

PARTICLE AND GAS EMISSIONS FROM LITHIUM-ION BATTERIES DURING THERMAL RUNAWAY FIRES

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Background

- **Widespread Use:** Lithium-ion batteries power various devices, including electric scooters, bikes, EVs, laptops, smartphones, and energy storage facilities.
- **Thermal Runaway in Lithium-Ion Batteries:** Thermal runaway is a chain reaction triggered by internal overheating in lithium-ion batteries, potentially leading to an uncontrollable release of heat, flammable gases, and toxic emissions.
- **Relevance to Electric Scooters:** Lithium-ion batteries are widely used in electric scooters for their lightweight, high-energy density, and rechargeable features.
 - However, their propensity for thermal runaway under unsafe conditions underscores the importance of understanding associated risks such as harmful gases and particulates emissions

Objective

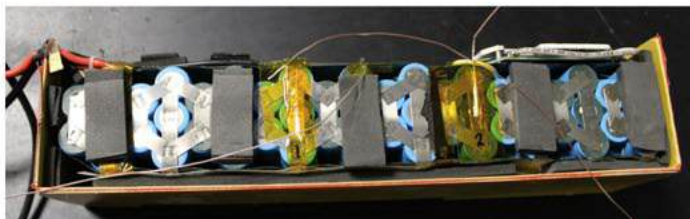
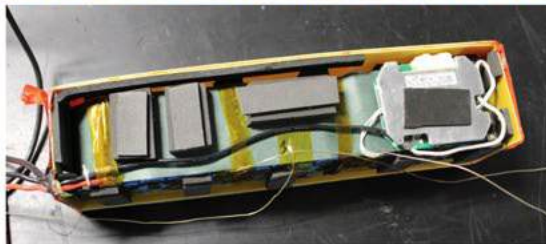
- To provide a detailed characterization of gaseous and particulate emissions from three Li Ion batteries (12ah 36V-0.43kW) subjected to thermal runaway fire via over-charging. These batteries are widely used in electric scooters.



Row	Parameter	Value
1	Chemistry	NMC
2	Size	335 mm x 75 mm x 75 mm
3	Weight	5.73 lbs.
4	C ₁ Capacity	12 Ah
5	Max Voltage	42 V
6	Nominal Voltage	36 V
7	Charge Current	3 A
8	Max Discharge Current: Cont., Peak	12 A, 24 A
9	Charge Temperature Range	0 to 45 °C
10	Cell Part Number	ICR 18650 / 26V

Battery Configurations

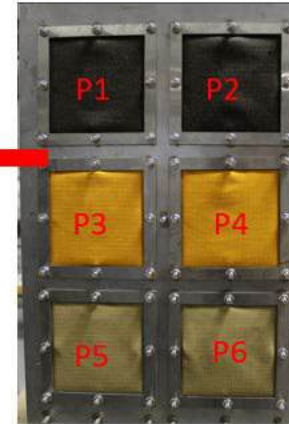
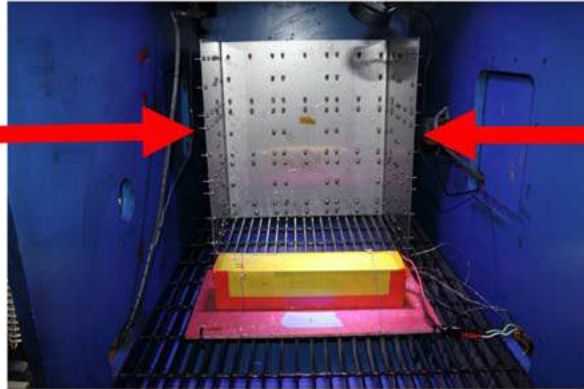
- Battery contains 50 cylindrical cells.
- Originally the battery will not overcharge due to battery management system (BMS) protection
 - The BMS was bypassed to allow overcharging to take place
 - Battery was instrumented with three internal thermocouple for surface temperature



Firefighters Gear Swatch Holder Inside the Blast Chamber

Clean and
Traditional Cab
Fabrics

SCBA Straps



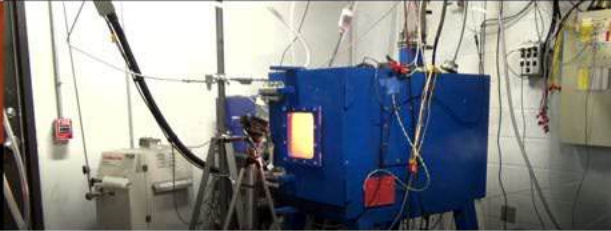
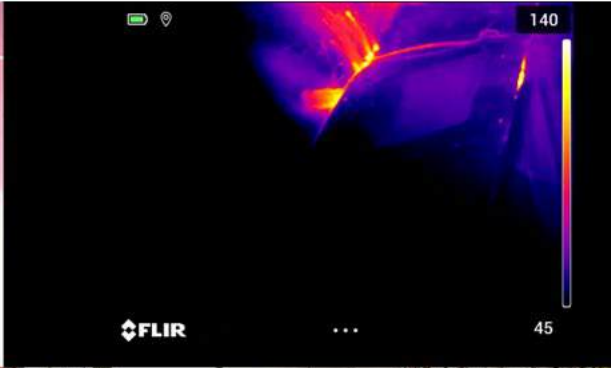
P: Position
Location

Gear outer Layers Exposed:

Tencate Advance Ultra
PBI Max
Tencate Millenia

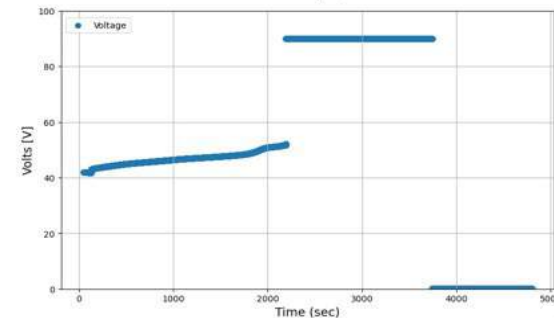
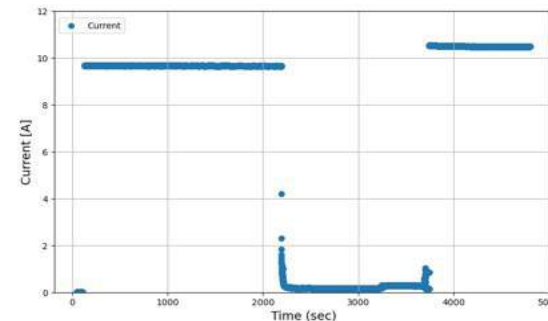
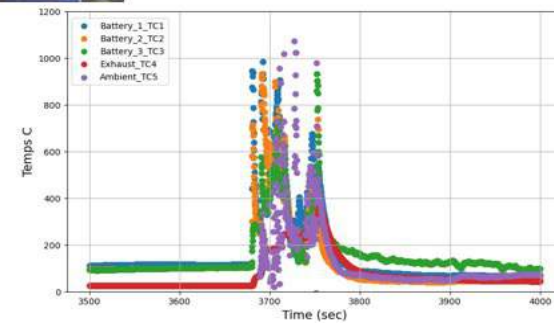
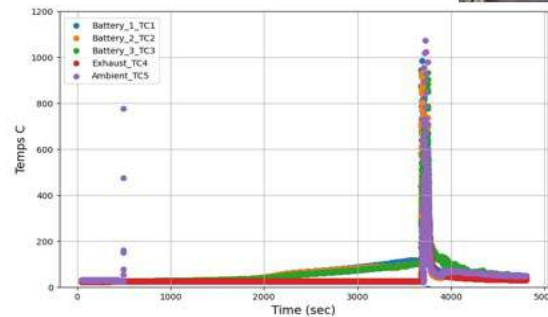
Gear Layers
Swatches (Outer
layer, moisture
barrier, thermal
insulator)

Battery Fire Visual for TEST 3



Current, Voltage and Temperature Profile Leading to Thermal Runaway-Test 3

- It took about 4800 seconds from start to finish
- Overcharging stopped around 2200 seconds
- Thermal runaway event started when TC1 temperature reached 117°C at 3680 seconds. Peak temperature reached $\sim 1100^{\circ}\text{C}$.
- Total high temperature fire event lasted about 90 seconds



Observations

- The CID trigger and voltage level were consistent for all three batteries.
- The thermal runaway inception temperature occurred at:
 - 117°C at ~3700 seconds for Test 3
 - 121°C at 4000 seconds for Test 1
 - 125°C at 4050 seconds for Test 2
- The peak temperature of 1100°C was similar for all tests
- The length of the high temperature runaway fire was:
 - ~200 seconds for Test 1. This was the longest likely due to lower air flow
 - ~90 seconds for Test 2 and test 3, likely due to a much higher flow in the blast chamber

Battery Weight Loss after Thermal Runaway Fire

- Battery debris remained after the battery fire was extinguished.
- Significant battery weight loss ranging from 44% to 63% of initial weight was observed.
- At higher air flow (Test 2 and Test 3), more burning occurred and battery lost more weight

	Pre-Weight	Post-Weight	Net Loss	Weight Loss
	g	g	g	%
Test 1	2676	1488	1188	44%
Test 2	2721	998	1723	63%
Test 3	2730	1127	1603	59%

Gaseous Species Measured by FTIR

- On average, < 200 seconds of thermal runaway, the most toxic species were:
 - CO and formaldehydes. CO concentration can reach 500 times the OSHA 8-hour 50 ppm limit, and 125 times the NIOSH 15-Minute limit of 200 ppm
 - Formaldehydes can reach 150 times the 8-hour 0.75 ppm limit, and 56 times the 15-minute of 2 ppm.

Mass by FTIR	Formula	Test 1 (g)	Test 2 (g)	Test 3 (g)
CARBON DIOXIDE	CO ₂	71.724	770.790	574.400
CARBON MONOXIDE	CO	16.634	98.990	34.693
NITRIC OXIDE	NO	0.010	0.462	0.393
NITROGEN DIOXIDE	NO ₂	<0.001	<0.001	0.009
HYDROGEN FLUORIDE	HF	0.003	0.014	0.018
HYDROGEN CHLORIDE	HCl	<0.001	<0.001	0.108
HYDROGEN CYANIDE	HCN	<0.001	0.046	0.018
FORMALDEHYDE	CH ₂ O	0.568	2.241	0.683
METHANE	CH ₄	0.977	5.704	1.703

Volatile Organic Compounds (VOC) by GC-FID

- VOC emissions were dominated by electrolytes that were reported undifferentiated, but they represent ethyl-, ethylene-, diethyl-, dimethyl- and propylene carbonate.
- Ethylene reached 446 times the OSHA 8-hour limit of 1 ppm, and 30 times the 15-minute limit of 5 ppm. 1,3 Butadiene reached 26 times the 15-minute OSHA limit of 1 ppm.

VOC (wt.% of Total VOC) by GC-FID	Test 1 (% of Total VOC)	Test 2 (% of Total VOC)	Test 3 (% of Total VOC)
ETHANE	1%	2%	1%
ETHYLENE	15%	23%	10%
PROPANE	0%	0%	0%
PROPYLENE	2%	3%	1%
ACETYLENE	2%	4%	2%
BUTANE	0%	0%	0%
TRANS-2-BUTENE	0%	0%	0%
1-BUTENE	1%	1%	0%
2-METHYLPROPENE (ISOBUTYLENE)	0%	0%	0%
PROPYLENE	0%	0%	0%
1,3-BUTADIENE	1%	1%	1%
2-METHYLPROPANE (ISOBUTANE)	0%	0%	0%
CIS-2-BUTENE	0%	0%	0%
2-METHYLBUTANE (ISOPENTANE)	0%	0%	0%
UNIDENTIFIED C4 OLEFINS	1%	1%	0%
C5-C6	1%	1%	2%
C6-C7	4%	7%	3%
C7-C8	1%	1%	0%
C8-C9	2%	0%	0%
C9-C10	0%	0%	0%
C10-C11	0%	0%	0%
C11-C12	1%	2%	0%
C12- C13 +	2%	5%	2%
ELECTROLYTES	66%	47%	75%
TOTAL	100%	100%	100%

Particulate Matter (mass, number & soot) Emissions During Runaway Fire

- $PM_{2.5}$ mass concentration in the vicinity of a diluted fire was a factor of 12,000 to 17,000 times higher than the new proposed EPA ambient $PM_{2.5}$ standard of $9 \mu\text{g}/\text{m}^3$.
- The soot or elemental carbon ranged from 3% to 6%.
- The dilute number concentration is comparable to that of an old model year diesel engine.

Particulate Matter Metrics			
Test #	PM2.5 (mg/m3)	Soot Concentration (mg/m3)	PN Concentration (#/cc)
1	159.48	4.38	2.71E+07
2	111.11	3.25	4.49E+07
3	111.90	6.85	6.47E+07

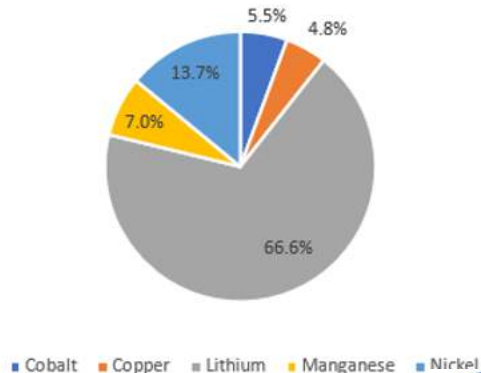
Soot vs Total PM Ratio			
Test #	Total Soot Mass (g)	Total Mass (g)	Mass Fraction (%)
1	0.005	0.18	2.75%
2	0.235	8.04	2.92%
3	0.510	8.33	6.12%

Particulate Matter (mass, number & soot) Emissions During Runaway Fire

- Lithium dominated the emissions followed by Cobalt, Manganese, Nickel and Copper
- Metallic elements dominates $PM_{2.5}$ in the range of 16% to 23%
- If we assume Li as Li_2O , the % weight will reach 34% to 49% of total $PM_{2.5}$ concentration
- These metals could be highly toxic depending on their chemical composition.

Elements	Test 1, mg/m ³	Test 2, mg/m ³	Test 3, mg/m ³
Cobalt	0.9	1.3	1.8
Copper	0.7	1.2	1.6
Lithium	19.5	14.9	15.2
Manganese	1.4	1.6	2.3
Nickel	2.3	3.1	4.8
Sum of Metals	24.8	22.1	25.7
$PM_{2.5}$	159.5	111.1	111.9
% of $PM_{2.5}$	16%	20%	23%

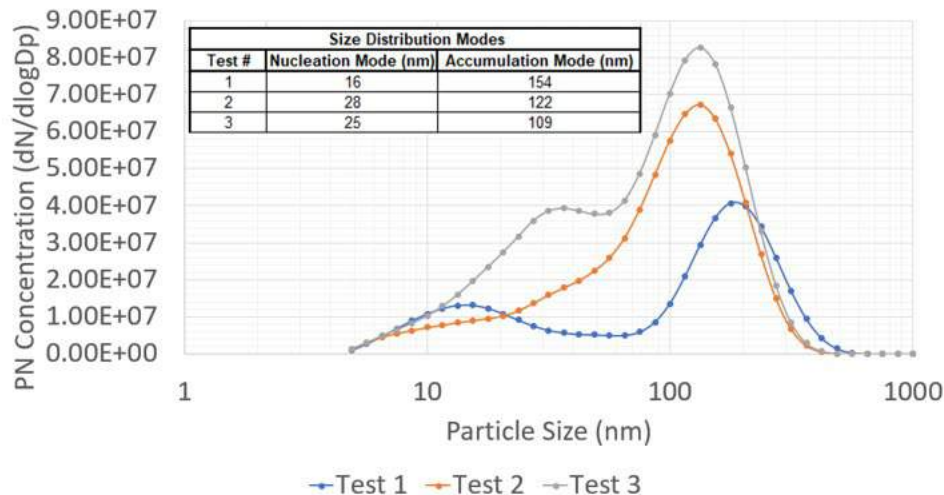
Average % Composition of Metallic Elements



Particle Size Distribution

- There is a small nuclei-mode with a geometric number mean diameter (GNMD) in the size range of 16 nm to 28 nm, and accumulation mode with a GNMD in the range of 109 to 154 nm.
- Although these particles can be filtered very effectively by an N95 mask, even a perfect mask will still expose the wearer to a significant concentration of particles.

Particle Number-Weighted Size Distributions



Observations-PPE SVOCs and Metals

- Many of the SVOCs were removed effectively especially with CO₂-based cleaning. Many of the SVOCs penetrated the outer layer to the vapor barrier but was removed via cleaning.
- The table below shows the sum of metallic elements on gear swatches after exposure and cleaning. The data clearly shows that the CO₂-based cleaning method is more effective. In addition, this suggests that performing two-cycle cleaning may help reducing the remaining metals on the gear swatches.

Outer Layer Type	Sum of Metallic Elements		
	Exposed	Water-Cleaned	CO2-Cleaned
	µg/cm ²	µg/cm ²	µg/cm ²
Test 1	688.623	5.12	2.49
Test 2	621.584	5.931	1.508
Test 3	494.255	7.177	4.213

- Clean cab fabric (like leather) showed less deposited metals compared to the traditional fabric, likely due to lower surface area.

Summary

- Three NMC scooter batteries were overcharged to induce thermal runaway in a blast chamber.
- Toxic gases (CO, CH₄, HCN, HF, formaldehyde), VOCs (ethylene, acetylene, butadiene), PM_{2.5}, and metallic particles (Li, Ni, Cu, Mn, Co) were measured, exceeding OSHA limits.
- Cleaning PPE swatches with water or CO₂ was highly effective (>99%). CO₂ cleaning outperformed water cleaning.
- PM_{2.5} levels were 12,000–17,000 times higher than the new EPA ambient standards of 9 µg/m³, with most particles in the respirable range (below 500 nm).
- This study highlights the extreme toxic emissions from Li battery thermal runaway fire.

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Questions

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