Fire and Gas Characterization Studies for Lithium-ion Cells and Batteries

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Motivation

Thermal Runaway

Thermal runaway is defined as the incident when an electrochemical cell increases its temperature through self-heating in an uncontrollable fashion.

- Thermal runaway propagates when the cell's generation of heat is at a higher rate than the heat it can dissipate.
- The intent of this project is to severely abuse a single cell such that it is most likely to enter thermal runaway with the presumption that a single cell may enter thermal runaway during transport.
- Under certain severe failure conditions, lithium-based rechargeable cells can emit gases which may be harmful to humans and/or may form a combustible mixture in sufficient concentrations. Examples may include, but are not limited to, carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), organic solvent vapors and hydrogen fluoride (HF).

Research Topic

Objective

The objective of the Li-ion battery (LIB) fire research is to develop data on fire hazards from two different types of lithium-ion battery chemistries (LFP and NMC) relative to fire size and production of venting gases and smoke.

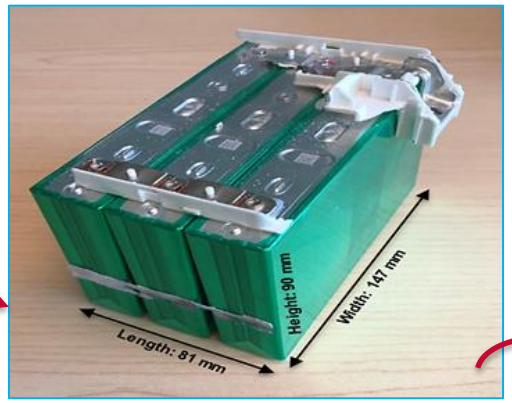
Effect of the cell chemistry. Changing the anode/cathode chemistries directly affects the heat released when the cell undergoes thermal runaway.

Size and configuration of LIB. The analysis proposed here will help to answer the question, *How do the results from single cell fire tests translate to large modules and battery systems?*

Test Samples

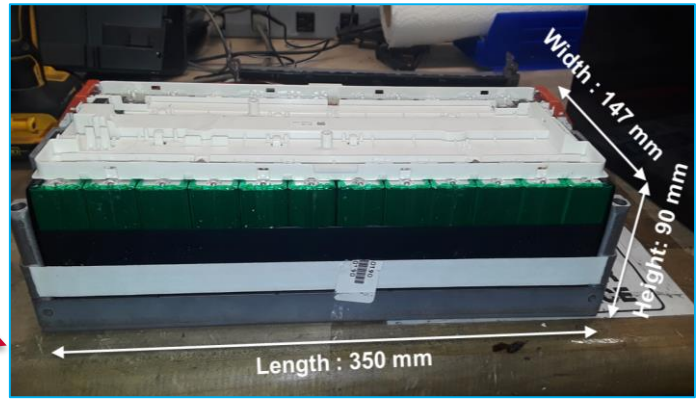
25 Ah, Single Cell

E = [2.7, 4.2] V



75 Ah, 3P Configuration

E = [2.7, 4.2] V



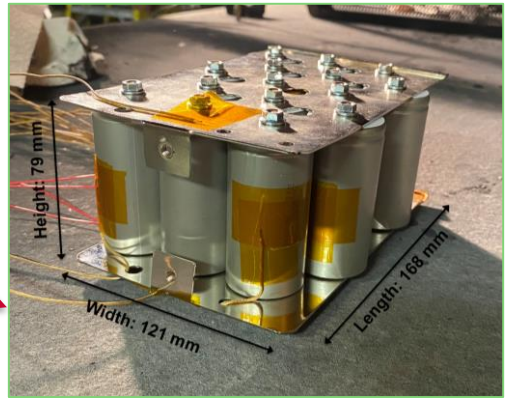
75 Ah, 3P4S Configuration

E = [10.8, 16.8] V

Single Cell | **Module** | **Battery**

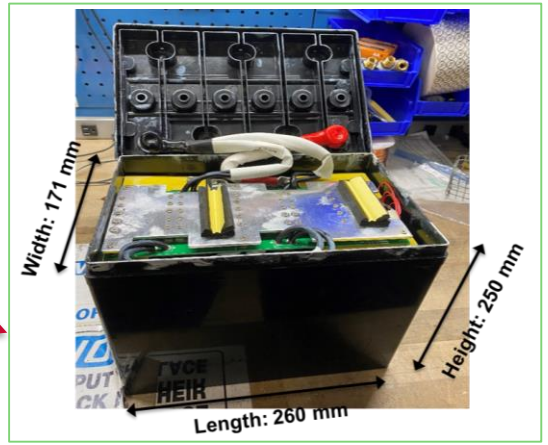
5.5 Ah, Single Cell

E = [2.0, 3.6] V



82.5 Ah, 15P Configuration

E = [2.0, 3.6] V



82.5 Ah, 15P4S Configuration

E = [8.0, 14.4] V

Test Setup

- *Cathode Chemistry* :

  NMC (Prismatic), **LFP** (Cylindrical)

- *Battery Scale* :

  Single Cell, Module, Battery

- *State of Charge*: **100% SOC**

- *Heater Specs*: 120 V, 10 W/in^2

  NMC: 4″ × 6″, LFP: 2″ × 2″

- *Heating Profile*:

  UL 9540A, “Test Method for Evaluating Thermal Runaway Fire Propagation”

  HR = **10 °C/min** to a hold temperature of **200 °C**

- *Temperature Measurements*: K-Thermocouple (30 AWG)

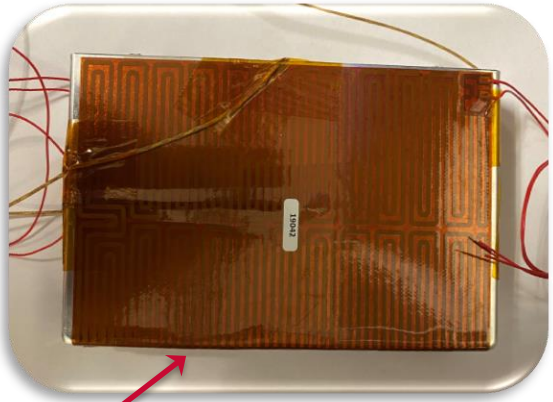
- *Gas Analysis*:

  Organic compounds. Fourier Transform Infrared Spectrometry (FTIR).

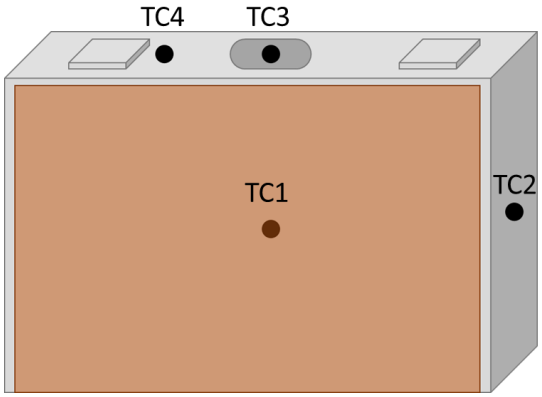
  Gas composition. Gas Chromatography – Mass Spectrometry.

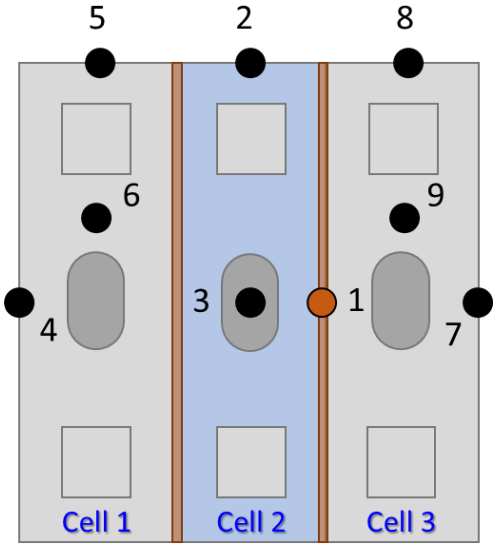
Trigger Cells and TC Configuration

NMC



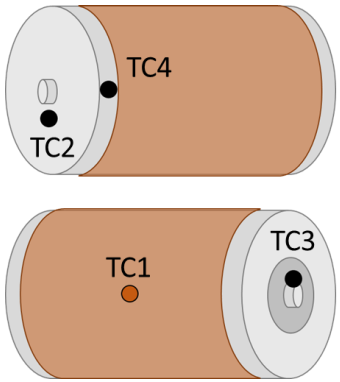
Flexible film heaters

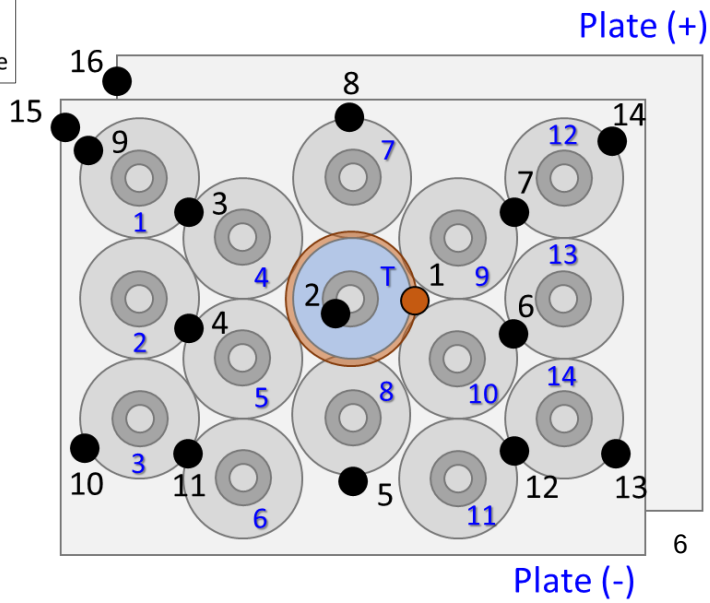




Initiating Cell
Cell
Vent
Heater
Thermocouple

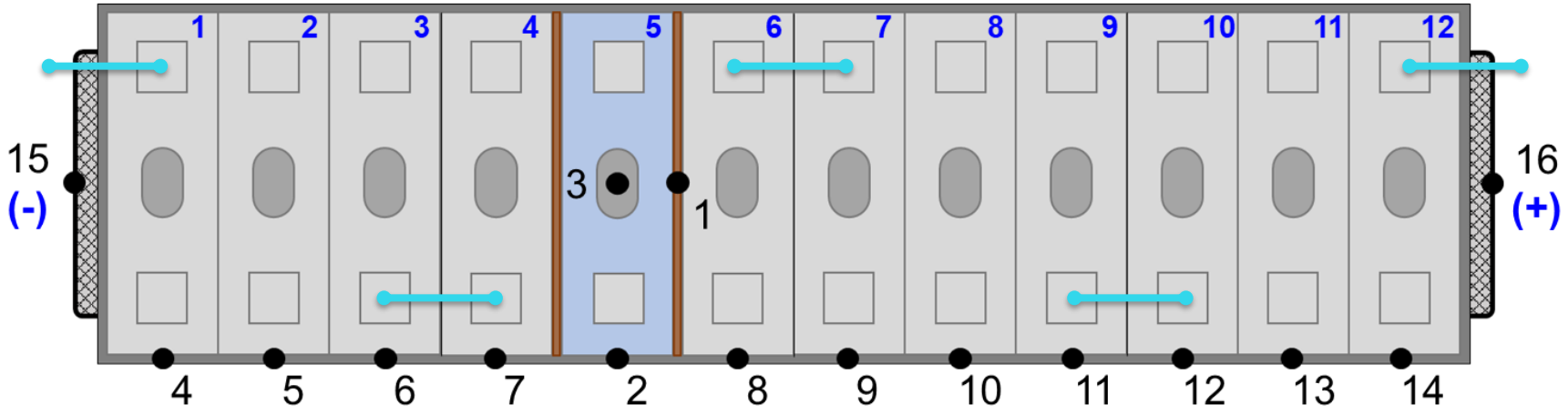
LFP



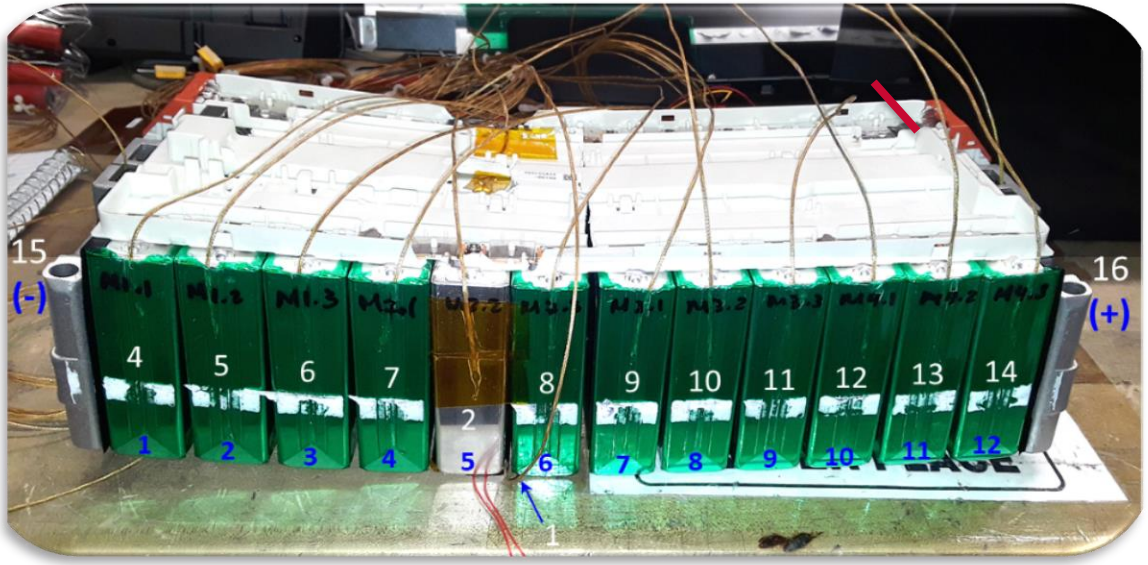


Trigger Cells and TCs Setup (NMC Battery)

Top View



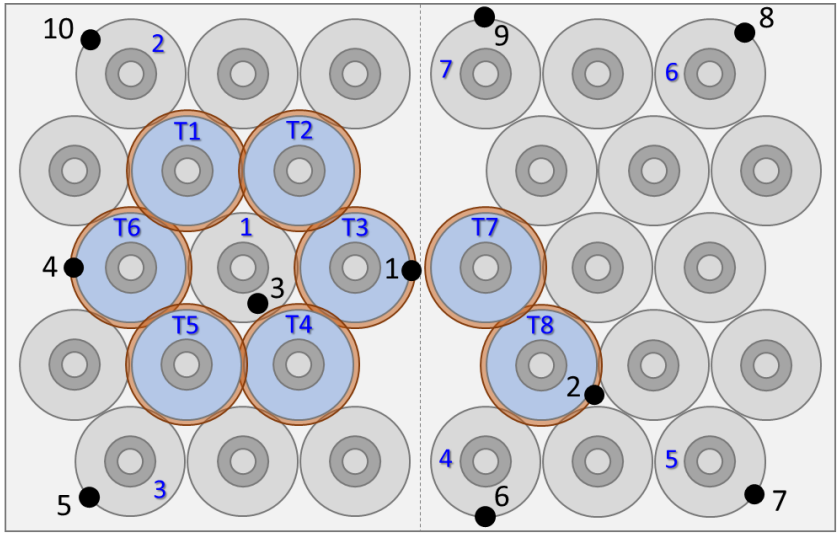
Initiating Cell
Cell
Vent
Heater
Thermocouple



3P4S Configuration

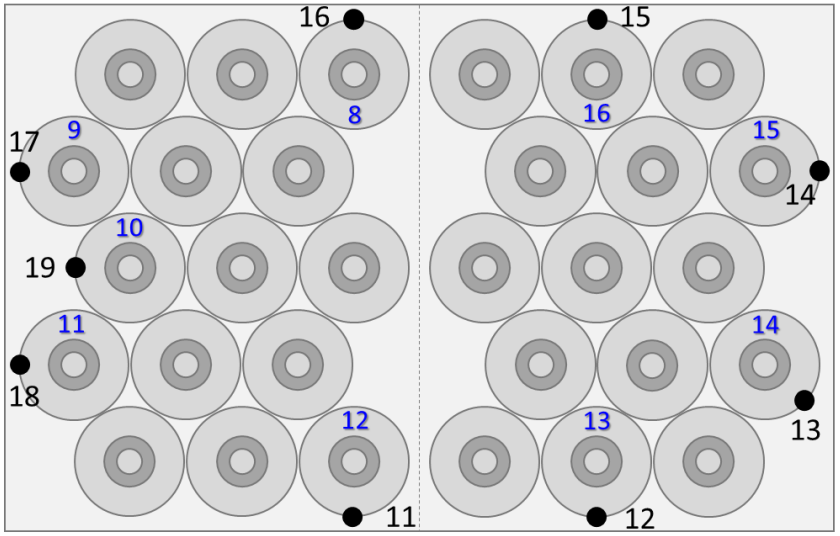
Trigger Cell and TCs Setup (LFP Battery)

Front



Module 1 Module 2

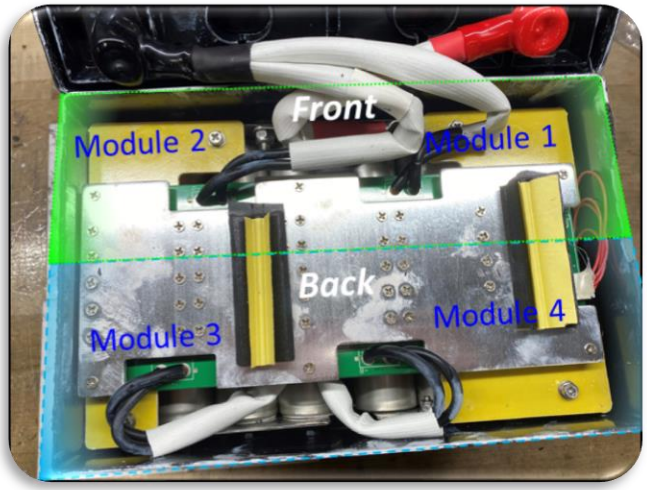
Back



Module 3 Module 4

- Initiating Cell
- Cell
- Vent
- Heater
- Thermocouple

15P4S Configuration

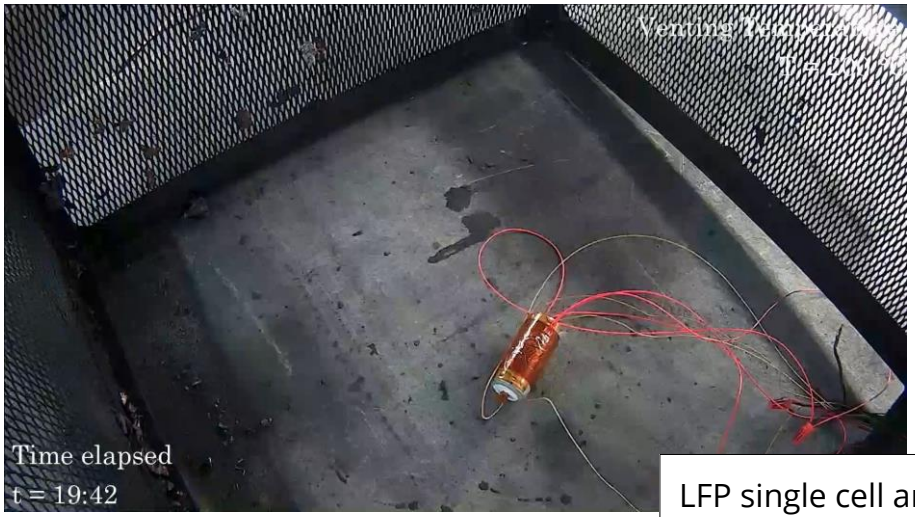


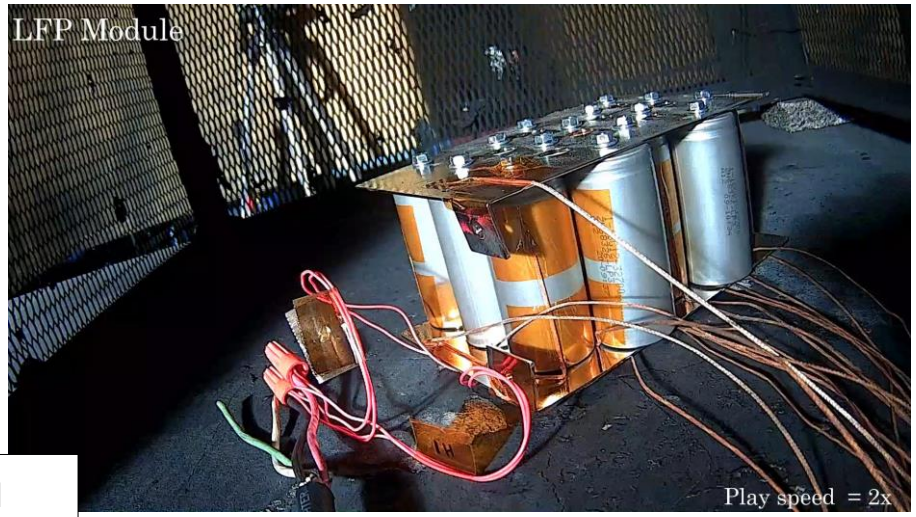
The module labels are only a reference to its position inside the battery.

RESULTS

Temperature Response

LFP – Temperature Response





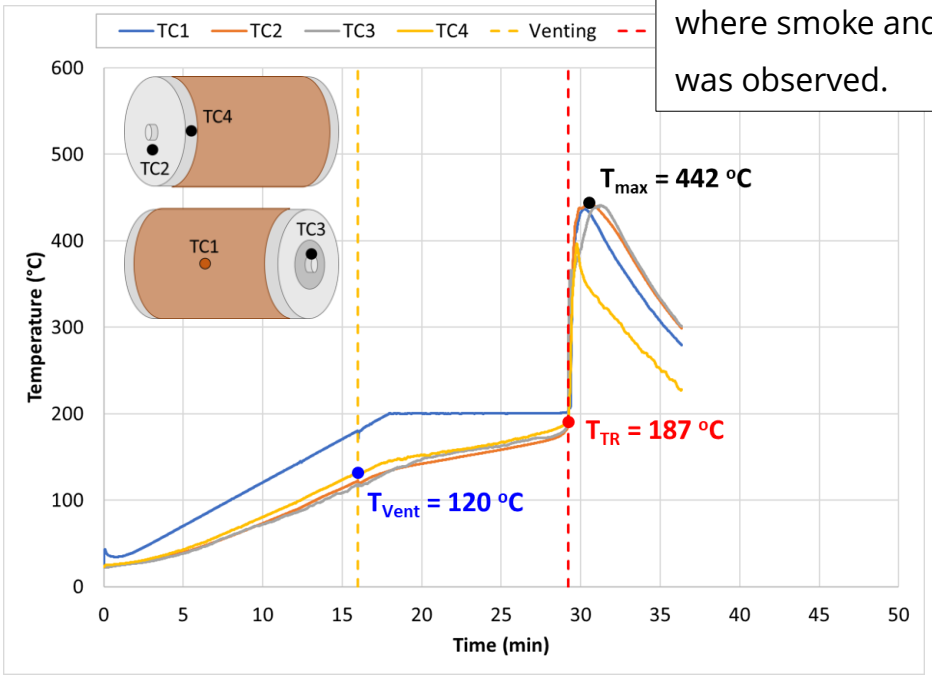
Smoke

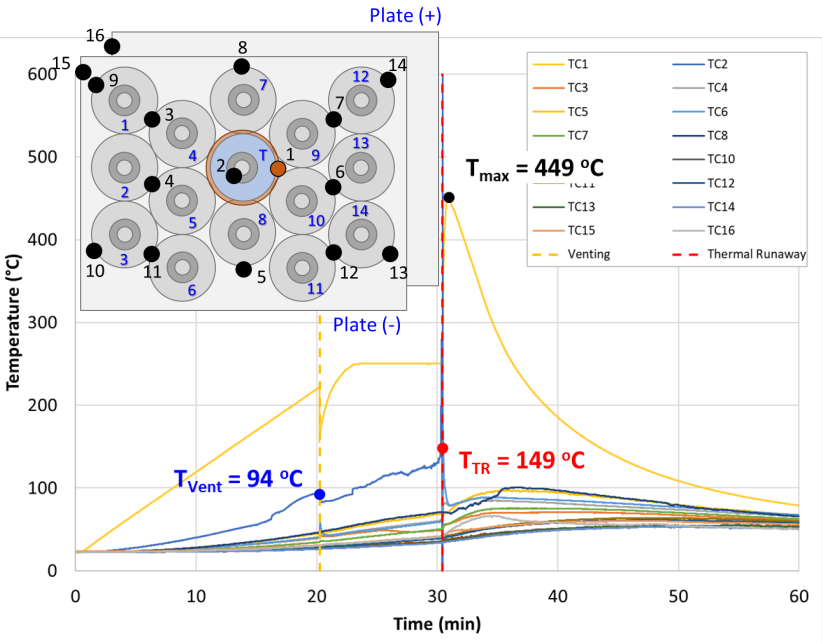
Single Cell

LFP single cell and module had one case where smoke and fire was observed.

Module

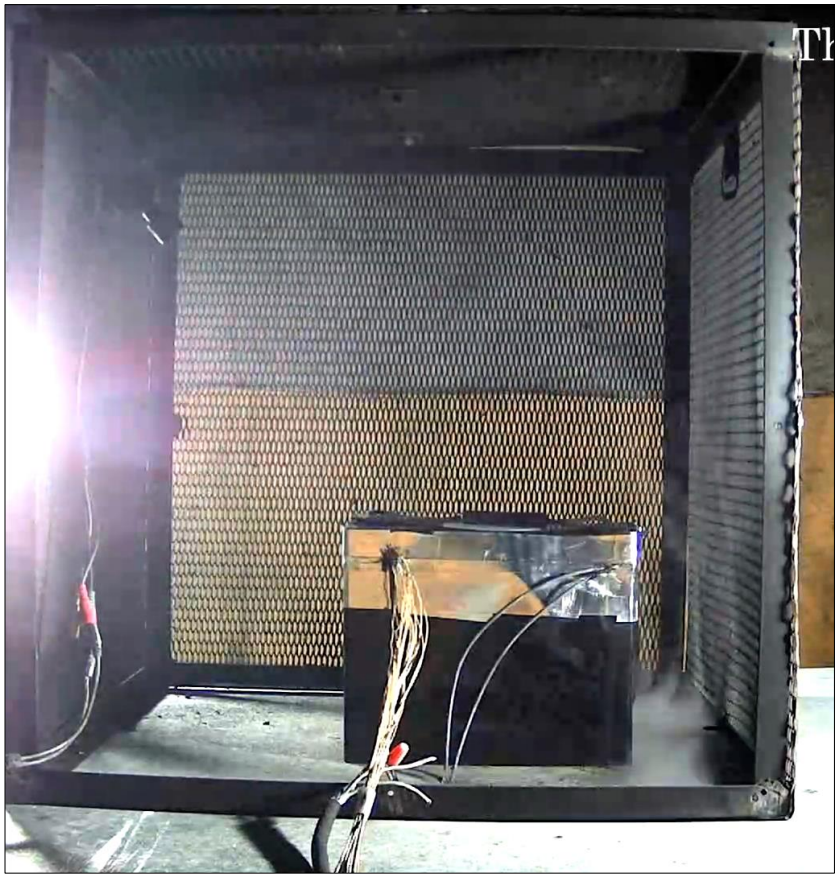
Smoke



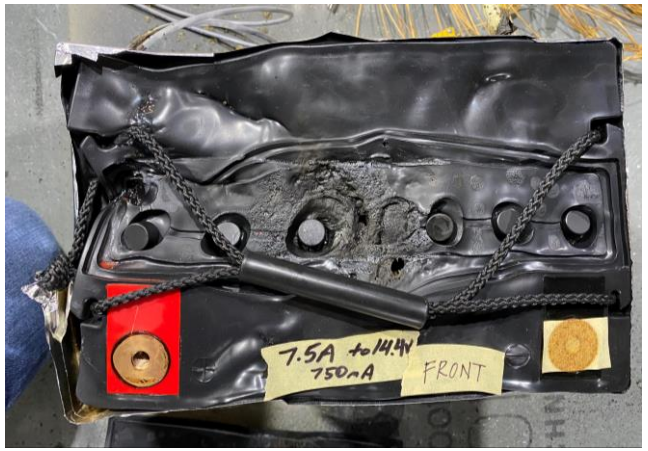


LFP Battery – Test

16.8 V; 82.5 Ah (**1.26 kWh**)

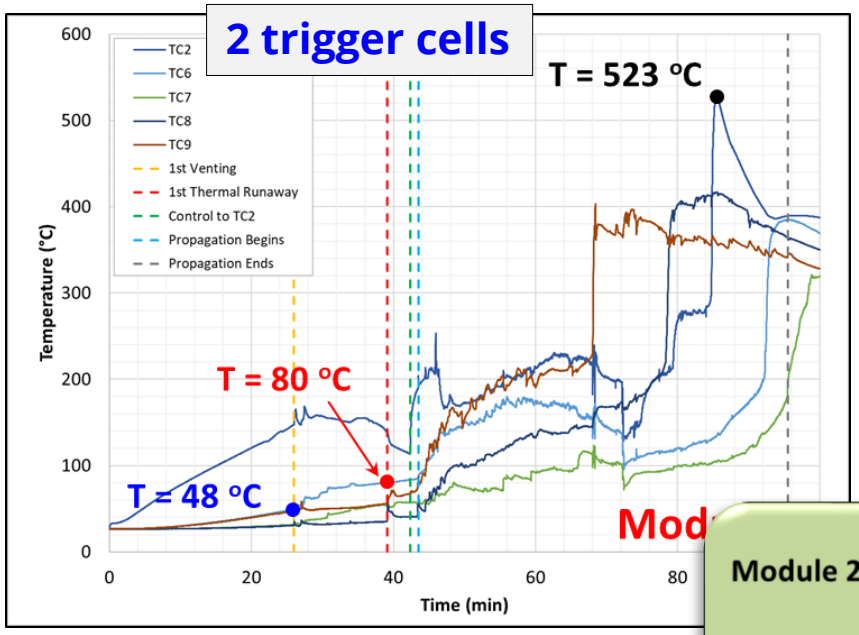


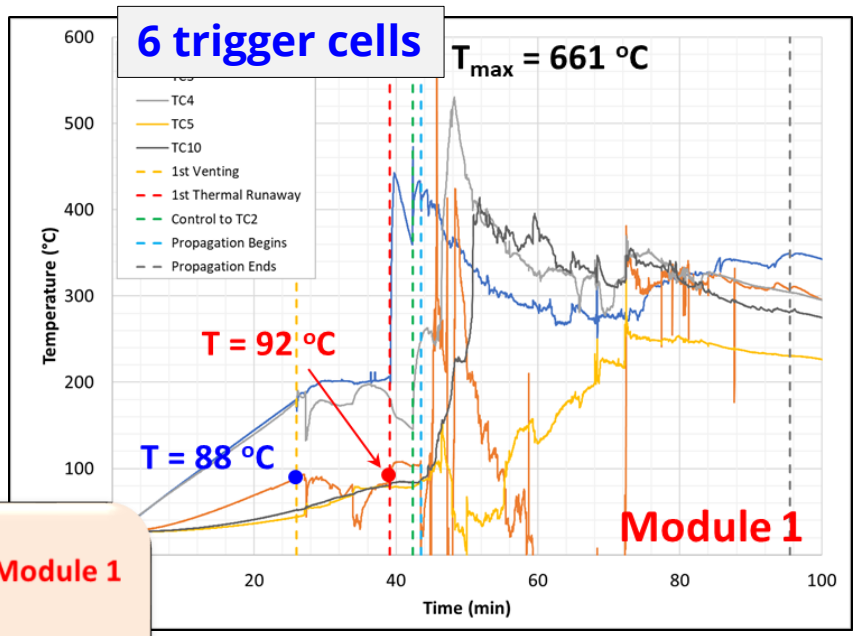
Battery after the test



- The outer plastic case was softened on all faces and breached in several locations where gas venting was observed.
- Some solidified piles of particulate, resembling plastic, were observed around areas where steady venting occurred.

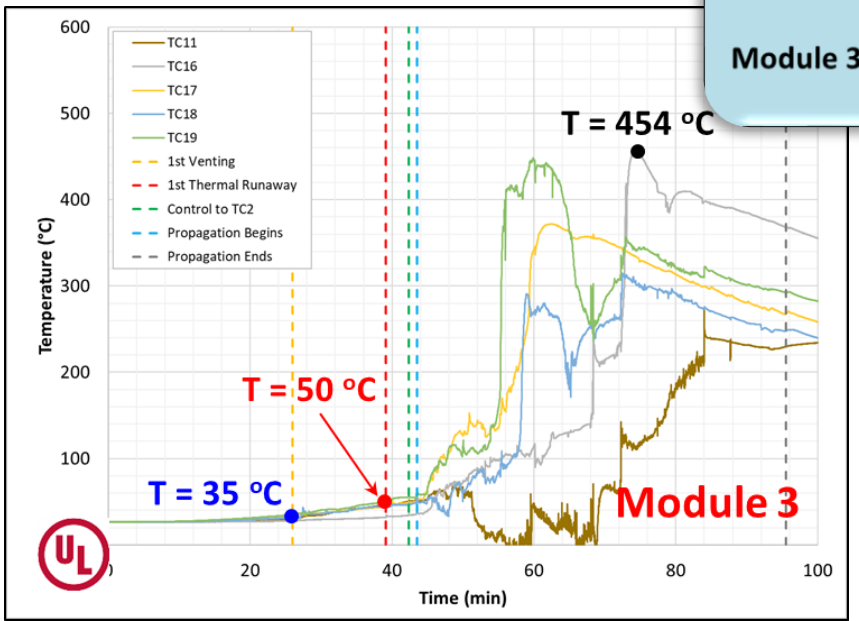
LFP Battery – Temperature Response

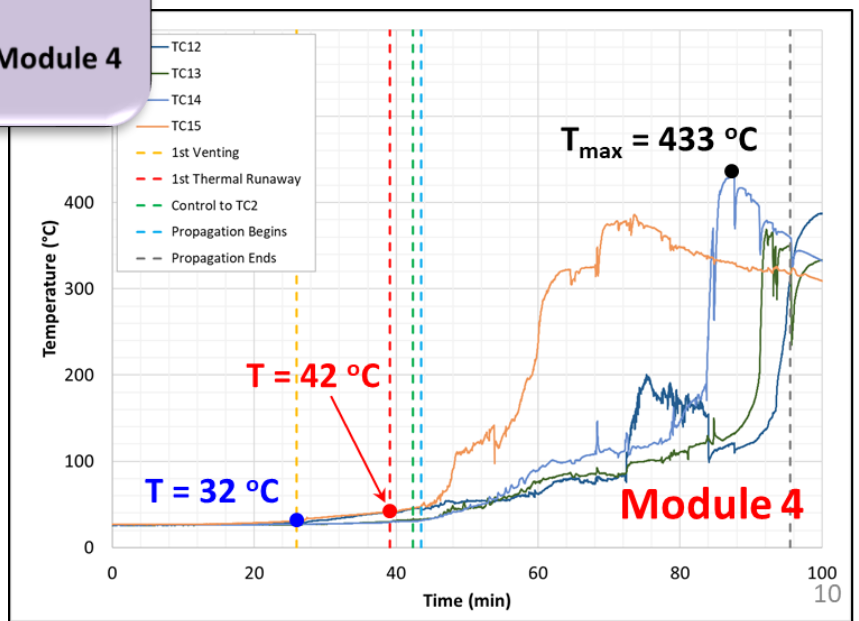




Module 2 | Module 1

Module 3 | Module 4

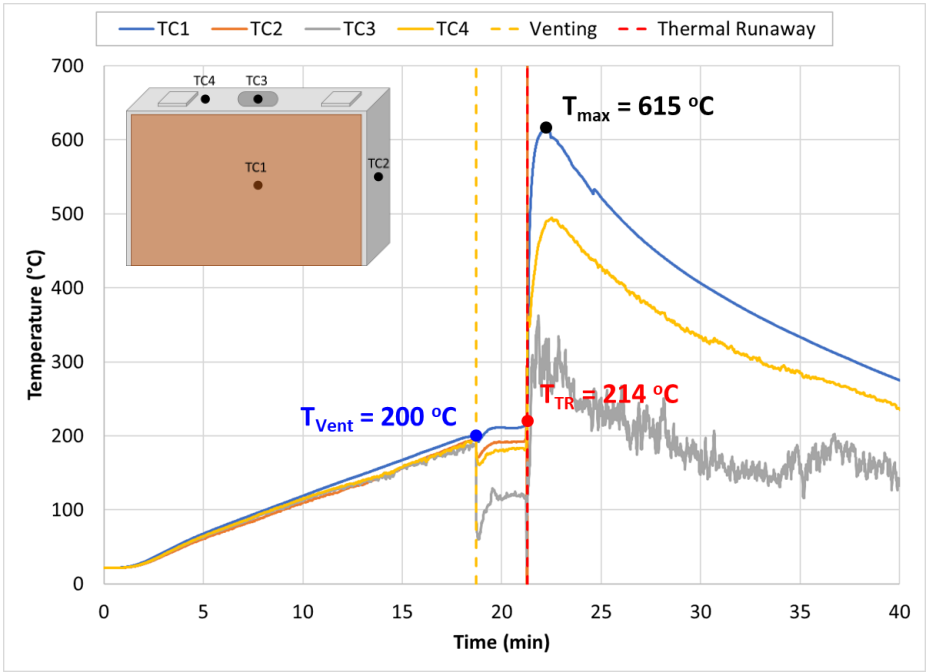


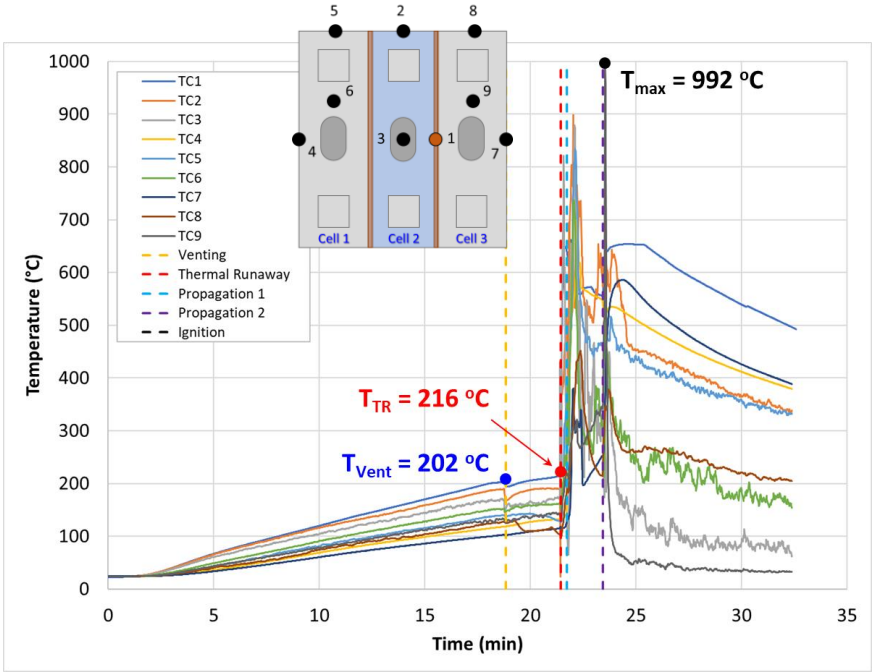


NMC – Temperature Response

Single Cell Only Smoke

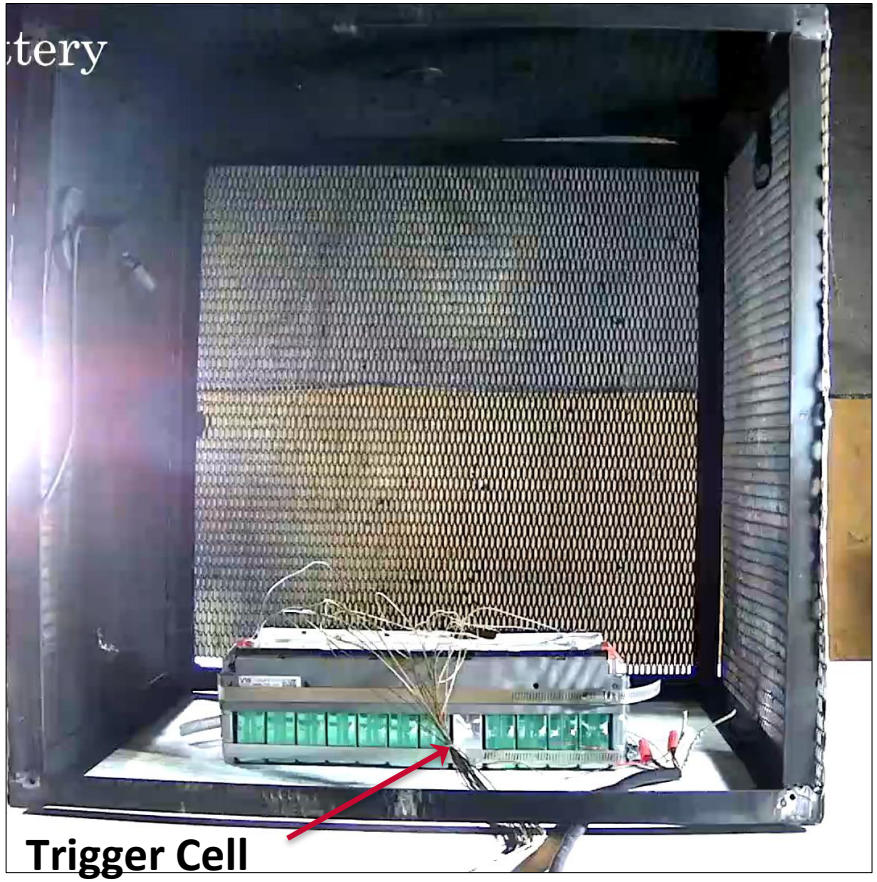
Module Smoke and Fire





NMC Battery – Test

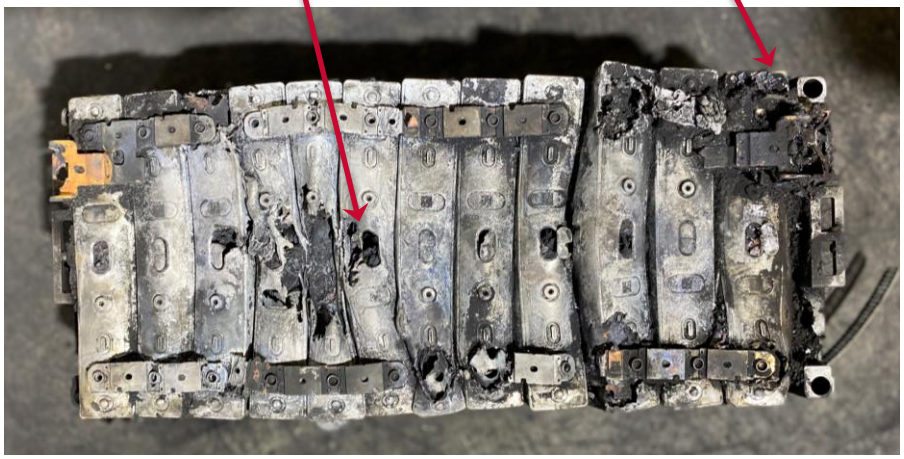
14.8 V; 75 Ah (**1.1 kWh**)



Flame jetted from the cell vents as well as ruptures on the sides of the cell casing.

Activated vent holes

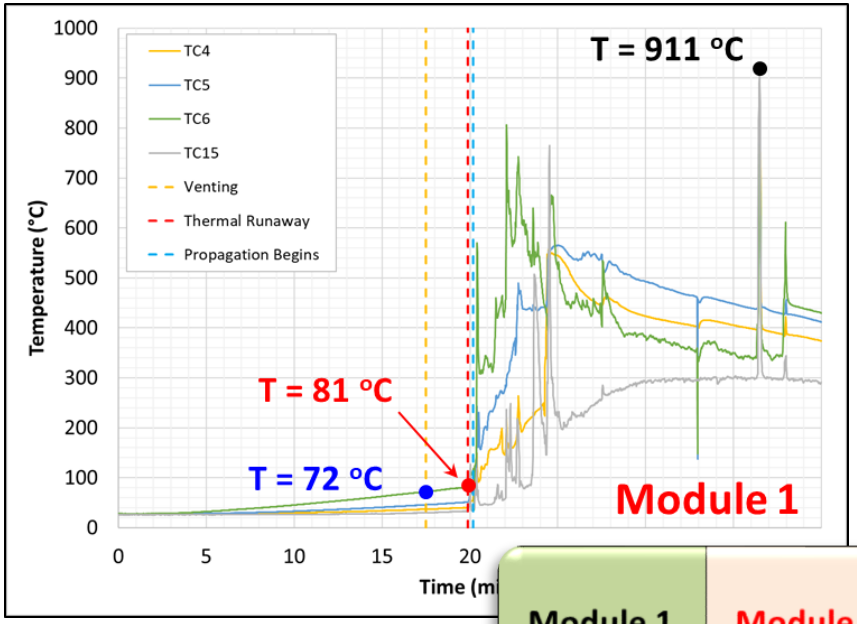
Cell metal casing melting

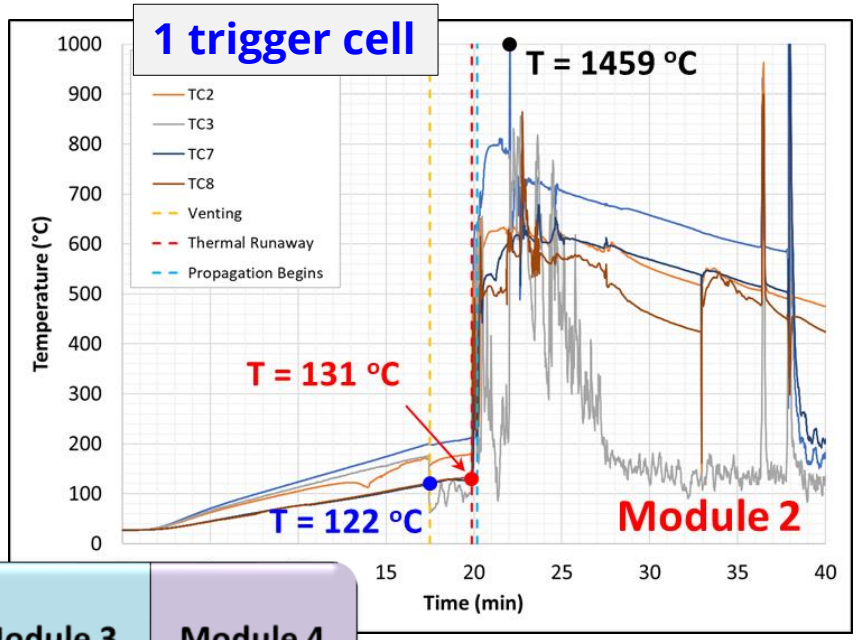


Cell rupture

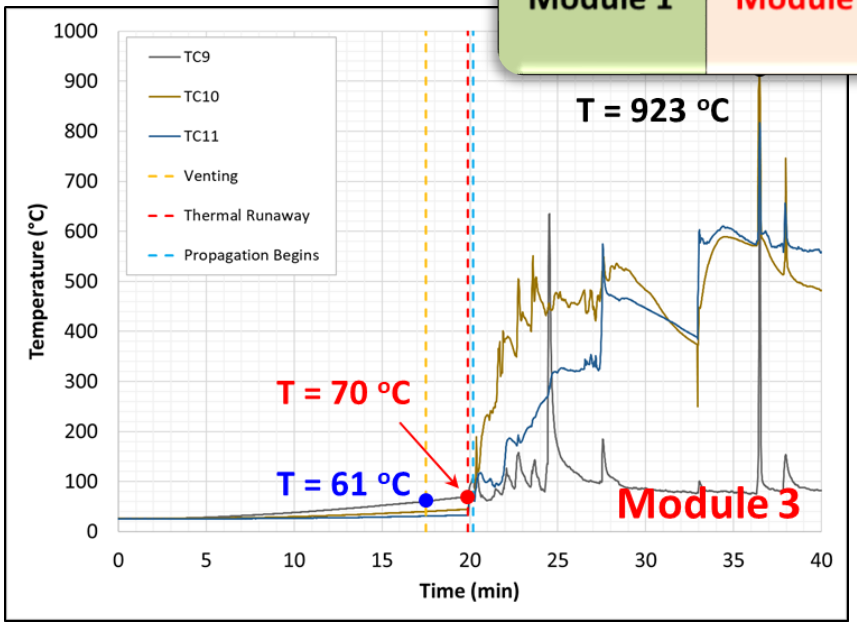
Thermal runaway occurred in all the cells.

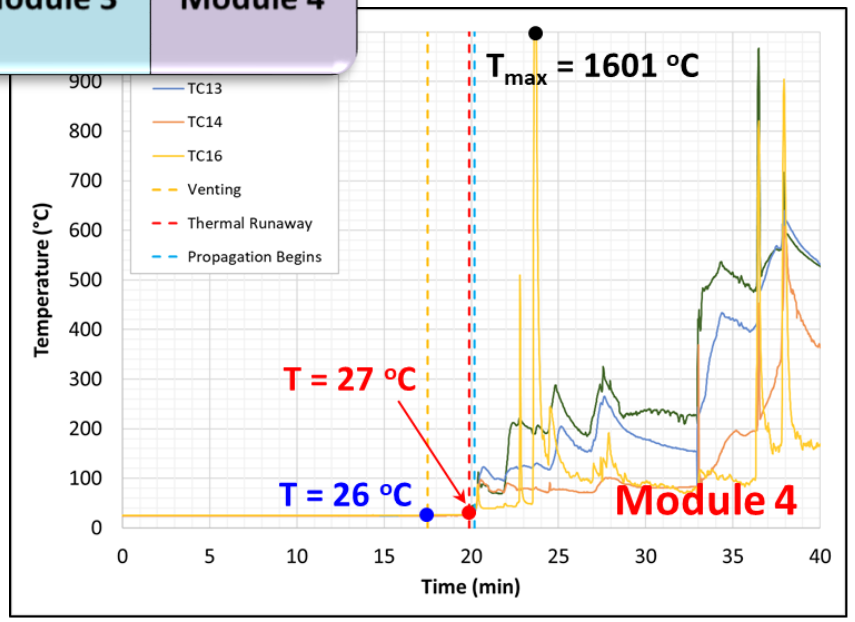
NMC Battery – Temperature Response





Module 1 | Module 2 | Module 3 | Module 4





Sample Size Effect

NMC	$T_{TR}\ [^oC]$	$t_{TR}\ [min]$	$T_{Max}\ [^oC]$	$t_{Max}\ [min]$
Single Cell	213	22	603	23
	214	21	615	22
	213	22	591	23
	211	23	609	24
Module	216	21	992	23
	216	20	764	21
Battery	170	20	1459	22

LFP	$T_{TR}\ [^oC]$	$t_{TR}\ [min]$	$T_{Max}\ [^oC]$	$t_{Max}\ [min]$
Single Cell	203	90	288	90
	187	34	405	36
	189	38	383	40
	187	29	442	31
Module	139	97	1093*	98
	149	30	449	31
Battery	92	39	661	45

RESULTS

Gas Analysis

Production of Venting Gases

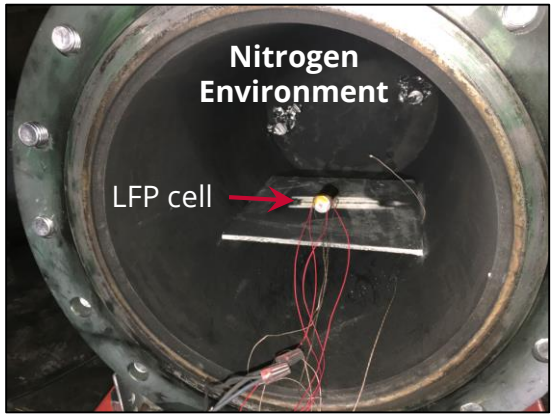
NMC	$SRR\ [m^2/s]$	Total Smoke Release	$HRR\ [kW]$	$CHR\ [MJ]$
Single Cell	0.5	14.9	0	0
	0.8	24.9	0	0
	3.2	26.7	0	0
	2.2	23.1	0	0
Module	2.4	70.6	58	2.9
	2.6	97.2	20	0.9
Battery	2.8	345.9	106	24.4

Chemical heat release (CHR) rate is not reported because external flaming did not occur. Total smoke release was calculated from the moment of venting until the end of visible gas and smoke release.

LFP	$SRR\ [m^2/s]$	Total Smoke Release	$HRR\ [kW]$	$CHR\ [MJ]$
Single Cell	0.2	2.0	3.3	0
	0.5	6.0	0.0	0
	0.4	7.9	0.0	0
	0.5	8.1	0.0	0
Module	0.4	42.3	33	9.5
	0.3	14.7	0	0
Battery	1.1	213.7	0	0

Cell Gas Composition - LFP

5.5 Ah Li-ion LFP cylindrical cells, **18 Wh**



Volume of gas released during thermal runaway in a single cell – **3 Liters**

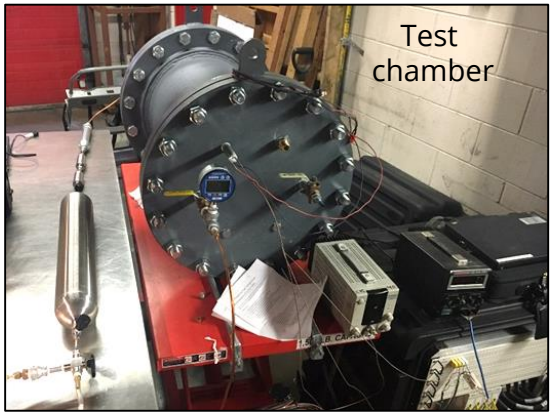
Component		Measured %	Component LFL
Carbon Monoxide	CO	23.76 % ‡	10.9 %
Carbon Dioxide	CO_2	26.65 %	N/A
Hydrogen	H_2	36.03 % ‡	4.0 %
Oxygen	O_2	0.92 %	N/A
Methane	CH_4	3.55 %	4.4 %
Ethylene	C_2H_4	3.20 % ‡	2.4 %
Ethane	C_2H_6	0.57 %	2.4 %
Propylene	C_3H_6	2.71 % ‡	1.8 %
Propane	C_3H_8	0.15 %	1.7 %
Propadiene	C_3H_4	0.01 %	1.9 %
N - Butane	C_4 (Total)	0.83 %	-
N - Pentane	C_5 (Total)	0.09 %	-
Hexane	C_6H_{14}	0.00 %	1.0 %
Dimethyl Carbonate (DMC)	$C_3H_6O_3$	1.08 %	Not specified
Ethyl Methyl Carbonate (EMC)	$C_4H_8O_3$	0.46 %	Not specified
Total	-	100 %	-
** Individual C4 Components*		-	-
Butane	C_4H_{10}	0.04 %	1.4 %
Butene	C_4H_8	0.60 %	1.5 %
Butadiene	C_4H_6	0.19 %	1.4 %
*** Individual C5 Components*		-	-
Pentane	n-C_5H_{12}	0.09 %	1.1 %

‡ Gases above combustible volume
LFL = Low Flammable Limit

Cell Gas Composition -NMC

Automotive battery

25 Ah Li-ion NMC prismatic cell, **95 Wh**



Volume of gas released during thermal runaway in a single cell – **41 Liters**

Component		Measured %	Component LFL
Carbon Monoxide	CO	0.00 %	10.9 %
Carbon Dioxide	CO_2	21.60 %	N/A
Hydrogen	H_2	54.00 % ‡	4.0 %
Oxygen	O_2	0.00 %	N/A
Methane	CH_4	6.10 % ‡	4.4 %
Ethylene	C_2H_4	3.46 % ‡	2.4 %
Ethane	C_2H_6	1.13 %	2.4 %
Propylene	C_3H_6	1.51 %	1.8 %
Propane	C_3H_8	0.59 %	1.7 %
Propadiene	C_3H_4	0.00 %	1.9 %
N – Butane *	C_4 (Total)	1.67 %	-
N – Pentane **	C_5 (Total)	0.22 %	-
Hexane	C_6H_{14}	0.05 %	1.0 %
Dimethyl Carbonate (DMC)	$C_3H_6O_3$	3.35 %	Not specified
Ethyl Methyl Carbonate (EMC)	$C_4H_8O_3$	6.32 %	Not specified
Total	-	100 %	-
** Individual C4 Components*		-	-
Butane	C_4H_{10}	0.38 %	1.4 %
Butene	C_4H_8	0.97 %	1.5 %
Butadiene	C_4H_6	0.27 %	1.4 %
*** Individual C5 Components*		-	-
Pentane	n-C_5H_{12}	0.16 %	1.1 %

‡ Gases above combustible volume
LFL = Low Flammable Limit

Summary

- The results from a single cell are not sufficient to elucidate the response of a module or a battery. The configuration of the module and battery including the heat conduction and dissipation paths determine the results of the thermal runaway.
- Complete propagation of TR was observed through all cells in the NMC modules and battery with fire in both cases.
- For the LFP modules and batteries, TR propagation was also observed without fire.
- Cathode chemistry has a large influence in the thermal response of the cell. The batteries with the cathode NMC developed a higher temperature than the LFP batteries.
- The effect of the sample size (single cell, module, battery) was reflected as an increase in the amount of gases released proportional to that produced by a single cell. The maximum temperature increased with increasing number of cells.
- Data obtained on the gases evolved should be analyzed for the volume of the chamber (room) or confined space that the battery system is located in, to understand worst case flammability and explosive as well as toxicity levels and help with the design of appropriate vent systems.

Acknowledgments

- Fire R&D (UL Northbrook)
  Dr. Pravinray Gandhi, Alex Klieger and team

- UL Electrochemical Safety Team
  Dr. Judy Jeevarajan
  Saad Azam (currently a graduate student at Dalhousie University)

Thank you!

Contact: **NFP.BatterySafety@ul.org**

THANK YOU