Texas A&M Engineering
TEEX
Extension Service

LITHIUM-ION BATTERY FIRES AND EMISSIONS CHARACTERIZATION

REPORT

November 2024

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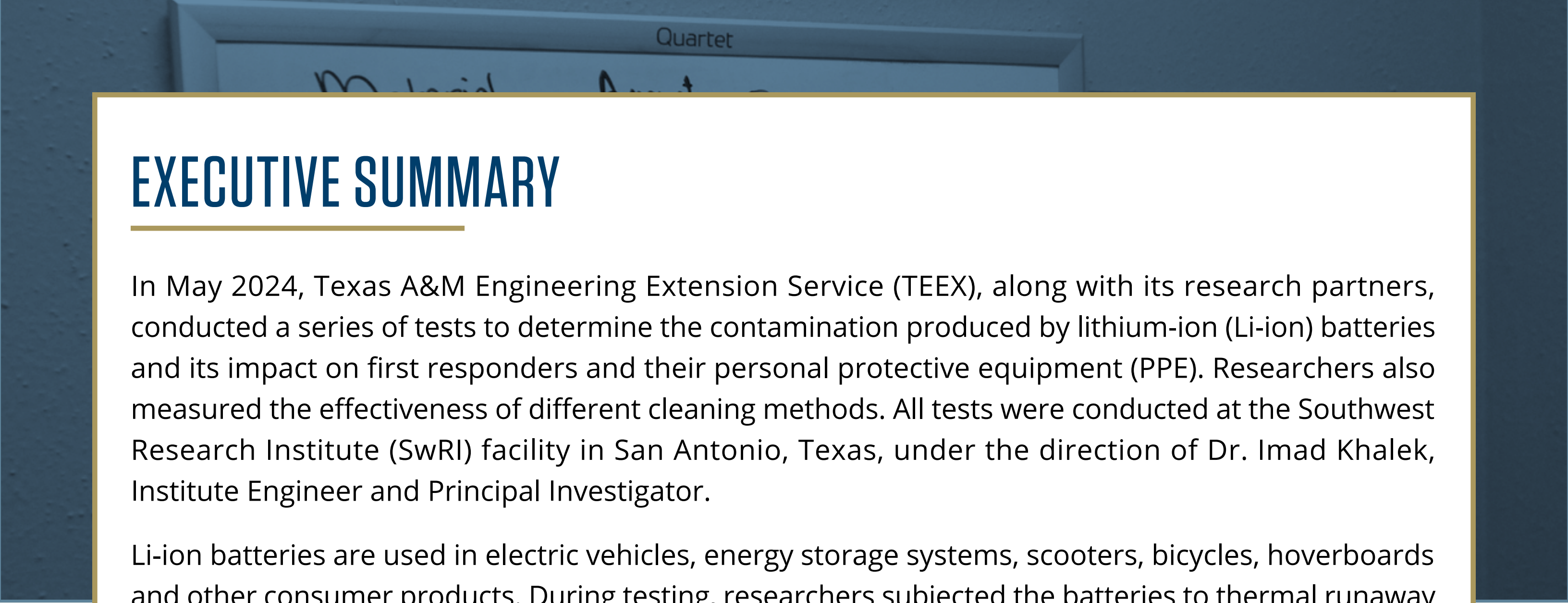

EXECUTIVE SUMMARY

In May 2024, Texas A&M Engineering Extension Service (TEEX), along with its research partners, conducted a series of tests to determine the contamination produced by lithium-ion (Li-ion) batteries and its impact on first responders and their personal protective equipment (PPE). Researchers also measured the effectiveness of different cleaning methods. All tests were conducted at the Southwest Research Institute (SwRI) facility in San Antonio, Texas, under the direction of Dr. Imad Khalek, Institute Engineer and Principal Investigator.

Li-ion batteries are used in electric vehicles, energy storage systems, scooters, bicycles, hoverboards and other consumer products. During testing, researchers subjected the batteries to thermal runaway by overcharge. The tests were conducted in a blast chamber where bunker gear swatches, apparatus fabric and self-contained breathing apparatus (SCBA) straps (referred to as equipment) were exposed to the byproducts of Li-ion battery fires. The tests measured 24 heavy metals and 75 semi-volatile organic compounds (SVOCs) resulting from the Li-ion battery fires.

Three separate tests were conducted:

- Test 1 exposed bunker gear swatches and equipment to Li-ion battery thermal runaway with an analysis of the chemical and metal particulates in the gear with no cleaning performed.
- Test 2 exposed bunker gear swatches and equipment to Li-ion battery thermal runaway and the bunker gear swatches were cleaned using traditional NFPA 1851 water-based extraction.
- Test 3 exposed bunker gear swatches and equipment to Li-ion battery thermal runaway, and the bunker gear swatches were cleaned using a liquid carbon dioxide (CO2) process.

The tests concluded that:

- Li-ion battery thermal runaway fires are an extreme emissions event, releasing highly toxic gases and particles that exceed the Occupational Safety and Health Administration (OSHA)-permissible exposure limits (PEL).
- During the tests, contamination in the blast chamber was extremely high. It ranged from 12,000 to 17,000 times more than the United States Environmental Protection Agency (EPA) ambient standard of $9\ \mu g/m^3$ for Particulate Matter (PM). Emissions were dominated by metallic particles and, to a lesser extent, soot.
- High concentrations of lithium, nickel, cobalt, manganese and copper were detected during each Li-ion thermal runaway event, with lithium being the most dominant.
- The traditional NFPA 1851 water-based cleaning of the PPE removed about 99.2% of all the metallic particles in the gear; liquid CO2 cleaning removed 99.8% of all the metallic particles.
- Some of the SVOCs remained in the gear after water-based cleaning. Cleaning efficiencies ranged from 21% to 92%. Liquid CO2-based cleaning was highly effective, with many SVOCs being undetected in the cleaned gear.
- Several metals, such as cobalt, manganese and lithium, remained in the gear regardless of the cleaning method used.

PROJECT DESCRIPTION

This study provides a detailed characterization of gaseous and particulate emissions from Lithium-ion batteries (36V 12Ah) containing 50 cylindrical cells subjected to thermal runaway via overcharging. These batteries are widely used in electric scooters and similar consumer products. All batteries were of Lithium-ion Nickel Manganese Cobalt (Li-NMC) chemistry.

Three tests were conducted, all with identical parameters. The Li-NMC batteries were forced into thermal runaway via overcharging. The Battery Management System (BMS) was bypassed to allow overcharging to occur. Testing was conducted inside a blast chamber with thermocouples affixed to the batteries to monitor battery surface temperatures before and during thermal runaway. High-speed cameras were also used to capture the thermal runaway event, in conjunction with Forward Looking Infrared (FLIR) technology to monitor internal battery temperatures.

Byproducts of the Li-ion battery fires were collected during testing and analysis, utilizing real-time measurements via Fourier Transform Infrared Spectroscopy (FTIR), Particle Size Distribution, Particulate Soot Mass, Semi-Volatile Organic Compounds (SVOC) and Metallic Compounds.

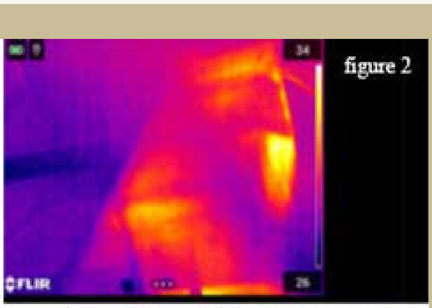

Figure 1 and 3: *Li-ion battery inside of blast chamber with three thermocouples attached to measure battery temperature.*

Figure 2: *Forward Looking Infrared Camera showing white-hot temperature signature of Li-ion battery cell failure.*

Figure 4: *View of blast chamber containing Li-ion battery, first responder PPE and equipment.*

During each test, various types of First Responder PPE and equipment were exposed to the byproducts of Li-ion battery fires. A specially designed testing rack was utilized to hold samples in place during testing. The materials exposed during Li-ion battery testing include:

- Bunker Gear – all three layers, including the outer shell, moisture barrier and thermal insulator.
- Apparatus Materials – clean and traditional cab configurations.
- Self-Contained Breathing Apparatus straps

During each of the three tests, the following components/materials were exposed by Li-ion batteries during thermal runaway.

- Six (6) full-thickness bunker gear samples.
- Two (2) apparatus clean cab fabrics.
- Two (2) apparatus conventional cab fabrics.
- Two (2) SCBA straps.

Only the bunker gear material was analyzed pre- and post-cleaning. All other materials were analyzed pre- and post-exposure. Test sample set 1 was exposed to Li-ion battery thermal runaway with no cleaning performed; only chemical and metal analysis were conducted. Bunker gear samples used in tests 2 and 3 were collected after testing and sent to the Emergency Technical Decon facility in Minnesota for cleaning and then returned to SwRI for analysis. Sample set 2 was cleaned using traditional NFPA 1851 water-based extraction. Sample set #3 was cleaned using a liquid carbon dioxide (CO2) process. The results of each cleaning method's effectiveness are discussed later in the report.

Figure 5: *(Left): Six swatches tested were full-thickness bunker gear, including the outer shell, moisture barrier and thermal liner. (Right): Six swatches tested are clean cab apparatus material, traditional cab material and SCBA shoulder straps.*

Figure 6: *Inside view of blast chamber with Li-ion battery in the foreground and PPE testing rack in the background.*

TESTING OBJECTIVES

The objectives of Li-ion battery testing include the following:

- Characterize emissions from three NMC Li-ion batteries experiencing thermal runaway fire.
- Measure gaseous species and particulate matter (PM) for each of the thermal runaway battery fire events:
- FTIR: CO, CO2, NO, NO2, HCN, HCl, HF, HCHO, CH4
  - GC-FID: Total VOCs
  - Particulate Matter (PM2.5), which is a particle size roughly 3% the diameter of a human hair, PM mass collected on a filter
  - Real-time black carbon mass
  - Real-time particle size distribution (5.6 nm to 560 nm)
  - Metals (EPA Method 6010/6020) – List of approximately 24 metals, including Li, Fe, Mg, Mn, Ni, Na, Co and others, up to 24 metals, excluding Hg
  - Semi-volatile Organic Compounds (SVOC) (EPA Method 8270E standard list + Toxic Industrial Chemicals)

One objective of this work was to expose various firefighter gear swatches, and perform metals and SVOC analyses, in addition to PM collected on filters and to quantify contamination. Another objective was to mearsure the efficiency of different cleaning methods provided to contaminated PPE and Equipment.

Figure 7 (Left): *Battery Test #3, where internal pressure from Li battery thermal runaway forced the blast chamber door to open.*

Figure 8 (Right): *Remains of Li-ion battery in blast chamber post-thermal runaway.*

TESTING RESULTS

- Three Li-NMC batteries (12ah 36V) containing 50 cylindrical cells were subjected to thermal runaway by overcharging them in a blast chamber one at a time. Thermal runaway could have been accomplished by other methods, including crushing, puncturing or applying an external heat source.
- Tests concluded that a Li-ion battery thermal runaway fire is an extreme emissions event of highly toxic gases and particles that are respirable and dominated by metallic compounds that well exceed the OSHA permissible exposure limits. High concentrations of lithium, nickel, cobalt, manganese and copper were detected in each test, with lithium being the most dominant.
- Particulate Matter in the dilute blast chamber was extremely high. It ranged from 12,000 to 17,000 times higher than the new EPA ambient standard (PM2.5) of 9 μg/m³. Emissions were dominated by metallic particles, with the highest being lithium. Other battery materials, such as nickel, manganese, and cobalt, were also detected. The concentration of metals ranged from 12 to 760 times their eight-hour OSHA limits, making them highly toxic, especially lithium.
- The use of a positive pressure self-contained breathing apparatus (SCBA) is highly recommended for all responders encountering Li-ion battery emergencies. Due to the high dilute particle concentration, even an effective passive mask such as an N95 will not effectively protect the wearer in the vicinity of such fires. NFPA 1971-compliant protective ensembles are necessary to protect the user from direct dermal contact with contaminants.
- In each test, peak temperatures inside of the blast chamber were observed in the 1100°C range (>2000°F). Temperatures increased each time a battery cell failed.
- There is a direct correlation between excessive voltage in a Li-ion battery and an increase in internal battery temperature. In each test, batteries became unstable, leading to thermal runaway when temperatures reached 117-125°C (242-257°F).
- PM2.5, soot mass, particle number and size distribution, metals, semi-volatile organic compounds (SVOCs) and gaseous emissions species were measured or collected from the exhaust of the blast chamber for further analysis. In addition, a set of PPE swatches placed in the blast chamber were exposed to battery fire products for metals and SVOC analyses before and after water-based and CO2-based cleaning.
- Although the mechanics of the thermal runaway fire were very similar for each test, the environmental conditions (still, windy conditions and variable wind conditions) in the blast chamber were different for each test.
- In each test, significant battery weight loss, ranging from 44% to 63%, was observed post-thermal runaway.

- Toxic gaseous species such as carbon monoxide, methane, hydrogen fluoride, hydrogen cyanide and formaldehyde were all measured. Volatile organic compounds (VOCs) were dominated by electrolytes; ethylene, acetylene and 1,3-butadiene, besides unidentified species in the C5-C7 and C11-C13 ranges. Carbon monoxide (CO) concentrations can reach 500 times the OSHA eight-hour 50 ppm limit, and formaldehydes can reach 150 times the 8-hour 0.75 ppm limit and 56 times the 15-minute limit of 2 ppm.
- Several toxic VOCs, such as ethylene, propylene, acetylene and 1,3-butadiene, were identified. Ethylene reached a level of 446 times the OSHA eight-hour limit of 1 ppm and 30 times the 15-minute limit of 5 ppm. 1,3-butadiene reached 26 times the 15-minute limit of 1 ppm.
- On average, each battery exhibited a thermal runaway condition for over 200 seconds, with the most toxic substances being carbon monoxide and formaldehyde.

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_2O	0.568	2.241	0.683
Methane	CH_4	0.977	5.704	1.703

Table 1: *Semi-Volatile Organic Compounds*

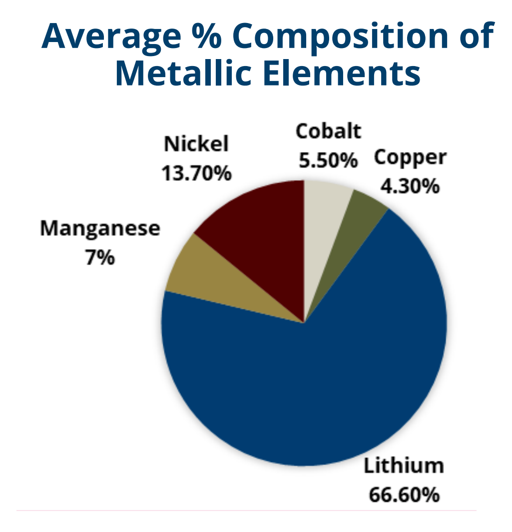

Figure 9: *Composition of Metallic Elements*

Elements	Test 1 (mg/m³)	Test 2 (mg/m³)	Test 3 (mg/m³)
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%

Table 2: *Summary of Metals Identified During Tests One Through Three.*

FINDINGS

Key findings on PPE exposure and cleaning effectiveness include:

- Up to 75 SVOCs were detected during testing, ranging from one-ring to five-ring PAHs. Tests with increased dilution of air in the blast chamber had a lower amount of SVOCs present.
- Penetration of SVOCs through the outer layer of the gear tested to the vapor barrier layer is possible. Water-based cleaning efficiency ranged from 21% to 92%. Many of the SVOCs penetrated the outer layer of the bunker gear, showing higher deposition in the vapor barrier. CO2-based cleaning was very effective, showing many compounds as undetected after cleaning.
- CO2-based cleaning proved effective in removing SVOCs that penetrated the outer layer of gear and were deposited in the vapor barrier.
    - The penetration of metallic particles to the vapor barrier level was very low. The outer layer of bunker gear proved effective in stopping most metals. All thermal liner values were near the detection limit.
    - One cycle of water-based and CO2-based cleaning of the exposed swatches was very effective for removing metallic compounds deposited on the outer layer of the gear samples. The cleaning efficiency was over 99% for most metals. CO2-based cleaning was slightly more effective than water-based cleaning. Using more than one cycle to clean could reduce some of the metals remaining on the surface of the gear's outer layer.
    - Iron, lead and magnesium proved to be the most difficult to remove from PPE, regardless of the cleaning method.
    - Even after cleaning, metals such as cobalt, copper, manganese and nickel remained on the bunker gear swatches at levels above the unexposed sample.
    - The PM2.5 collection was dominated by metallic elements with a small fraction of soot. Dominant elements were lithium, followed by nickel, manganese and cobalt.
    - Post thermal runaway analysis revealed apparatus clean cab fabric had less metals sticking to it, when compared with the traditional fabric materials; showing roughly half of the contaminates entrained in the fabric once exposed to a Li battery fire. This is likely due to the less porous surface of these materials, resulting in less particles sticking to the surface. The sum of metallic deposition averaged 226 ug/cm2 for clean cab materials and 418 ug/cm2 for traditional cab materials.
    - SCBA straps had the highest amount of contamination of any of the tested materials. The heavy metals contained in the SCBA straps were twice that of traditional apparatus fabric. This is likely due to the porous material construction of SCBA straps, resulting in a greater volume of particle entrainment. The sum of metallic deposition averaged 780 ug/cm2.

Outer Layer Type	Exposed (µg/cm²)	Water Cleaned (µg/cm²)	CO2-Cleaned (µg/cm²)
Test 1	688.623	5.12	2.49
Test 2	621.584	5.931	1.508
Test 3	494.255	7.177	4.213

Table 3: *Sum of Metallic Elements Pre- and Post-Cleaning. EPA Ambient Standard Is 9 µg/m³.*

CONCLUSIONS

- Quantifies the chemistry toxicity of Li-ion batteries that go into thermal runaway, the contaminants that first responders are exposed to when responding to Li-ion battery fires and the results of the two cleaning methods on contaminated bunker gear and equipment.
- Confirms that global Li-ion battery use is an emerging hazard for the first responder community. This hazard will only expand with the increased use of Li-ion batteries.
- Raises awareness of the human health and environmental risks associated with Li-ion battery fires.
- Provides information for the first responder community to shape their response protocols, such as apparatus positioning and cleaning efficiencies, and to develop and adopt standard operating procedures and guidelines for responding to Li-ion battery fires.
- Contributes to the body of knowledge to identify safe and successful methods for responding to Li-ion battery fires.
- Encourages the first responder community to rethink its approach to Li-ion battery fires because current water, foam and dry chemical suppression methods are ineffective.
- Emphasizes the need to perform testing and contamination analysis on larger Li batteries such as 400 and 800-volt Li-ion vehicle batteries and Battery Energy Storage Systems.

Abbreviations

Ah – Amp Hour
BMS – Battery Management System
CID – Current Interrupter Device
CO2 – Carbon Dioxide
EPA – Environmental Protection Agency
FLIR – Forward Looking Infrared
FTIR – Fourier Transform Infrared Spectroscopy
Li – Lithium Ion
Li-NMC – Lithium-Ion Nickel Manganese Cobalt
NFPA – National Fire Protection Association
OSHA – Occupational Health and Safety Administration
PAH – Poly Aromatic Hydrocarbon
PPE – Personal Protective Equipment
PM – Particulate Matter
PPM – Parts per Million
SCBA – Self Contained Breathing Apparatus
SVOC – Semi volatile Organic Compound
SwRI – Southwest Research Institute
TEEX – Texas A&M Engineering Extension Service
Ug – Microgram
V – Volt
VOC – Volatile Organic Compound

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- Mr. David Coatney, TEEX Agency Director
- Mr. Gordon Lohmeyer, TEEX Assistant Agency Director

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- Emergency Technical Decon – Provider of cleaning services for exposed bunker gear, including both water-based and liquid CO2 cleaning.
- Pierce Manufacturing – Siddons Martin – Supplier of apparatus fabric.

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