EVALUATION OF LITHIUM BATTERY THERMAL RUNAWAY VENT GAS COMBUSTION HAZARD

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Final report

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16. Abstract

The United Nations (UN) Subcommittee of Experts on the Transport of Dangerous Goods (SCOE TDG) approves proper shipping names (PSN) and assigns each PSN with a four-digit UN number. Currently, two UN numbers have been assigned to lithium batteries as either UN 3480, **Lithium ion batteries** (including lithium ion polymer batteries) or UN 3090, **Lithium metal batteries** (including lithium alloy batteries). This research seeks to support the UN SCOE TDG establish a more performance-based approach to classifying the various types of lithium-ion batteries for transportation. Performance based classifications will support a better understanding of the risks of transporting lithium batteries and promote the industry in further developing safer batteries. A proposed standardized test method was used to assess the combustion hazard from a lithium-ion battery that has undergone thermal runaway. Lithium cobalt oxide pouch cells (3.7 V, 4.8 Ah) and cylindrical cells (3.7 V, 2.6 Ah) were tested at various states of charge (SOCs) and heating rates. The cells were individually heated to induce thermal runaway inside of a pressure vessel, resulting in a venting of gases. The vent gases were analyzed for their constituent's volume, overall gas volume, and combustion energy. Key findings are as follows:

- The vent gas volume and combustion energy increased linearly with SOC for the pouch and cylindrical cells.
- The top three constituents as a percentage of the vent gas by volume across all SOCs and heating rates for the pouch and cylindrical cells were carbon dioxide, hydrogen, and carbon monoxide.
- The vent gas volume and combustion energy increased with the heating rate for the pouch and cylindrical cells.
- When comparing cells heated at 20°C/min to cells heated at 5°C/min, across the tested SOCs, the pouch cells released an average of 14.1% more vent gas and had an average of 34.4% greater combustion energy, the cylindrical released an average of 7.2% more vent gas and had an average of 13.0% greater combustion energy.

| 17. Key Words

1. Battery Cells - Thermal runaway
2. Battery Cells - Gas analysis
3. Battery Cells - Combustion energy
4. Battery Cells - Lithium-ion | | 18. Distribution Statement

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Acronyms

Acronym	Definition
FAA	Federal Aviation Administration
UN	United Nations
SCOE TDG	Subcommittee of Experts on the Transport of Dangerous Goods
PSN	Proper shipping names
PID	Proportional-integral-derivative
SOC	State of charge
Li-Ion pBVG	Premixed lithium-ion battery vent gas in air
CC/CV	Constant current/constant voltage
$LiCoO_2$	Lithium cobalt oxide
V	Volts
Ah	Amp-hour
Wh	Watt-hour
C	Celsius
mAh	Milliamp-hour
kJ	Kilojoule
kPa	Kilopascal
W	Watt

Executive summary

The transport of lithium batteries as cargo onboard transport aircraft creates a potential hazard to aircraft safety. Between January 23, 2006, and June 30, 2021, FAA has awareness of 322 aviation events with smoke, fire, extreme heat, or explosions involving lithium batteries [1]. Lithium batteries can undergo a process called thermal runaway; and can result in a rapid rise in temperature and pressure, accompanied by the venting of flammable gases [2]. Common causes of thermal runaway in a battery include damage (e.g. from mishandling of the package, improper packaging, etc.) and exposure to excessive heat. It can also occur spontaneously without any environmental or mishandling factors due to manufacturing defects. Thermal runaway can propagate to neighboring batteries when the heat from one battery causes an adjacent battery to overheat [3]. Propagation generally continues until either all batteries have undergone thermal runaway, or a reduction in heat transfer from the event, stops the chain reaction. Additionally, a buildup of flammable vent gas creates the risk of a catastrophic explosion [4]. The smoke detection and fire extinguishing systems in the aircraft lower cargo compartments can detect and suppress most fires. However, the current suppression systems may not be adequate to protect against lithium battery fires [4], [5] The United Nations (UN) Subcommittee of Experts on the Transport of Dangerous Goods (SCOE TDG) approves proper shipping names (PSN) and assigns each PSN with a four-digit UN number. Currently, two UN numbers have been assigned to lithium batteries as either UN 3480, **Lithium ion batteries** (including lithium- ion polymer batteries) or UN 3090, **Lithium metal batteries** (including lithium-alloy batteries) [6]. The current classifications do not reflect the wide range of potential hazards. The severity of the hazard created by batteries in thermal runaway can vary by state of charge (SOC), cell chemistry, cell size, heating rate, and other contributing factors [2], [7]. By further classifying the lithium batteries, more type-specific mitigation strategies could be used and may result in safer shipments of lithium batteries. A proposed standardized test method was used to assess the combustion hazard from lithium cobalt oxide pouch cells (3.7 V 4.8 Ah) and cylindrical cells (3.7 V 2.6 Ah) that were overheated at various states of charge (SOCs) and heating rates.

The vent gas volume and combustion energy increased linearly with SOC for the pouch and cylindrical cells. The top three constituents as a percentage of the vent gas by volume across all SOCs for the pouch and cylindrical cells were carbon dioxide, hydrogen, and carbon monoxide. When comparing cells heated at 20°C/min to cells heated at 5°C/min, across the tested SOCs, the pouch cells released an average of 14.1% more vent gas and had an average of 34.4% greater combustion energy, the cylindrical released an average of 7.2% more vent gas and had an average of 13.0% greater combustion energy. Therefore, this data suggests that the heating rate should be standardized for lithium battery combustion hazard analysis.

1   Introduction

1.1   Purpose

The United Nations (UN) Subcommittee of Experts on the Transport of Dangerous Goods (SCOE TDG) approves proper shipping names (PSN) and assigns each PSN with a four-digit UN number. Two UN numbers have been assigned to lithium batteries as either UN 3480, **Lithium ion batteries** (including lithium-ion polymer batteries) or UN 3090, **Lithium metal batteries** (including lithium-alloy batteries) [6]. The current classifications do not reflect the wide range of potential hazards [7]. This research seeks to help the UN further classify the various types of lithium batteries by using a proposed standardized test method to assess the combustion hazard associated with thermal runaway. By classifying the cells and batteries, more type-specific mitigation strategies could be used. This may reduce the risk of thermal runaway and help batteries ship in a safe manner. Performance based classifications will support a better understanding of the risks of transporting lithium batteries and promote the industry in further developing safer batteries.

1.2   Hazards

A single cell may be defined as a single encased electrochemical component and a battery defined as two or more cells electrically connected [8]. Lithium batteries can undergo a process called thermal runaway; and can result in a rapid rise in temperature and pressure, accompanied by the venting of flammable gases [2]. Common causes of thermal runaway in a battery include damage (e.g. from mishandling of the package, improper packaging, etc.) and exposure to excessive heat. Thermal runaway can also occur spontaneously without any environmental or mishandling factors due to manufacturing defects.

An important factor related to the hazard of thermal runaway is an event called thermal runaway propagation. Propagation occurs when the heat from one battery or cell causes an adjacent battery or cell to also overheat [3]. Propagation generally continues until either all batteries have undergone thermal runaway, or a reduction in heat transfer from the event stops the chain reaction. This process can create enormous amounts of heat, smoke, and flammable gases. Therefore, controls and mitigation techniques are crucial to prevent the propagation of thermal runaway.

The outcome of thermal runaway varies depending on the cell chemistry, the size of the cell or battery, the state of charge (SOC), and the manufacturer's design [7]. Additionally, the orientation and configuration in the package affect the thermal runaway. The more hazardous

outcomes can include flames, violent ejection of cell components, emission of flammable gas that can build up and later explode, or an explosion of the cell itself. Less hazardous outcomes include emission and dissipation of flammable vapors without ignition or the accumulation of flammable vapors with ignition but self-extinguishes.

The smoke detection and fire extinguishing systems in aircraft lower cargo compartments can detect and suppress most fires. However, the current suppression systems may not be adequate to protect against lithium battery fires. [4], [5]. One reason for this is because the 5%vol Halon 1301 knockdown concentration and the sustained 3%vol Halon 1301 in a Class C cargo compartment may not be sufficient at inerting lithium-ion battery vent gas and air mixtures [4], [5], [9]. At 5%vol Halon 1301 the flammability limits range from 13.80%vol to 26.07%vol of a premixed lithium-ion battery vent gas in air (Li-Ion pBVG) [5]. Testing suggests that 8.59 %vol Halon 1301 is required to render all ratios of the Li-Ion pBVG in air inert [5].

1.3   Combustion energy

The combustion energy is the amount of energy liberated after undergoing complete combustion with excess oxygen at standard conditions (25°C and 100 kPa). This is important because it incorporates both the flammability and volume of vent gas to create a one-parameter calculation to characterize the combustion hazard. This allows for direct comparison between various lithium batteries.

This research calculates the combustion energy by use of the gas analysis method as described by Quintiere, et al [10]. Essentially, the gas analysis method calculates the combustion energy by taking the summation of the products of the calculated masses of the dominant constituents and their corresponding heats of combustion. Ideally, the collection of the flammable gas constituents will occur in an inert environment to ensure that there are no reactions with oxygen. Other methods for measuring the combustion energy include the cone calorimeter and the oxygen bomb method [10].

2   Test setup

The test procedure follows previous studies with some modifications [2], [10], [11]. Modifications include specified charging procedures (Table 1) and insulating the test cell while overheating (Figure 1 and Figure 2). The cells are charged using constant current/constant voltage (CC/CV) charging, where it uses constant current until the voltage reaches a prescribed set point. Then, the prescribed voltage set point is held constant until the current reaches a prescribed set point. A general procedure overview and the modification details are below.

Lithium cobalt oxide (LiCoO₂) cells were tested in two different forms – cylindrical cells with dimensions 18 mm diameter, 65 mm length (18650 battery), and pouch cells with dimensions 5.4 x 47 x 95 mm. Further details about the cells' voltage (V), capacity (Ah), and resulting energy (Wh), are shown in Table 2. The initial starting temperatures of the cells were 21±2 °C. The individual cells were attached to a heater, wrapped with ceramic insulation on all sides except on the top, and vertically oriented (Figure 1 and Figure 2). The minimum ceramic insulation thickness is 20 mm. The individual cell configurations were contained in a 21.7 L stainless-steel pressure vessel. The cells were heated until the cell case temperature reached 200 °C or until the thermal runaway event occurred (Figure 3). A proportional-integral-derivative (PID) controller set the heating rate at 5°C/min, 10°C/min, 15°C/min, or 20°C/min for cells charged to 30%, 50%, 70%, or 100% SOC. The test matrix is shown in Table 3 and the gray regions represent the tested configurations.

A vacuum pump was used to evacuate the sealed pressure vessel to less than 0.7 kPa. Then, 101.3±0.3 kPa of nitrogen gas was inserted into the pressure vessel. Nitrogen gas creates an inert environment so that the flammable vent gas will not react with the test environment. This allows for measurements of the flammable gas components, ensuring that there is little to no interference from post-combustion products. Additional nitrogen gas is then inserted into the pressure vessel to a pressure of 124±0.3 kPa. This additional nitrogen, inserted after the thermal runaway event, allows the gases to mix and creates a positive pressure to force the mixed vent gas into the gas analyzers at the flow rate prescribed by the analyzer manufacturer manuals.

Each test recorded the pre-thermal runaway temperature and pressure, post-thermal runaway temperature and pressure after the temperature in the pressure vessel returned to its approximate pre-thermal runaway temperature, and the post-thermal runaway temperature and pressure after additional nitrogen gas is inserted into the pressure vessel. Gas chromatography with thermal conductivity and flame ionization detectors were used to measure hydrogen and hydrocarbon concentrations and a nondispersive infrared radiation analyzer was used to measure carbon monoxide and carbon dioxide concentration (Figure 4).

Table 1. Charging cycle

Charging cylindrical cells	Charging pouch cells
1. Charge at 1.25 Amps until the voltage reaches 4.2 V, then charge at 4.2 V. until the current drops to 0.05 Amps using CC/CV. 2. Rest 30 minutes. 3. Discharge the cell at 1.25 Amps until the voltage reaches 2.75 V. Note the total discharge time. Calculate the 100% capacity in Ah. 4. Repeat step 1 to recharge to 4.2 V. 5. Rest 30 minutes. 6. Discharge at 1.25 Amps for the appropriate fraction of the total time determined in Step 3 to arrive at the target SOC. The SOC is linear with the total discharge time.	1. Charge at 2.4 Amps until the voltage reaches 4.2 V, then charge at 4.2 V. until the current drops to 0.24 Amps using CC/CV. 2. Rest 30 minutes. 3. Discharge the cell at 2.4 Amps until the voltage reaches 3.0 V. Note the total discharge time. Calculate the 100% capacity in Ah. 4. Repeat step 1 to recharge to 4.2 V. 5. Rest 30 minutes. 6. Discharge the cell at 2.4 Amps for the appropriate fraction of the total time determined in Step 3 to arrive at the target SOC. The SOC is linear with the total discharge time.

Table 2. Experimental cells

Cell Style	Nominal Voltage, V	Capacity, Ah	Energy, Wh
Cylindrical	3.7	2.6	9.62
Pouch	3.7	4.8	17.76

Table 3. Test matrix

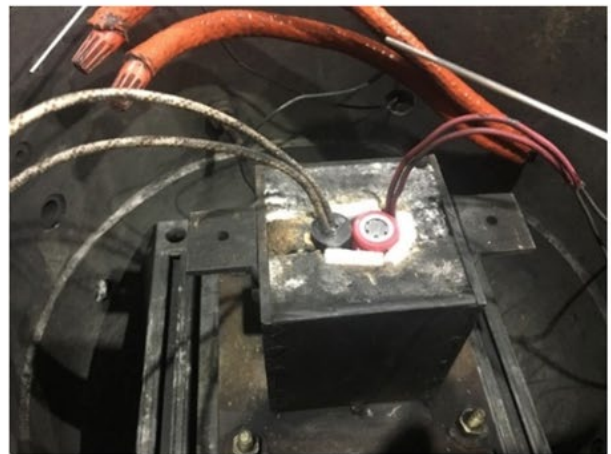|	30% SOC	50% SOC	70% SOC	100% SOC
5 °C /min				
10 °C /min	Not Tested	Not Tested	Not Tested	
15 °C /min	Not Tested	Not Tested	Not Tested	
20 °C /min				
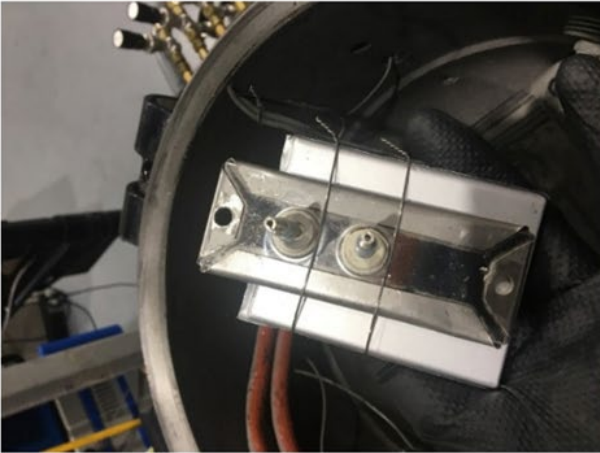
Figure 1. (a) Pouch cell attached to 75 W strip heater (b) Assembly wrapped in insulation

Figure 2. (a) Cylindrical cell attached to 100 W cartridge heater (b) Assembly wrapped in insulation
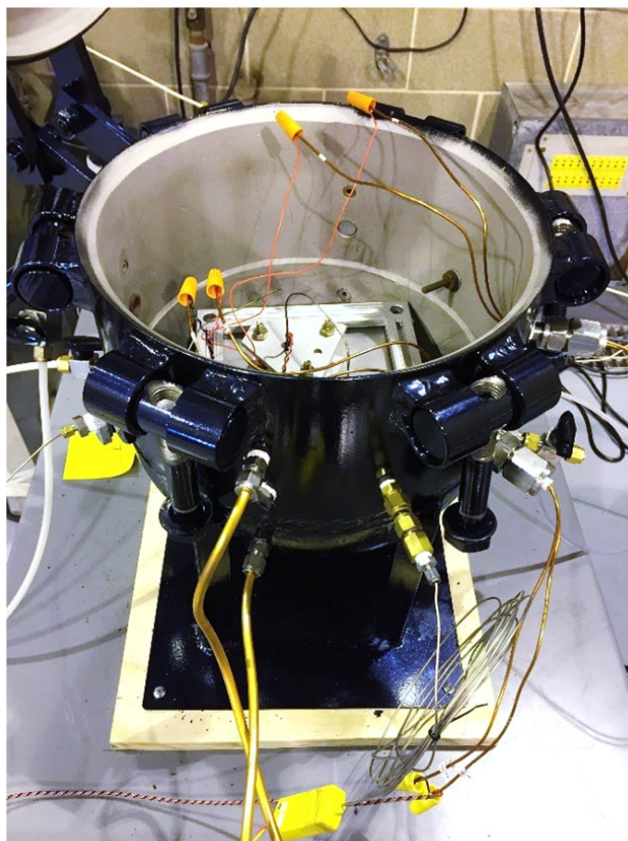
Figure 3. 21.7 L stainless-steel pressure vessel

Figure 4. Gas analyzers and calibration gases

3   Calculations and results

The test calculation follows previous studies [2], [10], [11]. The vent gas constituents as a percentage of the nitrogen diluted vent gas by volume after additional nitrogen was inserted into the pressure vessel were measured using various gas analyzers. The measured constituents are 1-butene, butane, propane, propylene, ethane, ethylene & acetylene, methane, total hydrocarbon content, hydrogen, carbon dioxide, carbon monoxide.

Gay-Lussac's Law, which states that the pressure of a given mass of gas is directly proportional to the temperature at a constant volume, was used to account for changes in pressure caused by heat produced after the thermal runaway.

The vent gas volumes were calculated using the pre- and post-thermal runaway pressures, the volume of the pressure vessel, and the Boyle-Mariotte Law, which states that the pressure of a given mass of gas is inversely proportional to the volume of gas at a constant temperature.

The vent gas constituents as a percentage of the vent gas by volume were calculated using the pre- and post-thermal runaway pressures, the pressure after thermal runaway with additional nitrogen added, the vent gas constituents as a percentage of the nitrogen diluted vent gas by volume after additional nitrogen was inserted into the pressure vessel, and Dalton's Law, which states that the total pressure exerted is equal to the sum of the partial pressures.

The combustion energy is calculated by taking the summation of the products of the calculated masses of the dominant constituents and their corresponding heats of combustion.

3.1   Pouch cells

The pouch cells as described in Table 2 were tested across various SOCs and heating rates as shown in Table 3. The individual test results for all gas constituents can be found in Appendix A-1 (Percentage of gas measurements for pouch cells) and Appendix B-1 (Volume of gas measurements for pouch cells).

The pouch cells heated at 20°C/min and charged to 30%, 50%, 70%, and 100% SOC released more vent gas than cells heated at 5°C/min (Figure 5). On average, a pouch cell heated at 20°C/min released 14.1% more vent gas than a pouch cell heated at 5°C/min. The vent gas volume increased linearly with SOC, and ranged from 1.3 L, for a pouch cell charged to 30% SOC and heated at 5°C/min, to 9.9 L, for a pouch cell charged to 100% SOC and heated at 20°C/min (Figure 5).
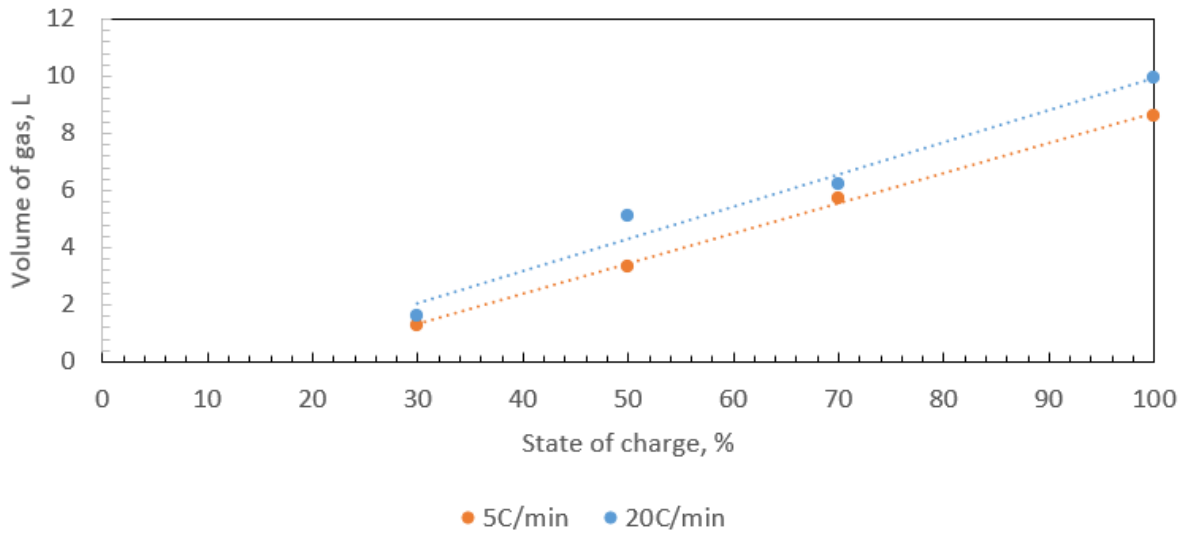
Figure 5. Vent gas volume versus the state of charge by the heating rate for pouch cells

The top three constituents as a percentage of the vent gas by volume across all SOCs in order from greatest to least were carbon dioxide, hydrogen, and carbon monoxide for the tested pouch cells. On average, the three gases contribute to $81\pm2\%$vol of the total gas mixture.

Measurements show that the percentage of carbon dioxide by volume decreased while carbon monoxide by volume increased with increasing SOCs (Figure 6). Many of the other gas constituents including hydrogen remain largely unchanged (Figure 6, Appendix B-1). The average concentration of hydrogen by volume in vent gas across all pouch cells was $24\pm4\%$vol.

Figure 6. Percentage of gas versus the state of charge by a constituent for pouch cells

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The pouch cells heated at 20°C/min and charged to 30%, 50%, 70%, and 100% SOC had greater combustion energy than cells heated at 5°C/min (Figure 7). On average, a pouch cell heated at 20°C/min had a 34.4% greater combustion energy than a pouch cell heated at 5°C/min. The combustion energy increased linearly with SOC, and ranged from 5.2 kJ, for a pouch cell charged to 30% SOC and heated at 5°C/min, to 114 kJ, for a pouch cell charged to 100% SOC and heated at 20°C/min (Figure 7).
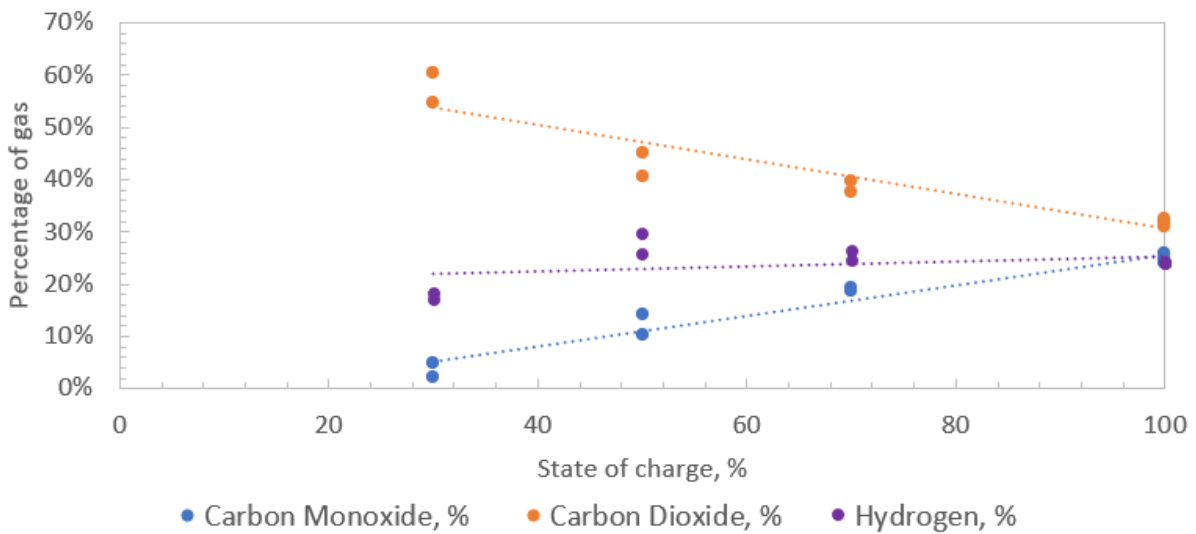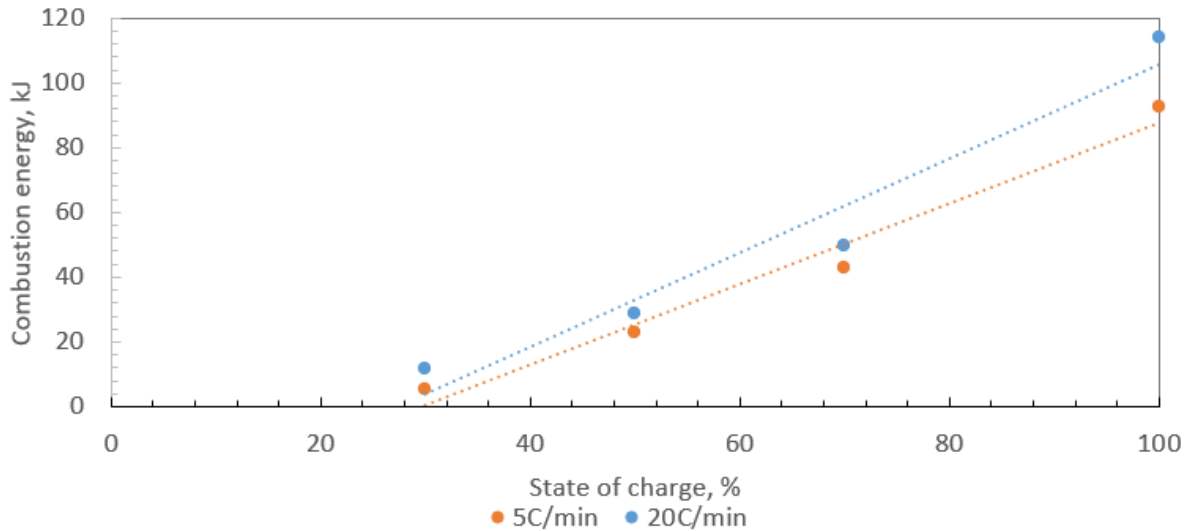

Figure 7. Combustion energy versus the state of charge by the heating rate for pouch cells

Although the percent change is greatest at low SOCs, the total difference in combustion energy was calculated to be greatest at high SOCs. The maximum percent change in combustion energy between a pouch cell heated at 5°C/min and 20°C/min was 129% and occurred in cells charged to 30% SOC (Table 4). The maximum total difference in combustion energy between a pouch cell heated at 5°C/min and 20°C/min was 21.5 kJ and occurred in cells charged to 100% SOC (Table 4).

Table 4. Combustion energy by heating rate and change between them by SOC, pouch cells

% SOC	Combustion Energy (5 °C/min), kJ	Combustion Energy (20 °C/min), kJ	Percent Change, %	Total Difference, kJ
30	5.2	11.9	129	6.7
50	22.9	29	27	6.1
70	42.9	49.6	16	6.7
100	92.5	114	23	21.5

3.2 Cylindrical cells

In addition to pouch cells, cylindrical cells as described in Table 2 were tested across various SOCs and heating rates as shown in Table 3. The individual test results can be found in Appendix C-1 (Percentage of gas measurements for cylindrical cells) and Appendix D-1 (Volume of gas measurements for cylindrical cells).

The cylindrical cells heated at 20°C/min and charged to 30%, 70%, and 100% SOC released more vent gas than cells heated at 5°C/min (Figure 8). Conversely, the cylindrical cell heated at 5°C/min and charged to 50% SOC released more vent gas than the cell heated at 20°C/min. On average, a cylindrical cell heated at 20°C/min released 7.2% more vent gas than a cylindrical cell heated at 5°C/min. The vent gas volume increased linearly with SOC, and ranged from 1.1 L, for a cylindrical cell charged to 30% SOC and heated at 5°C/min, to 3.75 L, for a cylindrical cell charged to 100% SOC and heated at 20°C/min (Figure 8).
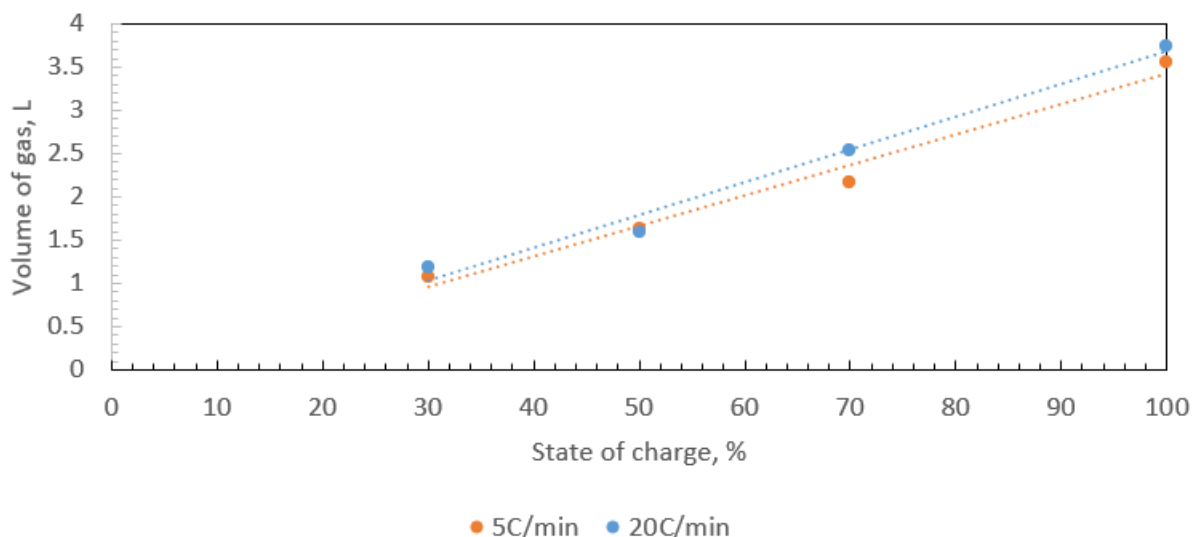
Figure 8. Vent gas volume versus the state of charge by the heating rate for cylindrical cells

The top three constituents as a percentage of the vent gas by volume across all SOCs in order from greatest to least were carbon dioxide, hydrogen, and carbon monoxide for the tested cylindrical cells. On average, the three gases contribute to 54±12%vol of the total gas mixture.

Measurements show that the percentage of carbon dioxide by volume decreased while carbon monoxide by volume increased with increasing SOCs (Figure 9). Many of the other gas constituents including hydrogen remain largely unchanged (Figure 9, Appendix D-1). The average concentration of hydrogen by volume in vent gas across all SOC cylindrical cells was 12±4%vol.
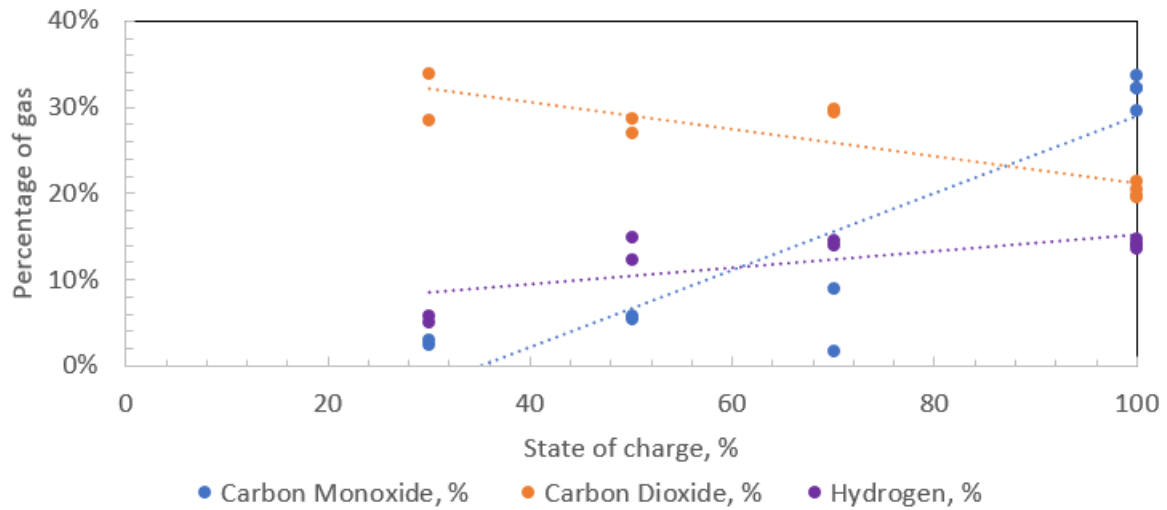
Figure 9. Percentage of gas versus state of charge by a constituent for cylindrical cells

The cylindrical cells heated at 20°C/min and charged to 30%, 50%, and 100% SOC had greater combustion energy than cells heated at 5°C/min (Figure 10). Conversely, the cylindrical cell heated at 5°C/min and charged to 70% SOC had greater combustion energy than the cell heated at 20°C/min. On average, a cylindrical cell heated at 20°C/min had a 13% greater combustion energy than a cylindrical cell heated at 5°C/min. The combustion energy increased linearly with SOC, and ranged from 4.5 kJ, for a cylindrical cell charged to 30% SOC and heated at 5°C/min, to 42 kJ, for a cylindrical cell charged to 100% SOC and heated at 20°C/min (Figure 10).
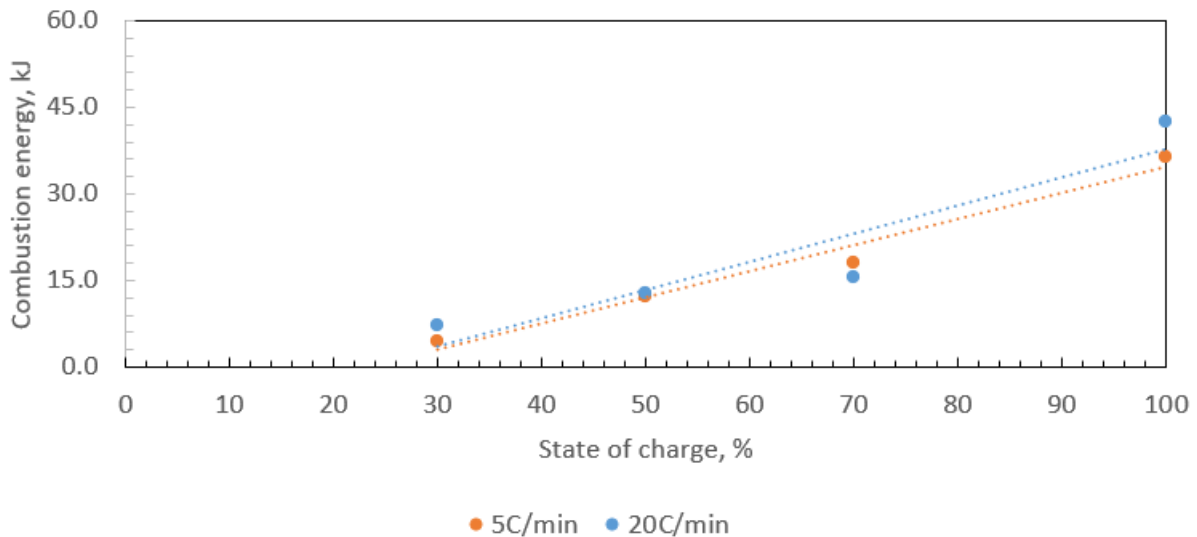

Figure 10. Combustion energy vs. the state of charge by the heating rate for cylindrical cells

Although the percent change is greatest at low SOCs, the total difference in combustion energy was calculated to be greatest at high SOCs. The maximum percent change in combustion energy between a cylindrical cell heated at 5°C/min and 20°C/min was 64% and occurred in cells charged to 30% SOC (Table 5). The maximum total difference in combustion energy between a cylindrical cell heated at 5°C/min and 20°C/min was 5.9 kJ and occurred in cells charged to 100% SOC (Table 5).

Table 5. Combustion energy by heating rate and change between them by SOC, cylindrical cells

% SOC	Combustion Energy (5°C/min), kJ	Combustion Energy (20°C/min), kJ	Percent Change, %	Total Difference, kJ
30	4.5	7.4	64	2.9
50	12.2	12.8	5	0.5
70	18	15.4	-14	-2.7
100	36.5	42.4	16	5.9

4   Analysis

The thermal runaway vent gas volume increased linearly with SOC for both the $LiCoO_2$ pouch (3.7 V 4.8 Ah) and $LiCoO_2$ cylindrical (3.7 V 2.5 Ah) cells. The vent gas volume for the pouch and cylindrical cells ranged from 1.3 L and 1.1 L, respectively, when charged to 30% SOC and heated at 5°C/min, to 9.9 L and 3.75 L, respectively, when charged to 100% SOC and heated at 20°C/min. For comparison, a previous FAA study measured the thermal runaway vent gas volume for $LiCoO_2$ pouch cells of size 5.4 x 47 x 95 mm (3.7 V 2.5 Ah), and for $LiCoO_2$ cylindrical cells of size 18650 (3.7 V 2.5 Ah) charged to 30% SOC [2]. The study measured 0.94 L and 0.47 L of vent gas for the pouch and cylindrical cells, respectively [2]. However, the previously mentioned FAA study used cells produced by different manufacturers.

The top three constituents as a percentage of the vent gas by volume across all SOCs for the tested pouch cells in order from greatest to least were carbon dioxide, hydrogen, and carbon monoxide (Figure 6). Cylindrical cells had the same three top constituents but differed from the pouch cells because the percentage of carbon monoxide by volume is greater than hydrogen by volume (Figure 9). This is in agreement with the previously mentioned FAA study that also found carbon dioxide, hydrogen, and carbon monoxide to be the top three constituents as a percentage of the vent gas by volume for the tested pouch and cylindrical cells charged to 30% SOC [2].

Hydrogen concentration is an important parameter in the combustion hazard analysis of lithium batteries because larger quantities of Halon 1301 than what is currently required in aircraft cargo fire suppression systems are required to inert hydrogen gas [5], [9]. Testing suggests that 27.7%vol Halon 1301 is the minimum inerting concentration for hydrogen and air mixtures [5]. The average concentration of hydrogen by volume in vent gas across all SOCs for the pouch and cylindrical cells were 24±4%vol and 12±4%vol, respectively. The previously mentioned FAA study measured the average concentration of hydrogen by volume in vent gas to be 17.0±1%vol and 7.3±2%vol for the pouch and cylindrical cells, respectively [2].

The combustion energy increased linearly with SOC for both the pouch and cylindrical cells. The combustion energy for the pouch and cylindrical cells ranged from 5.2 kJ and 4.5 kJ, respectively, when charged to 30% SOC and heated at 5°C/min, to 114 kJ and 42 kJ, respectively, when charged to 100% SOC and heated at 20°C/min.

The heating rate can greatly impact the vent gas combustion energy. The maximum percent change in combustion energy between similar cells heated at 5°C/min and 20°C/min occurred in cells charged to 30% SOC (Table 4 and Table 5). At 30% SOC, the percent change in combustion energy between heating rates of 5°C/min and 20°C/min was 129% and 64% for the pouch and cylindrical cells, respectively (Table 4 and Table 5). The maximum total difference in combustion energy between similar cells heated at 5°C/min and 20°C/min occurred in cells charged to 100% SOC (Table 4 and Table 5). At 100% SOC, the total difference between heating rates of 5°C/min and 20°C/min in combustion energy was 21.5 kJ and 5.9 kJ for the pouch and cylindrical cells, respectively (Table 4 and Table 5).

The effect of heating rate on the vent gas volume and combustion energy was considered. Typically, a cell heated at 20°C/min released more vent gas and had greater combustion energy than a cell heated at 5°C/min. This is because slower heating rates allow more time for the electrolyte inside of the cells to boil and vent than with cells heated at faster heating rates. Therefore, cells heated at slower rates have less electrolyte remaining in the cells once thermal runaway actually occurs which reduces the amount of vent gas and combustion energy over the same cells tested at faster heating rates. When comparing cells heated at 20°C/min to cells heated at 5°C/min, across the tested SOCs, the pouch cells released an average of 14.1% more vent gas, and the cylindrical cells released an average of 7.2% more vent gas. Furthermore, when comparing cells heated at 20°C/min to cells heated at 5°C/min, across the tested SOCs, the pouch cells had an average of 34.4% greater combustion energy and the cylindrical cells had an average of 13.0% greater combustion energy. This is in agreement with the previously mentioned FAA study which tested 22 cylindrical cells at 30 % state of charge and statistically determined that

heating rates at or above 15°C/min were more likely to produce a violent thermal runaway reaction than cells heated at less than 15°C/min [2]. The critical thresholds for a violent thermal runaway reaction were determined to be a maximum cell case temperature above 250°C and the release of over 0.5 L of vent gas [2]. Therefore, the heating rate should be standardized for lithium battery flammability hazard analysis. However, it should be noted that the cylindrical cell heated at 5°C/min and charged to 50% SOC and 70% SOC released slightly more vent gas and had slightly greater combustion energy, respectively than the cell heated at 20°C/min (Figure 8). By comparing the cylindrical cell results at 50% SOC and 70% SOC to the rest of the tests and the previous study, they are likely outliers due to a small data set.

5   Findings and conclusion

This report demonstrates a proposed test method used to assess the flammable gas hazard associated with lithium batteries that undergo thermal runaway. $LiCoO_2$ pouch and cylindrical cells, as described in Table 2, at various SOCs were individually placed inside of a pressure vessel and externally heated at heating rates ranging from 5°C/min to 20°C/min to induce thermal runaway. This resulted in a release of significant quantities of vent gas and an increase in vessel pressure. The vent gases were analyzed for their main constituents as a percentage of the total collected vent gas by volume, the vent gas volume, and the thermal runaway combustion energy. Key findings are as follows:

- The vent gas volume increased linearly with SOC for the pouch and cylindrical cells.

- The vent gas volume for the pouch and cylindrical cells ranged from 1.3 L and 1.1 L, respectively, when charged to 30% SOC and heated at 5°C/min, to 9.9 L and 3.75 L, respectively, when charged to 100% SOC and heated at 20°C/min.

- The top three constituents as a percentage of the vent gas by volume across all SOCs for the pouch and cylindrical cells were carbon dioxide, hydrogen, and carbon monoxide. On average, the three gases contribute to 81±2%vol and 54±12%vol of the total gas mixture for pouch cells and cylindrical cells, respectively.

- The average concentration of hydrogen by volume in vent gas across all SOCs for the pouch and cylindrical cells were 24±4%vol and 12±4%vol, respectively.

- The combustion energy increased linearly with SOC for the pouch and cylindrical cells.

- The combustion energy for the pouch and cylindrical cells ranged from 5.2 kJ and 4.5 kJ, respectively, when charged to 30% SOC and heated at 5°C/min, to 114 kJ and 42 kJ, respectively, when charged to 100% SOC and heated at 20°C/min.

- At 30% SOC, the percent change in combustion energy between heating rates of 5°C/min and 20°C/min were 129% and 64% for the pouch and cylindrical cells.

- At 100% SOC, the total difference between heating rates of 5°C/min and 20°C/min in combustion energy was 21.5 kJ and 5.9 kJ for the pouch and cylindrical cells.

- Increasing the heating rate increased the vent gas volume and its combustion energy for the pouch and cylindrical cells.

- When comparing cells heated at 20°C/min to cells heated at 5°C/min, across the tested SOCs, the pouch cells released an average of 14.1% more vent gas, and the cylindrical released an average of 7.2% more vent gas.

- When comparing cells heated at 20°C/min to cells heated at 5°C/min, across the tested SOCs, the pouch cells had an average of 34.4% greater combustion energy and the cylindrical had an average of 13.0% greater combustion energy.

These data agree with previous experiments which suggests that the heating rate should be standardized for lithium battery combustion hazard analysis.

6   References

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# A	Percentage of gas measurements for pouch cells

State of Charge	30	30	50	50	70	70	100	100	100	100
Initial Voltage, V	3.75	3.75	3.79	3.79	3.90	3.90	4.12	4.12	4.13	4.13
Intended heating rate, °C/min	5	20	5	20	5	20	5	10	15	20
Actual heating rate, °C/min	5.0	19.4	5.1	19.3	5.0	19.7	4.7	10.3	15.0	19.1
1-Butene, %	0.13%	0.21%	0.22%	0.21%	0.19%	0.21%	0.53%	0.53%	0.55%	0.56%
Butane, %	0.06%	0.09%	0.09%	0.08%	0.05%	0.04%	0.04%	0.04%	0.04%	0.04%
Propane, %	0.22%	3.02%	0.23%	0.21%	0.14%	0.13%	0.16%	0.14%	1.54%	0.16%
Propylene, %	0.57%	0.80%	1.05%	1.14%	1.10%	1.31%	2.06%	2.11%	2.17%	2.32%
Ethane, %	0.33%	0.45%	0.45%	0.44%	0.35%	0.33%	0.49%	0.46%	0.52%	0.52%
Ethylene & Acetylene, %	1.3%	1.3%	1.0%	1.0%	1.1%	1.4%	3.4%	3.7%	4.0%	4.1%
Methane, %	0.9%	1.4%	2.7%	2.5%	2.4%	2.2%	3.1%	3.0%	3.1%	3.2%
Hydrogen, %	17.0%	18.3%	25.7%	29.7%	24.6%	26.2%	23.8%	23.9%	24.2%	23.9%
Total Hydrocarbon Content, %	6.9%	8.1%	6.9%	6.8%	5.7%	6.2%	9.2%	9.3%	9.4%	3.7%
Oxygen, %	1.8%	1.6%	0.3%	0.5%	0.1%	0.0%	0.1%	0.0%	0.0%	0.1%
Carbon Dioxide, %	60.3%	54.8%	45.2%	40.5%	39.6%	37.7%	32.5%	31.8%	31.0%	31.4%
Carbon Monoxide, %	2.3%	4.9%	10.3%	14.3%	18.6%	19.4%	24.1%	24.8%	26.0%	24.6%

B   Volume of gas measurements for pouch cells

State of Charge, %	30	30	50	50	70	70	100	100	100	100
Initial Voltage, V	3.75	3.75	3.79	3.79	3.90	3.90	4.12	4.12	4.13	4.13
Intended heating rate, °C/min	5	20	5	20	5	20	5	10	15	20
Actual heating rate, °C/min	5.0	19.4	5.1	19.3	5.0	19.7	4.7	10.3	15.0	19.1
Total Volume, L	1.30	1.62	3.33	3.77	5.75	6.22	8.61	9.98	10.46	9.93
1-Butene, L	0.002	0.003	0.007	0.008	0.011	0.013	0.046	0.053	0.057	0.055
Butane, L	0.001	0.001	0.003	0.003	0.003	0.002	0.003	0.004	0.004	0.004
Propane, L	0.003	0.049	0.008	0.008	0.008	0.008	0.014	0.014	0.161	0.016
Propylene, L	0.007	0.013	0.035	0.043	0.063	0.081	0.178	0.210	0.227	0.231
Ethane, L	0.004	0.007	0.015	0.016	0.020	0.021	0.042	0.046	0.054	0.052
Ethylene & Acetylene, L	0.02	0.02	0.03	0.04	0.06	0.09	0.29	0.37	0.42	0.41
Methane, L	0.01	0.02	0.09	0.09	0.14	0.14	0.26	0.30	0.32	0.32
Hydrogen, L	0.22	0.30	0.86	1.12	1.41	1.63	2.05	2.39	2.53	2.37
Total Hydrocarbon Content, L	0.09	0.13	0.23	0.26	0.33	0.38	0.79	0.93	0.98	0.36
Oxygen, L	0.02	0.03	0.01	0.02	0.00	0.00	0.01	0.00	0.00	0.01
Carbon Dioxide, L	0.79	0.89	1.51	1.53	2.28	2.34	2.80	3.17	3.24	3.12
Carbon Monoxide, L	0.03	0.08	0.34	0.54	1.07	1.21	2.08	2.47	2.72	2.44

C Percentage of gas measurements for cylindrical cells

State of Charge, %	30	30	50	50	70	70	100	100	100	100
Initial Voltage, V	3.75	3.69	3.77	3.77	3.88	3.88	4.14	4.13	4.15	4.15
Intended heating rate, °C/min	5	20	5	20	5	20	5	10	15	20
Actual heating rate, °C/min	4.8	21.0	6.5	23.7	5.1	22.0	4.9	10.2	16.6	24.0
1-Butene, %	0.99%	2.26%	0.01%	1.22%	1.06%	0.87%	0.83%	0.85%	0.93%	0.89%
Butane, %	0.11%	0.20%	1.10%	0.15%	0.46%	0.00%	0.00%	0.00%	0.00%	0.00%
Propane, %	0.23%	0.47%	0.42%	0.44%	0.30%	0.21%	0.19%	0.18%	0.19%	0.45%
Propylene, %	0.69%	0.97%	1.37%	1.62%	1.40%	1.12%	1.63%	1.40%	1.59%	1.53%
Ethane, %	0.48%	0.58%	0.70%	0.82%	0.73%	0.48%	0.48%	0.49%	0.38%	0.45%
Ethylene & Acetylene, %	1.0%	1.1%	1.7%	2.1%	2.0%	2.0%	3.3%	3.5%	3.7%	3.8%
Methane, %	2.0%	1.9%	3.9%	4.2%	4.2%	3.3%	3.0%	3.5%	2.9%	3.2%
Hydrogen, %	5.2%	5.9%	15.0%	12.3%	14.0%	14.5%	14.0%	13.6%	14.3%	14.8%
Total Hydrocarbon Content, %	22.9%	24.7%	20.0%	21.0%	17.1%	14.4%	12.8%	12.7%	12.8%	12.5%
Oxygen, %	3.0%	4.0%	2.2%	2.2%	1.6%	5.1%	1.8%	1.1%	1.8%	2.5%
Carbon Dioxide, %	33.9%	28.5%	27.0%	28.8%	29.9%	29.4%	21.5%	19.7%	20.5%	19.7%
Carbon Monoxide, %	2.5%	3.0%	5.9%	5.5%	9.0%	1.7%	29.7%	32.3%	32.3%	33.7%

D   Volume of gas measurements for cylindrical cells

State of Charge, %	30	30	50	50	70	70	100	100	100	100
Initial Voltage, V	3.75	3.69	3.77	3.77	3.88	3.88	4.14	4.13	4.15	4.15
Intended heating rate, °C/min	5	20	5	20	5	20	5	10	15	20
Actual heating rate, °C/min	4.8	21.0	6.5	23.7	5.1	22.0	4.9	10.2	16.6	24.0
Total, L	1.07	1.19	1.63	1.60	2.16	2.53	3.56	3.87	3.93	3.75
1-butene, L	0.011	0.027	0.000	0.019	0.023	0.022	0.029	0.033	0.037	0.034
Butane, L	0.001	0.002	0.018	0.002	0.010	0.000	0.000	0.000	0.000	0.000
Propane, L	0.002	0.006	0.007	0.007	0.007	0.005	0.007	0.007	0.007	0.017
Propylene, L	0.007	0.012	0.022	0.026	0.030	0.028	0.058	0.054	0.063	0.057
Ethane, L	0.005	0.007	0.011	0.013	0.016	0.012	0.017	0.019	0.015	0.017
Ethylene & Acetylene, L	0.01	0.01	0.03	0.03	0.04	0.05	0.12	0.13	0.15	0.14
Methane, L	0.02	0.02	0.06	0.07	0.09	0.08	0.11	0.13	0.12	0.12
Hydrogen, L	0.06	0.07	0.24	0.20	0.30	0.37	0.50	0.53	0.56	0.55
Total Hydrocarbon Content, L	0.25	0.29	0.33	0.34	0.37	0.36	0.46	0.49	0.50	0.47
Oxygen, L	0.03	0.05	0.04	0.04	0.04	0.13	0.06	0.04	0.07	0.09
Carbon Dioxide, L	0.36	0.34	0.44	0.46	0.65	0.74	0.76	0.76	0.80	0.74
Carbon Monoxide, L	0.03	0.04	0.10	0.09	0.19	0.04	1.06	1.25	1.27	1.26