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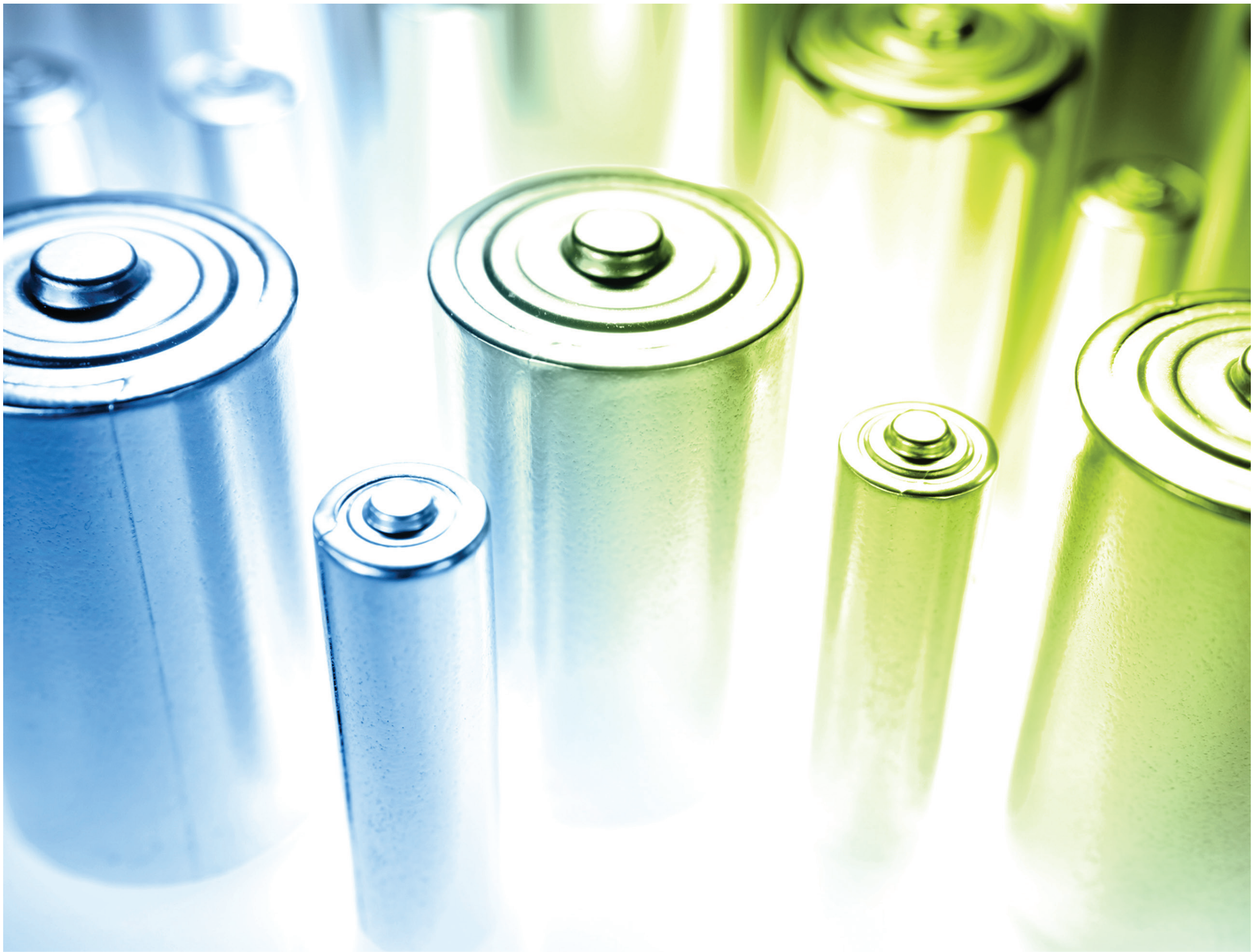
SUMMARY OF PRIOR ELECTROCHEMICAL BATTERY FIRE EMISSIONS CHARACTERIZATION STUDIES



Technical Brief, December 2020

INTRODUCTION

Lithium-ion batteries (Li-ion batteries or LIBs) have become one of the most popular battery types for electric vehicle (EV) and stationary energy storage system (ESS) platforms given their high energy density, low maintenance, and longevity, which are important features to support long-term operation and high-current applications. Utility-scale battery ESS has also been shown to be an effective way to stabilize the electric grid and support the utilization of renewable energy sources. There is increasing demand for renewable energy sources, such as solar and wind, in order to meet renewable energy targets, reduce utility carbon footprint, and obtain long-term cost benefits. However, there is a gap between the demand and supply of renewable energy since geological, seasonal, and temporal conditions can affect power generation from renewable sources. Grid-level stationary battery ESS have become an important element for efficiently utilizing electricity generated from renewable energy sources, allowing for adequate balancing between the supply and demand by storing excess electrical energy during peak generation hours to be used during other periods. As a result, deployment of stationary battery ESS has been increasing.

Several incidents of LIBs catching fire and exploding have been reported from stationary and vehicle platforms and consumer products (Kong et al., 2018). However, a limited understanding exists of the hazards associated with LIBs when a cell failure occurs. One potential outcome of a failure is a fire event, which brings risks from the combustion, explosion, and exposure to hazardous materials that may result (EPRI, 2019). Public reports of some experimental testing methods for live fire battery burn testing exist that can inform discussions of risk associated with LIB fire events. This report summarizes relevant testing methods and subsequent air emissions characterization of off-gassing and combustion plumes from these prior test reports. The results can be used to set initial expectations for potential outcomes of a LIB fire incident, and to understand gaps in current knowledge and assessment tools. Gaps can be subsequently addressed to continually advance safety and risk discussions and improve protocols.

BASICS LIB DESIGN

There are four components that make up a LIB: anode (negative electrode), cathode (positive electrode), separator, and electrolyte. Battery cell discharges and charges occur by Li-ions shuffling between the cathode and anode, which are separated by a separator, through the electrolyte. The cathode determines the energy capacity and power delivery of LIBs; therefore, LIBs are characterized by cathode chemistries. Many different battery chemistries can be used in the cathode of LIBs including Lithium Cobalt Oxide (LCO), Lithium Manganese Oxide (LMO, also known as spinel), Lithium Iron Phosphate (LFP), Lithium Nickel Manganese Cobalt (NMC), Lithium Nickel Cobalt Aluminum Oxide (NCA), and more. LIBs can be packaged in four different cell types: cylindrical, prismatic, pouch, and button cells. Therefore, there are many types of LIBs using different battery chemistries packaged in different cell types with varying energy capacity that may lead to unique patterns and magnitudes of hazards.

SAFETY ASPECTS OF LIBS

A concern with LIBs is thermal stability; instabilities can lead to thermal runaways resulting in hazardous outcomes. Thermal runaway can be defined as "a self-enhanced increasing temperature loop"(Kong et al., 2018) where the temperature of the battery will continue to increase once the temperature reaches above 150°C-180°C (Warner, 2019) (**Figure 1**), which then can lead to off-gassing, fires, and explosions accompanied by associated emissions. It should be noted that the exact temperatures, above which varying indications of battery fire event are triggered, could vary by additives in the electrolyte and the coating of the separator (Warner, 2019). Thermal runaways of LIBs can be initiated via multiple pathways, such as overcharge, short circuit, exposure to heat, and vibration. Mitigation efforts can be made at three different stages of the thermal runaway process: 1)

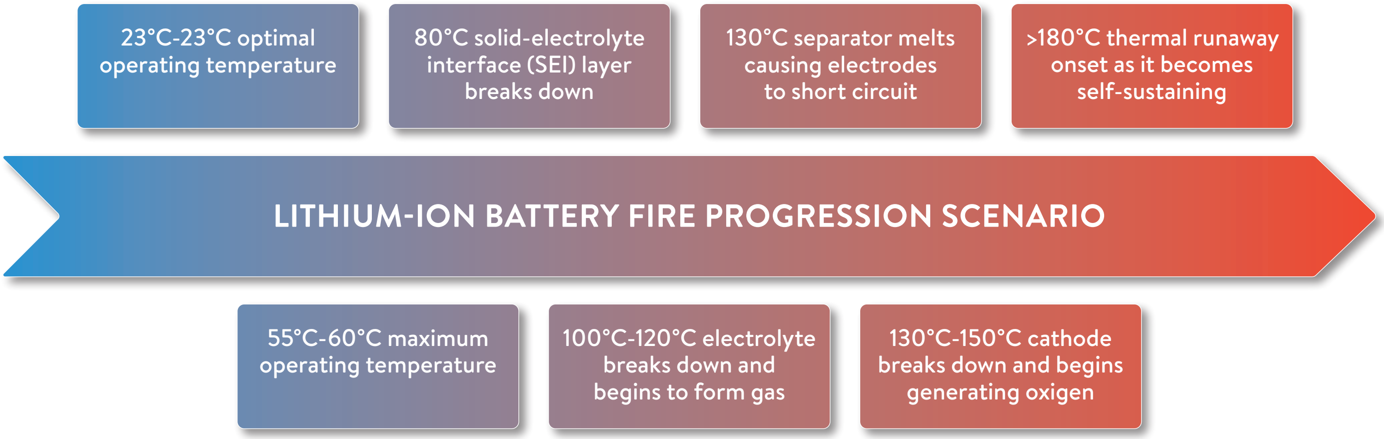


Figure 1. *Impact of temperature on a Li-ion battery cell (figure was modified from Warner, 2019)*

before thermal runaway – e.g. adding flame retardants in the LIB electrolyte to increase thermal stability and prevent thermal runaway, 2) during thermal runaway – e.g. implementing separator shutdown (closing the pores of the separator through a melting process leading to cell shutdown), cell venting to release the gases in a more controlled way rather than in an uncontrolled explosion, and 3) after thermal runaway – e.g. safe extinguishment of any fires (Warner, 2019).

Along with design and engineering efforts to improve the safety and reduce the failure rates of these battery ESS, the probability and expected magnitude and pattern of the potential hazards from LIB cell failures must be carefully assessed to accurately inform associated risks. One way to gather such data is to conduct experimental tests simulating plausible incident scenarios. Qualitative and quantitative findings from such experiments can help inform safety system designs, especially for large-scale ESS, in order to protect on-site workers, first responders, and nearby communities from potential exposures. Even though the cell failure rate can be exceedingly low, given the large quantity of LIBs in a large utility-scale ESS, it is important to accurately assess the associated hazards in case of a cell failure.

OBJECTIVES OF THIS REPORT

- Review existing publicly available information on LIB fire experiments and summarize the basic experimental designs used in different studies;
- Summarize gas emissions associated with battery behaviors post induced cell failures; and
- Characterize common themes, insights, and gaps on the testing and air emissions from these existing studies.

EXPERIMENTAL DESIGNS FROM PRIOR STUDIES

Seven studies were identified that conducted LIB burn testing experiments, representing a variety of experimental designs (**Table 1**) and battery characteristics such as state of charge (SOC). Six out of seven studies conducted experiments on a cell to module level using from a minimum of one to a maximum of 12 battery cells in a test. One study (study #2) included 14,400 battery cells by directly using a stack of battery modules used in Tesla vehicles. It is important to mention that utility-scale ESS often have a storage capacity of a few to hundreds of megawatt-hours (MWh) (International Renewable Energy Agency (IRENA), 2019); therefore, even the largest-scale experiment reviewed in this report is smaller by at least a factor of 10 compared to the energy capacity typically used in a utility-scale ESS.

Table 1. *LIB burn testing experiment studies reviewed in this report.*

Study ID	Citation	Number of Tests, Number of Cells, Battery Chemistries, and Cell Types	Experimental Setup	Gas Measurements
1	Andersson et al., 2013	Seven experiments were performed using various SOC (0% to 100%). - five tests used LFP pouch cells (n=5 cells per test) - one used LFP cylindrical cell (n=9) - one used laptop battery pack (n=12) The energy capacity of each test ranged from 110 to 830 Wh.	Pouch cell for automotive applications, optimized cylindrical cell for electric vehicles (type 26650), and laptop LFP batteries were used. Tests were conducted in a Single Burning Item apparatus (EN13823) and batteries were secured by using steel wire or steel net to avoid possible projectiles. A propane burner was placed underneath the batteries that were on a small table with the tabletop consisting of wires.	Fourier Transform InfraRed spectrometry (FTIR) was used to measure emission of HF, POF_3 and PF_5. FTIR simultaneously obtains absorption spectra across a wavelength range relevant for a large number of gaseous compounds. Particulate matter was removed by filters. The FTIR was calibrated specifically for the analytes of interest, for individual compounds and mixtures.
2	Blum, 2016	Two experiments were conducted using Tesla NCA cylindrical battery pack (n=14,400 for each test) at 100% SOC. The energy capacity of each battery pack was 100,000 Wh.	Tesla Powerpack containing cylindrical cells (type 18650) were tested. Two 52-inch long by 38-inch wide by 86-inch high steel cabinets each with 16 energy storage pods, and each storage pod containing two modules of 450 cells, called Powerpack, were installed: one for external test and one for internal test. The cabinets had coolant pumps, reservoirs, and fans and radiators within the front door, and a vent at the top. Both tests were performed outdoors in open air, on a concrete pad, exposed to natural weather conditions. The Powerpack is exposed to a propane burner for 60 minutes to simulate a fire scenario where the fire originates outside of the Powerpack for the external test, while individual cells were induced to thermal runaway using heater cartridges for the internal test.	Gas samples were pumped from the exhaust vent and measured by MultiRAE Lite PGM-6208 (CO, Cl_2, CH_4) and a PortaSensII portable gas leak detector (HF).
3	Nedjalkov et al., 2016	Three scenarios were tested using one NMC in a pouch cell (172 Wh) at 100% SOC for each test.	Three different scenarios: 1) a single bare Li-ion cell mounted within a barrel partly shut by a cover (to prevent explosion and retain the emitted gases), 2) a battery from scenario #1 wrapped within a specially-developed textile composite structure for fire prevention, and 3) experimental set-up from scenario #2 with the barrel sealed with a gas filtration unit (5-stage filtration: coarse particle separator, activated charcoal, potassium permanganate, activated alumina, and fine particulate filter) mounted on top were tested in a barrel with a nail penetration device to create an internal failure (n=1 for each test).	Gas samples were collected in absorbent tubes and analyzed by gas chromatography (GC) for larger molecules [VOC >C4, e.g. benzene, ethylmethylcarbonate (EMC), diethyl carbonate (DEC)[and smaller components (<C4) by quadropole mass spectrometry (MS). HF gas samples collected in wash bottles and measured via ion chromatography and conductivity. Photoacoustic spectroscopy detected CO.
4	Consolidated Edison and NYSERDA, 2017	NCM battery cells from 4 different manufacturers, and LFP, T1 by Toshiba, and BM-LMP batteries were tested at SOCs ranging from 25% to 100%. One battery cell was used in each test and some tests were repeated. No information on the energy capacity of each cell was provided.	Chamber (30*30*30 inch) testing using radiant electric heat and outdoor large-scale burn testing using propane burner were conducted. 37 chamber testing reported battery type- and SOC- specific gas emissions and heat release rates. The large-scale burn testing was conducted in a walled off shipping container with a series of ventilation ports cut into the room in order to identify any unforeseen risks posed by larger systems in addition to verifying modeling results. The partially enclosed large-scale tests were secured overnight for observation of re-ignition, then intentionally re-ignited 24 hours later to determine remaining fire load. A large variety of different battery chemistries by different manufacturers and SOCs were tested.	FTIR (HCl, HF, HCN, CO, CO_2, O_2, SO_2, NO, NO_2, hydrocarbons (e.g. CH_4, ethane, ethylene, benzene, toluene). MSA Ultima sensors (O_2, H_2, F_2, Cl_2). Gas bags collected samples for later analysis of fluoride compounds, metals, gases).

Table continued on next page.

***Table 1 (continued).** LIB burn testing experiment studies reviewed in this report.*

Study ID	Citation	Number of Tests, Number of Cells, Battery Chemistries, and Cell Types	Experimental Setup	Gas Measurements
5	Larsson et al., 2017	A wide range of battery chemistries (LCO, LFP, NCA-LATP, and laptop pack), cell packaging (prismatic hard Al-can, pouch, and cylindrical), and SOCs (0%, 25%, 50%, 75%, and 100%) were tested with each test containing 2 to 10 cells. Energy capacity of each test ranged from 92 to 138 Wh.	The experiments were conducted in a well-ventilated SBI apparatus (EN13823). Cells were exposed to an external propane fire.	FTIR was used to measure fluorinated compounds (HF, POF$_3$, and PF$_5$) after calibration for these compounds. Gas washing bottles were used to validate results from FTIR.
6	Sturk et al., 2019	Two experiments were conducted with one LFP pouch cell (116 Wh) and one NMC/LMO pouch cell (287 Wh) with each test including 5 cells at 100% SOC.	This study focused on investigating conditions of venting, the amount of gas released, and the composition of gases formed by heating two types of automotive grade Li-ion cells in an oxygen free environment -- the top of the test vessel was fitted with an inlet for nitrogen gas -- preventing ignition of vented gases. The walls of 60 L insulated test vessel were electrically heated to around 70 C° to limit condensation of gases during the test. One test for LFP cell and one for NMC/LMO cell were conducted by heating the bottom of the test vessel using a plate heater generating a maximum temperature of 350 C° at a rate of 7 C°/min.	FTIR [HF, POF$_3$, CO$_2$, CO, electrolyte solvents [e.g. diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonates (EMC)]; Gas wash bottles and IC (HF) to validate FTIR. Gas bags collected samples for later gas chromatography mass spectrometry (GC-MS) to validate FTIR data for electrolyte solvents.
7	Peng et al., 2020	One LFP pouch cell (219 Wh) was used for each of the four experiments at SOC of 0%, 50%, 75%, and 100% (n=1 for each test).	An LFP battery cell (PL15181210), widely used in electric buses, was tested by being placed upon a supporting mesh in a well-ventilated chamber (150*150*180 cm). A 3 kW electric heater was set under the battery at a vertical distance of 10 cm to simulate a radiative heat condition as well as an electric spark igniter.	Paramagnetic analyzer (O$_2$); Non-dispersive infrared sensor (CO$_2$). FTIR (CO, HF, SO$_2$, NO2, NO, HCl).

Battery chemistries listed in the table are as follows:

BM-LMP: bio-mineralized lithium mixed metal phosphate

LATP: $Li_{1.2}Al_{0.2}Ti_{1.8}(PO_4)_3$

LFP: lithium iron phosphate – $LiFePO_4$

LMO: lithium ion manganese oxide – $LiMn_2O_4$

NCA: lithium nickel cobalt aluminum oxides

LCO: lithium cobalt oxide – $LiCoO_2$

NMC: lithium nickel manganese cobalt oxide – $LiNiMnCoO_2$

Table 2. *Summary of Visual Observations of LIB Fire Tests*

Study ID	Observations
1	Outbursts of vented gases (both light and dark smoke) were observed with cells with 100% SOC. Fires/flames started around at 1-minute time point and lasted from 18 to 33 minutes with fires from batteries with lower SOC lasting longer.
2	External: The test lasted for 3 hours and 45 minutes. Popping sounds and light and dark smokes were observed, while no violent projectiles, explosions, or bursts were observed during the entire course of test (while exposed to the burners, in a free burn state, or after flames were no longer visible). Flames were mostly confined within the Powerpack though some weaker flames emanated from the exhaust vent, the front thermal door grill, and around the front thermal door seal. Internal: The test lasted for 1 hour and 30 minutes. The cell failures were contained within the initiator pod with induced cells. Popping sounds and light and dark smoke was observed but without violent projectiles, explosions or bursts. No flames or other signs of fire were observed.
3	Scenario #1 showed that the cell expands until it bursts open and catches fire, but no explosions were observed. Video record of scenario #2 showed an abrupt outgassing of the cell.
4	Rising smoke plumes were observed through door gaps and out of top vents in the burn container. The module testing showed that the exhaust fan was eventually overstressed by the heat and smoke following several consecutive fire tests. The cell failures seemed to happen within 10 minutes of being exposed to heat in both chamber and module testing. Off-gassing and rupturing were observed when the temperatures reached 120°C. LFP, LTO, and BM-LMP cells often off-gassed without flame, but the emitted constituents were the same as batteries with failure at higher temperatures.
5	Distinct peaks in heat release rate were only observed with 100% SOC cells happening between 3 to 8 minutes after the heat was applied, but not with the lower SOC cells. Test results were reported for the maximum of 30-minute window. No descriptions were provided for fires/explosions/smoke.
6	The venting duration for NMC/LMO was approximately 2 minutes compared to 45 minutes for LFP cells indicating higher reactivity of NMC/LMO cells. Since the experiments were conducted in an oxygen-free environment, no smoke, fire, explosion, and projectiles were reported.
7	Ignition time, the time from the exposure to electric radiation to the appearance of a continuous flame, were inversely associated with SOC. The largest length of a jet flame was more than 55 cm for the fully charged battery. Cells with higher SOCs also showed a longer combustion flame as well as a larger scale of fire. Tests lasted for from 20 to 30 minutes.

There are also smaller ESS, such as demonstration scale systems below 1MW in operation, to which the findings from these experiments are likely to be more directly relevant.

Each study was unique in how the experiment was designed. One study (study #6) was conducted in an oxygen-free environment, while all other experiments were conducted in fully ventilated conditions. One study (study #3) initiated cell failure using a nail penetration of a battery cell, while all others used heat exposure to initiate the thermal runaways either by using a propane burner or an electric heater/plate. For this suite of prior tests, internal heating (such as that performed with a flexible film heater) was not used, although it is a more common approach in subsequent battery fire tests (Energy Storage Research Group, pers. comm.). While the range of experimental designs provides the opportunity to assess varying hazards that could be present under different LIB fire scenarios, it makes it difficult to compare the results across the studies. The test methods used here also differ from the American National Standards Institute (ANSI) accredited test method, ANSI/CAN/UL 9540A (commonly referred to as UL9540A), for assessing LIB systems during failure and fire (EPRI, 2020). This is because UL 9540A focuses primarily on flammability, with emissions (and emissions only hydrocarbons and hydrogen halides) as a secondary focus. Data collected during UL9540A analysis are used as inputs to a fire protection engineering analysis to assist with design of explosion protection and fire suppression systems.

Table 2 summarizes some visual observations as well as the experimental duration. No study observed explosions or projectiles, in part by how the studies were designed, while outbursts of cells and flames were commonly observed. Test durations ranged from 20 minutes to 3 hours and 45 minutes.

CONCEPTS OF EXPOSURE LIMIT

Table 3 summarizes various exposure limits, where available, of the gases examined in the seven reviewed studies in this report. It's important to define, and recognize the differences between, various exposure limit concepts. National Institute for Occupational Health and Safety (NIOSH) has recommended exposure limits (RELs) to provide guidelines for upper exposure limits to hazardous substances in the workplace, while Occupational Safety and Health Administration (OSHA) sets up legal permissible exposure limits (PELs) in the United States to protect workers' safety. These values are developed based on the chemical properties of the substance, experimental studies on animals and humans, and toxicological and epidemiological data. Both PELs and RELs use time-weighted averages (TWA). These are the levels of average airborne exposure in any 8-hour (PEL), or up to 10-hour (REL), work shift of a 40-hour week established as the highest level of exposure an employee may be exposed to without incurring the risk of adverse health effects, which shall not be exceeded. There are three additional metrics to consider: 1) short-term exposure limit (STEL), a 15-minute TWA exposure that should not be exceeded at any time during a workday, 2) ceiling limit (CL), the value should not be exceeded at any time, and 3) immediately dangerous to life and health (IDLH), the values used for respirator selection criteria and to characterize high-risk exposure concentrations. There are two main purposes of IDLH including: 1) to ensure that the worker can escape from a given contaminated environment in the

Table 3. *Example Exposure Limits by Gas Type*

Substance	Regulatory Limits by OSHA	Recommended Limits by NIOSH	
	8-Hour TWA PEL STEL CL	Up to 10-Hour TWA REL STEL CL	IDLH
	ppm (mg/m^3)		
Acrolein	PEL: 0.1 (0.25)	REL: 0.1 (0.25) STEL: 0.3 (0.8)	2 (5)
Benzene	PEL: 1 (3.2) STEL: 5 (16)	REL: 0.1 (0.32) STEL: 1 (3.2)	500 (1,600)
Biphenyl	PEL: 0.2 (1)	REL: 0.2 (1)	15.8 (100)
CO	PEL: 50 (55)	REL: 35 (40) CL: 200 (229)	1,200 (1,374)
CO_2	PEL: 5,000 (9,000)	REL: 5,000 (9,000) STEL: 30,000 (54,000)	40,000 (72,000)
DEC	-		
EC	-		
EMC	-		
HCl	CL: 5 (7)	CL: 5 (7)	50 (70)
HCN	PEL: 10 (11) [skin]	STEL: 4.7 (5)*	50 (55)
HF	PEL: 3 (2.5)	REL: 3 (2.5) CL: 6 (5)	30 (25)
NO	PEL: 25 (30)	REL: 25 (30)	100 (120)
NO_2	CL: 5 (9)	STEL: 1 (1.8)	13 (23.4)
SO_2	PEL: 5 (13)	REL: 2 (5) STEL: 5 (13)	100 (250)
Styrene	PEL: 100 (425) CL: 200 (850)	REL: 50 (215) STEL: 100 (425)	700 (2,975)
Toluene	PEL: 200 (750) CL: 300 (1020)	REL: 100 (375) STEL: 150 (560)	500 (1,875)

* There is also potential for dermal absorption

event of failure of the respiratory protection equipment, and 2) to indicate a maximum level above which only a highly reliable breathing apparatus, providing maximum worker protection is permitted (CDC, 2017). These values are reported in either ppm or mg/m3 (conversion factors are available for various substances to convert between ppm and mg/m3). There are also guidelines set by the American Conference of Governmental Industrial Hygienists – threshold limit value (TLV), which can be adopted by individual workplaces, though these are not regulatory requirements. Metrics that are likely to be more relevant for first responders entering battery fire situations are STEL, CL, and IDLH, while PEL and REL in addition to STEL may be relevant for nearby communities. It is important to note that these PELs have not been updated since its establishment in 1971. OSHA acknowledges that these limits are not necessarily sufficiently protective of workers' health as shown by industrial experience, developments in technology, and scientific data. These exposure limits can be used as a starting point, but workplace-specific decisions should be made to protect their workers utilizing other existing information developed by various technical, professional, industrial, and government organizations. Exposure limits for other gases can be obtained from OSHA (https://www.osha.gov/dsg/annotated-pels/index.html).

RESULTS AND DISCUSSION FROM PRIOR STUDIES

GAS EMISSIONS

A wide range of gases may be emitted from LIBs during a thermal runaway event. Battery chemistry, state of charge, ventilation status, size of the room, and the heat transfer environment are known factors that could influence thermal runaway processes and their results. In total, there were more than 20 different gases that the seven reviewed studies attempted to measure, and most were detected. The summary tables for gas emissions focused on the gases that had reported concentrations. It is important to note that the reported emission concentrations were from field/laboratory experiments and are not necessarily representative of the concentrations expected from real battery fire events considering potentially varying ventilation and dilution environments. Some of the numeric values were estimated from the reported figures and a range was provided if the same test was repeated.

1. HF, POF$_3$, and PF$_5$

This section summarizes the findings on the fluorinated compounds from the reviewed studies. When the electrolyte (LiPF$_6$) in a LIB is heated in a dry and inert environment, it can decompose and produce PF$_5$. Then, when PF$_5$ reacts with water, POF$_3$ and hydrogen fluoride (HF) can be produced. PF$_5$ is highly reactive and can decompose easily, while POF$_3$ is stable at both room temperature and at an elevated temperature (Andersson et al., 2013).

All 7 studies measured, detected, and quantified HF. **Table 4** summarizes HF emission levels (emissions concentrations) that were reported in either ppm or mg/m^3, from the reviewed studies for easy comparisons between the detected emissions levels to the exposure limits. Other reported HF emissions levels can be found in **Table 5**. Exposure to HF at low levels can irritate the eyes, nose, and the respiratory tract, while exposure to high concentrations of HF could cause death from an irregular heartbeat or from fluid build-up in the lungs (CDC, 2018). NIOSH has a CL for HF, which is the amount of exposure that is never safe, of 6 ppm (5 mg/m^3), as well as an IDLH of 30 ppm (25 mg/m3), above which there could be immediate danger for human life and health without a highly reliable personal protective equipment. All reported peak HF emissions in **Table 4** exceeded the CL of 6 ppm except for the test that used filtration system in Study #3, and at least one test in each study that measured peak HF emissions exceeded the IDLH of 30 ppm. In other words, even though these studies (study #1, #3, and #7) are much smaller in scale compared to a large utility-scale ESS, the peak concentrations exceeded the safe exposure levels. This is an important finding indicating that there is a highly likely hazard of elevated HF concentrations during a LIB fire event for first responders as they enter the fire scene. It is difficult to compare the HF emissions level reported in the other studies (**Table 5**) to the exposure limits since the units used in those studies vary widely.

Table 4. *Summary of HF (IDLH= 30 ppm or 25 mg/m^3) emissions by study and test reported in ppm or mg/m^3*

Study ID	Battery Chemistry	Cell Packaging	Nominal Energy Capacity (Wh)	SOC (%)	Metric	HF Conc	Unit	Equipment
1	Considering multiple cells (LFP cells + laptop battery)	Pouch or Cylindrical	112-829	0-100	Peak	15-50	ppm	FTIR
2	NCA (external ignition)	Cylindrical	100,000	100	Peak	> 100 (over scale)	ppm	Porta Sens II
	NCA (internal ignition)					26		
3	NMC	Pouch	172	100	Total	Not Reported	ppm	Ion chromatography
	NMC + fire prevention					1800		
	NMC + gas filtration					3 filtration		
7	LFP	Pouch	219	0	Peak	20	mg/m^3	FTIR
				25		60		
				50		115		
				100		165		

Nonetheless, it can still be concluded that the production and detection of HF were clear in all studies and HF emissions from an ESS fire event, which will be larger in scale, would likely result in levels dangerous to human health. It is unclear if there is a positive correlation between HF emissions and SOC given that the results are mixed when comparing the results from study #4, #5 and study #7. Findings from study #5 and #6 suggest that LFP cells produce more HF compared to LCO, NCA-LATP, and NMC/LMO cells, and findings from study #5 indicate that pouch cells may result in higher HF concentrations compared to cylindrical cells. Studies #1, #5 and #7 indicated that the peak HF values were typically observed directly after the peak HRR was observed, and then dropped shortly thereafter. Study #2 showed a steady rise in HF values for both internal (lower rate of increase) and external (higher rate of increase) ignition. Internal ignition test values dropped over time at the end of the test, while external ignition test values remained high through the entire fire. Study #6 also demonstrated a slower build-up and drop-off of HF.

Three studies attempted to measure other fluorinated gases – study #1 and #5 measuring both PF_5 and POF_3 and study #6 measuring POF_3. Due to the high reactivity of PF_5, it is expected that quantification of PF5 would be challenging as shown in study #1 where no PF5 was detected in any of the tests. PF_5 was detected qualitatively but could not be quantitatively calibrated in study #5. POF_3 was detected in study #1 at 5%-40% of the HF emissions on a weight basis only when directly burning the electrolytes, but none was detected in the cell fire tests likely due to the emission levels below the detection limit. The maximum POF_3 concentrations were 11 ppm (5-cells) and 19 ppm (10-cells) in study #5. Since no exposure limits are set for POF_3 and PF_5, and their toxicity and health effects are not well established, it is difficult to know the implications of these findings. Nonetheless, the chlorine analogues of POF_3 and PF_5 are known to be very toxic even at very low levels warrants the need for continued efforts to measure emission of these gases from battery fires.

Table 5. *Summary of HF emissions by study and test reported in other units than ppm or mg/m^3*

Study ID	Battery Chemistry	Cell Packaging	Nominal Energy Capacity (Wh)	SOC (%)	Metric	HF Conc	Unit	Equipment
1	LFP Type 1 (*2)	Pouch	112	100	Total	14-18	mg/g	FTIR
	LFP Type 1 + water mist			100		17		
	LFP Type 1			0		32		
	LFP Type 1			50		39		
	LFP Type 2	Cylindrical	829	100		15		
	Laptop Battery Pack	Not Reported	746	100		7.3		
4	NCM (*4)	Prismatic or pouch	Not Reported	25	Peak	ND-500	ppm/kg in 0.44 m^3	FTIR
	NCM (*9)			50		ND-2100		
	NCM (*4)			75		ND-1200		
	NCM (*2)			100		100		
	NCM (*11)			25		100-5800		
	LFP (*2)			25		ND-1100		
	LFP			50		600		
	LFP			100		600		
	Ti			50		300		
	Ti			100		600		
	BM-LMP			50		100		
	BM-LMP (*2)			100		100		
	All Cells			-	Average	0.009	ppm/kg in 1 m^3	
	Not Reported		7,500-55,000	Not Reported	30-Min Release Rate	1.70E-07	kg/s	
5	LCO	Prismatic hard Al-can	128	0	Normalized Total	23	mg/Wh	FTIR
				25		20		
				50		25		
				75		24		
				100		23		
	LFP	Pouch	128	0		198		
				25		175		
				50		195		
				75		170		
				100		150-175		
	LFP	Pouch	112	0		103		
				25		85		
				50		65-160		
				75		65		
				100		45-55		
	LFP	Cylindrical	92	50		12		
				100		24		
	LFP	Cylindrical	132	100		52		
	NCA-LATP	Pouch	138	100		55		
	Laptop battery pack	Cylindrical	124	100		15		
6	LFP	Pouch	116	100	Normalized Total	36	g/kWh	Wash Bottles
						16		FTIR
	NMC dioxide /LMO spinel		287			23		Wash Bottles
						6		FTIR

Table 6. *Summary of CO emissions by study and test*

Study ID	Battery Chemistry	Cell Packaging	Nominal Energy Capacity (Wh)	SOC (%)	Metric	CO Conc	Unit	Equipment
2	NCA (external ignition)	Cylindrical	100,000	100	Peak	50	ppm	MulitiRAE
	NCA (internal ignition)			100		2000		
3	NMC + fire prevention	Pouch	172	100	Average	25,000	ppm	Photoacoustic spectroscopy
	NMC +filtration			100		1,000		
4	All Cells (cell-level)	Prismatic or pouch	Not Reported	Varies	Average per single cell	0.279	ppm/kg in 1 m^3	FTIR
7	LFP	Pouch	219	0	Peak	< 5	ppm	FTIR
				25		75		
				50		200		
				100		250		

2. CO

Four studies reported CO concentrations (**Table 6**). Inhalation of CO is known to be associated with headache, dizziness, vomiting, and nausea, while extremely high concentration may also lead to unconsciousness or even death (CDC, 2016). Overall, both peak and average CO emissions from LIB fires were shown to exceed the exposure limits and could pose health hazards. The peak CO from study #2 internal ignition test was well above the IDLH of 1,200 ppm at 2,000 ppm (the maximum detection level for the given device), and the 50% and 100% SOC batteries from study #7 exceeded the CL of 200 ppm, but the emissions were below the exposure limit from the 0% and 25% SOC batteries. CO emission from the internal ignition test was more than 40-fold higher than the emission from the external ignition test in study #2, which is opposite of the pattern shown for HF where the external ignition led to a higher concentration. This suggests that the emission patterns of different gases are likely to vary by the LIB fire scenario. In other words, a difference in how the cell failure was initiated could increase emissions for one gas, while decrease it for another.

Table 7. *Summary of HCl emissions by study and test*

Study ID	Battery Chemistry	Cell Packaging	Nominal Energy Capacity (Wh)	SOC (%)	Metric	HCl Conc	Unit	Equipment
4	NCM	Prismatic or pouch	Not Reported	25	Peak	ND-1,200	ppm/kg	FTIR
	NCM			50		ND-4,600		
	NCM			75		ND-3,000		
	NCM			90		5,500-10,000		
	NCM			100		1,400-5,800		
	LFP			25		ND-<100		
	LFP			50		600		
	LFP			100		600		
	T1			50		10,000		
	T1			100		100		
	BM-LMP			50		1,700		
	BM-LMP			100		900-5,900		
	All Cells			Varies	Average	0.057	ppm/kg in 1 m^3	
7	LFP	Pouch	219	0	Peak	4	mg/m^3	FTIR
				25		3		
				50		6		
				100		8.5		

Table 8. *Summary of HCN emissions by study and LIB type*

Study ID	Battery Chemistry	Cell Packaging	Nominal Energy Capacity (Wh)	SOC (%)	Metric	HCN Conc	Unit	Equipment
4	NCM	Prismatic or pouch	Not Reported	25	Peak	ND - 200	ppm/kg	FTIR
	NCM			50		ND-2100		
	NCM			75		ND - 100		
	NCM			90		ND		
	NCM			100		<100 - 7000		
	LFP			25		ND-<100		
	LFP			50		<100		
	LFP			100		<100		
	T1			50		ND		
	T1			100		200		
	BM-LMP			50		300		
	BM-LMP			100		ND-200		
	All Cells			Varies	Average	0.003	ppm/kg in 1 m^3	

3. HCl

HCl has a ceiling limit of 5 ppm (7 mg/m^3) and IDLH of 50 ppm (70 mg/m3), and exposure above the safe limit can irritate the skin, nose, eyes, throat, and larynx (CDC, 2019). None of the peak concentrations reported in study #7 exceeded the IDLH, while battery at 100% SOC exceeded the ceiling limit (**Table 7**). Based on results from study #4, there is a potential for hazard considering the utility-scale LIB ESS. Considering a typical electric vehicle battery unit of approximately 500 kg, the calculated average HCl emission is around 28.5 ppm (0.057 ppm/kg × 500 kg) in 1 m3, which is well above the ceiling limit for HCl. Overall, the hazard to HCl during a LIB fire cannot be excluded, though more evidence is required.

4. HCN

Exposure to HCN can lead to mild (e.g. headache, dizziness, nausea, vomiting) to more severe (gasping, irregular heartbeats, seizures, and even death) symptoms (ATSDR, 2014). Study #4 was the only study that reported HCN emission levels. IDLH for HCN is 50 ppm. A similar calculation that was done for HCl can be done with HCN, which will result in 1.5 ppm (0.003 ppm/kg × 500 kg) in 1 m^3 (**Table 8**). The hazard of HCN seems low based on this study, but it is difficult to draw conclusions based on a single study.

Table 9. *Summary of selected hydrocarbon emissions by scenario and equipment in Study #3*

Study ID	Battery Chemistry	Cell Packaging	Nominal Energy Capacity (Wh)	SOC (%)	Metric	A Gas Mixture Conc	Unit	Equipment
3	NMC	Pouch	172	100	Average:		Area/L	GC
					EMC	$>1E^7$		
					DEC	$>1E^7$		
					EC	$>1E^5$		
					Benzene	$>1E^5$		
					Toluene	$>1E^5$		
					Styrene	$>1E^4$		
					Bipheynyl	$>1E^5$		
	NMC + fire prevention				Average:		Area/L	GC
					EMC	$>1E^7$		
					DEC	>1E7		
					EC	$>1E^6$		
					Benzene	$>1E^6$		
					Toluene	$>1E^6$		
					Styrene	$>1E^6$		
					Biphenyl	$>1E^7$		
					Average:		ppm	MS
					Benzene	$>1E^2$		
					Toluene	$>1E^2$		
					Acrolein	>1E1		
					CO	$>1E^4$		
					CO_2	$>1E^4$		
	NMC + gas filtration				Average:		Area/L	GC
					EMC	$>1E^4$		
					DEC	$>1E^3$		
					EC	ND		
					Benzene	ND		
					Toluene	$>1E^3$		
					Styrene	ND		
					Biphenyl	ND		
						$>1E^1$	ppm	MS
						$>1E^1$		
						$>1E^0$		
						$>1E^3$		
						$>1E^3$		

5. Hydrocarbons

Several gases were chosen as constituents of interest in study #3 based on their "quantity, dangerousness, and toxicity" (**Table 9**). Results were presented for the scenarios with and without a 5-layer filtration system, for compounds such as battery electrolytes, benzene, and toluene. Filtration was able to reduce the concentrations of gases at least by a factor of 10. These findings are significant in that the potential health hazards of gas emissions from battery fires could be significantly reduced, though the applicability of these findings to a large ESS needs to be further investigated. Study #6 measured several electrolytes, but the data and implications thereof were not discussed in the paper.

6. SO2, NO, and NO2

None of the tests exceeded the IDLH levels for SO_2, NO, and NO_2 in study #7 (**Table 10**). There seems to be minimal hazard from NO. NO_2 emissions from LFP batteries at 50% and 100% SOC exceeded the CL (9 mg/m^3) by OSHA, indicating a potential health risk associated with NO_2 exposure from LFP battery fires, especially at the utility-scale ESS.

Table 10. *Summary of Emissions of SO_2, NO, and NO_2 by study and test*

Study ID	Battery Chemistry	Cell Packaging	Nominal Energy Capacity (Wh)	SOC (%)	Metric	Conc	Unit	Equipment
7	LFP	Pouch	219	0	Peak SO_2	5	mg/m^3	FTIR
				25		60		
				50		105		
				100		115		
				0	Peak NO	7		
				25		9		
				50		15		
				100		6		
				0	Peak NO_2	3		
				25		3.5		
				50		11		
				100		12.5		

Table 11. *HRR and THR by study and battery type*

Study ID	Battery Chemistry	Cell Packaging	Nominal Energy Capacity (Wh)	SOC (%)	Metric	HRR	Unit	Metric	THR	Unit
1	LFP (*2)	Pouch	112	100	Peak	44-48	kW	Total	6826-6645	kJ
	LFP + water mist			100		42			7130	
	LFP			0		9.5			7356	
	LFP			50		14			7460	
	LFP	Cylindrical	829	100		26			2409	
	Laptop Battery Pack	Not Reported	746	100		50			3036	
4	All Cells	Prismatic or pouch	Not Reported	25-100	Mean	2-4	kW per 100-800 g mass loss	Not Reported		
				25-100	Peak	2-8		Not Reported		
5	LCO	Prismatic hard Al-can	128	0-100	Normalized Peak	243-729	W/Wh	Normalized Total	17-19	kJ/Wh
	LFP	Pouch	128	0-100		78-633			45-50	
	LFP	Pouch	112	0-100		116-491			66-75	
	LFP	Cylindrical	92	50-100		207-315			27-30	
	LFP	Cylindrical	132	100		235			50	
	NCA-LATP	Pouch	138	100		384			50	
	Laptop Battery Pack	Cylindrical	124	100		460			28	
7	LFP	Pouch	219	0	Peak	3.7 ± 0.5	kW	Total	4165 ± 356	kJ
				25		25.8 ± 1.6			5644 ± 317	
				50		70.2 ± 7.2			6388 ± 431	
				100		80 + 2.6			6660 ± 419	

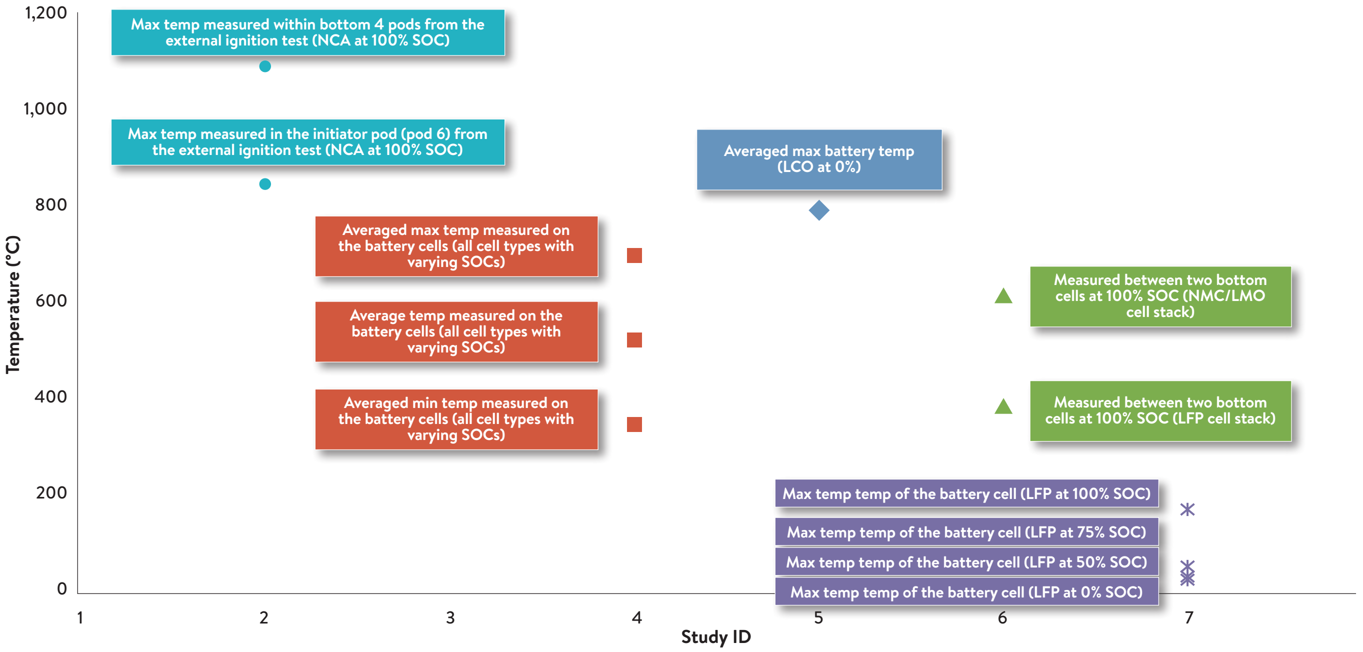


Figure 2. *Battery cell temperatures by study*

HEAT RELEASE RATES (HRR) AND BATTERY TEMPERATURES

HRR is one of the key parameters for characterizing the energy released and potential fire hazard of a LIB fire. HRR is defined as the rate at which energy is generated by the burning of a fuel and oxygen mixture. A positive correlation between SOC and HRR was shown in study #1 and #7 (**Table 11**). HRR as well as total heat release (THR) seem to vary quite widely depending on the cell packaging as well as battery chemistry. For example, an LFP pouch cell produced a higher HRR (42 kW) compared to an LFP cylindrical cell (26 kW) even though cylindrical cell has a higher energy capacity (112 vs. 829 Wh). Study #5 showed that the production of HF was correlated to increases in HRR (Larsson et al., 2017). Peak HRR did not always correlate with THR (e.g., study #1 vs. #7). This may provide some insights about how different cell types could result in higher peak gas emissions corresponding to higher peak HRR, while the total gas emissions may be affected by THR.

Five studies reported battery temperatures during the fire using thermocouples on the battery cells (**Figure 2**). Overall, most battery cells (except for the cells at 0%, 50%, and 75% SOC in study #7) reached beyond the temperature of 100 C°-120C° where battery failures can be initiated (Warner, 2019). Similar to the widely varying concentrations of some gases, the range of observed battery temperatures was also wide. There are differences in the experimental setup, battery chemistries, SOC, and energy capacity that would have contributed to these differences. The observed battery temperatures were highest in study #2, which is anticipated given the scale of the experiment. Study #6 showed that the battery temperature was higher in the NMC/LMO cell stack compared to the LFP cell stack, while the normalized total HF emission was higher for the LFP cell than the NMC/LMO cell (**Table 5**). Battery cell temperatures in study #7 were particularly lower compared to all other studies. Even though the energy capacity of the LFP cells in study #7 was higher (219 Wh) compared to the LFP cell in study #6 (116 Wh), the observed maximum temperatures were lower in study #7. One difference between study #6 and #7 was that #6 was conducted in an oxygen-free environment. This reinforces the importance of keeping in mind that how the experiments are set up will affect the study results. In other words, the interpretations of the results of different experimental studies on battery fire should be carefully done as the results can be sensitive to both external (e.g., experimental setup) and internal factors (e.g., battery chemistry, cell type, SOC, etc.) that are likely to vary across different studies.

WATER AS AN EXTINGUISHING AGENT

The ideal battery extinguisher should be both highly thermally conductive and highly electrically insulation. Water has good heat remove capability but is electrically conductive. Many other extinguisher types have equal or poorer heat remove capability to water and all are often electrically conductive due to their reliance on water as a dispersion medium (DNV GL, 2017). All studies that conducted extinguishing tests concluded that water is the superior to or equally effective cooling agent as other special extinguishing agent (e.g. dry chemicals, clean agents, or foam), but with the potential for shorting neighboring cells, which can initiate a new thermal runaway. Two studies (study #1 and #5) showed that the addition of water could lead to higher peaks of HF over short periods of time, but without affecting the total released amount (Andersson et al., 2013; Larsson et al., 2017). Higher peaks of toxic gases will pose greater health risks to first responders, especially considering the gases that were shown to be produced at higher than IDLH levels. Thus, appropriate personal protective equipment should be used and the timing of applying water to the batteries as compared to the timing of the entrance of first responders to the scene should be carefully planned.

CONCLUSION AND NEXT STEPS

Review of these studies revealed that LIB fires can release a range of different gases at varying emission rates. It is generally agreed that there is very limited understanding of the human health impact of LIB fires from an ESS due to the limited number of studies available as well as the question of scaling-up the findings from small-scale tests to a utility-scale ESS. Even though firm conclusions of the magnitude of potential hazards of some of the gases were not possible considering the differences in scale between the experiments and utility-scale ESS, proper protective equipment should be used whenever entering a LIB fire scene as some of the gases were shown to be emitted at dangerous levels. For example, the peak HF emission from the external ignition experiment from study #2 was more than two times higher than the IDLH. Additionally, the full suite of emitted compounds is not yet known as these studies focused on gaseous chemicals and did not include sampling of airborne particulate matter. Additional studies investigating emissions measured before, during, and after water suppression was applied would be helpful, given the current importance of this suppression technique.

Notwithstanding the limitations of the studies evaluated, the gases detected in these studies have known toxicity and potential implications for first responders as well as nearby communities. Study #4 recommended the use of self-containing breathing apparatus (SCBA) as an effective means of protecting first responders from inhalation risks. However, there could be other routes of exposure (e.g., dermal exposure) that need to be considered, which was not discussed in any of the reviewed studies, likely due to the expectation that first responders will wear fire protective suits. The possibility of dermal exposure due to particulate material that is moved due to advection, tracking across surfaces, or through dropping off of a suit in areas where workers or others are not in protective suits has not yet been assessed. None of the studies included in this review directly measured substances on a surface, though study #1 mentioned that some substances could be found on the wall following splashing and bursting events. Future studies should consider examine the level of potential exposure via skin contact and how to protect first responders from such hazards.

In addition to protecting first responders, the protection of workers at ESS and people in nearby communities of ESS should be considered. Proper ventilation of an ESS space is a major conceptual change to ESS fire suppression designs, but important to reduce the concentrations of gases when first responders enter the room and allow oxygen to infiltrate. At the same time, the gases released into the ambient air should not be at high concentrations to avoid putting nearby workers or the public that are without any personal protective equipment at risk.

Alternative battery-ESS (BESS) designs may consider adapting the concept of filtration as it was shown to be very effective in reducing the concentration of HF in study #3.

Based on the review of these studies, there are a few things that future studies and research communities focusing on this topic should consider. One of the main limitations is the scale of these experiments. Six out of seven studies reviewed in this report conducted their testing at the module level with a maximum of 12 cells in a test, while one study used an electric vehicle-size battery system, which is still much smaller than what would be used in a large utility-scale ESS. Though small-scale tests do provide useful information, it is not clear how relevant the results are to large scale ESS with larger capacity and multiple layers of safety features already in place. Scaling-up the results (such as by capacity, energy density or other metrics) is possible, but it is not ideal given how there could be multiple factors that may be different between a fire from a single LIB vs. a large system. Nonetheless, there is some evidence that scaling-up efforts could be reasonable. Study #1 compared their findings to the results from a typical plug-in hybrid electric vehicle (PHEV), which would typically have 432 cells of 9,700 Wh. They found the extrapolation of their results using a conversion factor based on the nominal capacity led to a similar order of HF emissions from the vehicle fire test. Furthermore, the internal ignition test in study #2 reported that the failures of LIBs did not lead to thermal runaways of battery cells outside of the initiator pod, which indicates that the emission levels might not be so different in a larger utility-scale ESS if the cell failure would be contained within the given cell-/module-level. Overall, the reasonableness of scaling-up effort from cell-/module-size experiment results to utility-scale ESSs needs to be further investigated.

A couple studies also mentioned how gas emissions from LIBs are relatively small compared to plastic fires (though with higher peaks). These studies did not include any plastic parts, except for the laptop battery packs, that are likely to be part of real ESS. It could be worthwhile to perform separate burn testing of the plastics and the battery cells themselves to separate the differences between the two. As the primary purpose of conducting these experiments is to protect those who may become exposed to these hazards, it is important to understand what the total exposure would be, whether that is from LIBs or other parts that make up an ESS, and should consider the impact of safety features that would reduce the total potential hazards from battery fires.

An additional challenge is that the results from the reviewed reports could not be directly compared across studies due to substantial variation in experimental designs that could affect the pattern and magnitude of potential emissions (e.g., battery chemistries, cell packaging, nominal energy capacity, state of charge, etc.). Also, the metrics and units used in different studies for different gases were not consistent. This also makes it difficult to compare these levels to the exposure limits set by OHSA and/or NIOSH. The efforts and resources spent on conducting these experiments can be better used if the results could be more easily interpreted. Future studies should report the results in units that can be easily compared across studies and that can be compared to the known exposure limits (ppm or mg/m^3) and also report the room size and ventilation rates. In addition, those results can be normalized using the nominal energy capacity, which will make it easier to examine how different battery chemistries and cell packaging may affect the emission levels. Lastly, a study that has a well-defined question (objective) and organized experimental setup would provide much more useful information compared to a study that tests multiple hypothesis that does not necessarily help answering any specific questions. Study #2 provided limited information with only two experiments using one battery type, but this was the study that reported the results in a useful manner. It clearly showed how external ignition and internal ignition may lead to different outcomes at levels that are comparable to exposure limit values. This brings up the question of how different initial abuse would affect the behavior of battery fires as well as gas emissions. In summary, future experiments should consider how their test results can be a valuable addition to what is already known both in terms of its scope and how it's reported.

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