

Evaluating thermal runaway risks in high energy density cells



PRESENTED BY

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Energy Storage Safety Forum 2020



Lithium-Ion Battery Challenges

- **Energetic thermal runaway**
 - Anode and cathode decomposition reactions
- **Electrolyte flammability**
 - Low flashpoint electrolyte solvents
 - Vent gas management
 - Fuel-air deflagrations
 - Wide flammability range of decomposition products
- **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**
- **However... From 2014-2016 there were 171,500 vehicle fires per year, almost entirely from gasoline vehicles¹**

Capabilities of Power Source R&D Group

10,000 sq. ft. dry room space

Synthesis of battery materials

Prototyping for thermal batteries, Li primary, and Li-ion cells and batteries

Battery design & development

Performance and abuse testing

Battery calorimetry facilities

Forensics and analysis

Fundamental electrochemistry

Modeling and simulation*

Environmental testing*

High hazard test facilities (Burn Site)*



*Facilities leveraged from our Partners in SNL Experimental Sciences Center

Battery Abuse Testing Laboratory (BATLab)

Comprehensive abuse testing platforms for safety and reliability of cells, batteries and systems from mWh to kWh

Cell, module, and battery system hardware deliverables for testing

Mechanical abuse

- Penetration
- Crush
- Impact
- Immersion

Thermal abuse

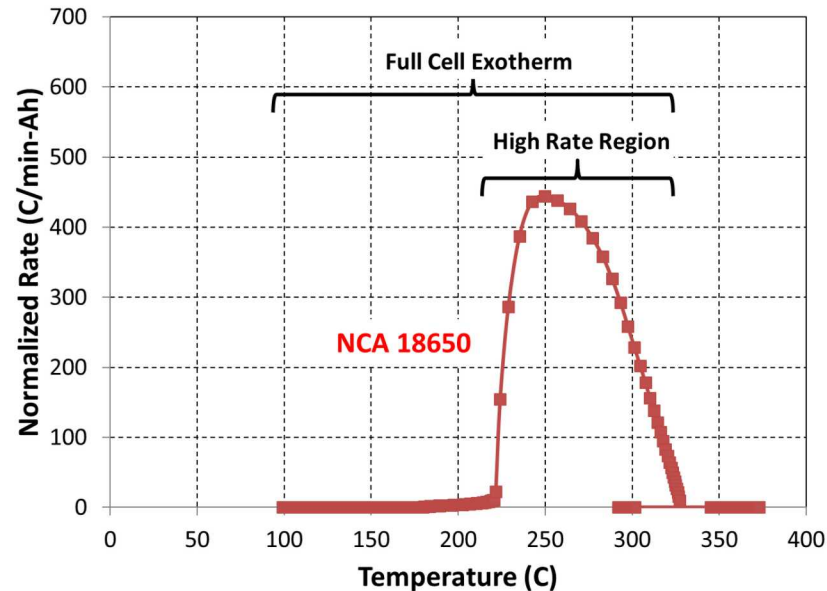
- Over temperature
- Flammability measurements
- Thermal propagation
- Calorimetry

Electrical abuse

- Overvoltage/overcharge
- Short circuit
- Overdischarge/voltage reversal

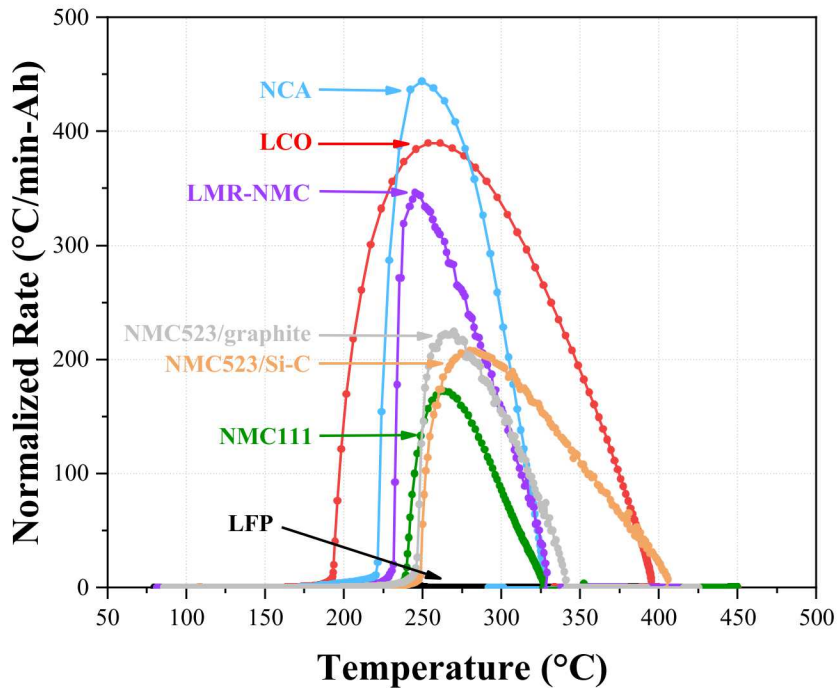


Characterizing Thermal Runaway



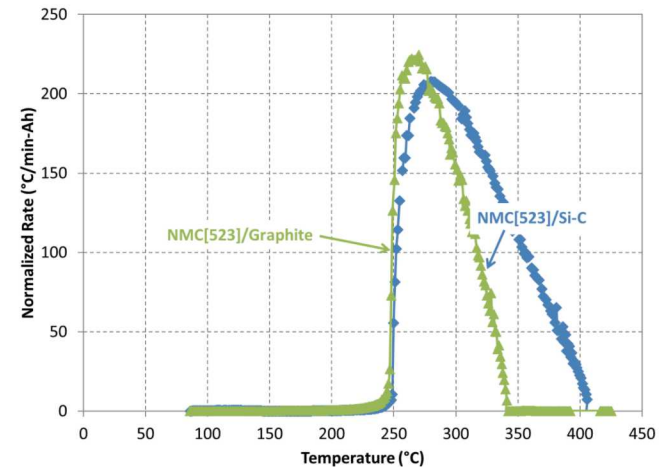
- Begins when self heating reactions exceed natural losses to surroundings
 - Upon self heating, a cell experiences further decomposition leading to an accelerated heating rate effect
 - ARC testing - sets natural losses to 0
- We evaluate two primary values:
 - Peak heating rates
 - Total enthalpy of the exothermic process
(The enthalpy of the high rate region can also be determined)
- High rate behavior:
 - Best potential for evaluating the likelihood of thermal runaway
 - Identifies the threshold for thermal runaway

Characterizing New Materials



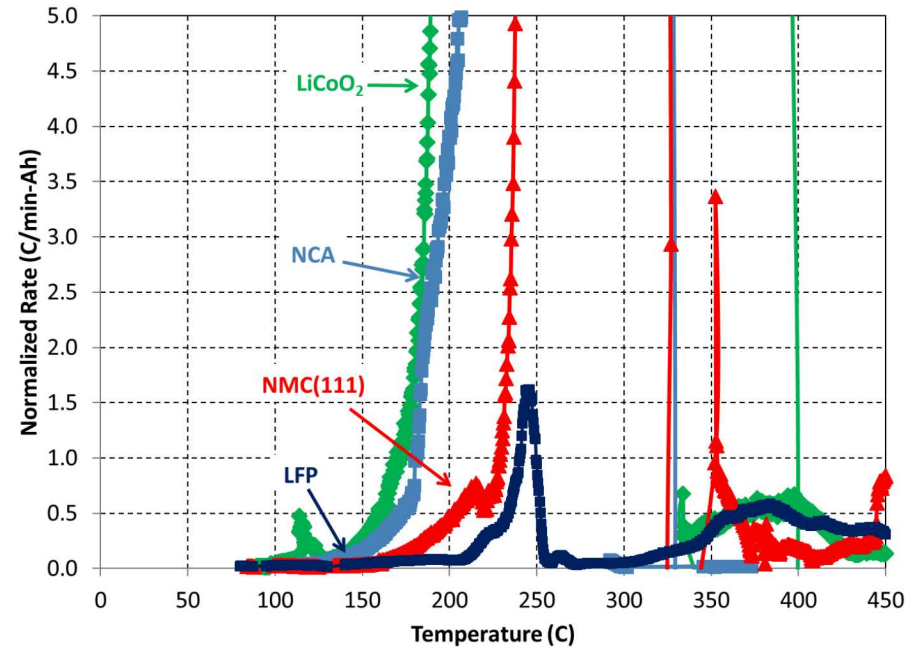
- ARC data depicts behavior of various chemistries
- Peak heating rates and total energy of thermal runaway
- Newer materials (LFP):
 - Significantly reduced thermal runaway intensities
 - Limited energy density

- ARC has been a powerful tool in performing these evaluations of new materials
- Work is generally performed on 18650 cells



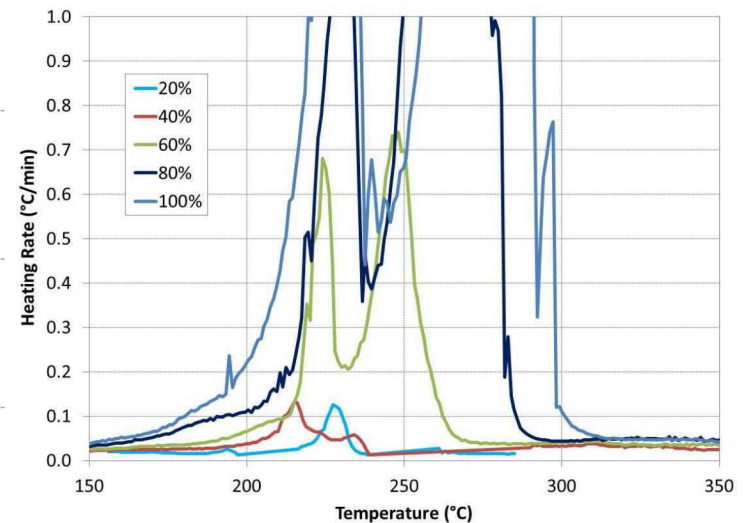
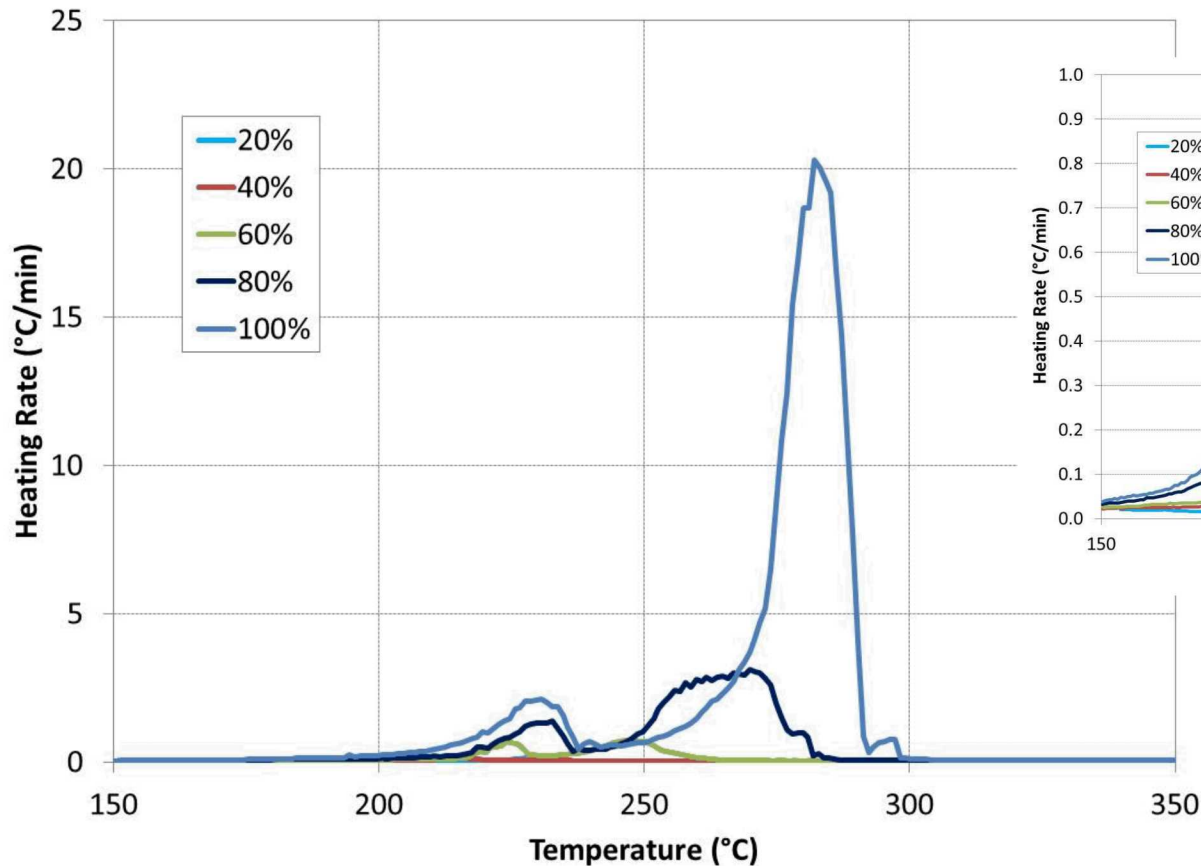
7 Chemistry vs. Energy Density

- Cell chemistries such as LTO and LFP
 - Labeled as lower risk materials
 - Energy density also significantly lower
- Typically normalize to cell level capacity or energy density
- Low capacity cells - inactive materials are a larger portion of the total mass of a system
- Materials comparison done on 18650 cells of 1-2 Ah, normalized to cell capacity

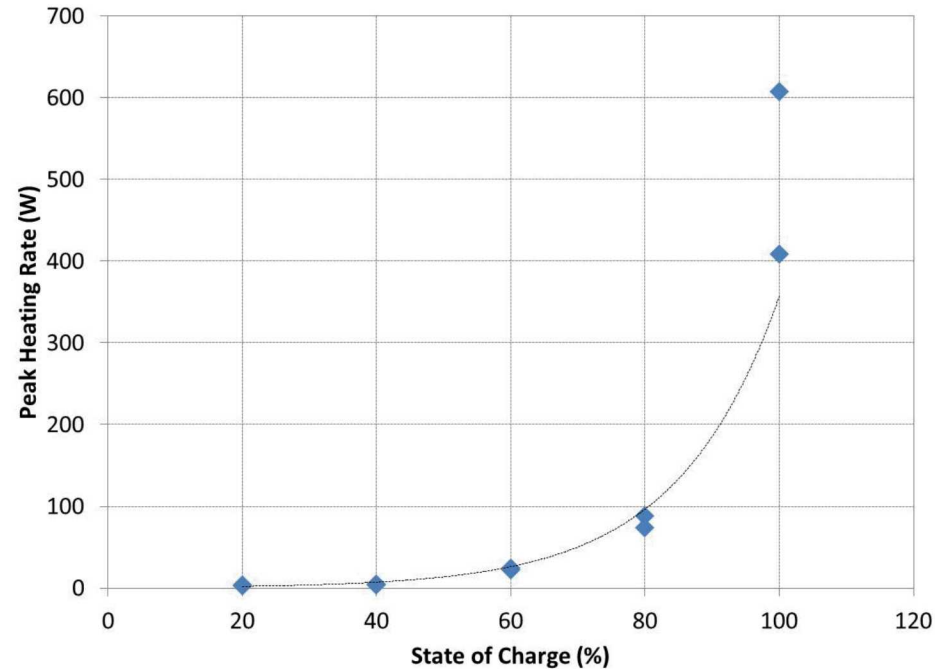
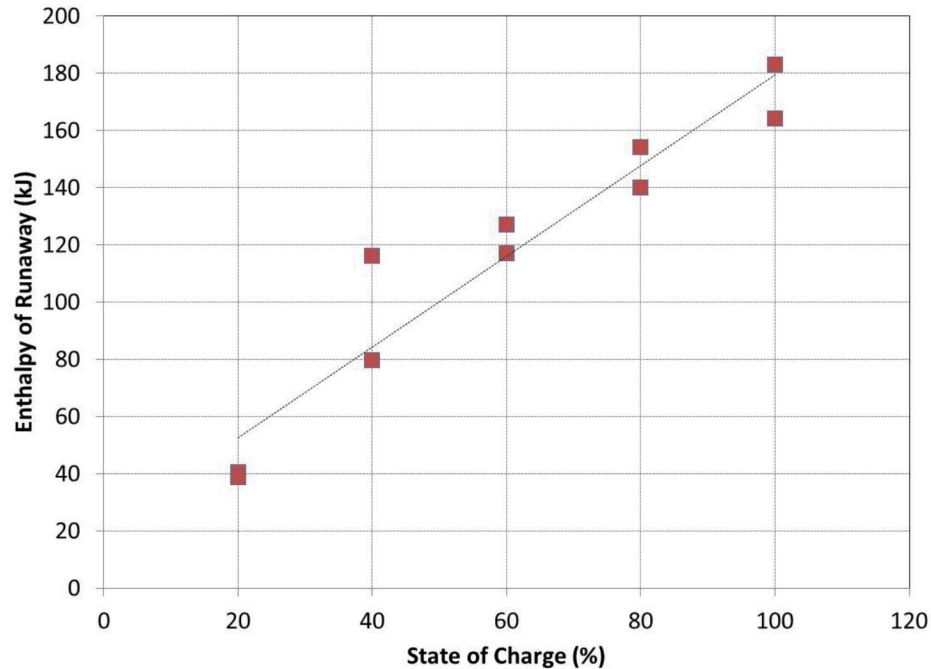


SOC and Thermal Runaway – A single cell case study

- 16 Ah Automotive (PHEV) pouch cells (mixed LiMn_2O_4 spinel)
- Significant impact observed above 60% SOC
 - Very low self heating rate at 40% and 20%

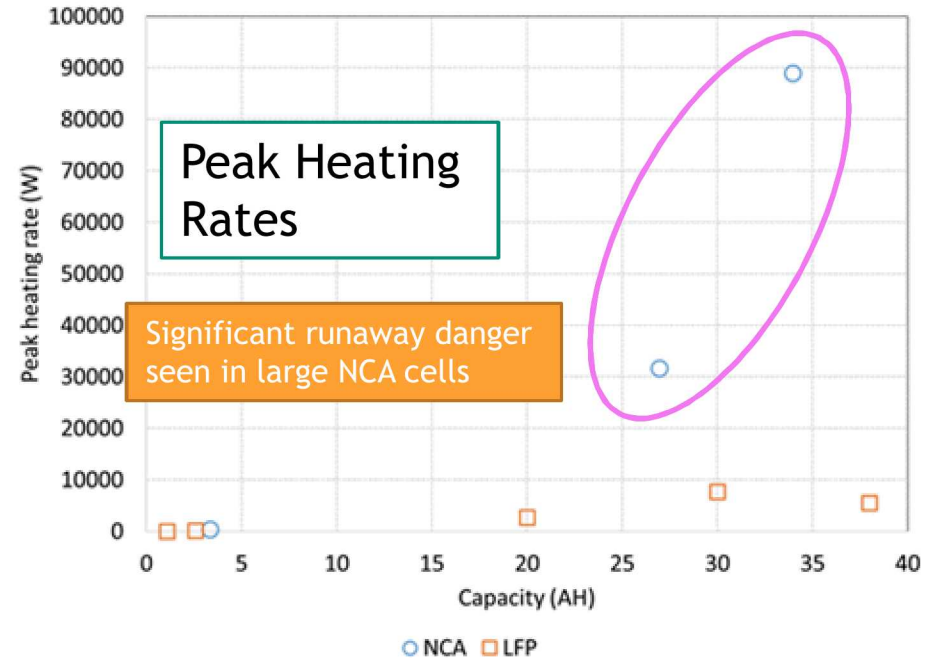
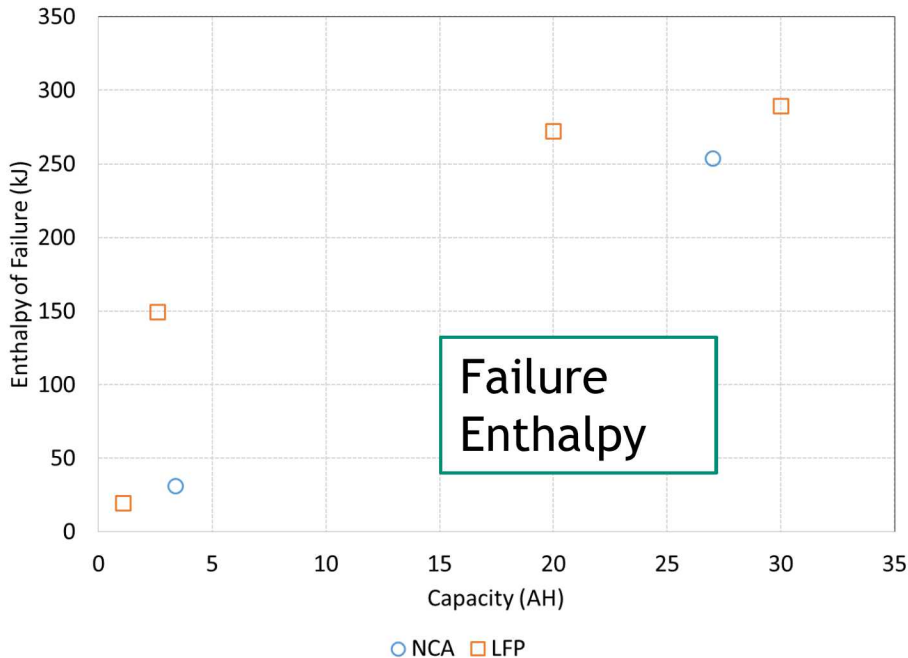


Impact of SOC on Runaway – A single cell case study

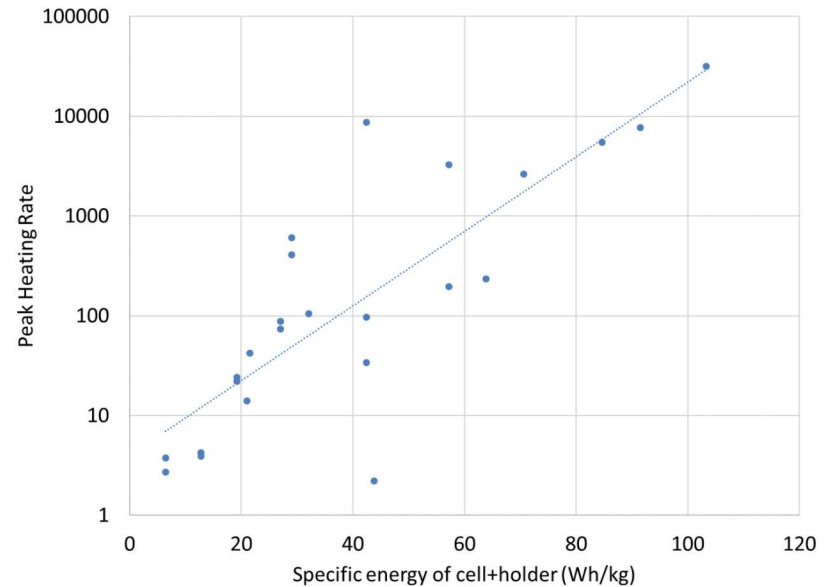
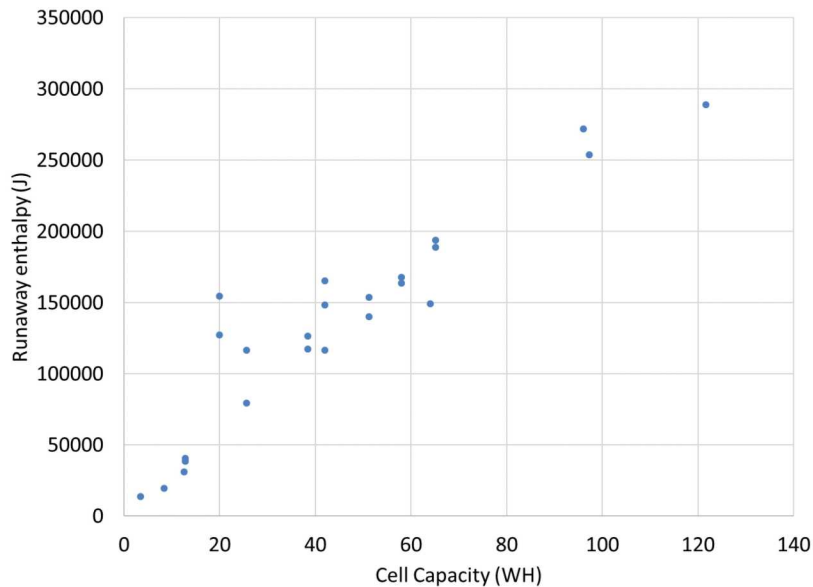


- Nearly linear relationship between total heat release (kJ) and cell SOC
 - Similar to data for cell size
 - Suggests failure enthalpy is based largely on the stored energy available
- Heat release rates (e.g. runaway reaction kinetics) follow an almost exponential relationship with cell SOC
 - Traditionally thought to cause a greater risk of thermal runaway

Cell Size vs. Chemistry

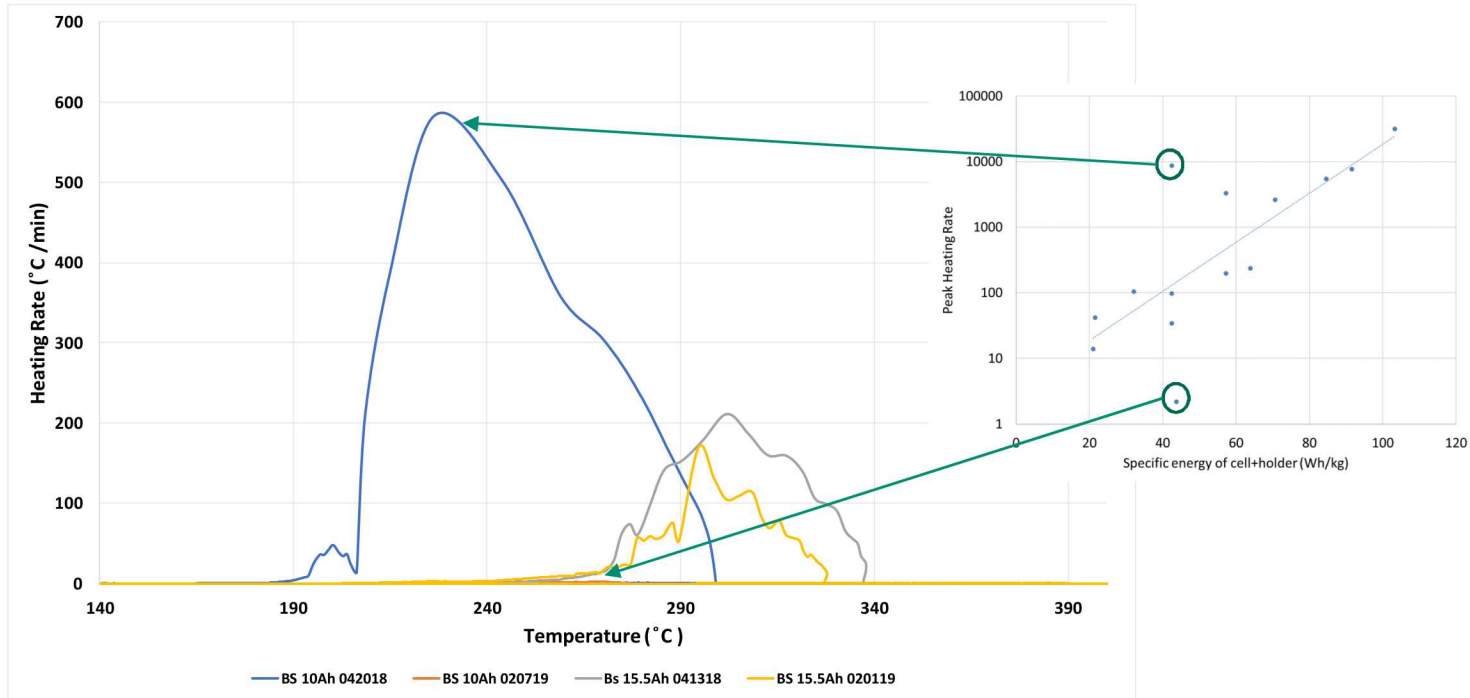


- Enthalpy – proportional to capacity
 - Similar for both chemistries
 - Early data suggests that failure enthalpy is largely tied to the available stored energy
- Peak heating rates significantly higher for large NCA cells
- High peak heating rates are generally thought to carry a higher thermal runaway risk

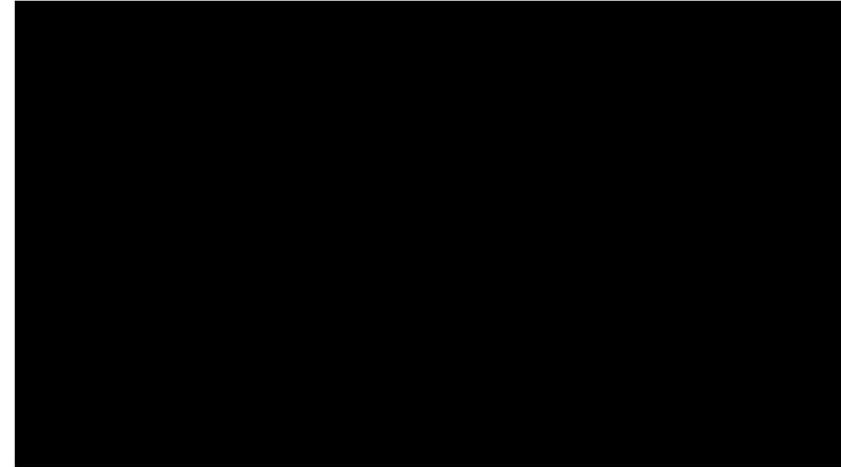
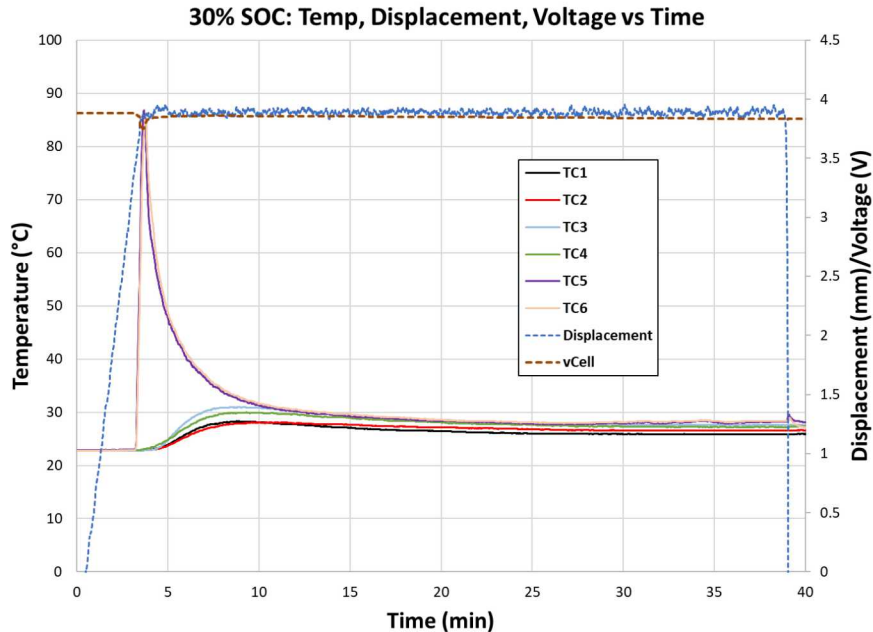


- Test data from the following:
 - Cell capacity = 1.08 to 38 AH (3.5-122 WH)
 - Chemistries = LFP, NMC and NCA
 - Formats = 18650, 26650, pouch cell, and large cylindrical*
- Total energy of runaway maintains a linear relationship to cell capacity
- Pairing peak heating rate with specific energy of the tested system results in an exponential pattern
- Peak heating rates do not give a complete story for runaway severity
 - Excludes gas generation and peak temperatures
 - May be the best metric we have for predicting likelihood of thermal runaway
 - When heating rates do not exceed natural heat loss - thermal runaway will not normally occur

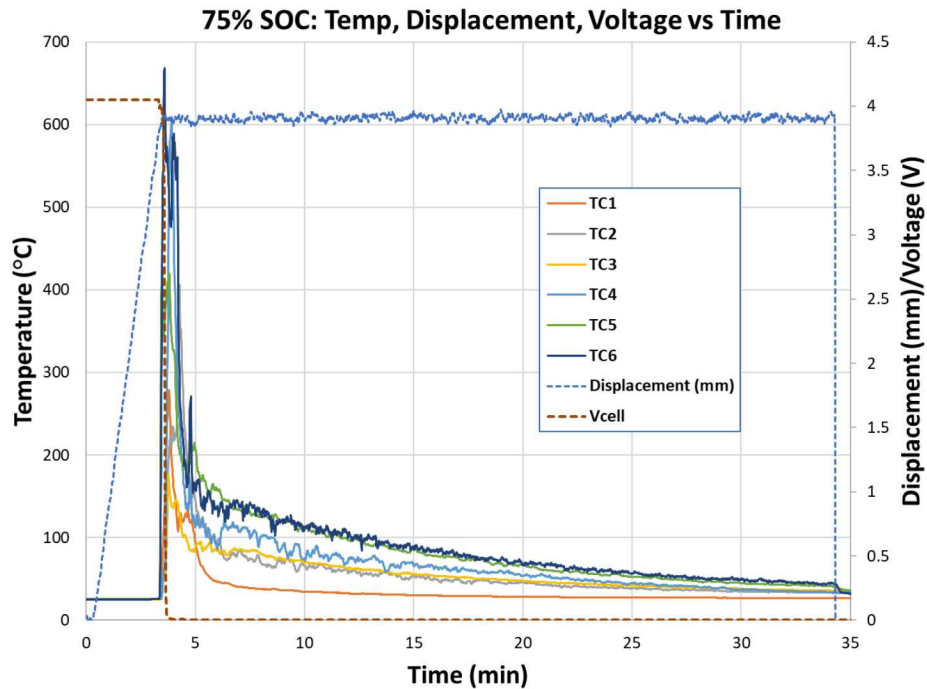
*steel cylindrical cells with machined stamped vents



- Cell from single supplier responsible for the most abnormal runaway patterns
- COTS pouch cell from a second tier supplier
- Suggests cell construction has an important role to play as well
- Large heating rates observed here may be indicative of an internal short circuit developing during failure, or self ignition of electrolyte
 - Would lead to significant heating due to the rapid self discharge

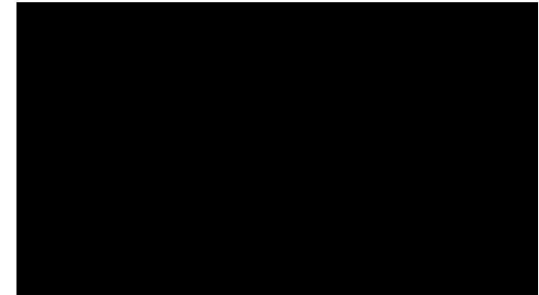
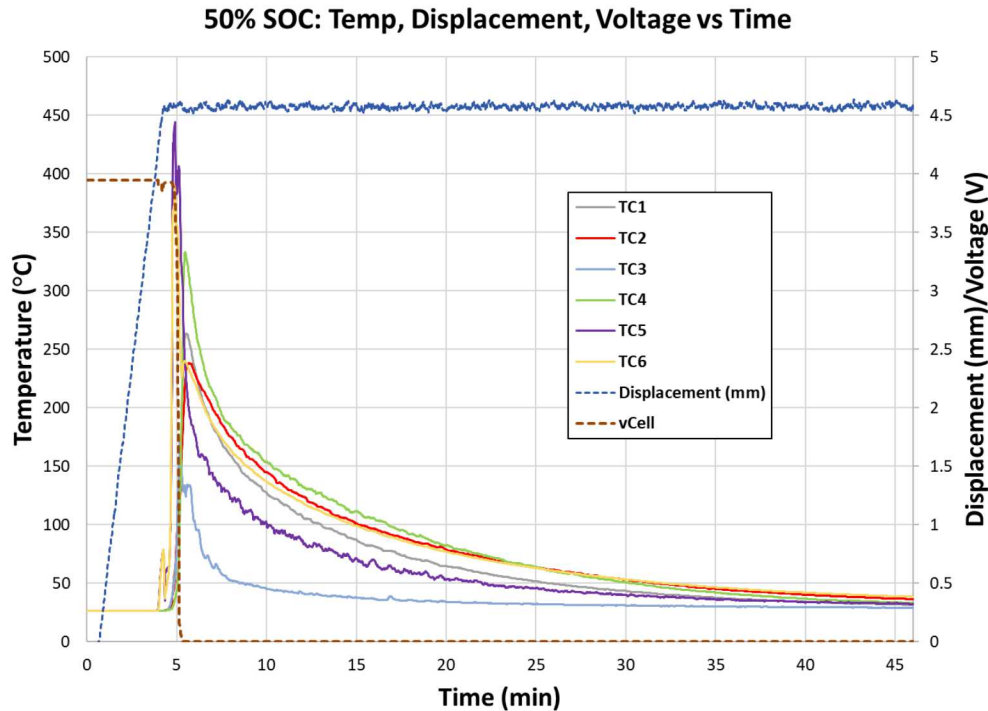


- Collaborative comparison of mechanical results with ORNL
- Displacement of ~4.0 mm
- Force reached was just under 2,200 N
- Voltage drop of 3.88 V to 3.75 V
- Some self heating but no major venting or self-ignition, max temp = 86.8°C
- Some leakage of electrolyte observed



- 75% SOC test
- By this SOC a full cell runaway with self-ignition is observed
- Displacement of ~4.1 mm
- Force reached of ~ 2,050 N
- Full voltage loss
- Significant thermal runaway event with self-ignition max temp = 668.3 °C

Impact of SOC on mechanical abuse testing – Testing of large format cells



- 50% SOC test
- Thermal runaway event observed but no self ignition
- Displacement ~4.7 mm
- Force ~ 2,120 N
- Full voltage loss
- Thermal runaway event, max temp = 444.6 °C
- Heavy venting of electrolyte products observed - sufficient to obscure vision in the test chamber

First Glance:

- Peak heating rates are highly dependent on:
 - Cell chemistry
 - State of Charge
 - Cell format
- Digging deeper reveals primary driver may simply be the component level energy density
- Component level = cell + inactive material in intimate contact with cell
- May have implications on propagation mitigation strategies
 - Mitigate failure by simply reducing system level energy density
- Open question: Is it possible to break this trend and achieve a low risk of thermal runaway, with a significantly high energy density?

Total Enthalpy – tied directly to total stored energy

Pouch cells – higher variance observed

Mechanical testing at various states of charge shows the impact may go beyond just the energetics of the initial runaway

- At 50% SOC, a milder thermal runaway event is observed that on its own may be less likely to propagate to a broader system
- However, significant venting still occurs, ultimately filling the room
- The potential flammability of this gas may pose significant risk in some situations

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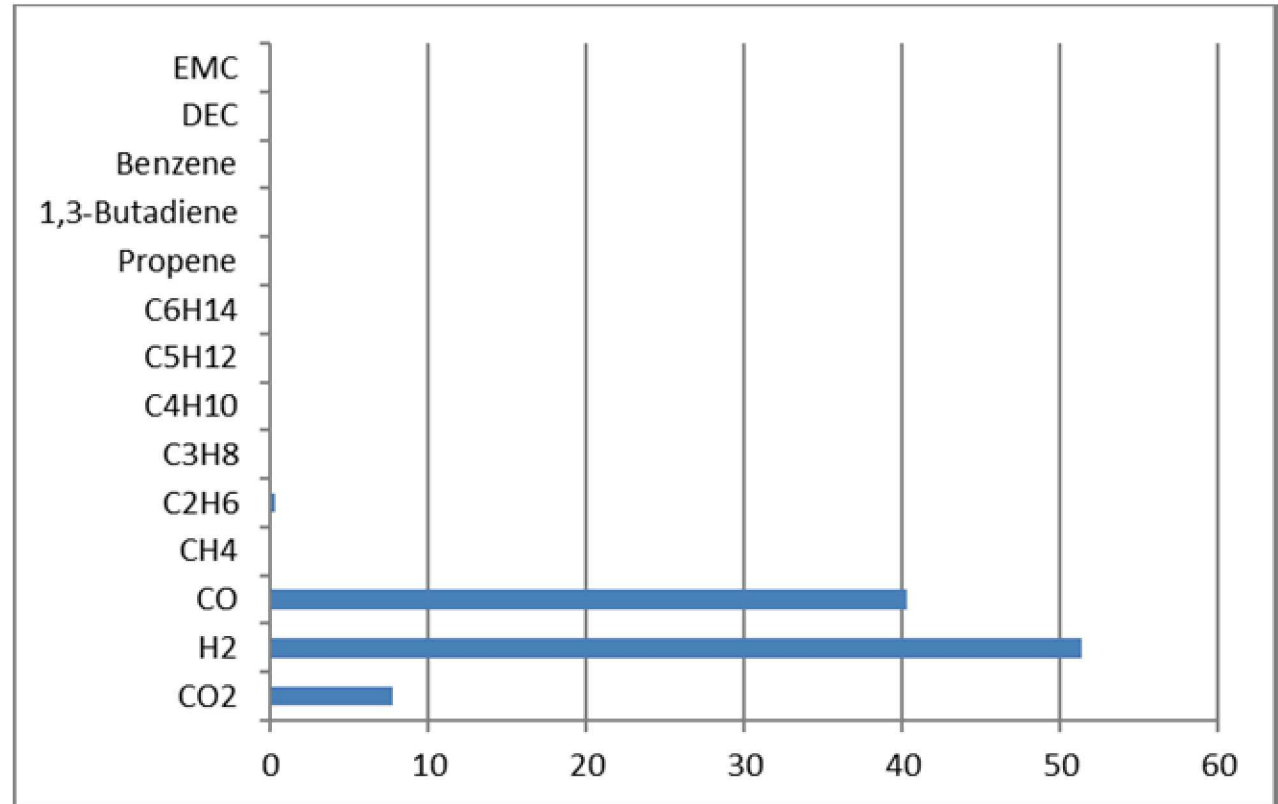
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Extra slides – sample gas analysis



- Most prominent constituents observed are CO, H₂ and CO₂
- N₂ and O₂ were subtracted out for this comparison
- N₂ and O₂ present were roughly equivalent to in-air proportions, suggesting little combustion occurred



FTIR results of the vent gasses of a COTS cell

- FTIR peaks show an initial venting at ~19 minutes
- The initial gas observed shows DMC (dimethyl carbonate) gas most prominently
- CO_2 rapidly becomes apparent after this initial venting
- Some CO develops over time, peaking 6 minutes after the initial vent
- Some CH_4 peaks may be present (but overlap with DMC)

