Fire and Smoke Characterization and Fire Suppression of Lithium-Ion Cells, Modules and Batteries

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Electrochemical Safety Research Institute
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Discoveries in Safety™

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"Going Green – The Effect on Aircraft Cabin and Fire Safety"

Motivation

Thermal runaway is defined as an accelerating release of heat inside a cell due to a series of uncontrollable exothermic reactions manifesting as an uncontrolled increase in cell temperature.

The events accompanying thermal runaway can vary quite a bit: venting or smoke or fire or combinations of these can be observed.

Arizona Battery Energy Storage System

Surprise, AZ, US. April 19 , 2019
Courtesy: UL FSRI AZ Battery Explosion Report, 2020

Delivery Electric Bike Catches Fire

Manhattan, NY, US. August 31 , 2021
Courtesy: FREEDOMNEWS TV - NIGHT EDITION
https://www.youtube.com/watch?v=w5ilNMe1lA8

Thermal Runaway

Objective

The objective of the Li-ion battery (LIB) fire study is to measure the fire size, smoke and gases evolved during the thermal runaway of LFP and NMC cathode chemistries. The study included thermal runaway tests on the cell, module and battery level to understand the scaling effects on fire size and gas composition released during the thermal runaway events.

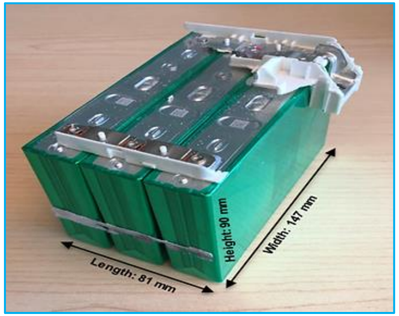
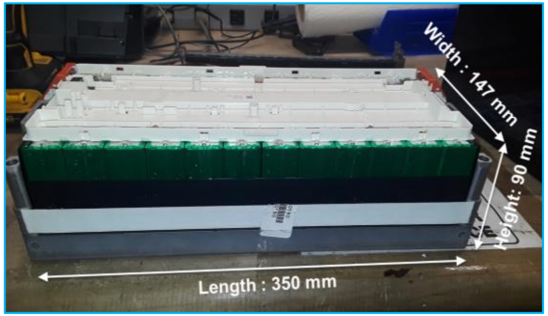
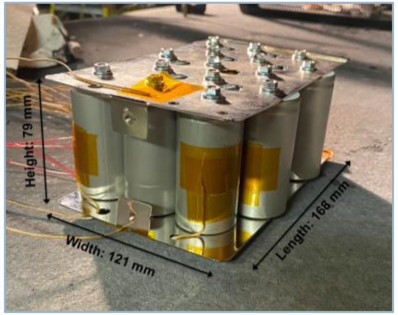
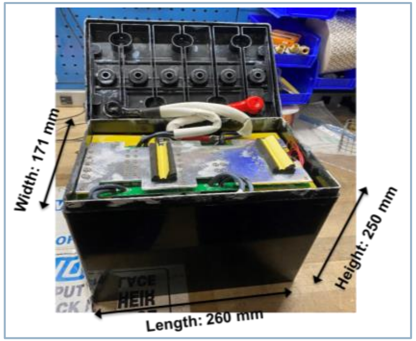
Additional cell-level tests were conducted in an inert environment to collect gases released during thermal runaway gases that would normally combust in air and analyze the compositions and associated lower flammability limits, maximum closed vessel deflagration pressures, and burning velocities.

Motivation

The intent of this study 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** or use in an EV.

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).

Test Samples

	Single Cell	Module	Battery
NMC			
	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**
LFP			
	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**

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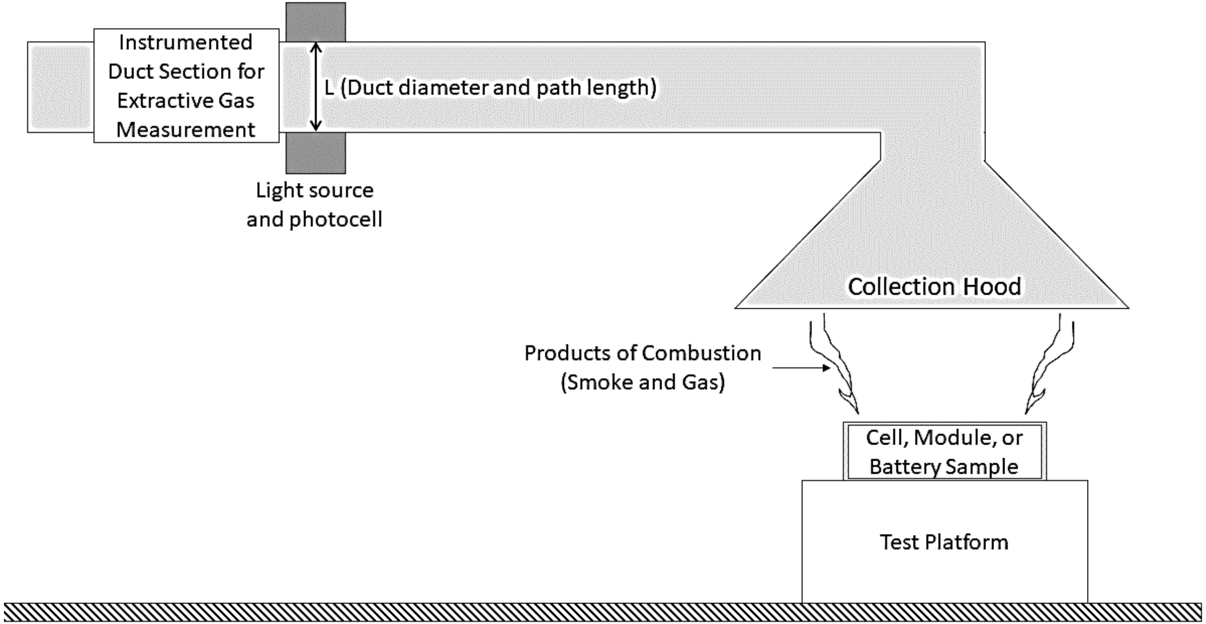
Test Setup – Open Air



Setup used to analyze the composition and quantity of gases released and to measure chemical heat release rate using an oxygen consumption calorimeter.

Heating Profile:

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

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

State of Charge:

100% SOC

Heater Specs:

120 V, 10 W/in^2

NMC: 4" × 6", LFP: 2" × 2"

Test Setup

Cell Voltage

- *Voltmeter*
  - National Instruments DAQ

Heater Power

- *Voltmeter; Ammeter*
  - GW Instek PSU 150-10

Chamber Pressure

- 0 to 100 psig diaphragm pressure transducer
- Vacuum to 45 psig diaphragm pressure transducer

Oxygen Concentration

- *Paramagnetic Analyzer*
  - Siemens Ozymat 6

Temperature

(Chamber, Venting, Thermal Runaway)

- *Thermocouple*
  - Type K thermocouples (30 AWG)

Total unburned hydrocarbon concentration

- *Flame Ionization Detection*
  - JUM Model 3-300A

Gas Composition

- *Gas Chromatography – Mass Spectrometry (GC-MS)*
  - Thermo Fisher Gas Chromatograph model Trace 1310 with a Mass Spectrometer model ISQ 7000 single Quadrupole detector, Thermal Conductivity Detector, Flame Ionization Detector

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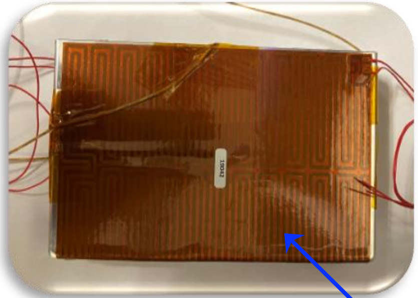
Trigger Cells and TC Configuration – Single Cell and Module

Trigger Cells with Heaters

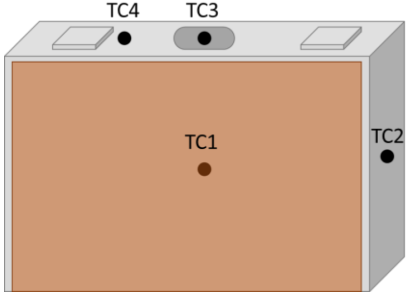
NMC

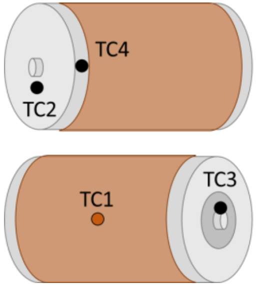


LFP

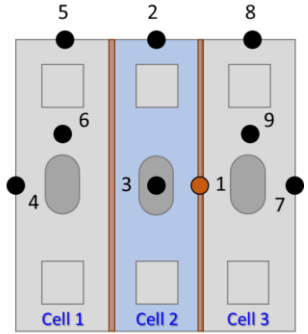
Flexible film heaters

Single Cell – TC Layout

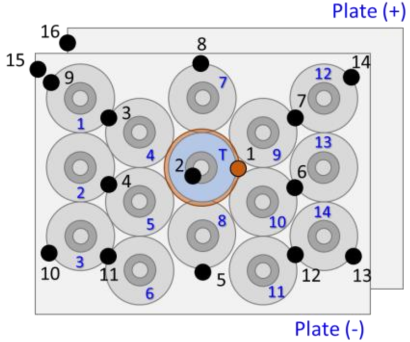




Module – TC Layout



- Initiating Cell
- Cell
- Vent
- Heater
- Thermocouple



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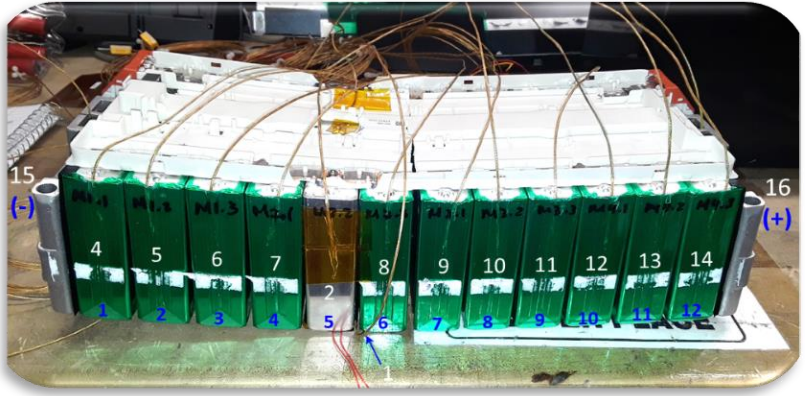
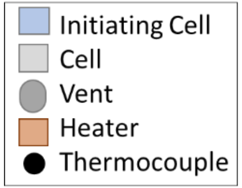
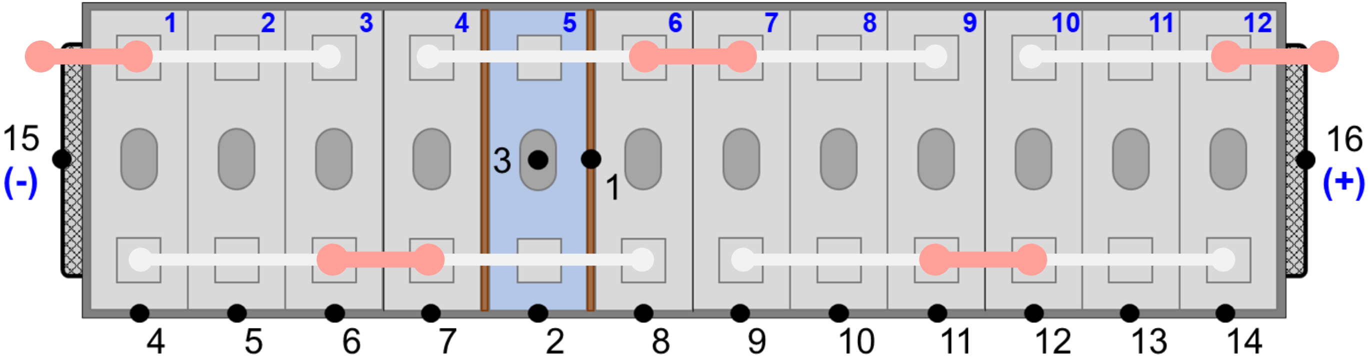
Trigger Cells and TC Configuration (NMC Battery)

Top View

3P4S Configuration

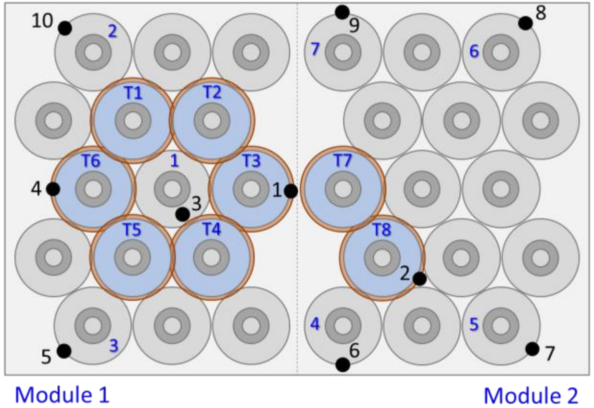




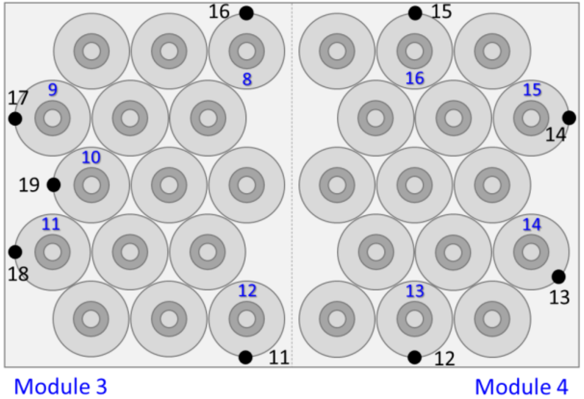


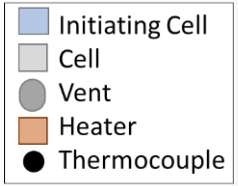
Trigger Cells and TC Configuration (LFP Battery)

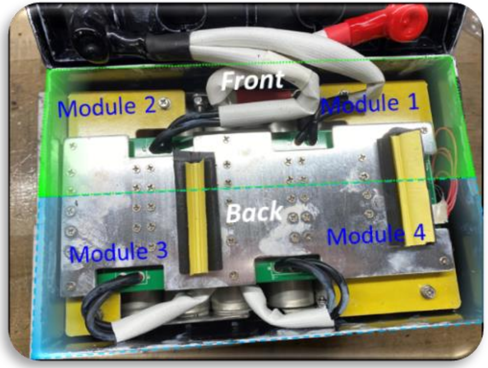
Front



Back







15P4S Configuration

Eight trigger cells were used with the LFP battery because the results of the LFP modules showed that a single trigger cell was not sufficient to propagate thermal runaway.

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

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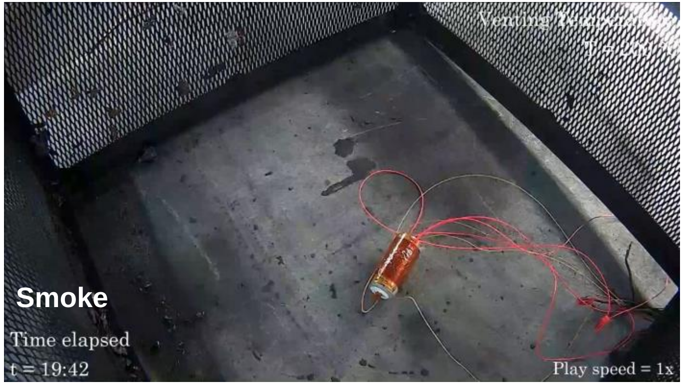
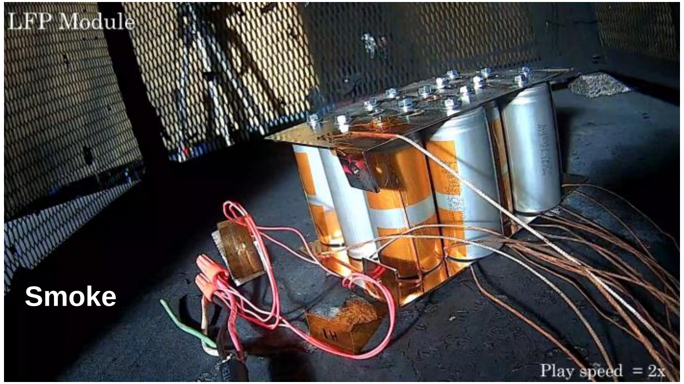
Thermal Response

Results

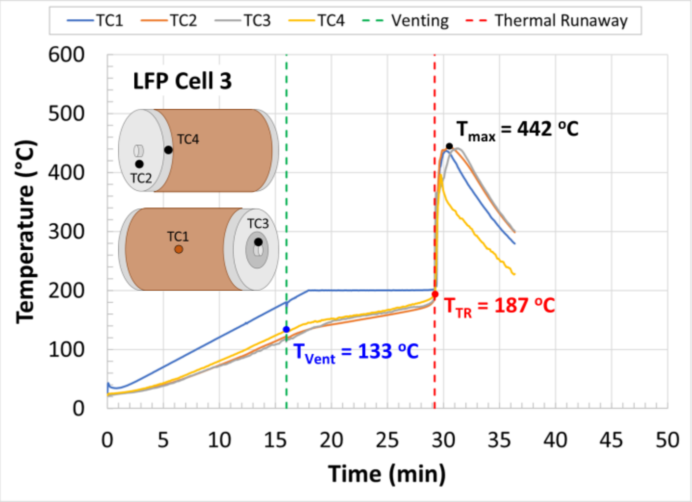
LFP – Temperature Response

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

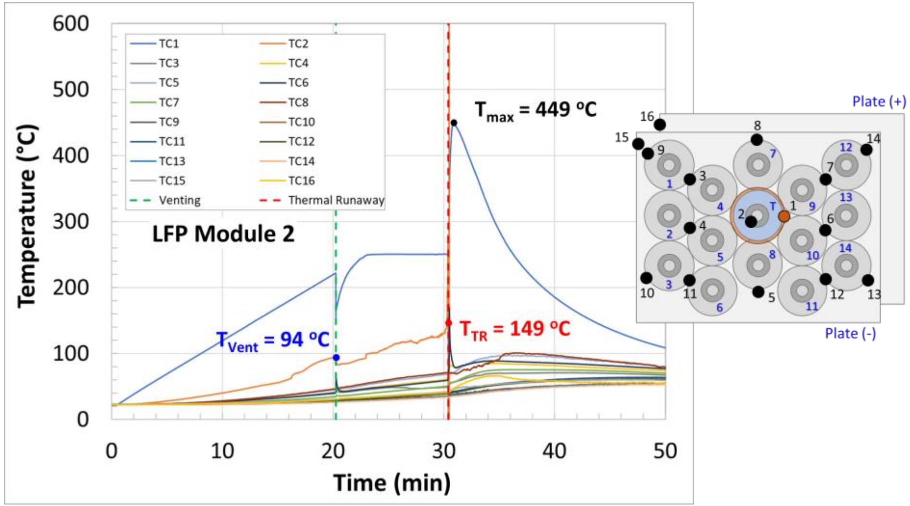




Single Cell



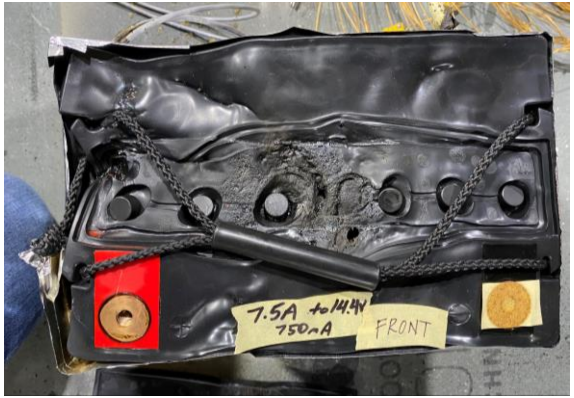
Module



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.

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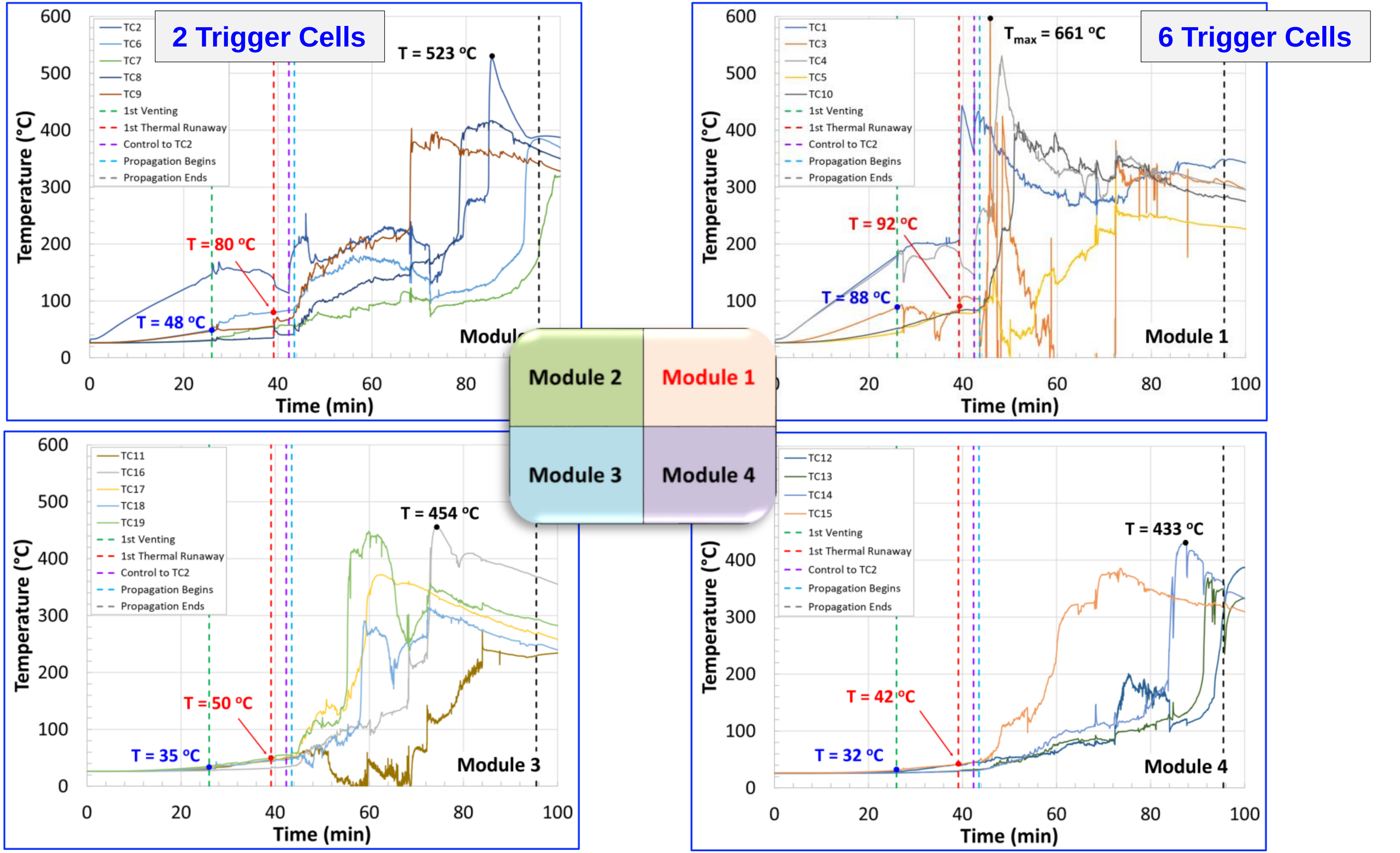
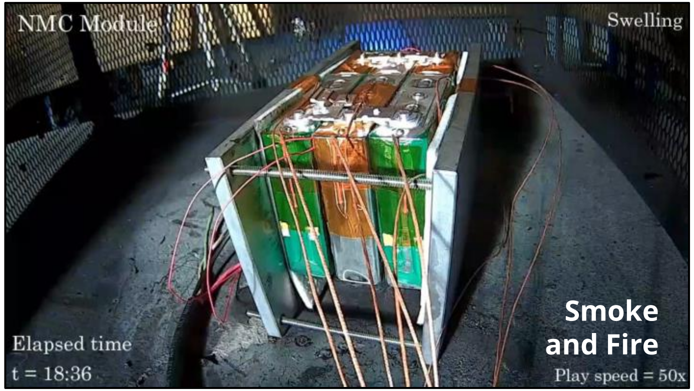
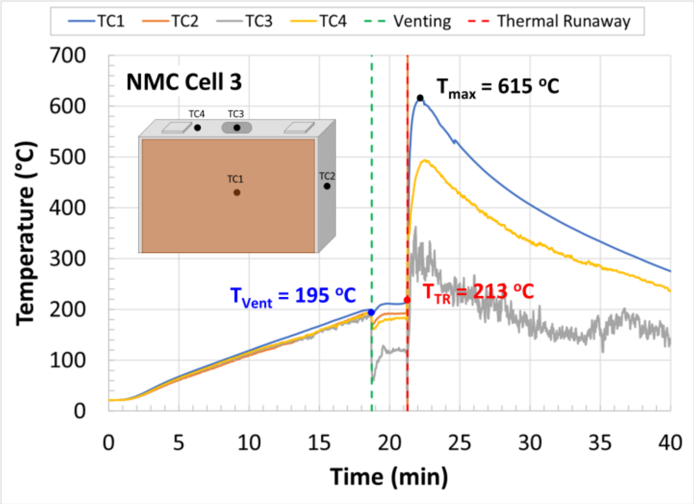
LFP Battery – Temperature Response



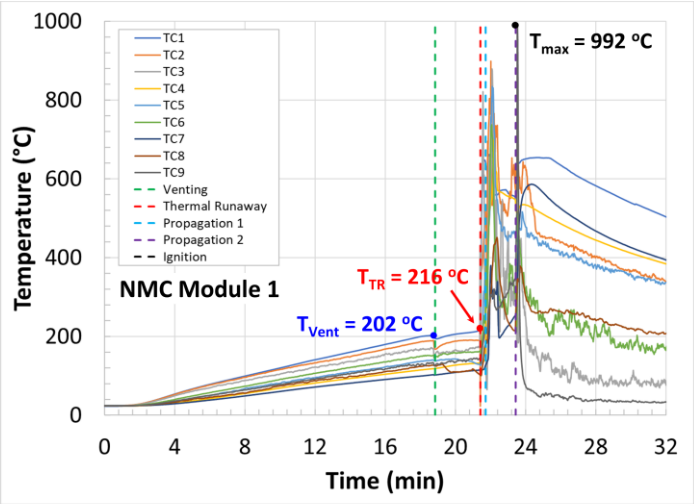
NMC – Temperature Response

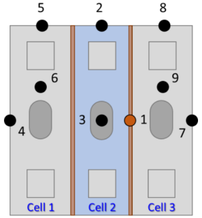


Single Cell



Module





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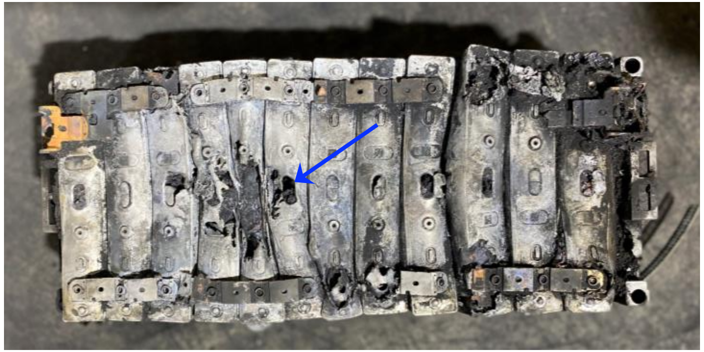
NMC Battery Test

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

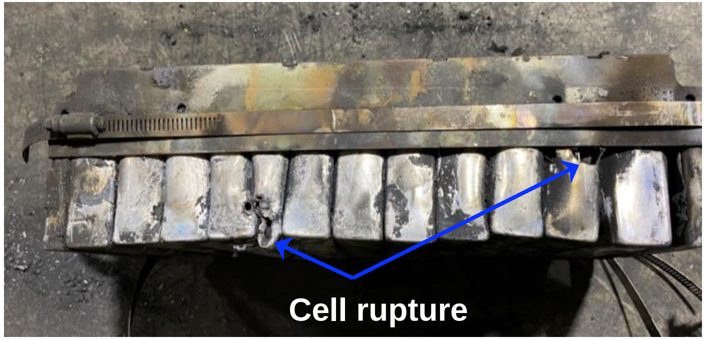
Flame jetted from the cell vents as well as ruptures on the sides of the cell casing.

Battery after the Test



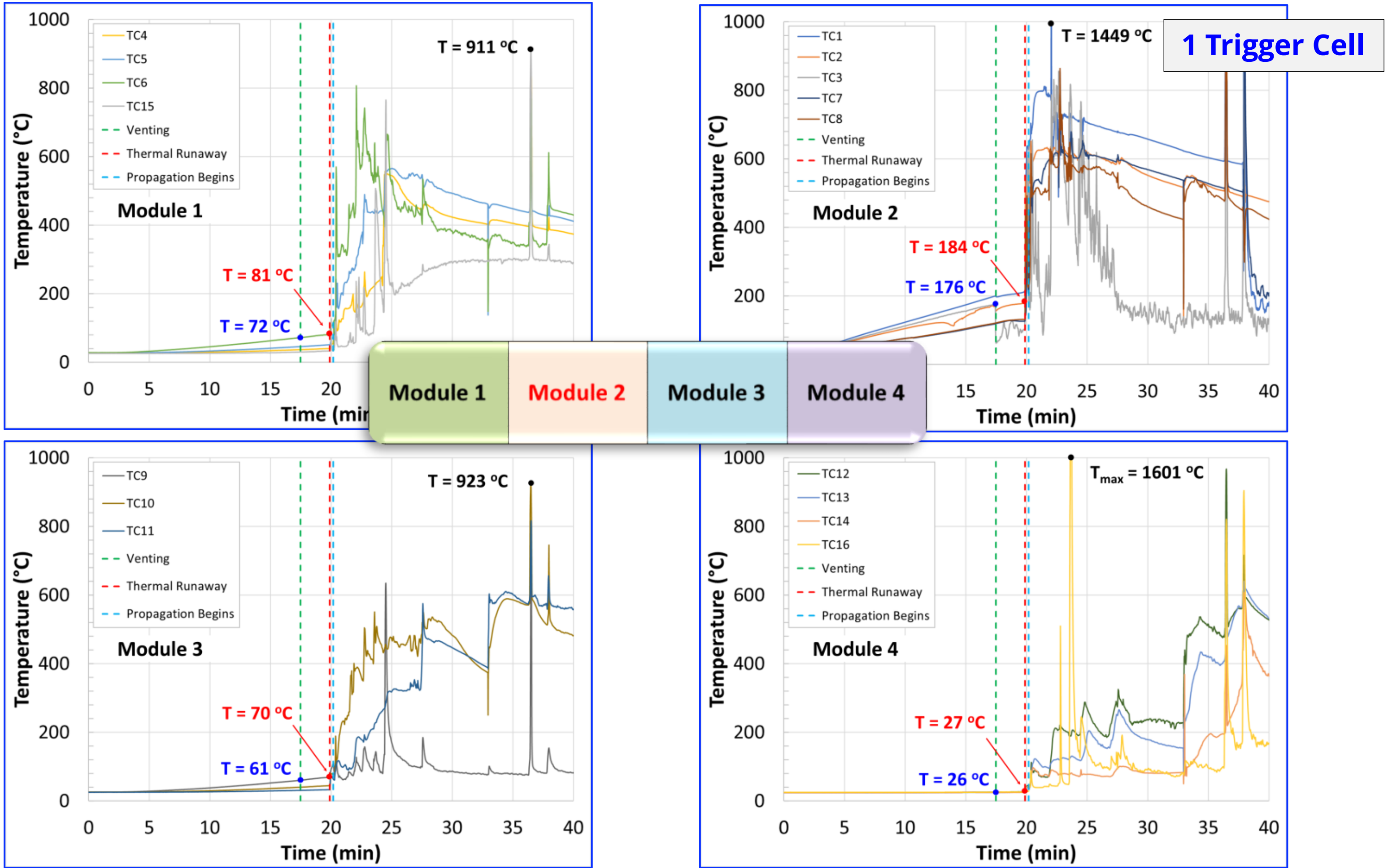
Cell metal casing melting

Activated vent holes



* Thermal runaway occurred in all the cells.

NMC Battery – Temperature Response



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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

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Gas Analysis

Results

Production of Venting Gases in Open Air

Chemistry	Test Level	Mass Loss (g) / (%)	Total Hydrocarbons Peak Release Rate (L/min)	Total Hydrocarbons Volume (Thermal Runaway) (L)	Carbon Dioxide Peak Release Rate (L/min)	Carbon Dioxide Volume (Thermal Runaway) (L)	Carbon Monoxide Peak Release Rate (L/min)	Carbon Monoxide Volume (Thermal Runaway) (L)	Hydrogen Peak Release Rate (L/min)	Hydrogen Volume (Thermal Runaway) (L)
NMC	Single cell 1	250 / 37	13.7	10	10.0	3	16.4	5	6.3	8
	Single cell 2	250 / 37	16.7	14	15.3	2	42.1	8	21.5	8
	Single cell 3	281 / 41	54.4	13	47.3	7	34.0	8	33.4	19
	Single cell 4	255 / 37	51.3	13	45.0	6	42.2	8	31.4	16
	Module 1	891 / 43	109.7	39	470.8	248	76.9	35	43.7	39
	Module 2	891 / 42	119.5	33	189.2	56	68.5	20	NR	NR
	Battery	4005 / 41	113.3	165	471.1	1403	33.8	90	52.4	83
LFP	Single cell 1	103 / 74	14.7	1	< 3.1	BDL	< 0.6	BDL	< 4.6	BDL
	Single cell 2	24 / 18	4.0	2	< 3.1	BDL	1.5	BDL	< 4.6	BDL
	Single cell 3	24 / 17	3.0	2	< 3.1	BDL	< 0.6	BDL	< 4.6	BDL
	Single cell 4	25 / 18	4.5	2	< 3.1	BDL	< 0.6	BDL	< 4.6	BDL
	Module 1	402 / 17	5.5	7	104.7	265	< 0.6	BDL	8.3	4
	Module 2	79 / 3	4.3	2	< 3.1	BDL	< 0.6	BDL	< 4.6	BDL
	Battery	1368 / 12	35.8	357	< 18.1	BDL	< 0.1	BDL	16.8	196

Production of Venting Gases

NMC	SRR [m^2/s]	Total Smoke Release [m^2]	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

Smoke

Fire

LFP	SRR [m^2/s]	Total Smoke Release [m^2]	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

Fire

Smoke

Fire

Smoke

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Total smoke release was calculated from the moment of venting until the end of visible gas and smoke release.

Thermal Runaway
in an Inert Environment

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Thermal Runaway in an Inert Environment

Thermal runaway tests were also conducted in an inert environment to characterize the gases evolved with subsequent analysis of lower flammability limit (LFL), burning velocity, and maximum closed vessel deflagration pressure that may be utilized as inputs for deflagration protection and prevention systems.

Fire and deflagrations can result from a mixture of flammable vapors with air and a source of ignition. One way to prevent fire and explosion is to control the amount of flammable gases to a safe level using mitigation methods. Below the LFL, the mixture of gases and air is too lean to support combustion. As the concentration of vented gases continues to increase and goes above the LFL, a fire or explosion may result if a viable ignition source is present.

Gas Composition - LFP

Test in Inert Environment

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

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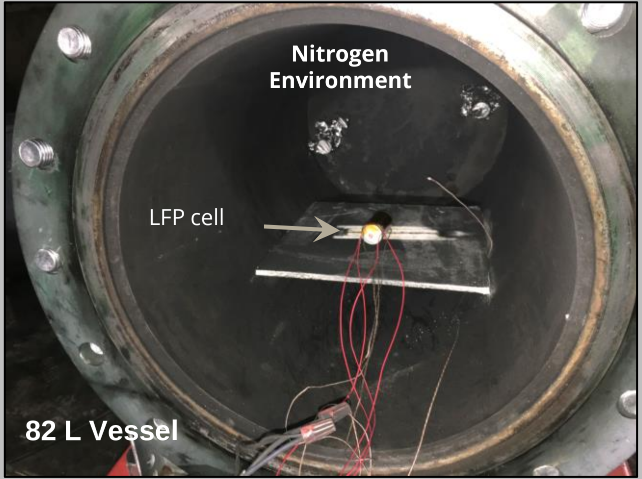
5.5 Ah Li-ion LFP cylindrical cells, **18 Wh**



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

Gas Composition - NMC

Test in Inert Environment

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

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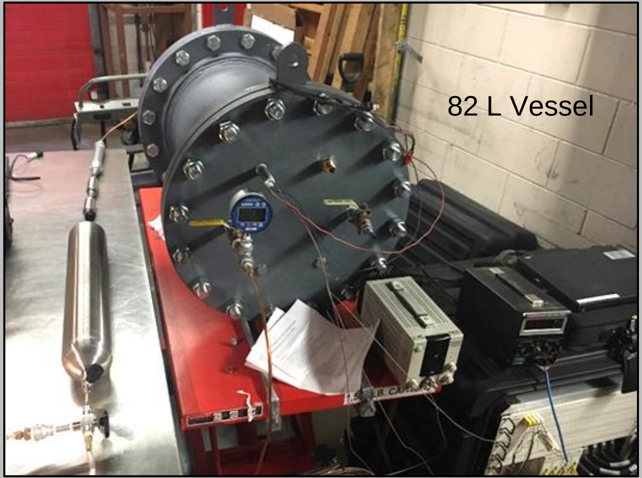
25 Ah Li-ion NMC cylindrical cells, **95 Wh**



1-gallon 316 stainless steel sample gas cylinder

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

Summary

- The heating test in open air provided information on the fire hazards, whereas the heating test in an inert environment provided information to quantify deflagration hazards.
- 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.

Summary

- 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.

- **Hydrogen fluoride** was **not detected** above the detectable limit of 20 ppb on the ion chromatograph for either cell chemistry in any of the tests.

- 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 Schraiber and team

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Dr. Judy Jeevarajan

Saad Azam (currently a graduate student at Dalhousie Univ.)

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