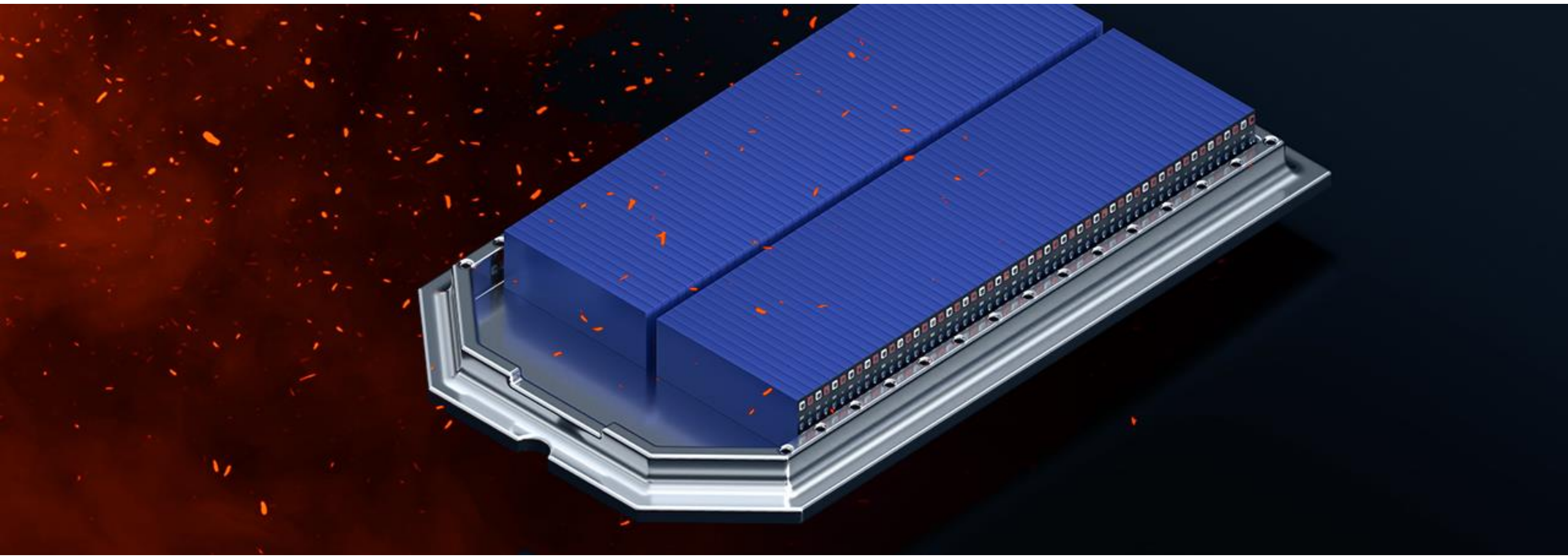

Gas analysis in lithium-ion battery risk mitigation and incident response

Li-Ion batteries (LIBs) are the dominating technology in battery-operated devices. LIBs have become the preferred choice for various applications, including consumer electronics, electric vehicles (EVs), and renewable energy storage systems.

In addition to the multiple benefits of LIBs, these batteries can also pose hazards to people. LIBs are capable of entering a self-sustaining series of exothermic reactions, called thermal runaway (TR). TR is a chain reaction of different chemical reactions in a LIB. TR can be triggered for example by external heat, mechanical battery damage such as penetration, short circuit or overcharging the battery. In TR, the battery cell temperature often increases extremely rapidly and toxic gases are released. The result can be an uncontrolled battery fire leading to an explosion and emitting of toxic fumes. Released gases include toxic gases like HF, HCl, HCN, CO as well as explosive gases i.e. hydrogen and toxic hydrocarbons , i.e. formaldehyde.

Fire, explosion and toxic gases caused by TR can be a danger to people: both the public, and first responders attending the LIB related incident site. The specific risks and required mitigation strategies vary from one incident to another: they are affected by e.g. varying battery chemistries, environmental conditions and size of the battery pack in question. Gas concentrations greatly vary during thermal runaway, and can shoot from zero to thousands of ppm within minutes. There typically is a complex mixture of various gases present, making the gas analysis challenging. Good quality gas measurements are necessary to understand the situation specific risks and to select correct protective actions – in order to prevent serious harm to people. Measuring released gases is a crucial part of the situation assessment in all LIB related incidents.

This document demonstrates the usage of a portable FTIR multi-gas analyzer, Gasmet's GT5000 Terra, in LIB people safety gas measurements, through a field research project example.

Lithium-ion battery safety research, County of San Diego

The objective of the field research project was to collect information on the exposure risks first responder confront at incident sites involving damaged LIBs. This information will then be reviewed and aid in the development of best practices to efficiently protect first responders and the public from harm caused by damaged LIBs.

Behavior of thermally abused batteries was studied to determine what kind of hazards the progress of thermal runaway causes, depending on the battery chemistry, cell number and geometry. Among potentially released toxic gases, HF was one of the main gases of interest, as it is a regular cause of first responder injuries.

The research project was organized by the County of San Diego, in collaboration with US EPA, Cal Transportation, UCLA, Massachusetts Fire Services and local CST team. Several measurement equipment manufacturers were also involved, including Gasmet.

Materials & methods

Various LIB packs were placed inside an enclosed wooden structure (see Figure 1). The battery packs were thermally abused to initiate thermal runaway. The progress of thermal runaway was then followed with cameras as well as through gas monitoring equipment. Afterwards, the hazmat crews opened the doors to extinguish and remove the LIB debris.

Figure 1. Wooden test enclosure. Gas analysis equipment on table in front of the enclosure.

The duration of each test was approximately 10 minutes. Testing mostly involved skateboard batteries where the number of cells, LIB chemistry, amount of charge and types of enclosure were the changing parameters. In terms of battery chemistries, both NMC and LiFePO4 batteries were tested. In the final day test the LIB's were placed into thermal runaway with encasement and uninhibited explosions within the wooden structure took place (Figure 2).

Figure 2. Uninhibited fire on the last day of the study. Firetruck ready for extinguishing in the background.

Gasmet GT5000 Terra was one of the measurement instruments employed in the research (Figure 3). The gas library used for the analysis of results from GT5000 Terra has been optimized for LIB safety related measurements. The gases and their measurement ranges utilized in the study are listed in Table 1. Sampling of formed and released gases was performed by placement of the GT5000 sampling probe inside the wooden structure at approximate breathing zone height to emulate toxic gas exposure for first responders.

Figure 3. Gas analysis equipment employed in the research. GT5000 Terra in the center.

Table 1. Measured gases and their measurement ranges.

Compound name	Range	Unit
Water	3	vol-%
Carbon dioxide	30 000	ppm
Methane	2000	ppm
Nitrous oxide	100	ppm
Carbon monoxide	1000	ppm
Hydrogen fluoride	30	ppm
Hydrogen chloride	50	ppm
Hydrogen cyanide	100	ppm
Dimethyl carbonate	200	ppm
Ethyl methyl carbonate	200	ppm
Ethylene carbonate	100	ppm
Diethyl carbonate	100	ppm
Propylene carbonate	100	ppm

Formaldehyde	50	ppm
Acetaldehyde	200	ppm
Methanol	200	ppm
Ethanol	200	ppm
Isopropanol	100	ppm
Acetic acid	100	ppm
Methyl acetate	100	ppm
Ethane	200	ppm
Hexane	50	ppm
Isopentane	200	ppm
Ethylene	200	ppm
Propene	200	ppm
Acetylene	200	ppm
Benzene	200	ppm
Toluene	200	ppm
Styrene	100	ppm
Ammonia	100	ppm

Results & discussion

Toxic gases at levels exceeding the exposure limits were measured in all of the performed tests, e.g. HF, HCl, HCN and formaldehyde were released. Battery chemistry influenced the released gases significantly: NMC batteries (Figure 4) showed higher concentrations of HF than $LiFePO_4$ batteries (Figure 5) which in turn showed significantly higher formaldehyde concentrations than NMC batteries.

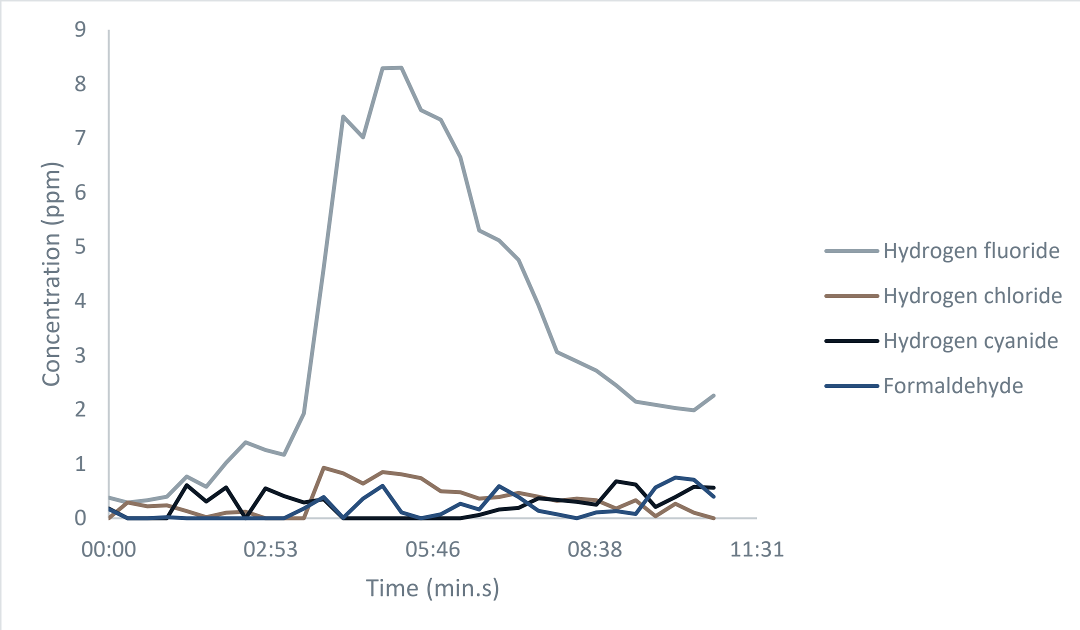

Figure 4. Concentrations of most important toxic gases released during thermal abuse of 4 NMC cells.

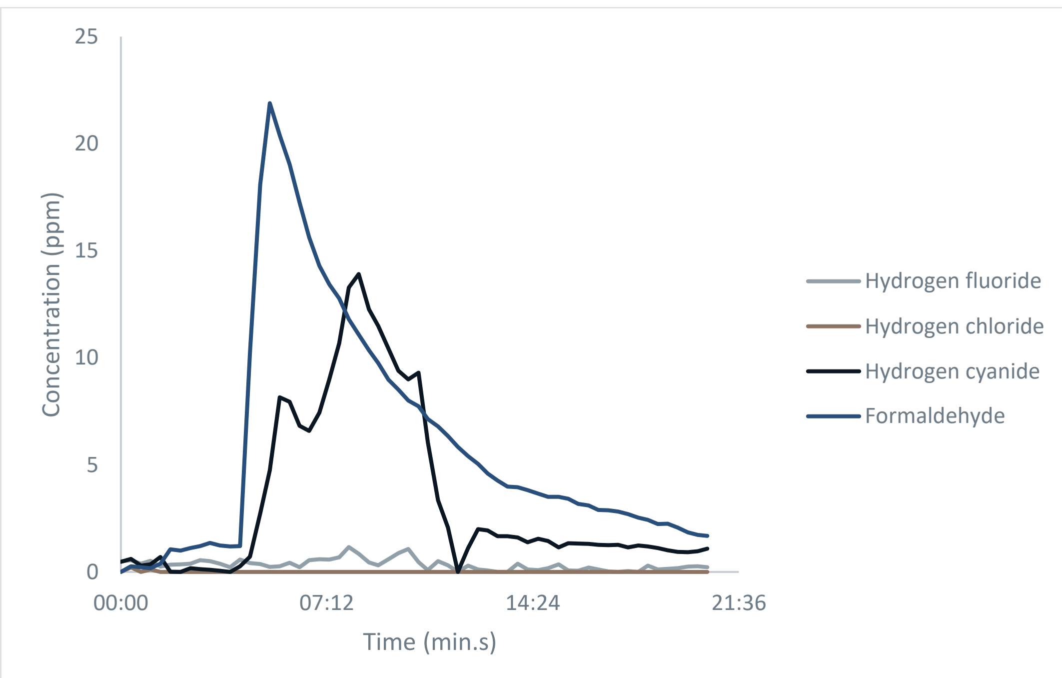

Figure 5. Concentrations of most important toxic gases released during thermal abuse of cylindrical LiFePO4 batteries, 4 cells.

The concentrations achieved dangerous levels extremely quickly, typically, within 1-2 minutes. Table 2 shows the peak concentrations of some of the key toxic gases as well as their exposure limits. Comparing these values shows that the peak concentration of most of the mentioned components greatly exceeded the OSHA PEL (permissible exposure limit) values.

Table 2. Measured peak concentrations of key toxic components in comparison to permissible exposure limits.

Compound	Peak concentration	OSHA PEL
HF	28.52 ppm	3 ppm
HCN	74.17 ppm	10 ppm
HCl	2.55 ppm	5 ppm
Formaldehyde	36.15 ppm	0.75 ppm
Methanol	736.52 ppm	200 ppm
Acetic acid	78.24 ppm	10 ppm

The peak gas concentrations show that there is a significant risk to health of first responders and any other people present at a LIB fire scene. Of the most important toxic gases discussed here, HF and HCl are corrosive and poisonous, HCN is highly toxic and flammable and formaldehyde is a carcinogen, and can also cause respiratory and skin irritation. Figures 4 and 5 show that there were smaller but still hazardous concentrations of toxic gases prior to and after the peak concentrations. As the peak concentrations are very high, dangerous levels of toxic gases can also persist after the thermal runaway or even after extinguishing the fire.

The released gas mixture included, in addition to the already mentioned gases, mix of carbonates as well as flammable organics. Even though the gas matrix was complicated and rapidly varying, the <5 ppm hazardous concentrations were easily detected by GT5000 Terra. During the tests, the GT5000 Terra became the site reference unit to give all clear for first responders entry to the wooden structure after each test. Emitted soot did not affect the GT5000 Terra operation, unlike some of the other instruments.

Conclusion

A significant driver for this study was to observe HF gas levels since an employee was previously injured by the corrosive fumes when responding to a LIB fire event. The Gasmet GT5000 Terra showed that in a significant number of thermal runaway tests, the corrosive HF gas along with HCN and formaldehyde were present in levels above safe work-place limits. Even though battery chemistry affected the gases released, both NMC and LiFePO4 batteries produced hazardous gases in concentrations exceeding the exposure limits. To ensure safety, it is crucial to have an instrument that can detect low concentrations, as for many of the key components, small concentrations can already be very dangerous. For instance, HF needs to be accurately measured at levels of 3 ppm. The GT5000 Terra performed faultlessly, regardless of the complex gas matrix and quickly changing concentrations.

The study demonstrates the importance of gas detection when protecting people in LIB related incidents. The collected data further proves GT5000 Terra to be an essential tool for the global first responders in a world where safety concerns are becoming a daily issue due to the ever- increasing number of LIB hazmat events. Optimized gas library eliminates difficulties typically associated with these kinds of measurements. The GT5000 Terra offers also unmatched versatility in the safety applications – it can also be employed for Identifying unknown gases at HAZMAT Incident sites when using its Extended reference library containing 5,500+ gases and vapors.