- Greg Krumdick (ANL)
- Kevin Gering (INL)
- Mason Harrup (INL)
- Ram Nagubandi (Binrad)
- Leslie Pinnel (A123)
- Tony Gozdz (A123)
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- Andy Jansen (ANL)
- Bryant Polzin (ANL)
- David Wood (ORNL)
- Rob Tenent (NREL)
- Anne Dillon (NREL)
- Tom Wunsch
- Mani Nagasubramanian
- Bill Averill
- Pete Roth
- Dan Doughty
- Kyle Fenton
- Josh Lamb
- Mike Russell
- Jill Langendorf
- Lorie Davis
- Dave Johnson
- Denise Bencoe
- June Stanley

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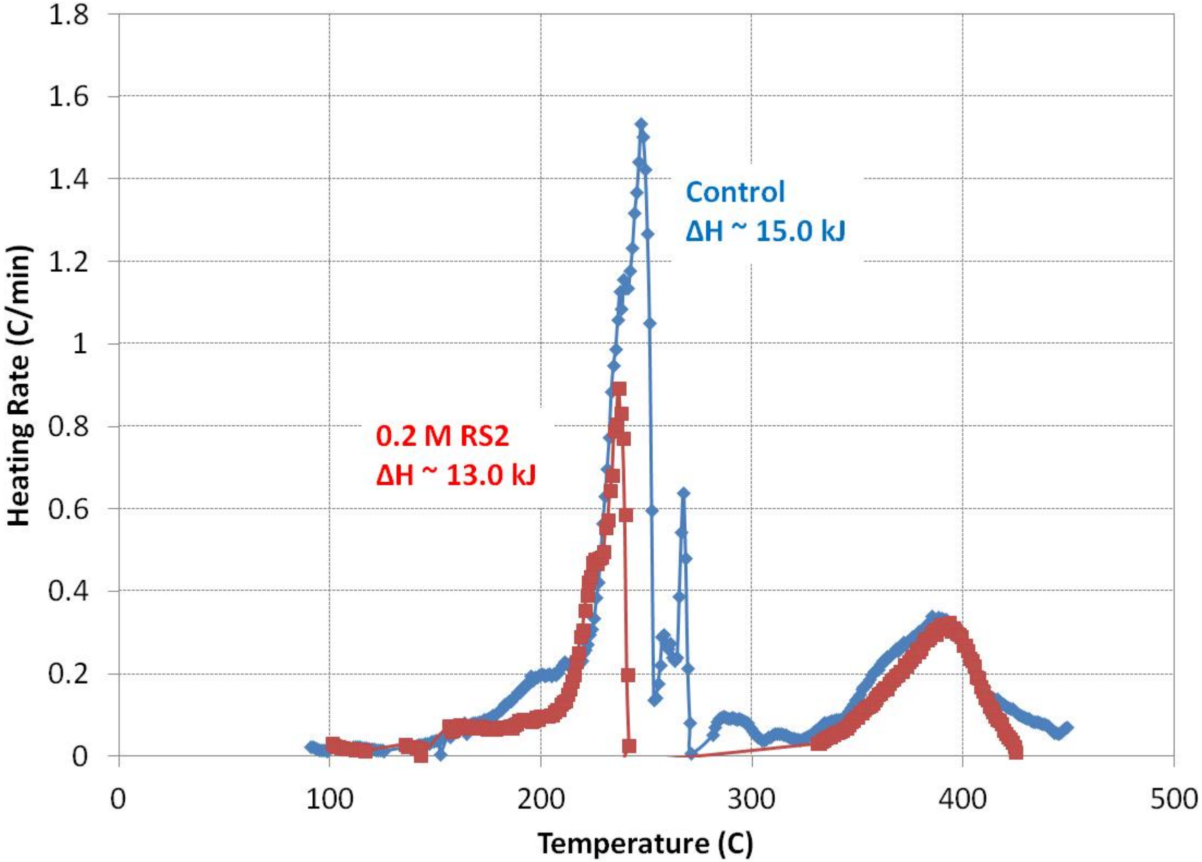
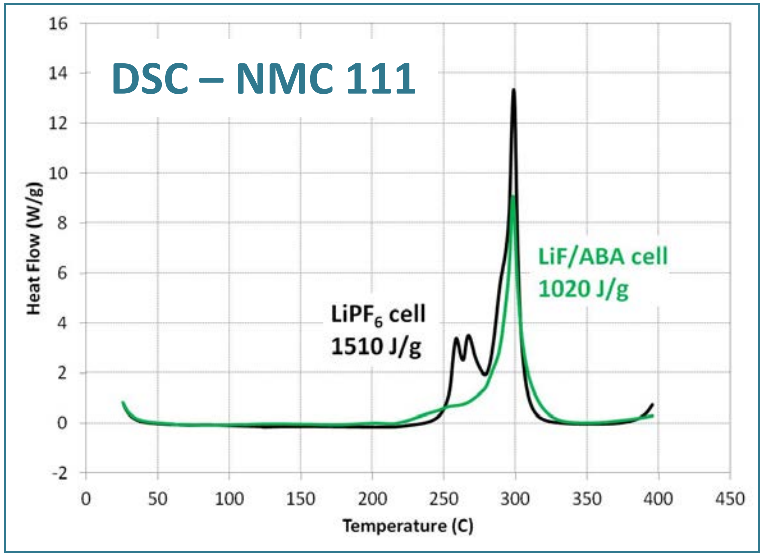
Technical Backup Slides

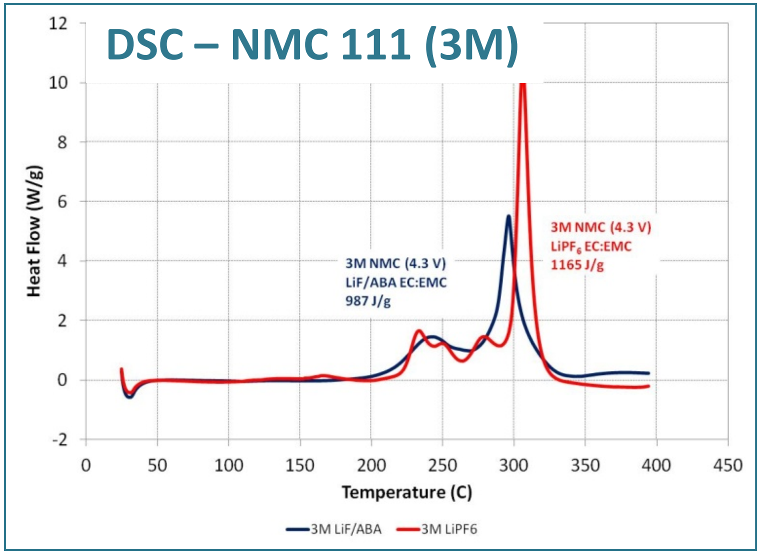
RS2 Overcharge Shuttle – ARC Measurements

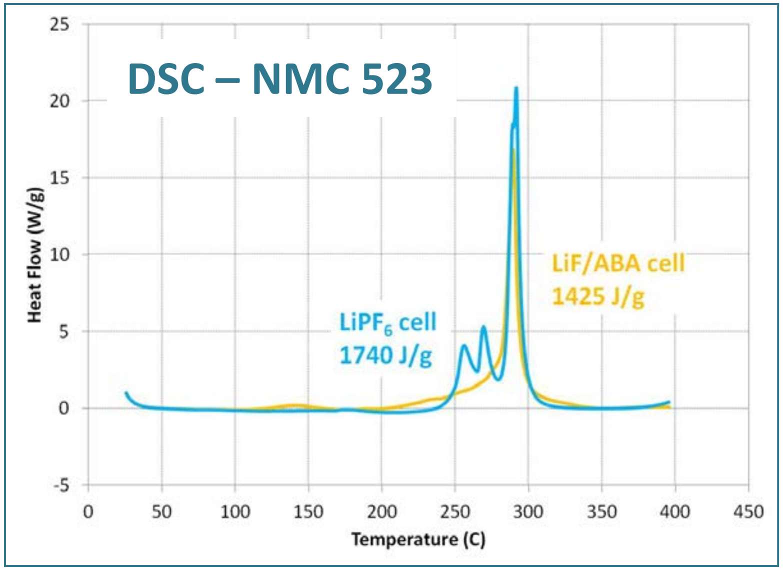


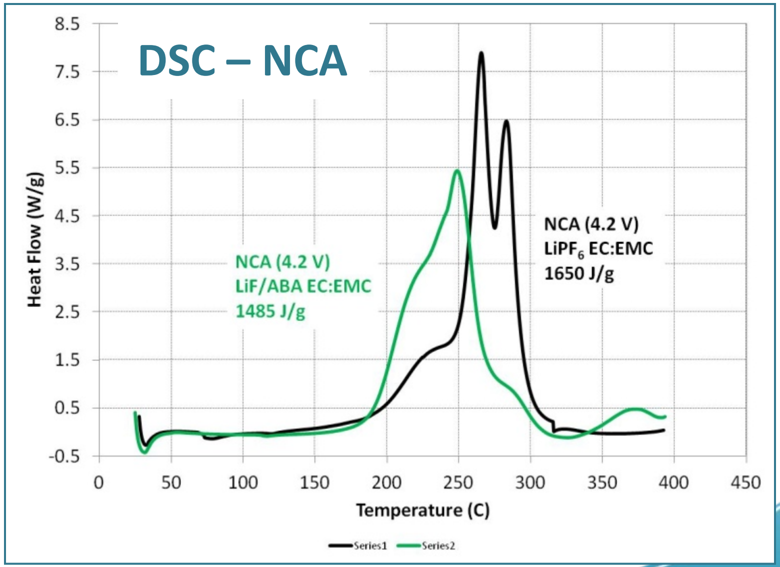
RS2 and control cells show comparable runaway profiles/enthalpies

LiF/ABA Electrolyte + Cathode DSC









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