

Lithium Battery Thermal Runaway Vent Gas Analysis at Various Heating rates

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Abstract

Lithium-ion batteries are extremely prevalent in today's society, powering everything from cell phones to automobiles, and are shipped in bulk quantities on cargo aircraft. These cells, however, have the potential to undergo a process called thermal runaway, during which the cell vents a flammable gas mixture. The extreme temperatures reached during thermal runaway have the potential to ignite this gas mixture, posing a potential hazard to the aircraft in which they are shipped. In order to understand and mitigate this hazard, there is a need to further understand the resulting combustion hazard. This study outlines a potential standardized test method for the classification of a cell's thermal runaway combustion hazard by analyzing the flammable vent gases. 18650-sized 3.7 V 2600 mAh lithium cobalt oxide cells at 30 % state of charge were heated at 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min.

A critical threshold for a violent thermal runaway reaction was determined to be a maximum cell case temperature above 250 °C coupled with the release of over 0.5 L of vent gas. It was statistically determined that heating rates at or above 15 °C/min were more likely to produce a violent thermal runaway reaction. There was a 34.3 % difference in the maximum cell case temperature between a standard and a violent thermal runaway reaction. There was a 53.5 % difference in the thermal runaway vent gas volume between a violent and standard thermal runaway reaction. There was a 48.4 % difference in the pressure rise between a standard and violent thermal runaway reaction. There was a 101 % difference in the total volume of hydrogen found in the thermal runaway vent gas between a standard and a violent thermal runaway reaction. The calculated average lower flammability limit (LFL) of the vent gas was 15.1 ± 2.1 % for a violent thermal runaway reaction and 12.0 ± 2.0 % for a standard thermal runaway reaction.

The maximum flammable airspace (MFA) per cell was 4.2 ± 1.0 l per cell and 3.1 ± 0.8 l per cell for a standard thermal runaway reaction. There was a 31.1 % difference in the MFA per cell between a standard and a violent thermal runaway reaction.

Keywords: Lithium-ion, Batteries, Combustion energy, Thermal runaway, Gas analysis

Introduction

Lithium-ion batteries are extremely prevalent in today's society, powering everything from cell phones to automobiles, and are shipped in bulk quantities on cargo aircraft. These cells, however, have the potential to undergo a process called thermal runaway, during which the cell vents a flammable gas mixture. The flammability hazard from thermal runaway can vary by state of charge (SOC), cell chemistry, cell size, and other contributing factors. Thermal runaway causes an uncontrolled ion exchange, which can result in a rapid rise in temperature and pressure accompanied by the venting of flammable gases. The cell's high-energy release can cause the vented flammable gases or adjacent materials to ignite and propagate fire. Additionally, the overpressure can cause structural damage to the aircraft. Between January 23, 2006, and January 22, 2020, there were 268 events involving smoke, fire, extreme heat, or explosions caused by lithium batteries on cargo and passenger aircraft [1].

The objective of the study was to outline test procedures, measurements, and calculations to create a framework for potential guidelines for a standardized test method to determine a cell's flammability hazard. However, this paper does not reflect the FAA policies or position. This study examined various heating rates to determine the effects on a cell's thermal runaway. The study analyzed the collected gases for hydrogen, carbon monoxide, carbon dioxide, and hydrocarbon content. The gas and pressure measurements were used to determine the lower flammability limit (LFL) of the vent gases. The study calculated the maximum flammable airspace (MFA) per cell after thermal runaway.

Experimental Method

The test procedure followed the thermal runaway initiation methods described in DOT/FAA/TC-20/1259 [2]. The individual battery cells were contained in a 21.7 L stainless-steel pressure vessel and heated using a film heater until the cell case reached 200 °C or until thermal runaway occurred. A proportional-integral-derivative (PID) controller set the heating rate at 5 °C/min, 10 °C/min, 15 °C/min, or 20 °C/min. The slope of the cell case temperature vs. time graph from 30 °C to 140 °C was used to calculate the actual heating rate. A vacuum pump evacuated the sealed pressure vessel to less than 0.7kPa. Then, a nitrogen bottle inserted 101.3kPa of nitrogen gas into the pressure vessel. Nitrogen gas has inert properties and does not interfere with the gas analyzers.

The inert properties of nitrogen are important to retain the flammable gases for measurement. A pressure transducer quantified the pressures generated from thermal runaway vent gases and measured the pressure spikes. The percent pressure-rise calculations used the difference of the maximum pressure and the original pressure divided by the original pressure (Eq. 1).

$$\%P_R = \frac{P_m - P_{om}}{P_{om}} \quad (\text{Eq. 1})$$

Where: $\%P_R$ = Percent pressure rise

P_m = Maximum measured pressure

P_{om} = Measured pressure before thermal runaway

Each test recorded the post-thermal runaway pressure after the ambient temperature returned to its approximate pre-thermal runaway temperature. Gay-Lussac's Law accounted for small temperature differences in the pressure vessel (Eq. 2). The thermal runaway vent-gas volume calculations used Boyle's Law with the recorded pre- and post-thermal runaway pressures and the volume of the pressure vessel (Eq. 3).

$$P_o = P_{om} * \frac{273.15 * T_F}{273.15 * T_o} \quad (\text{Eq. 2})$$

Where: P_o = Temperature adjusted pressure before thermal runaway

T_F = Ambient temperature after thermal runaway

T_o = Ambient temperature before thermal runaway

$$V_{vg} = \frac{P_f * V_{pv}}{P_o} - V_{pv} \quad (\text{Eq. 3})$$

Where: V_{vg} = Vent gas volume

V_{pv} = Pressure vessel volume

P_f = Pressure after thermal runaway

Additional nitrogen gas was used to fill the pressure vessel to 124 kPa. This addition allows the gases to mix and creates a positive pressure to force the mixed vent gas into the gas analyzers. Gas chromatography with a thermal conductivity detector and flame ionization detector measured hydrogen and hydrocarbon concentrations. The nondispersive infrared radiation sensor measured carbon monoxide and dioxide concentration. The vent-gas composition calculations used Dalton's Law with the pressure measurements and the gas analyzers' measurements (Eq. 4-6).

$$X_{vg} = \frac{P_f - P_o}{P_{F2}} \quad (\text{Eq. 4})$$

Where: X_{vg} = Percent volume of vent gas

P_{F_2} = Pressure after thermal runaway with additional nitrogen

$$X_{C_{vg}} = \frac{X_{C_{vg+N_2}}}{X_{vg}} \quad (\text{Eq. 5})$$

Where: $X_{C_{vg}}$ = Percent volume of constituent in vent gas

$X_{C_{vg+N_2}}$ = Percent volume of constituent in vent gas and nitrogen

$$V_{C_{vg}} = X_{C_{vg}} * V_{vg} \quad (\text{Eq. 6})$$

Where: $V_{C_{vg}}$ = Volume of vent gas constituent

Le Chatelier's mixing rule accurately calculates the flammability limits of mixtures containing hydrogen, carbon monoxide, methane, and simpler paraffin hydrocarbons [3]. However, calculated flammability limits are less accurate in mixtures containing vapors such as ether or acetone [4]. Therefore, the mixing rule should not be used indiscriminately [4].

The method for calculating the flammability limits of mixed gases can be summarized as [4]:

1. Calculate the constituents of the mixed gas without air.
2. Create binary gases by combining part or all of a nonflammable gas with one or more flammable gases and then recalculate the gas constituents.
3. Record the flammability limits of the mixtures' constituents from tables or curves.
4. Calculate the flammability limits of the mixture using Le Chatelier's mixing rule equation (Eq. 7).

$$L = \frac{100}{\frac{p_1}{N_1} + \frac{p_2}{N_2} + \frac{p_3}{N_3} + \dots} \quad (\text{Eq. 7})$$

Where: L = Either the LFL or the upper flammability limit (UFL)

p_1, p_2, p_3, \dots = Percentages of the mixture's constituents

N_1, N_2, N_3, \dots = Either LFL or UFL of the individual constituents

Note that the study used the actual total percentage when the constituents did not add up to 100 percent. The study estimated the MFA. The MFA is the maximum headspace volume that is likely to create a flammable mixture when exposed to the flammable vent gas from a single specified cell. The calculated average LFL and the measured average volume of thermal runaway vent gas determined the estimation (Eq. 8).

$$MFA = \frac{V_{vg}}{LFL} * 100 \quad (\text{Eq. 8})$$

Where: *MFA* = Maximum flammable airspace volume per cell
LFL = Lower flammability limit

Results

A two-sample t-test compares the means of two control groups [5]. The test statistically determines if changing an independent variable of the control groups significantly affects the dependent variable. For example, this study compared the thermal runaway reaction of 18650 sized cells for heating rates below 15 °C/min and at or above 15 °C/min. The heating rate is the independent variable, and the thermal runaway reaction is the dependent variable. This test statistically determines if changing the heating rate affects the cell's thermal runaway reaction.

There was a very significant difference in the maximum thermal runaway case temperature for heating rates below 15 °C/min (mean (*M*)=228 °C, standard deviation (*SD*)=35 °C) and heating rates at or above 15 °C/min (*M*=288 °C, *SD*=54 °C); $t(20)=3.1$, $p=0.0053$. The low p-value suggests that the heating rate significantly affects the maximum thermal runaway cell case temperature. Specifically, our results suggest that heating rates at or above 15 °C/min are very likely to increase the maximum cell case temperature.

A two-sample t-test compared the thermal runaway vent gas for heating rates below 15 °C/min and at or above 15 °C/min. There was an extremely significant difference in the volume of the vent gas for heating rates below 15 °C/min (*M*=0.38 l, *SD*=0.055 l) and heating rates at or above 15 °C/min (*M*=0.57 l, *SD*=0.14 l); $t(20)=4.3$, $p=0.0003$. The low p-value strongly suggests the heating rate affects the thermal runaway vent gas. Specifically, heating rates at or above 15 °C/min are extremely likely to increase the volume of thermal runaway vent gas.

A critical threshold for a violent thermal runaway reaction was determined to be a maximum cell case temperature in excess of 250 °C and the release of greater than 0.5 l of vent gas. This threshold is not universal and would likely change by cell type and states of charge. This threshold is used to demonstrate the impact of heating rate on the resulting flammability hazard. Slower heating rates allow more time for the electrolyte inside of the cells to boil and vent than faster heating rates. Therefore, more electrolyte remains in the form of potential energy.

Heating rates at or greater than 15 °C/min were more likely to produce a violent thermal runaway. Violent reactions occurred in 0/5 tests (0 %) at 5 °C/min, 1/7 tests (14%) at 10 °C/min, 3/5 tests (60 %) at 15 °C/min, and 4/5 tests (80 %) at 20 °C/min. Results were grouped by reaction type to determine the variation between standard and violent thermal runaway reactions. This will represent how heating rates affect thermal runaway.

Violent thermal runaway reactions produced a greater maximum cell case temperature than standard thermal runaway reactions. High

temperatures can cause flammable gases and surfaces to auto-ignite. There was a 34.3 % difference in the maximum cell case temperature between a standard and a violent thermal runaway reaction (table 1). The mean difference in the maximum cell case temperature was 92 °C. There was a 95 % confidence interval ranging from 64.9 °C to 119 °C.

Table 1. Maximum cell case temperature and reaction type.

Reaction Type	Number of Tests	Maximum Cell Case Temperature, °C		
		Mean	SD	standard error of the mean (SEM)
Standard	14	222	28.6	7.64
Violent	8	314	30.5	10.8

Violent thermal runaway reactions produced a greater volume of vent gas than standard thermal runaway reactions. There was a 53.5 % difference in the thermal runaway vent gas volume between a violent and standard thermal runaway reaction (table 2). The mean difference in vent gas volume was 0.27 l. There was a 95 % confidence interval ranging from 0.22 l to 0.31 l.

Table 2. Thermal runaway vent gas volume and reaction type.

Reaction Type	Number of Tests	Thermal Runaway Vent Gas Volume, l		
		Mean	SD	SEM
Standard	14	0.37	0.028	0.007
Violent	8	0.64	0.070	0.025

Violent thermal runaway reactions resulted in a greater pressure rise than standard thermal runaway reactions. Overpressure can cause structural damage to an aircraft and result in catastrophic system failure. There was a 48.4% difference in the percent pressure rise between a standard and violent thermal runaway reaction. The mean difference in the percent pressure rise was 3.11 % (table 3). There was a 95% confidence interval ranging from 1.69 % to 4.54 %. The violent thermal runaway reaction had a maximum of 11.9 % pressure rise. The standard thermal runaway had a maximum of 5.6 %.

Table 3. Percent pressure rise and reaction type

Reaction Type	Number of Tests	Percent Pressure Rise, %		
		Mean	SD	SEM
Standard	14	4.88	0.46	0.02
Violent	8	8.00	2.52	0.89

Hydrogen is a major contributor to the constituents of lithium-ion thermal runaway vent gas. Hydrogen has a wide flammability range from 4.95 % to 76.5 % by volume [3]. Violent thermal runaway reactions produced a greater volume of hydrogen than standard thermal runaway reactions. There was a 101 % difference in the total volume of hydrogen found in thermal runaway cell vent gas between a standard and a violent thermal runaway reaction (table 4). The mean difference in the total volume of hydrogen was 0.045 l. There was a 95 % confidence interval ranging from 0.037 l to 0.053 l.

Table 4. Hydrogen Volume and Reaction Type

Reaction Type	Number of Tests	Hydrogen Volume, L		
		Mean	SD	SEM
Standard	11	0.022	0.005	0.001
Violent	5	0.067	0.011	0.005

This study separated the gas concentrations used for the calculation of the LFL by reaction type (table 5). Standard thermal runaway reactions produced a more flammable gas mixture than violent thermal runaway reactions. The calculated LFL of the produced gases was 15.1 ± 2.1 % for a violent thermal runaway. The calculated LFL of the produced gases was 12.0 ± 2.0 % for a standard thermal runaway reaction. There was a 22.9 % difference in the calculated LFL between a standard and a violent thermal runaway reaction.

Table 5. Gas species, concentration, and LFL

Gas Specie	Standard Thermal Runaway, %vol	Violent Thermal Runaway, %vol	LFL, %vol
carbon dioxide	17.3 ± 2.91	34.9 ± 2.71	0
carbon monoxide	4.71 ± 0.41	3.84 ± 0.39	12.5
ethane	0.27 ± 0.05	0.46 ± 0.16	3.00
ethylene	2.16 ± 0.45	1.67 ± 0.24	3.10
hydrogen	5.98 ± 0.86	10.3 ± 0.70	4.95
methane	1.02 ± 0.28	1.27 ± 0.35	5.30
propane	0.10 ± 0.01	0.14 ± 0.07	2.10
propylene	0.07 ± 0.01	0.26 ± 0.18	2.40

\pm Confidence intervals based on a 95% confidence interval

Violent thermal runaway reactions produced a greater MFA per cell than standard thermal runaway reactions despite their higher LFL. This is because a violent thermal runaway reaction produced 53 % more vent

gas than a standard thermal runaway reaction. The MFA after a violent thermal runaway reaction was 4.23 ± 1.04 l per cell for a violent thermal runaway reaction and 3.09 ± 0.75 l per cell for a standard thermal runaway reaction. There was a 31.1 % difference in the MFA per cell between a standard and a violent thermal runaway reaction.

The cell case temperature, when apparent and rapid self-heating initiates, is referred to as the thermal runaway onset temperature. There was no statistical difference in the thermal runaway onset temperature for heating rates below 15 °C/min ($M=158$ °C, $SD=12$ °C) and heating rates at or above 15 °C/min ($M=150$ °C, $SD=9$ °C).

Conclusions

Cylindrical LiCoO₂ cells at 30% SOC, of type 18650 3.7V 2600mAh were tested. Tests included heating the cells at 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min. The results suggest that the heating rate significantly affects an 18650-sized cell's thermal runaway. Heating rates at or above 15 °C/min were more likely to produce a violent thermal runaway reaction. A standardized test method should prescribe the heating rate. Additional tests need to verify if the heating rate boundaries and their relation to standard and violent thermal runaway reactions in 18650 cells at 30% SOC translate to other lithium-ion cells.

References

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