APPLICATION NOTE

FTIR ANALYSIS OF LI-ION BATTERY THERMAL RUNAWAY

PROBLEM

Under some circumstances, damaged Li-ion batteries can experience thermal runaway behaviour that constitutes a fire and/or explosive safety hazard. In addition, the chemical make-up of Li-ion batteries produces toxic and corrosive emissions during such events. When these batteries (Figure 1) are employed in enclosed environments (e.g. cars, homes, offices, etc.), the toxic emissions and fire potential from a damaged battery can be especially hazardous. The detection and speciation of emissions from a Li-ion battery before and during a thermal runaway event is therefore important for understanding the break down mechanisms and for developing new battery designs that can reduce these safety hazards.

BACKGROUND

Volumetric energy densities for Li-ion batteries can range between 250 – 700 WhL^{-1}, depending on the details of the internal chemistry [1]. This is twice the energy density of a standard NiCd battery and up to 7 times that of lead acid batteries. This means that a relatively small Li-ion battery can deliver power at appropriate voltage and with sufficient battery life for applications such as portable electronics, uninterrupted power supplies (UPS), electric vehicles (EVs), marine vehicles, and solar power storage. These properties have made Li-ion batteries the fastest growing rechargeable battery technology.

Li-ion batteries function by transferring lithium ions between a graphitic carbon anode and a lithium cobalt (III) oxide ($LiCoO_2$) cathode. The transfer occurs through an

Figure 1 - Li-ion Battery Technology.

electrolyte that consists of lithium hexafluorophosphate ($LiPF_6$) dissolved in a mixture of alkyl carbonate solvents [2]. The latter includes ethylene carbonate (mandatory for a solid electrolyte interphase, SEI) along with dimethyl-, diethyl-, and ethyl-methyl carbonates (EC, DMC, DEC, and EMC, respectively). The electricity-producing chemical reaction that occurs in a Li-ion battery is (left to right = discharging, right to left = charging):

$$LiC_6 + CoO_2 \rightleftarrows C_6 + LiCoO_2$$

$LiPF_6$ has excellent properties as an electrolyte, however, elevated temperatures in batteries using this electrolyte can produce thermal runaway that constitutes a significant fire, explosion, and toxicity hazard [2] [3]. Thermal runaway is a phenomenon in which the anode, cathode, and electrolyte all react to produce large amounts of heat, increasing the cell's temperature and internal pressure. Thermal runaway within a Li-ion battery can be initiated by different causes. Physical damage to the battery may short out internal cells or there may be an external short circuit; both types of short circuit can raise the battery temperature and initiate thermal runaway.

Overcharging, external heating, improper cooling, or an external fire can also raise the temperature of the battery to the point where thermal runaway occurs [4].

While the detailed mechanism of thermal runaway in Li-ion batteries is not fully understood, recent studies have provided some insights. When a runaway event occurs, there is rapid gas evolution as the alkyl carbonate is thermally broken down to produce gases such as CO_2, CO, and hydrogen along with volatile organic compounds (VOCs) that include methane, ethane, ethylene, and monofluoroethane [5]. In addition, the decomposition of the $LiPF_6$ electrolyte releases PF_5 which is hydrolyzed on exposure to moist air to produce POF_3 and HF, both highly reactive and toxic fluorine compounds. The hydrogen and VOC emissions from the battery can ignite, producing a fire [6] or, should conditions allow them to accumulate, an explosion. The products from the breakdown of $LiPF_6$ (PF_5, POF_3, HF) and their reaction with the organic materials produce toxic organofluorine compounds and CO, which represent a toxicity hazard in the environment around a damaged battery [7].

Mitigation of the risks associated with the use of Li-ion batteries has been the subject of much study over the past two decades and recent reviews are available [8] [9] [10]. The work has produced changes in battery design that improve thermal separation between cells, significantly reducing the potential for thermal runaway. Battery fire analysis has been an important part of this work, providing data and mechanistic insights into the origin and course of Li-ion battery fires.

Fourier Transform Infrared (FTIR) spectroscopy is an effective and convenient analytical tool that is routinely used in a wide variety of analytical applications, including fire analysis. FTIR spectroscopy measures the absorbance of a broadband infrared beam as it passes through a sample of gas. Different molecular species (i.e. gases) absorb infrared radiation at different wavelengths and this provides a fingerprint that identifies the presence of that gas in a sample. The absorbance measured for each species is proportional to its concentration multiplied by the pathlength through which the beam travels and is used to quantify the concentration of that gas in the sample. Figure 2 displays the specific fingerprint (signature) for each gas molecule.

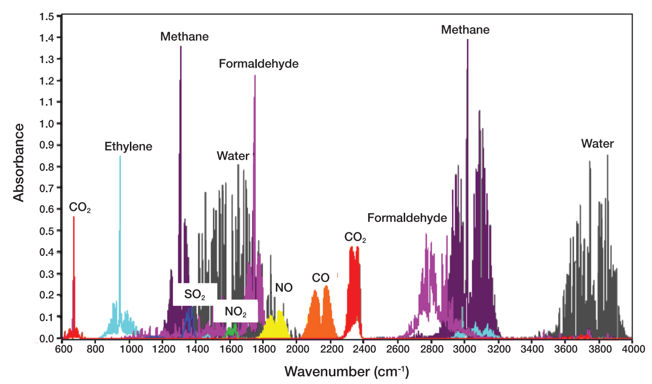


Figure 2 - FTIR spectra showing absorbance for different molecules. Each molecule has a specific "fingerprint".

FTIR is a powerful tool for fire analysis. Unlike gas chromatography (GC), it provides a real-time, continuous concentration measurement of the gases emitted during a fire. The FTIR measurements can be used to fully characterize a thermal runaway event, from inception to completion. Table 1 provides a list of the some of the gases associated with battery fire analysis that can be detected and quantified using FTIR spectroscopy. All gases can be measured by FTIR, except for gases without a molecular dipole moment such as nitrogen, oxygen, and hydrogen as well as noble gases (argon, etc.).

The use of FTIR in fire analysis is well established and there are published standards specifying how FTIR spectroscopy should be employed in this application. ISO 19702:2015 - "Guidance for sampling and analysis of toxic gases and vapours in fire effluents using Fourier Transform Infrared (FTIR) spectroscopy" specifies the requirements for FTIR sampling systems that are used in small and large-scale fire testing and analysis [11]. The

Ambient Gases	Nitrogen Gases	Acid Gases	VOCs/HAPs	Carbonates	Toxic Gases
CO	NO	HCl	Formaldehyde	EC	Ethylene Oxide
CO_2	NO_2	HBr	Methanol	DMC	Propylene Oxide
H_2O	NH_3	SO_2	Ethylene	DEC	HCN
CH_4	N_2O	COS	Propylene	EMC	HF
Ozone			Hydrocarbons		H_2SO_4

Table 1 - Gases that are detectable using FTIR spectroscopy. Gases highlighted in blue are toxic and of special interest.

standard provides guidance for the use of the FTIR instrument, the collection and use of calibration spectra, and gives recommendations for sampling parameters such as pressure, scan rates, etc. ISO 19702:2015 is commonly used to guide the analysis of toxic emissions during upholstery and vehicle fires.

The requirements of battery fire testing analysis differ from those for the analysis of large-scale fires that occur with upholstery or vehicles. Larger fires tend to have a slower, more progressive gas release whereas in Li-ion battery fires large amounts of gas can be released in a relatively short time. This produces different sampling requirements in the two fire analysis applications since relative concentrations and dilution factors are different for analyzing the two types of fires. For FTIR analysis, this means that the gas cell pathlength through which the infrared beam travels must be adjusted to avoid saturation of the absorbance signal when gases of interest are more highly concentrated.

Figure 3 illustrates the effects of inappropriate and appropriate gas cell pathlengths in an FTIR measurement. As a general rule measurement for battery thermal runaway analyses deal with %-level concentrations and it is best to use a short pathlength gas cell such as a 2 cm cell (as shown in Figure 4). If a long pathlength cell (e.g. 5 m) is the only option, then dilution of the sample gas with an FTIR-inactive gas such as nitrogen is required to produce measurable absorbances. Long pathlength cells are most appropriate for the measurement of battery cell venting samples with concentrations of interest that are at the ppm level. The standard, ANSI/CAN/UL 9540:2019 – "Test method for evaluating thermal runaway fire propagation in battery energy storage systems" directly addresses the use of FTIR for the analysis of fires in Li-ion and other high energy density batteries [12]. Section 8.2.12 of this standard states that: "Vent gas composition shall be measured using a Fourier Transform Infrared Spectrometer with a minimum resolution of 1 cm^{-1} and a pathlength of at least 2 m."

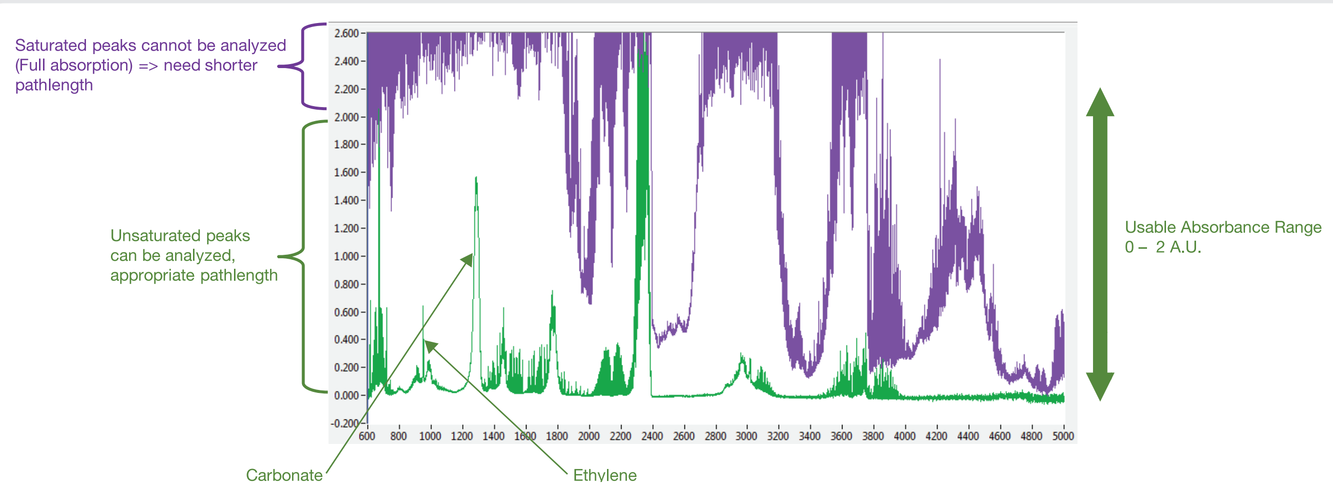


Figure 3 - The importance of gas cell pathlength in FTIR spectroscopy. Quantitative measurements are only possible when absorbances are within the usable range.

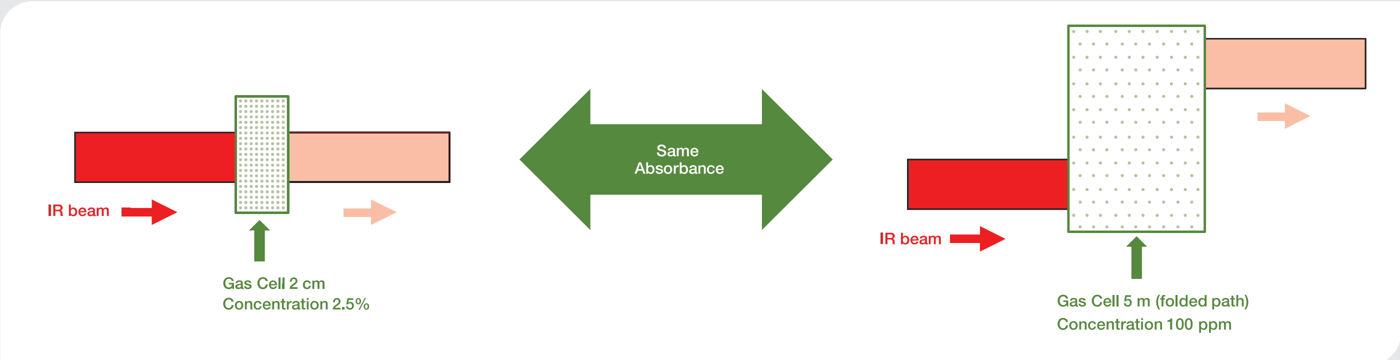


Figure 4 - Schematic of FTIR sampling arrangement for two different concentrations of the same analyte giving the same absorbance in an FTIR analysis.

SOLUTION

MKS Instruments' MultiGas™ FTIR Gas Analyzer (pictured in Figure 5) is a field proven, rugged FTIR instrument with an integrated, heated (to 191°C) gas cell, an integrated pressure sensor, and internal heated gas lines that make it well-suited for Li-ion battery emissions testing. The MultiGas™ FTIR has high time resolution (5 Hz) which allows for rapid, effectively continuous measurements. It can be configured for either thermal runaway analysis (high concentration, short pathlength measurements) or cell emission testing (low concentration, long pathlength measurements), offering interchangeable gas cells with pathlengths of 5.11 m, 35 cm, or 2 cm. The option of either liquid nitrogen or thermoelectric cooled detectors allows for convenient installation of the FTIR instrument in a variety of environments. The instrument has a large calibrations library, with over 250 gases and library search software. The MultiGas FTIR Gas Analyzer has been proven in many applications, including fire testing, exhaust gas analysis and compliance, gas process control and gas manufacturing (i.e. purity, blending, etc.).

Figure 5 - MKS Instruments MultiGas™ FTIR Gas Analyzer.

Figure 6 illustrates two examples of typical sampling configurations that are employed with the MultiGas FTIR Gas Analyzer. The pump can be placed either before or after the FTIR and sample lines are heated prior to the analyzer to avoid condensation that can produce inaccurate measurements. The upper configuration in Figure 5 uses a short pathlength (2 cm) gas cell and it is commonly used for the analysis of battery thermal runaway since an event generates several liters of undiluted gas with %-level concentrations of the components of interest. The lower configuration in Figure 5 employs a long pathlength (5.11 m) gas cell. It is used where dilution of the analyte gas is needed or where ppm level contaminants in vented gases are to be measured.

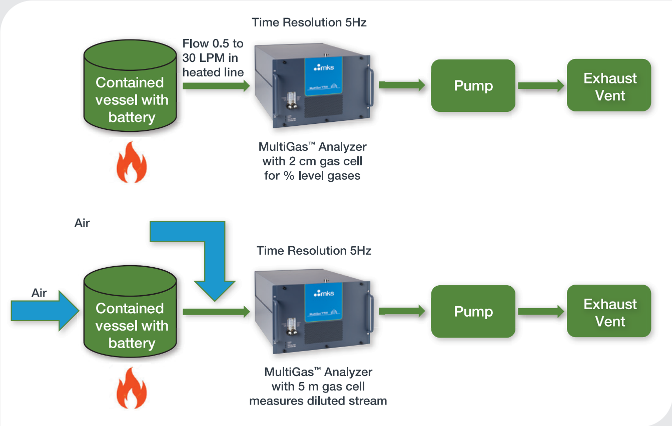


Figure 6 - Typical sampling configurations with the MultiGas™ FTIR Gas Analyzer. Top configuration is with a short pathlength cell, measuring % level of gas. Bottom configuration is for diluted gas or a slow gas release.

Figure 7 shows data for the concentrations of several species contained in a diluted sample gas from a Li-ion battery thermal runaway event, using an arbitrary time scale. The measurement used the diluted sample configuration shown at the bottom of Figure 6. The concentration traces show that the emissions are initially dominated by large amounts of CO and CO_2, with lesser amounts of ethylene, formaldehyde, and carbonates. While some battery thermal runaway events generate significant concentrations of HF, this battery did not. Finally, the traces for formaldehyde and dimethyl carbonate showed that more complex chemical interactions are occurring as the event proceeds.

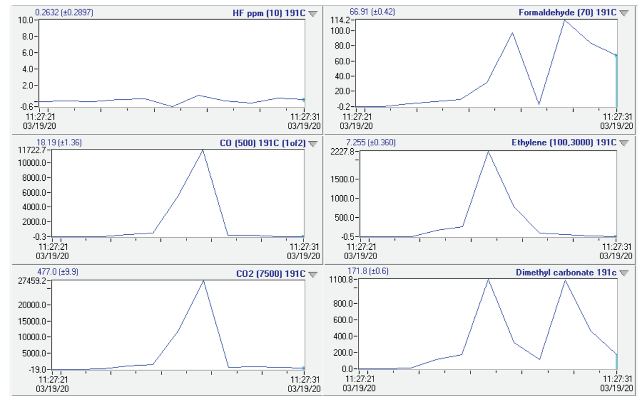
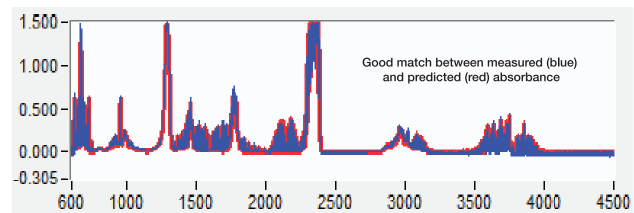


Figure 7 - Concentration timelines using MultiGas™ Analyzer.

The MultiGas software uses a sophisticated chemometric algorithm to extract the concentration of many gases from the measured absorbance spectrum. Figure 8 shows a typical absorbance spectrum during a battery thermal runaway test. The image at the top shows a typical spectral match between the software's predicted absorbance spectrum (red) and the observed absorbance spectrum (blue). The match is seen to be excellent, with the predicted spectrum accounting for all of the spectral features in the measured spectrum. This means that all gases in the sample are accounted for in the predicted spectrum. The software also includes search algorithms which identify gases present, such as what is presented in the table at the bottom of Figure 8. The estimated uncertainty in the measurement is output as a Goodness of Fit (GOF) statistic while the quality of the match between the component and observed spectra is signified by the Hit Quality Index (HQI) statistic which is a measure of the closeness of fit between the unknown spectrum and each reference spectrum.



Gas Calibration Name	Conc	GOF	HQI	Comment
ETHYLENE (100,3000) 191C	158.453	5.981	0.038	User-defined
CO (500) 191C (1OF2)	298.856	14.586	0.049	Likely present
CO2 (7500) 191C	1161.384	61.463	0.053	Likely present
H2O (5000) 191C	375.169	20.883	0.056	Likely present
DIMETHYL CARBONATE 191C	116.433	9.661	0.083	Likely present
CH4 (250) 191C	65.232	5.573	0.085	Likely present
CO% (1) 191C (2OF2)	0.030	0.003	0.104	Likely present
PROPYLENE (200,1000) 191C	71.630	12.156	0.168	Likely present
PENTANE (500) 150C	17.454	2.998	0.170	Likely present
COS (100) 150C	1.172	0.296	0.247	Likely present
MEOH (10) 191C	14.962	4.278	0.278	Likely present
ETHYLMETHYL CARBONATE 191C	20.022	6.466	0.311	Likely present
ETHANE (500) 191C	19.382	6.526	0.323	Likely present
ISOBUTYLENE (500) 191C	28.196	10.175	0.344	Likely present
DIESEL (C1 4500) 191C	22.518	17.009	0.636	Possible
ETHYLENE OXIDE 150C	3.413	3.572	0.786	Possible
FORMALDEHYDE (70) 191C	6.099	4.973	0.671	Possible
H2SO4 (50) 150C	2.332	1.399	0.534	Possible
ISOPENTANE (500) 191C	16.077	2.724	0.168	Possible
PROPANE (1000) 191C	6.226	4.616	0.628	Possible
1,3 BUTADIENE (80) 191C	2.585	6.861	1.138	Unlikely
ACETALDEHYDE (500) 191C	9.460	14.590	0.954	Unlikely
ACETIC ACID 150C	-2.028	4.660	1.096	Unlikely
ACETONE 191C	-0.364	3.739	1.344	Unlikely
ACETYLENE (1000) 191C	0.797	7.775	1.340	Unlikely

Figure 8 - Observed and predicted spectrum for a diluted sample from a Li-ion battery thermal runaway test, as measured by the MultiGas™ Analyzer and quantified by the gas search algorithm.

The data presented clearly show the power of the MultiGas FTIR Gas Analyzer for characterizing Li-ion battery fires. The interchangeable, heated gas cells permit easy switching between analyses requiring dilution to analyses without dilution. Extremely high time and wavenumber resolution of the instrument (5 Hz and 0.5 cm^{-1}, respectively), coupled with the small volume gas cells, allow for fast measurements that differentiate difficult-to-separate signals from species such as HF, HCl, HCN, NO_X, etc. All MultiGas instruments use the same calibrations which means that the user does not need to create instrument-specific calibrations.

Finally, MKS Instruments provides a "Battery Testing" applications package with the MultiGas Analyzer that requires minimal user input and includes an automated gas search software. The package includes calibrations for HF, HCl, HCN, and typical electrolyte components such as ethyl methyl carbonate, diethyl carbonate, methyl carbonate as well as other VOCs.

CONCLUSION

Li-ion batteries are finding many uses in today's consumer technology and, because of this, battery fire testing has become important for the development of safe designs for consumer batteries. FTIR is a powerful analytical tool for the analysis of the gases emitted from Li-ion batteries during a thermal runaway and fire event. FTIR spectroscopy can simultaneously and accurately measure the concentrations of multiple gases emitted during a thermal runaway event in real time. MKS Instruments' MultiGas FTIR Gas Analyzer is ideally suited to the application of Li-ion battery fire testing, as it provides high time resolution measurements of either diluted or undiluted sample gases through the flexible selection of a variety of gas cells and detectors. The MultiGas Analyzer features a battery testing application package specific to the analysis of Li-ion battery fires that requires minimal user input for accurate and repeatable measurements.

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APP NOTE - Battery Thermal Runaway_02/21

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