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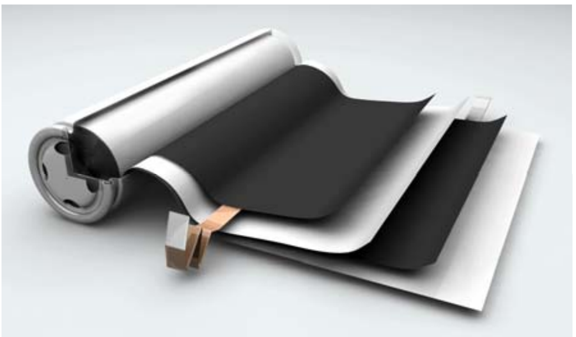
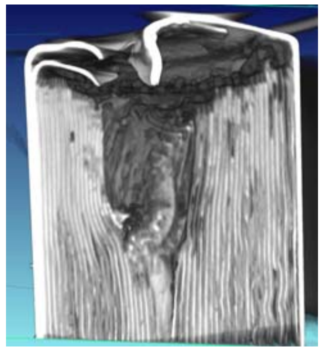

Quantifying Thermal Runaway and Improvements Through Materials Development

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Sandia National Laboratories

Next Generation Batteries 2015/Battery Safety

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Lithium-Ion Battery Safety Challenges

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- **Energetic thermal runaway**
  - **Anode and cathode decomposition reactions**
- **Electrolyte flammability**
  - **Low flashpoint electrolyte solvents**
  - **Vent gas management**
  - **Fuel-air deflagrations**
- **Thermal stability of materials**
  - **Separators, electrolyte salts, active materials**
- **Failure propagation from cell-to-cell**
  - **Single point failures that spread throughout an entire battery system**
- **Managing residual stored energy**
- **Diagnostics/prognostics to understand stability in the field**

Battery Field Failures in Vehicles

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Field failures could include:

- Latent manufacturing defects
- Internal short circuits
- Misuse or **abuse conditions**
- Ancillary component issues

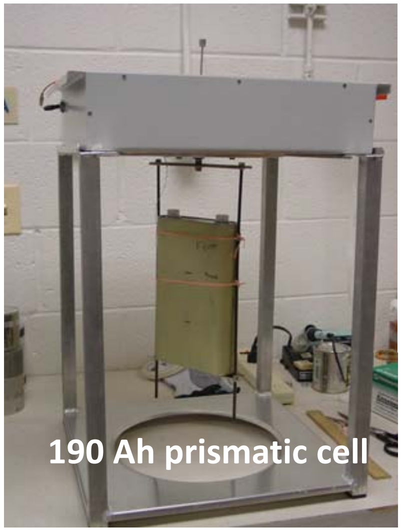
Even in cases where the battery is **not the root cause** of a failure, they can **contribute to the severity** of the failure scenario

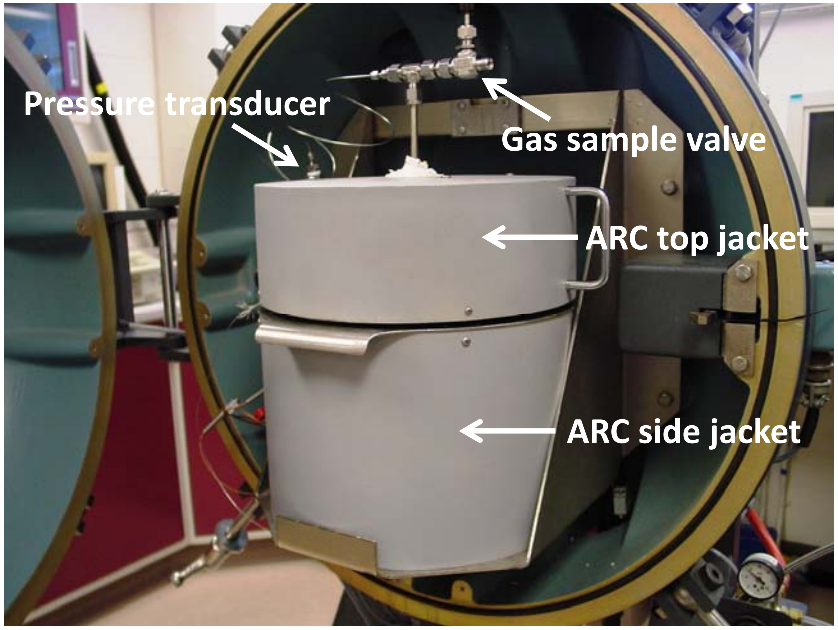
Fisker incident in the wake of Super Storm Sandy , New Jersey, 2012

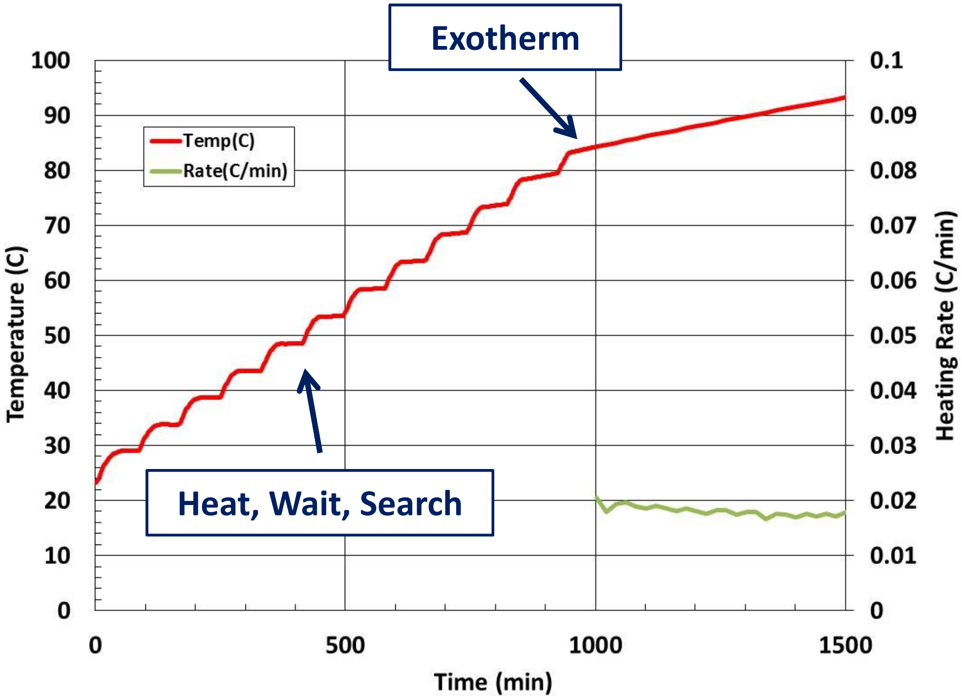
Outline

- **Calorimetry of lithium-ion cells**
- **Practical considerations for calorimetry measurements**
- **Specific examples highlighting the impact of:**
  - **Cell chemistry**
  - **Cell size (Ah)**
  - **State of charge**
- **Opportunities for improving thermal runaway performance**

Accelerating Rate Calorimetry (ARC)

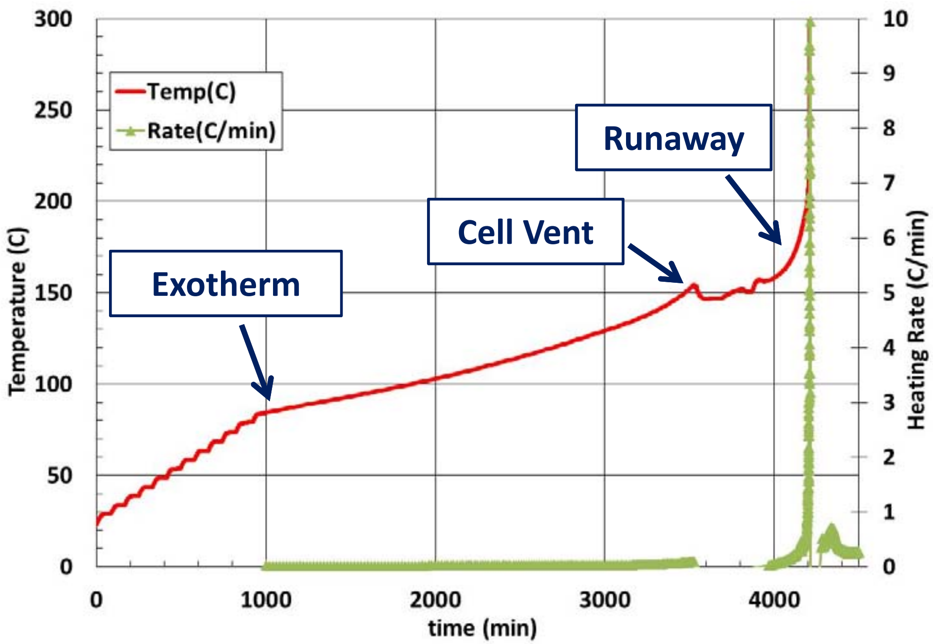


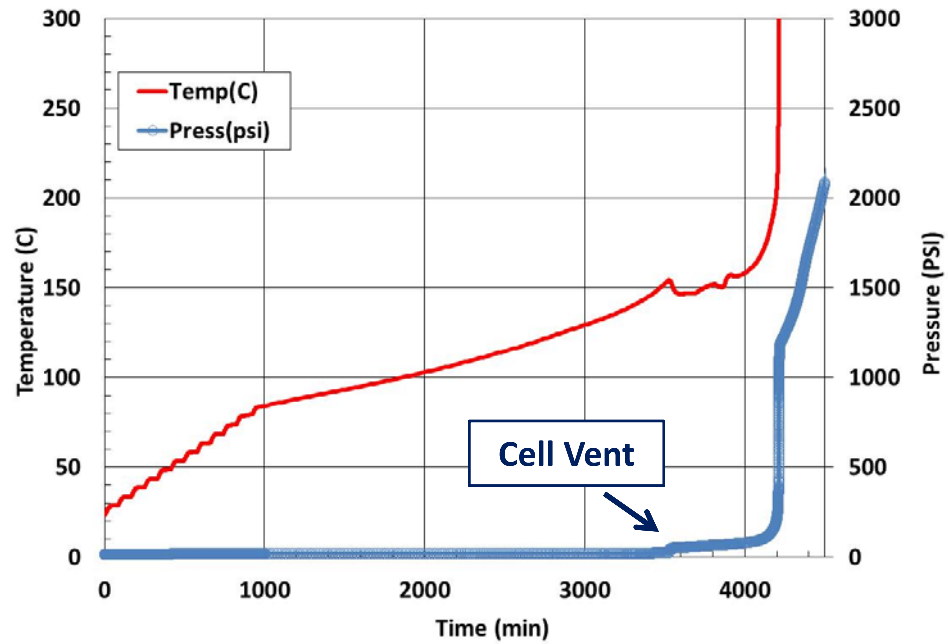




Operating in Exotherm mode, the ARC follows the heat generated by the bomb (cell) and stays adiabatic

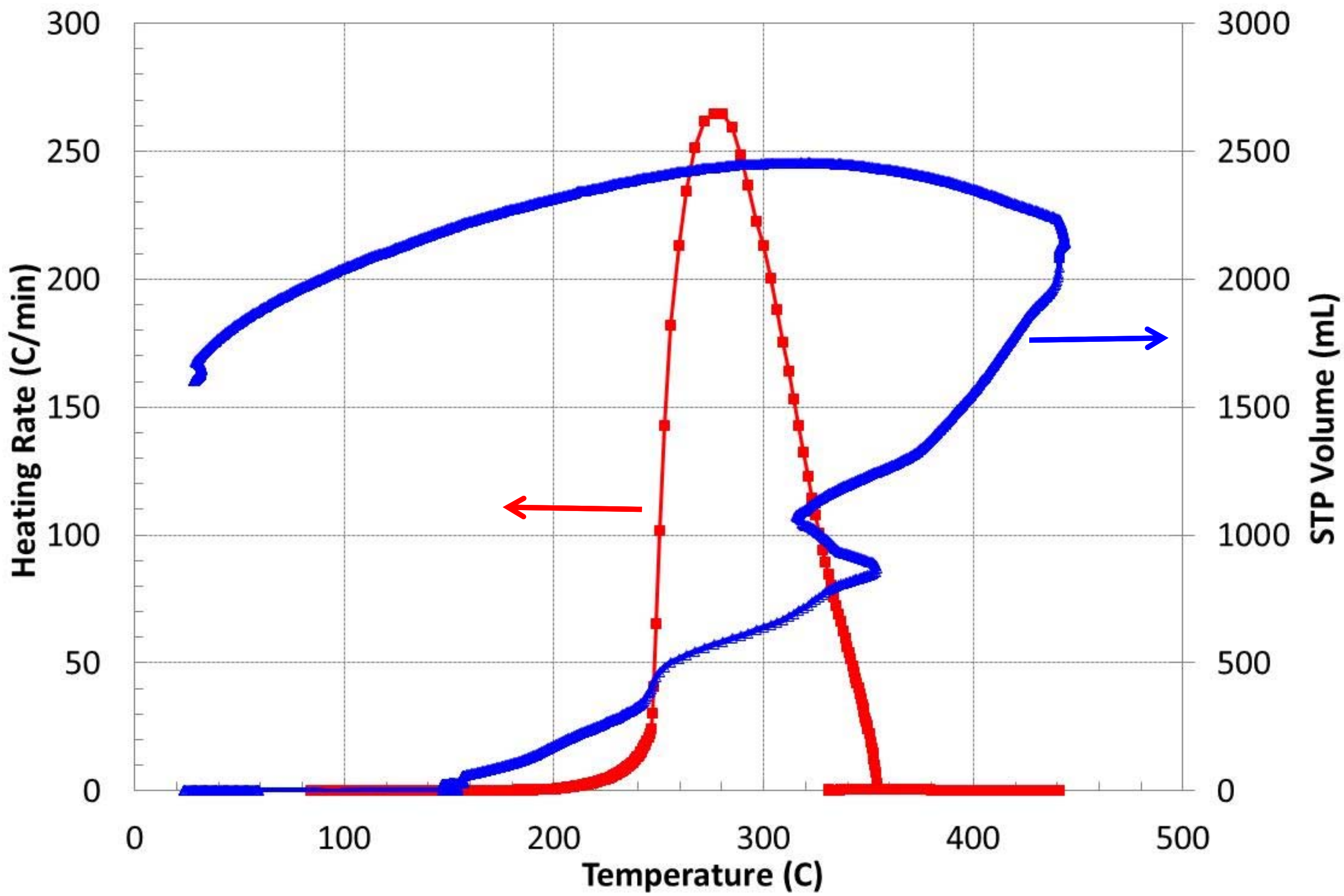
Lithium-ion Cell ARC Profiles



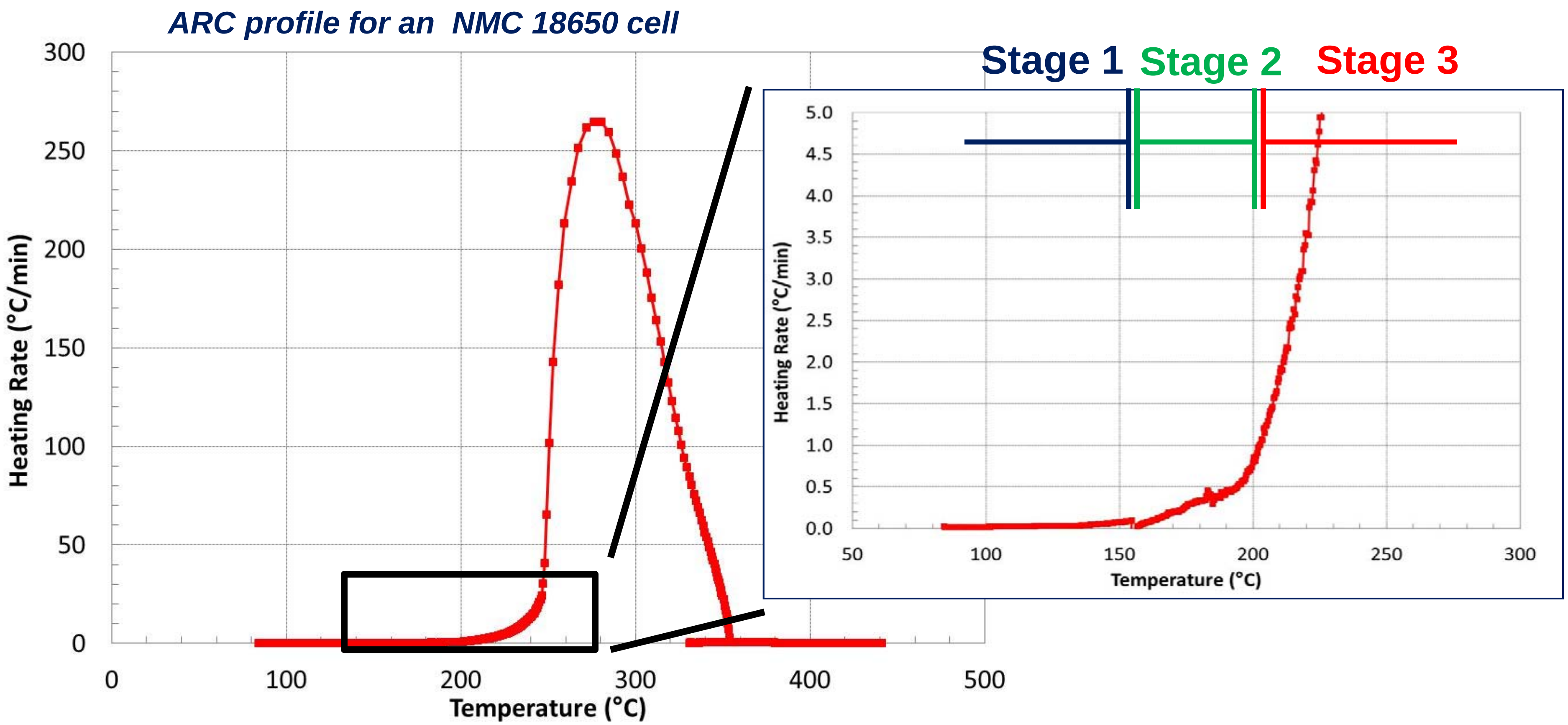


Anatomy of a lithium-ion cell thermal runaway measured by ARC

Lithium-ion ARC Profile

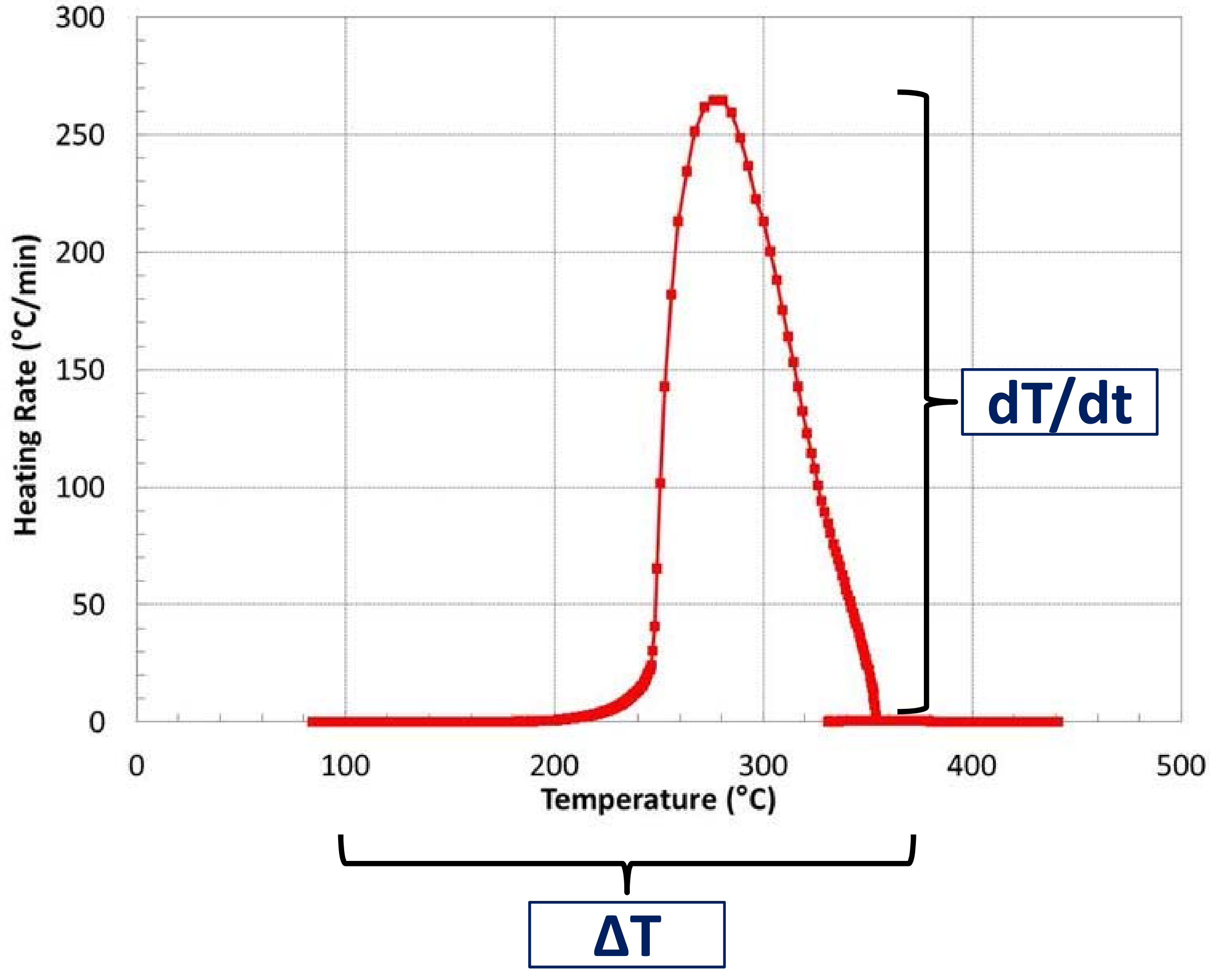


Stages of Thermal Runaway



Stage 1: < 160°C – Onset (SEI layer breakdown, electrolyte degradation, etc.)
Stage 2: 160°C - 200°C – Acceleration (cell vent, accelerated anode and electrolyte degradation, onset of cathode decomposition)
Stage 3: > 200°C – Runaway (full cell materials degradation, energetic release and uncontrolled rapid disassembly)

Runaway Thermodynamics



- ARC → dT/dt (C/min), ΔT (C)

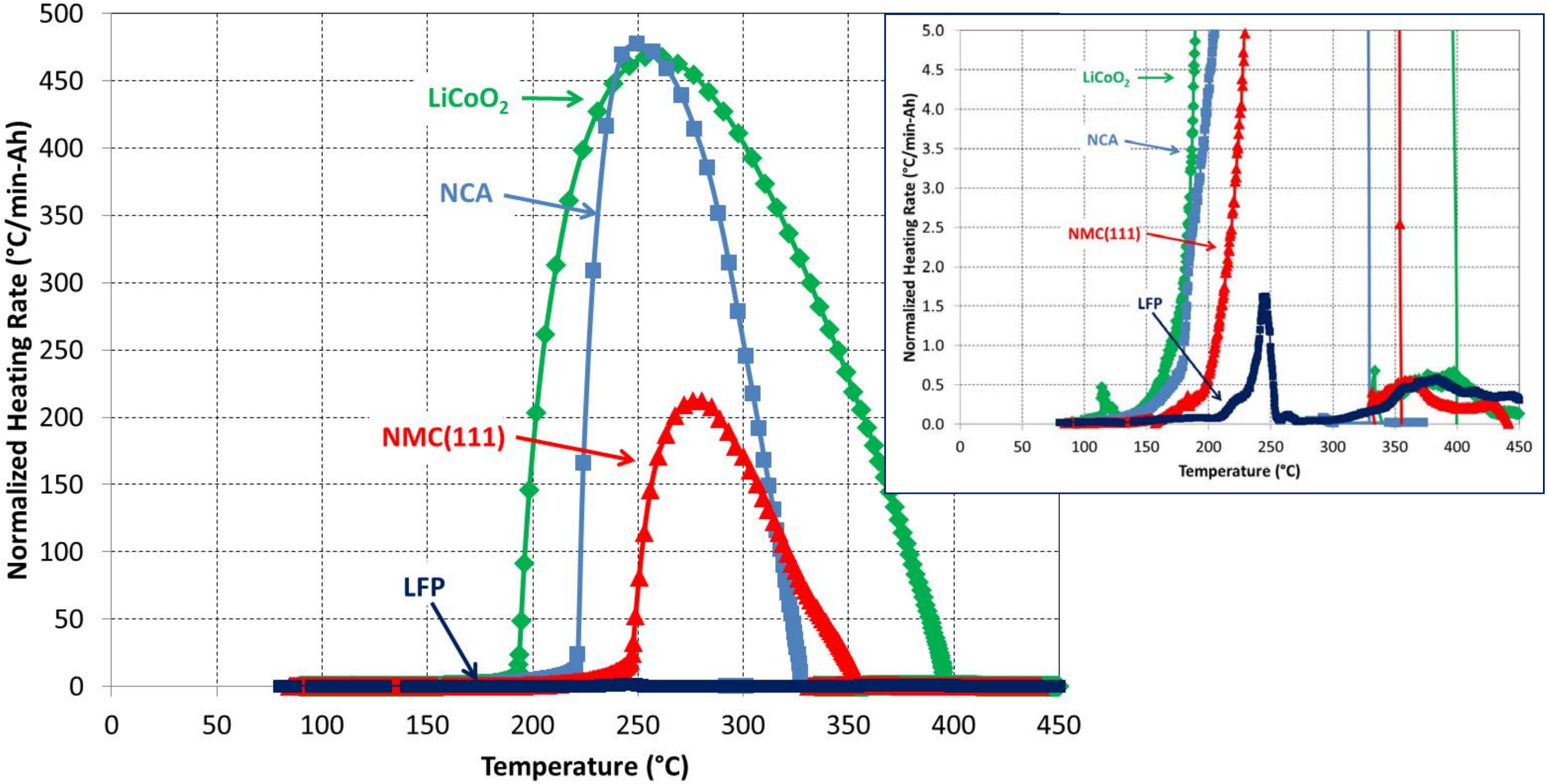
For known (or measured) C_p, J/g-K)

- dT/dt → W (J/s)
- ΔT → kJ

Thermodynamic parameters can be used to understand fundamental battery degradation phenomenon and to support battery design or risk mitigation design

Impact of Cell Chemistry

Accelerating rate calorimetry (ARC) of 18650 cells with different cathode materials



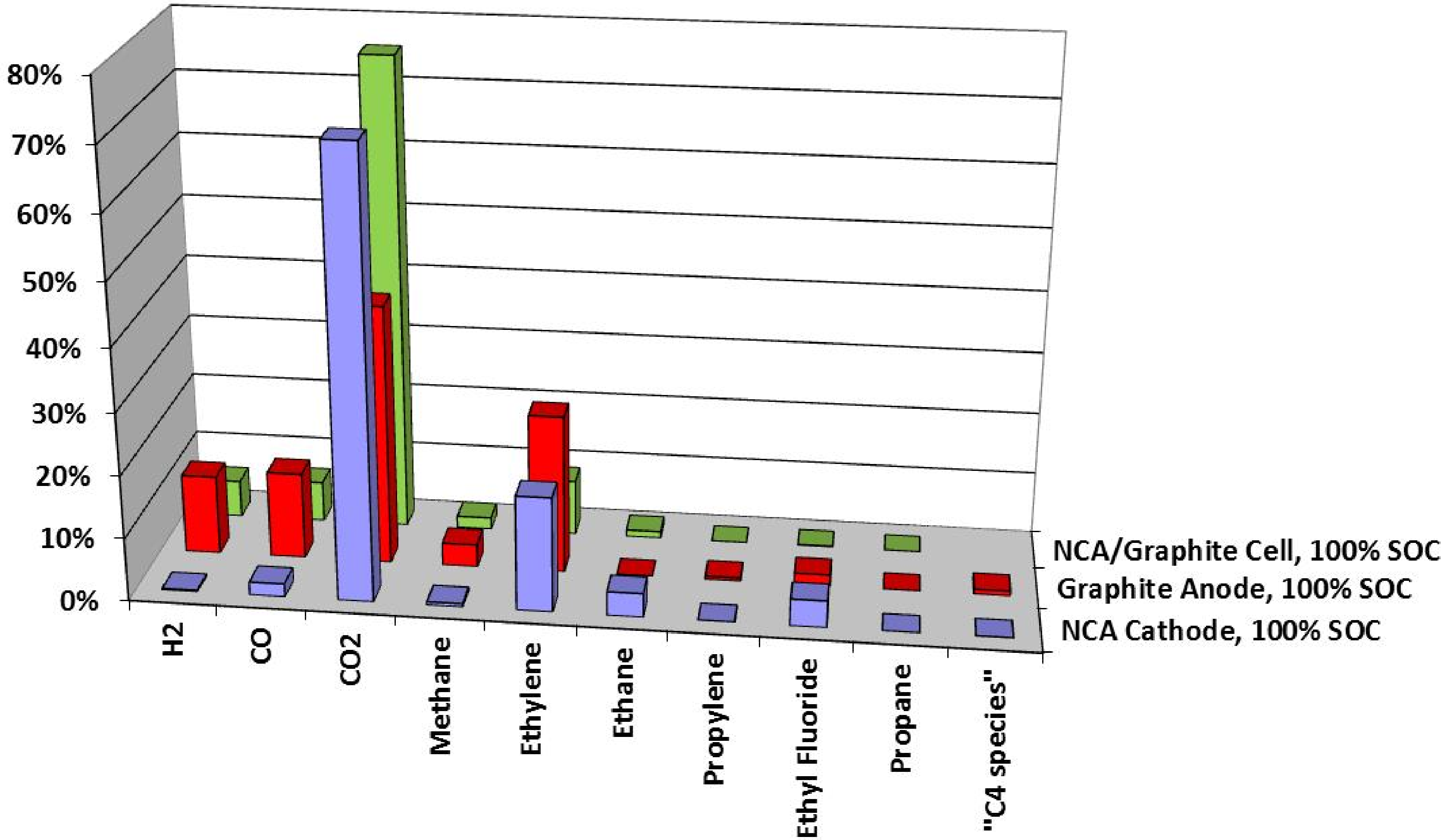
- ***All measurements at 100% SOC and for cells with 1.2 M $LiPF_6$ in EC:EMC (3:7)***
- ***Differences in runaway profiles are related to oxygen release and combustion at different cathodes***

Runaway Thermodynamics of Different Cell Chemistries

Cell Type	Capacity (Ah)	Runaway Enthalpy (kJ/Ah)		Peak Heating Rate (W/Ah)
		Full Cell	High Rate Region	
LCO 18650*	1.2	28.4	15.9	281
NCA 18650*	1.0	21.6	9.8	266
NMC 18650*	0.95	22.0	8.3	105
LFP 18650*	1.08	12.8	2.4	2

- ***Comparable total (full cell) heat release (kJ/Ah) for all cell chemistries***
- ***Heat release rates (e.g. runaway reaction kinetics) are very different for the cell chemistries***

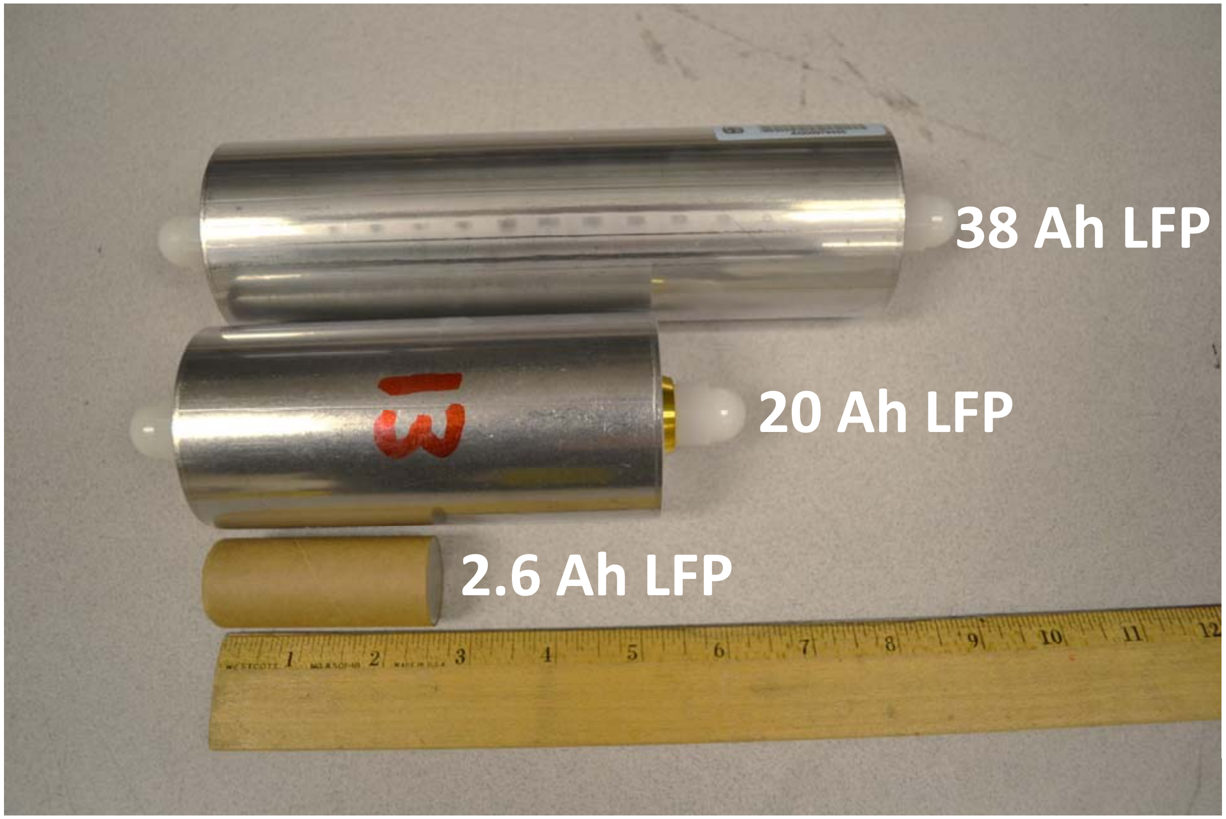
Vent Gas Analysis from the ARC



18650 cell electrodes separated from a cell at 100% SOC and repackaged in 18650 cans
Grab samples collected during an ARC experiment and analyzed
Analysis show significantly more H_2 and CO generation at the anode interface

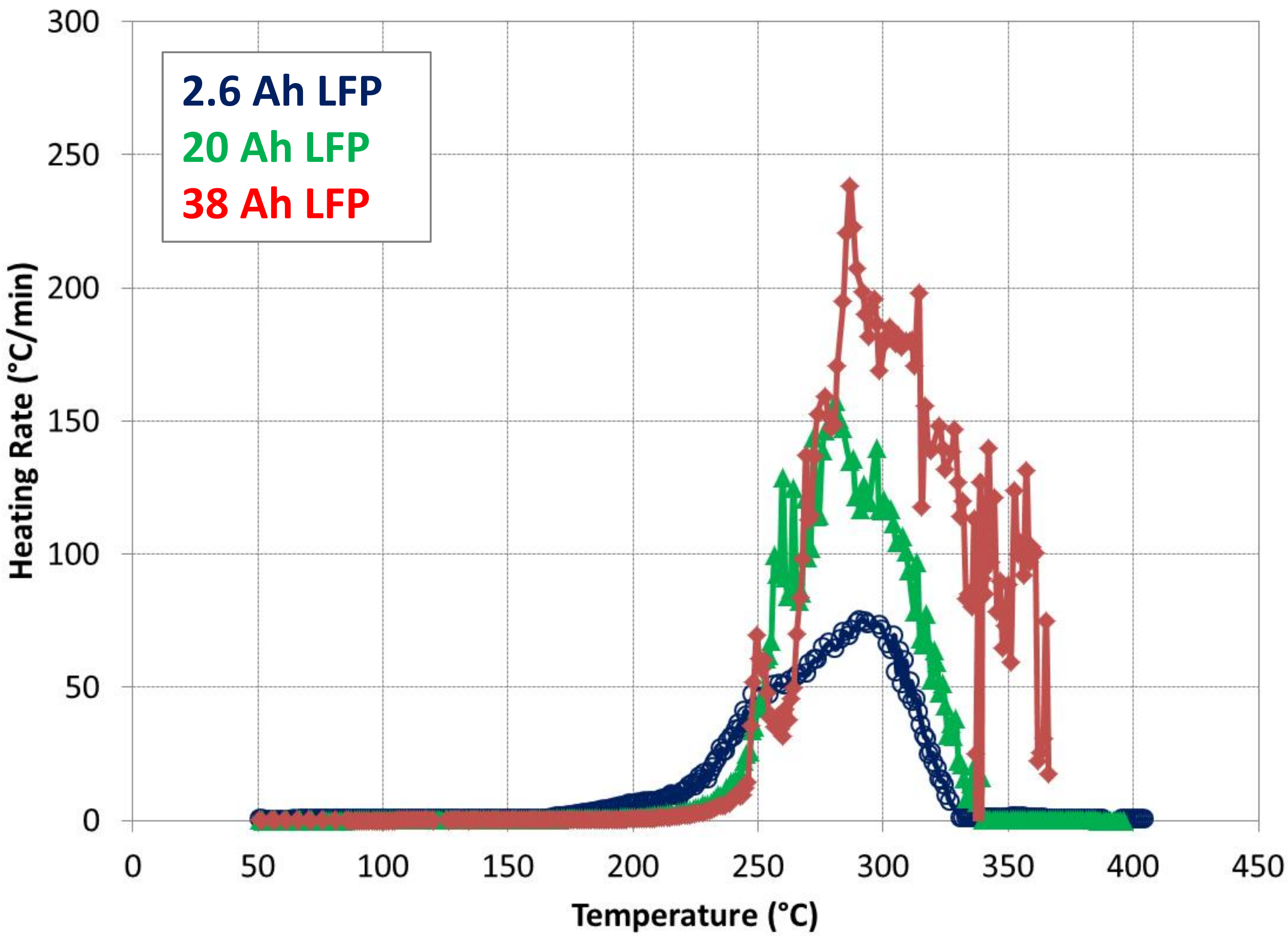
Impact of Cell Size on Runaway

- ***Evaluation of heat and gas generation as a function of cell size from 2-50 Ah***
- ***Using COTS cells and controlling cell chemistry and format as much as practical***
  - ***3 cylindrical LFP cells* and 3 cylindrical NCA cells***



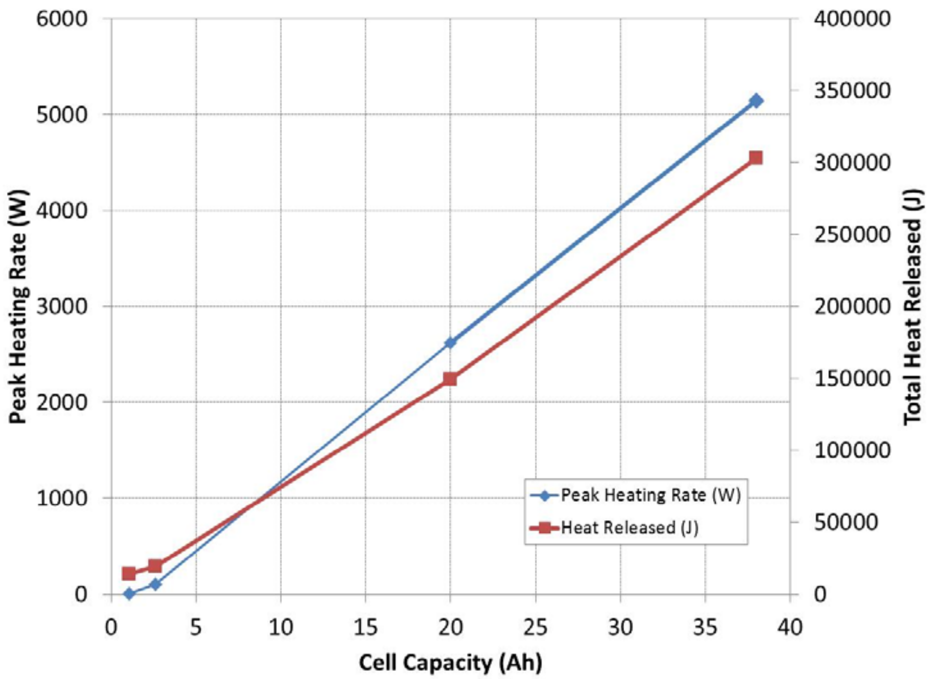
*** Will also show some data for 1.1 Ah LFP 18650 cells for comparison***

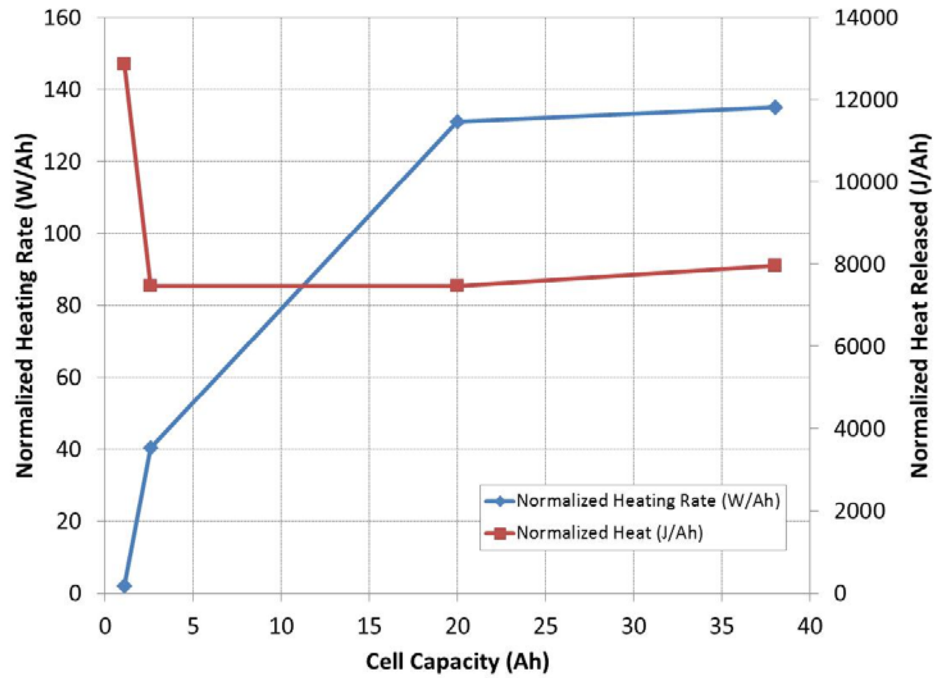
Impact of Cell Size on Runaway



As measured, the LFP cells show the expected trends where larger capacity cells show larger heating rates and larger temperature rise during thermal runaway

Impact of Cell Size on Runaway

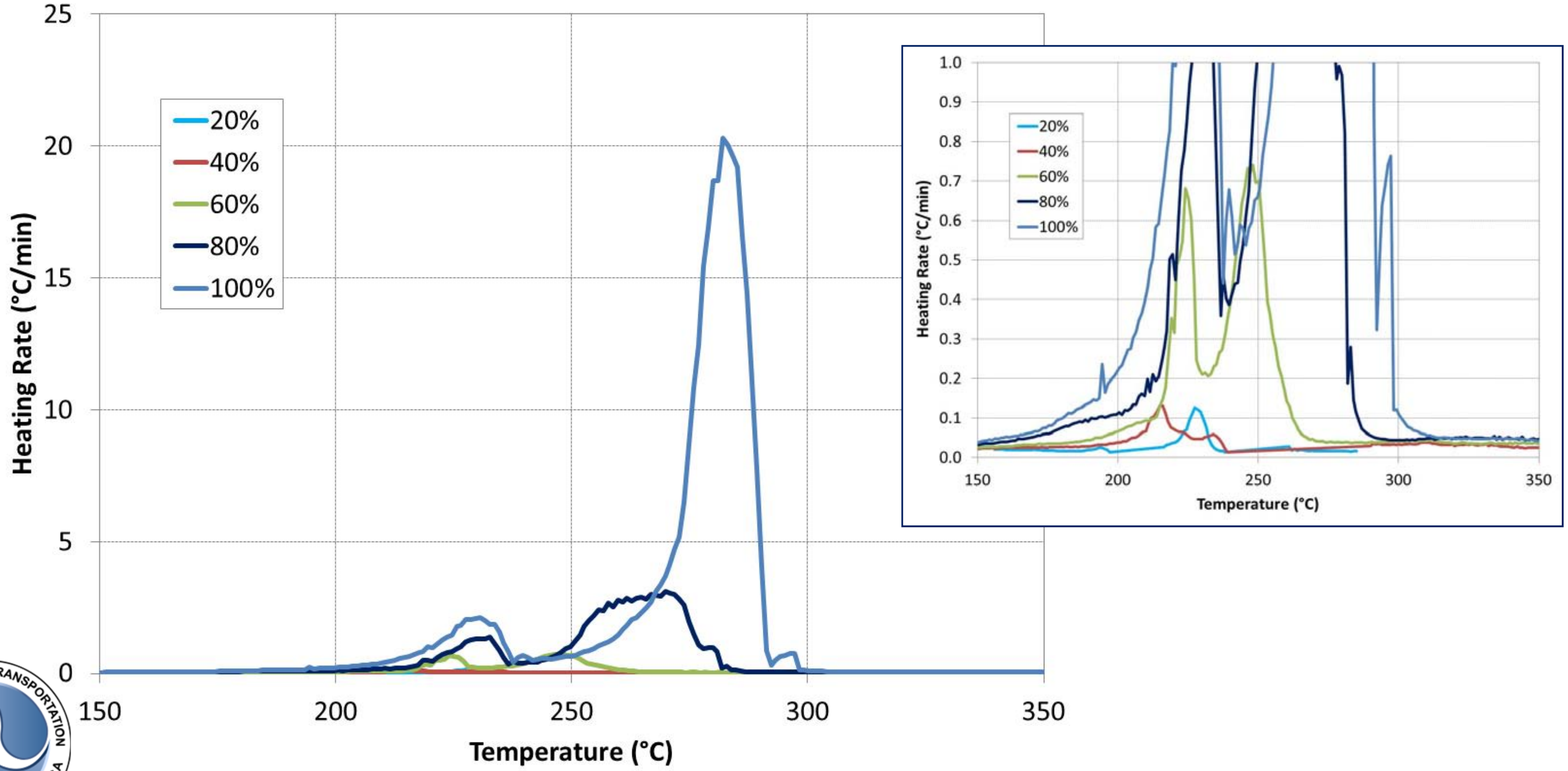




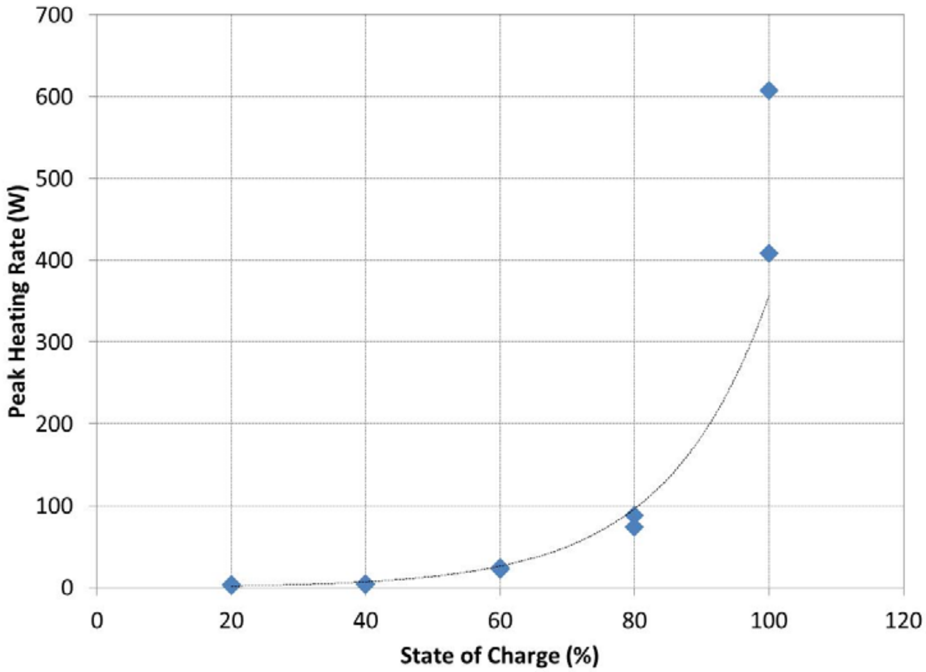
Total heat output and heating rate both scale with increasing cell capacity
Normalized heat output (J/Ah) is almost constant at ~7500-8000 J/Ah for 2.6-38 Ah cells

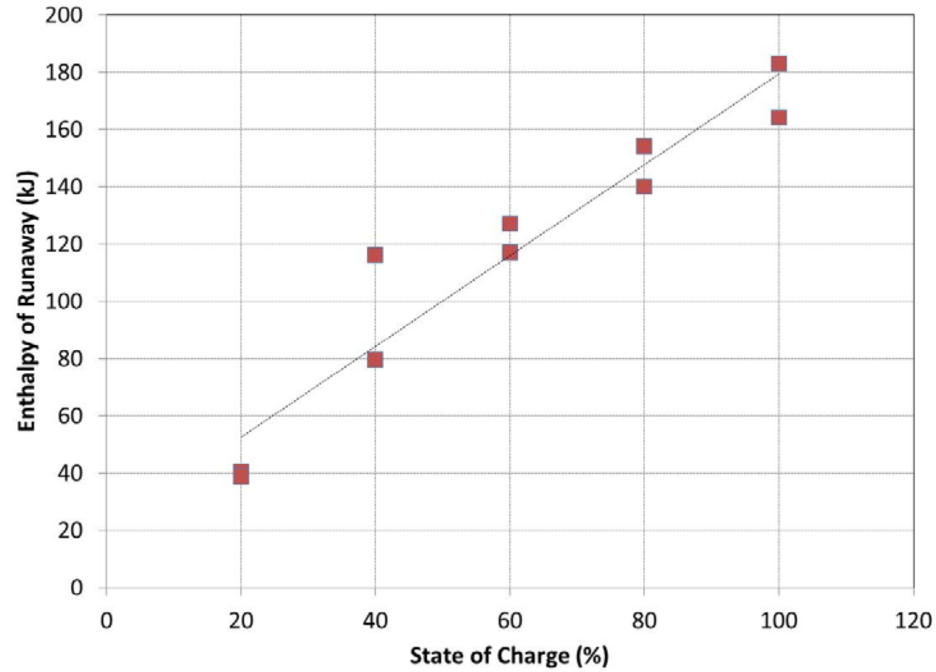
Impact of SOC on Runaway

- *16 Ah automotive (PHEV) pouch cells (mixed $LiMn_2O_4$ spinel)*
- *The objective is to provide data to support an acceptable discharge state in dealing with stranded energy in a rechargeable energy storage system (RESS)*



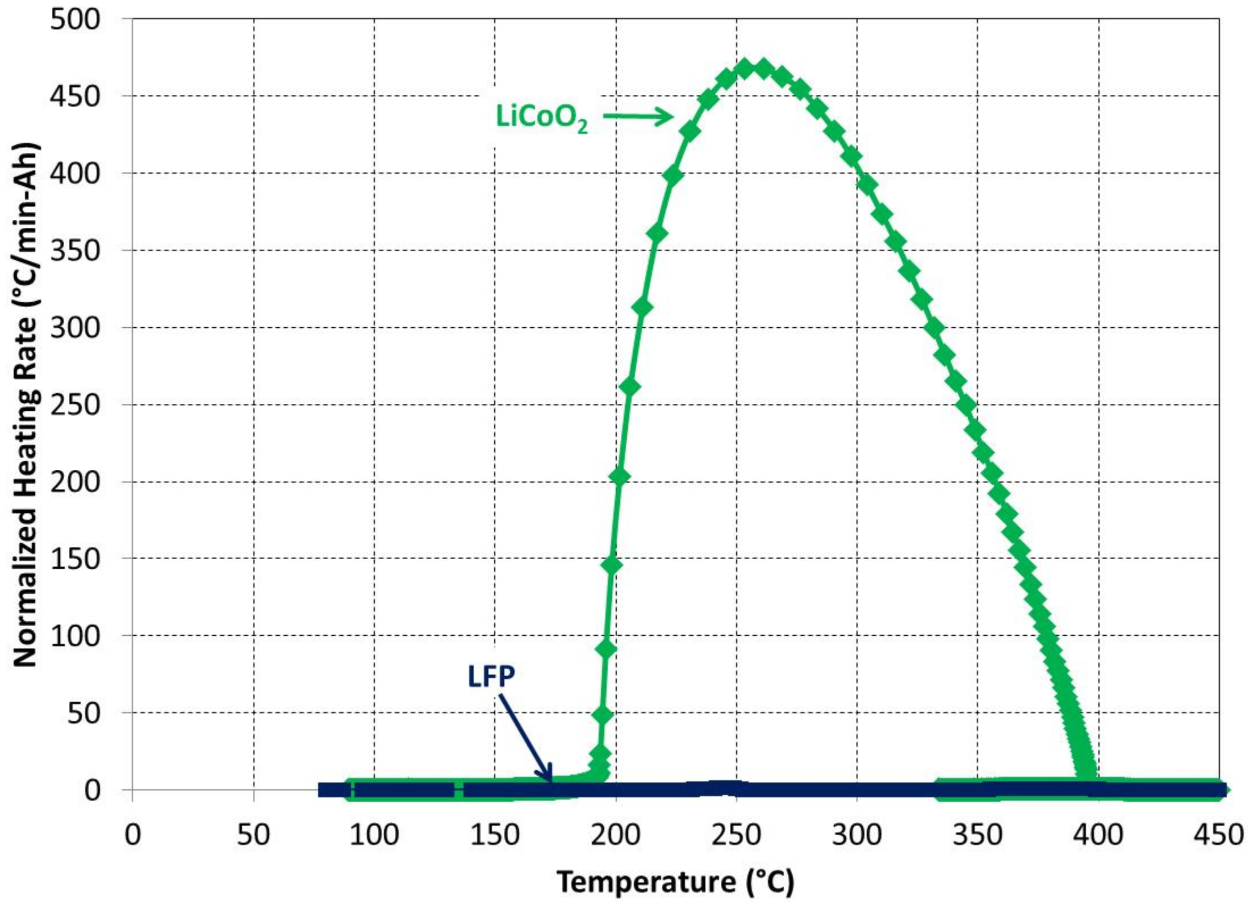
Impact of SOC on Runaway





Results show a nearly linear relationship between total heat release (kJ) and cell SOC
Heat release rates (e.g. runaway reaction kinetics) follow an almost exponential relationship with cell SOC
Results show a significant reduction in heat release rate between 40-60% SOC (validates a best practice of handling and shipping cells at ~50% SOC)

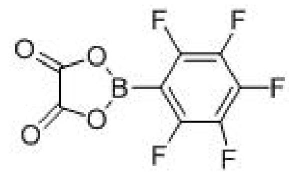
What can we do about it?



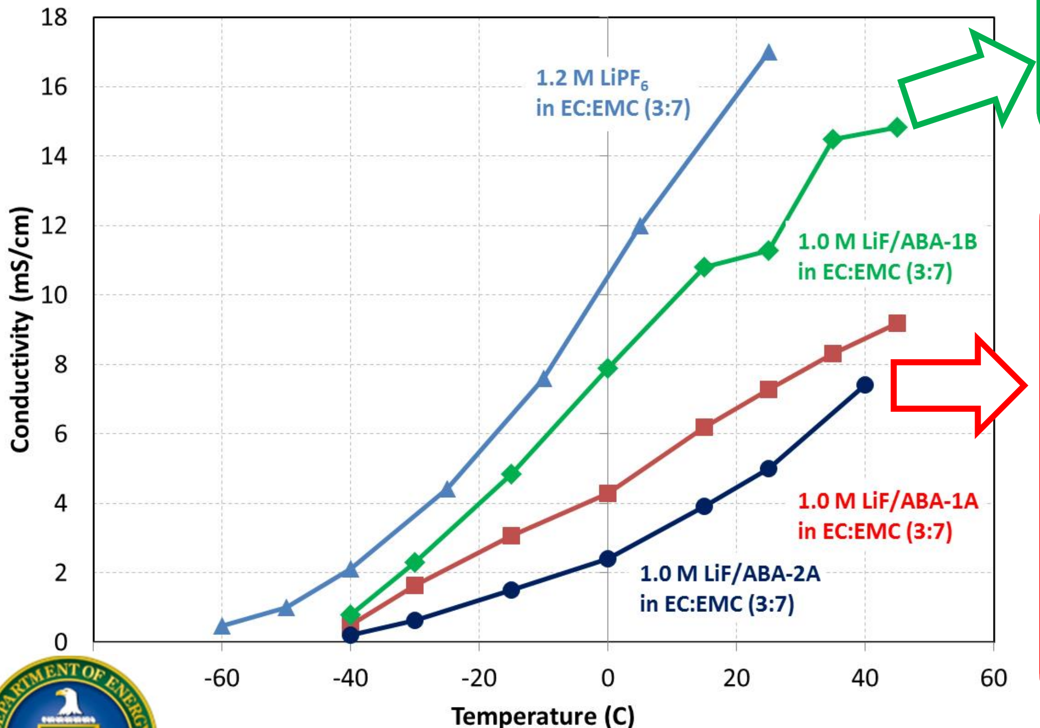
Can we change the thermal runaway behavior of higher energy chemistries to be more like that of LFP without sacrificing energy and performance?

Abuse Resilient Components

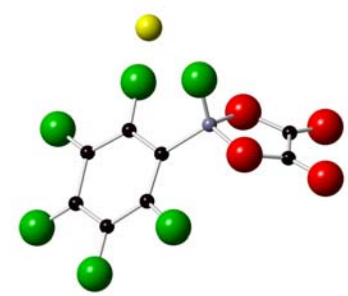
Electrolytes based on LiF and anion binding agents (ABAs)



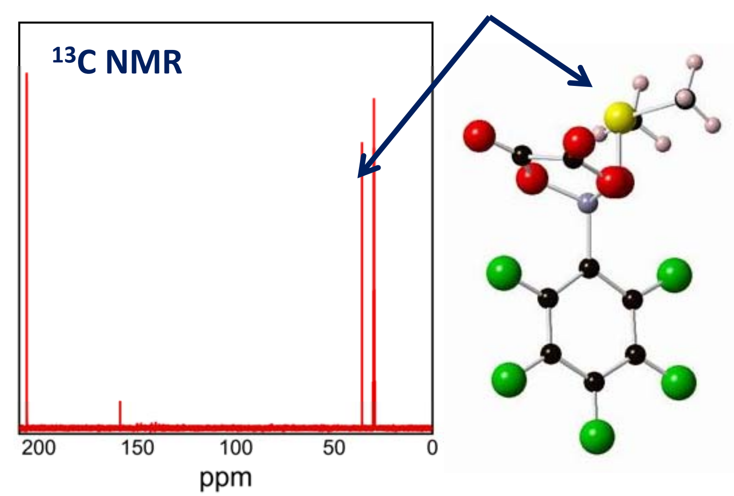
Perfluorophenyloxaltoborate (ABA -1)



Free LiF-ABA



DMSO coordinated to ABA-1A

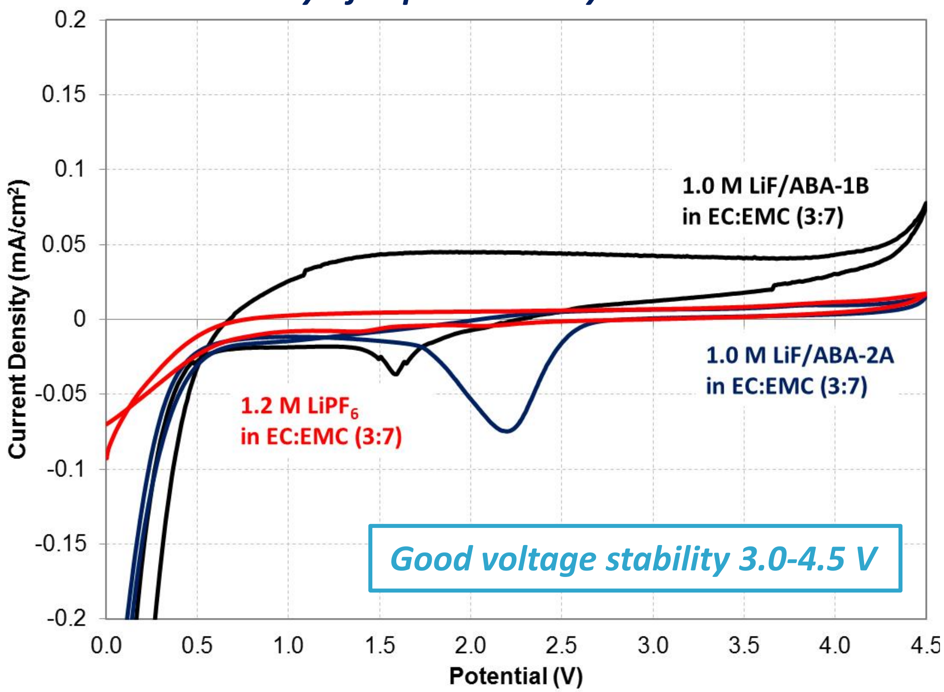


Improved performance of new ABA-based electrolytes

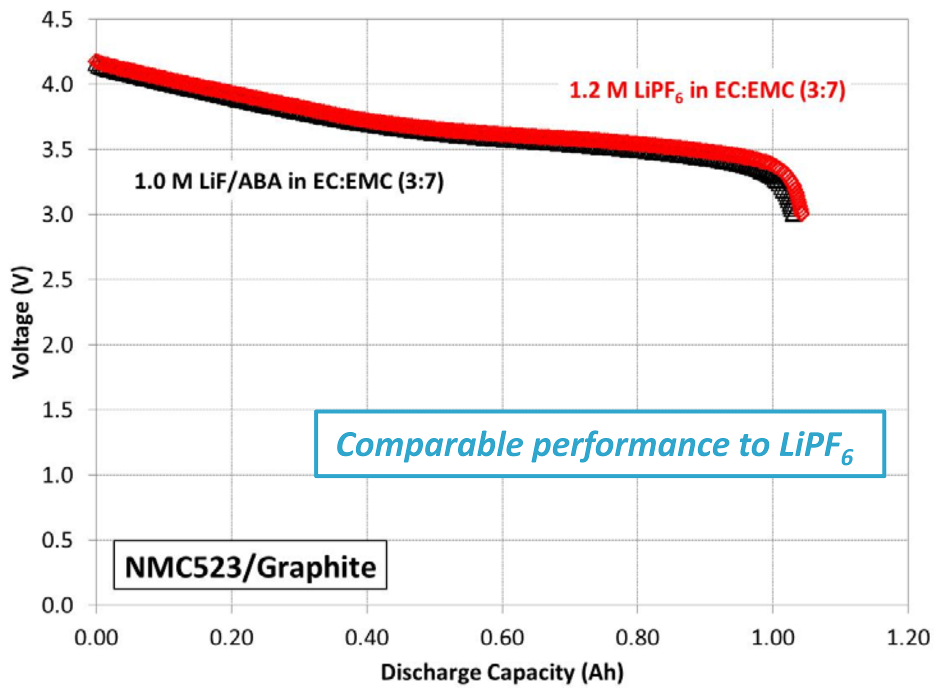
Abuse-Resilient Components

LiF/ABA Electrochemical Performance

Voltammetry of Liquid Electrolytes



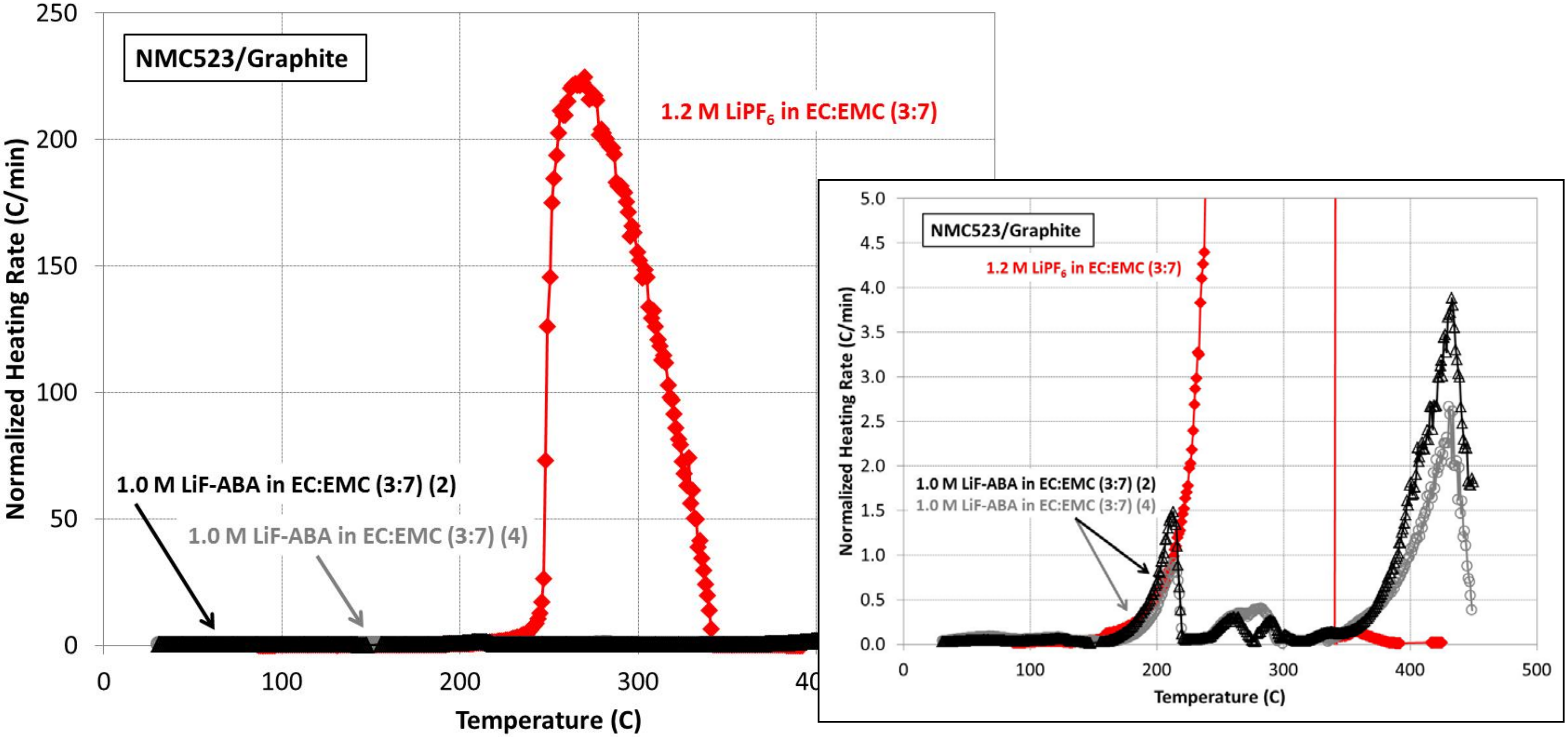
18650 Cell Performance



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

Abuse-Resilient Components

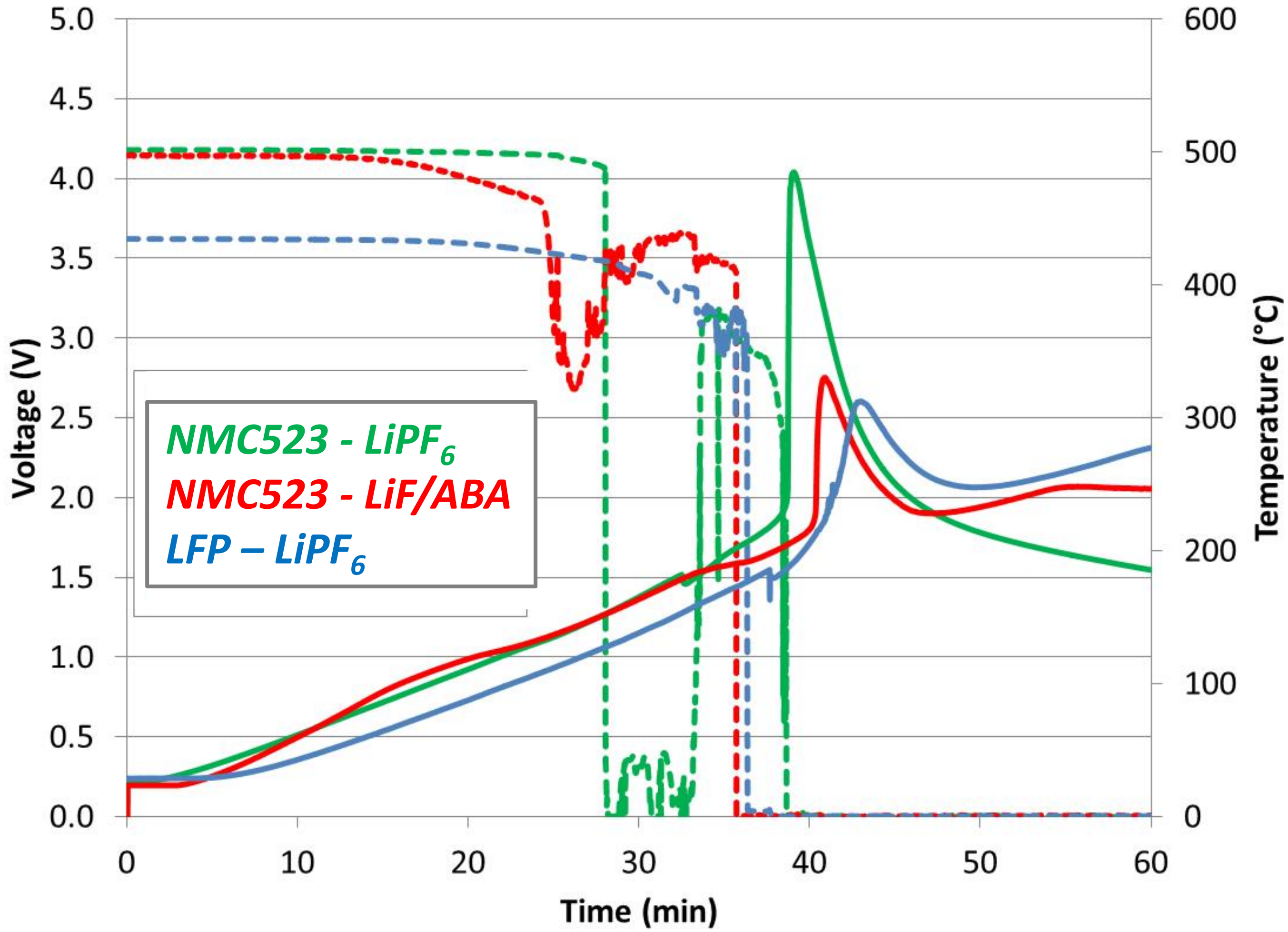
LiF/ABA Impact on Cell Thermal Runaway Response



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

Advanced Electrolytes

Thermal Abuse Tolerance of LiF/ABA

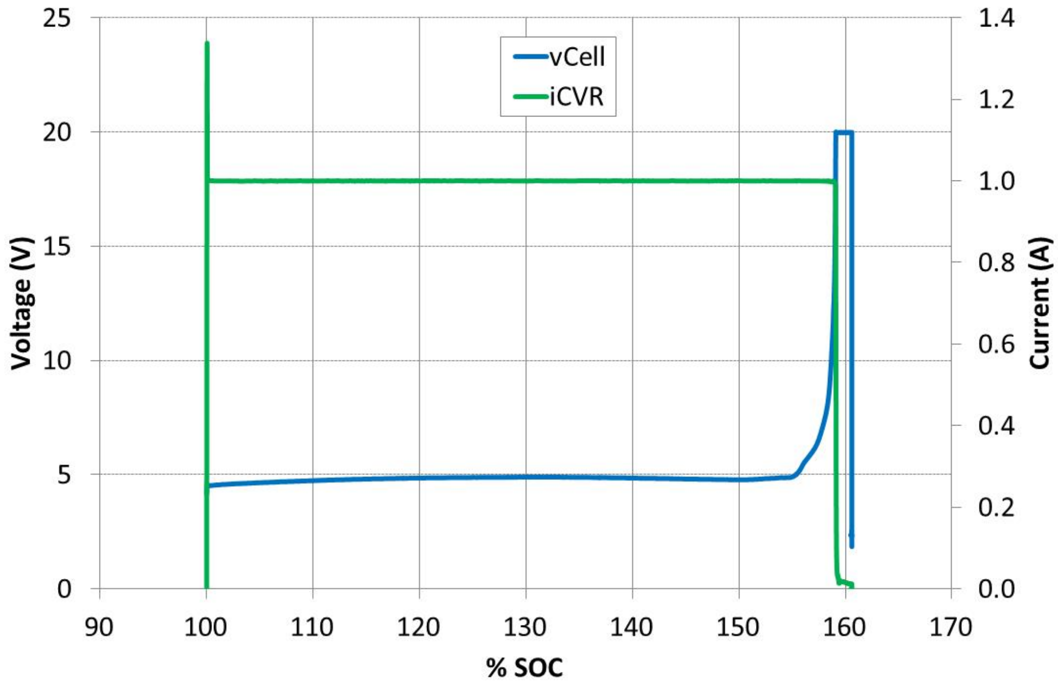


LiF/ABA NMC cells show thermal abuse tolerance comparable to LFP cells

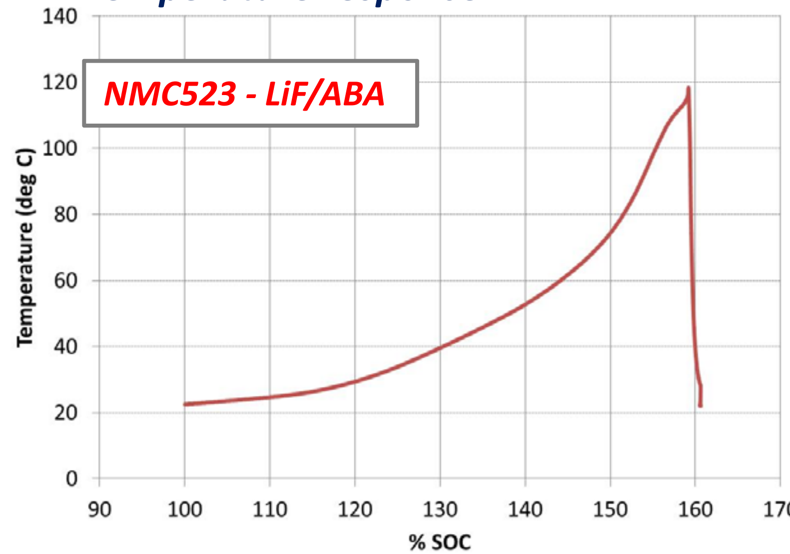
Advanced Electrolytes

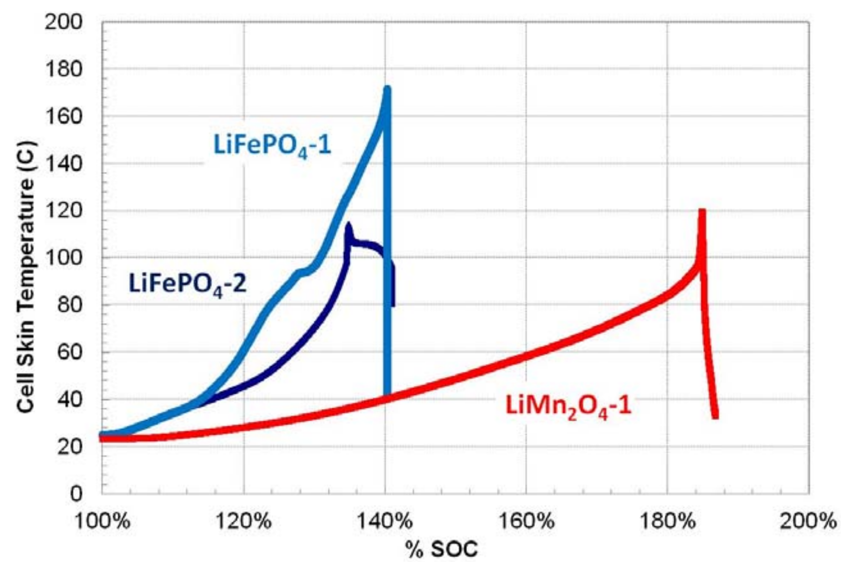
Overcharge Abuse Tolerance of LiF/ABA

Voltage and Charge Current



Temperature response





LiF/ABA NMC cells show consequences of overcharge abuse comparable to LFP cells

Summary

- Accelerating rate calorimetry (ARC) can be used to quantify the energetics of thermal runaway in lithium-ion cells
- Total heat release (kJ) and heat release rates (W) are nearly linear as a function of cell size (3-40 Ah for LFP cells)
- Total heat release (kJ) is nearly linear as a function of SOC while the heat release rates (W) are nearly exponential as a function of SOC for the cell type studied
- Electrolytes based on LiF/ABA salts have been shown to mitigate the severity of thermal runaway in lithium-ion cells without sacrificing significant performance

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