Overheat and Overcharge

Thermal Runaway Vent Gas Analysis of Lithium Manganese Oxide Cells

Presented to: <Audience>

By: Matthew Karp

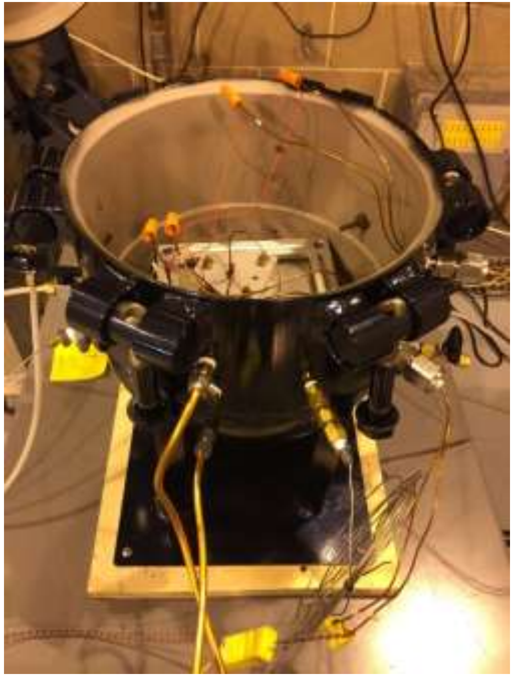
Date: April 27, 2017

Scope of Test

- All tests were conducted with CR123a 3V lithium manganese dioxide ($LiMnO_2$) spiral cell primary batteries
- The cells were forced into thermal runaway using the overheat and overcharge method
- Tests were conducted in a 21.7L pressure vessel, where a pressure transducer and thermocouple were used to quantify the gas release from each lithium battery cell
- The maximum temperature rise and peak pressure rise were annotated

Test Equipment

- Experiments were conducted in a 21.7L stainless steel pressure vessel
- Temperature measurements were taken at the battery's approximate vertical center with an 1/16" thermocouple
- Flexible heaters were used to bring the batteries into thermal runaway while conducting the overheat method
- A DC power supply was used to overcharge the batteries while conducting the overcharge method



Test Apparatus

Test Procedure

I. The pressure vessel is vacuumed to less than 0.1 psia

II. The pressure vessel is filled to 14.7 psia with nitrogen gas

    I. Nitrogen gas is used because of its inert properties and to prevent interference with the gas analyzers

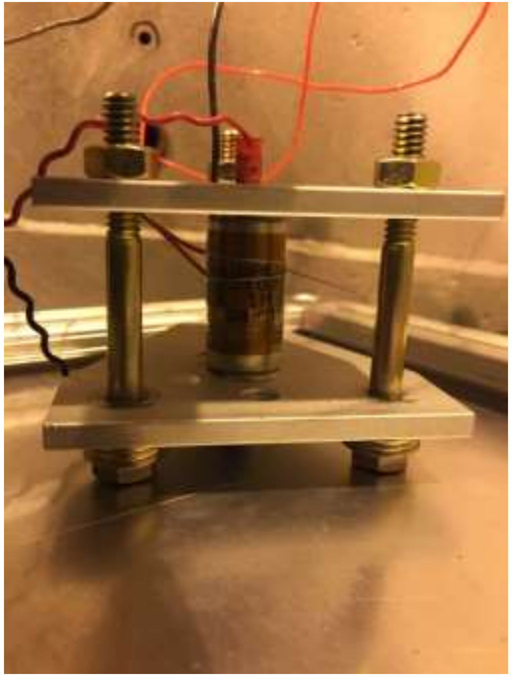
III. The battery is forced into thermal runaway and the vent gases are released

IV. More nitrogen is added to the pressure vessel until the pressure reaches 18 psia, this creates a positive pressure to feed into gas analyzers

V. The samples are analyzed for gas composition

Overheat with Battery Holder

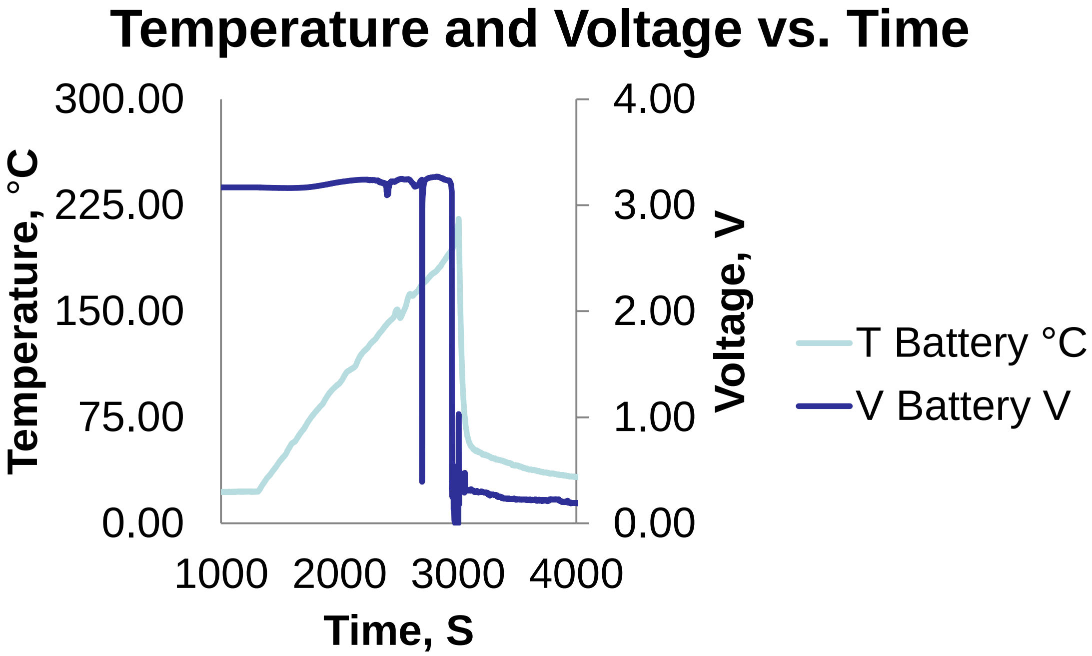
- The batteries were heated at 5-10 °C/min until thermal runaway is induced
- The battery cells were wrapped in a flexible heater
- Temperature was measured at the vertical center of the cell case
- Tests were conducted with the battery holder, so that the battery's voltage can be measured throughout testing



Battery holder setup

Temperature and Voltage

- As the battery's temperature is increased the voltage increases from 3.17V to 3.24V
- As the battery is brought into thermal runaway the battery's voltage drops to approximately 0V



The above graph shows how the voltage drops as the battery is brought into thermal runaway

Federal Aviation Administration

Overheat with Battery Holder

- The battery holder prevents the battery vent mechanism from activating
- This causes the internal pressure to increase and the battery to fragment

Fragmented battery after overheat method

Overheat without Battery Holder

•The batteries were heated at 5-10 °C/min until thermal runaway is induced

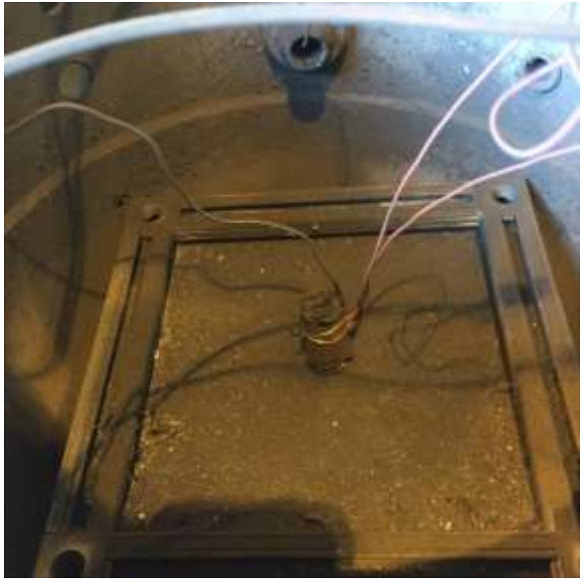
•The battery cells were wrapped in a flexible heater

•Temperature was measured at the vertical center of the cell case

No battery holder setup

Overheat without Battery Holder

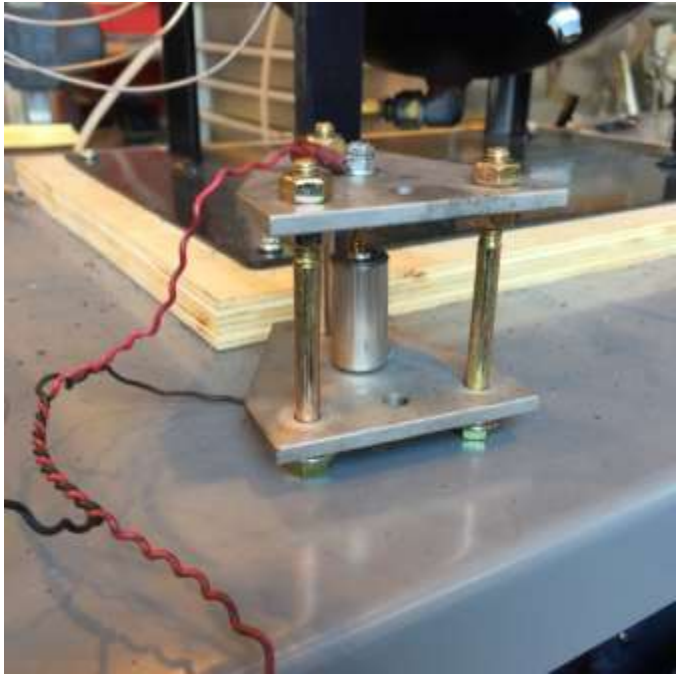
- Without the battery holder, the battery vent mechanism was able to function properly
- The battery's internal components did not fragment or eject



Post test, no battery holder

DC Overcharge Method

- The DC overcharge method did not consistently bring the tested battery cell into thermal runaway.
- All DC voltage tests were conducted in the modified battery
    - The modified battery holder has a spring in place between the positive terminal of the battery and the positive charge terminal plate. This is used to allow the venting mechanism to function



DC overcharge setup

DC Overcharge Method

- What did work
  - 6V charge for 4 to 5 hours, followed by 1 to 2 days rest without charge, then overcharge to 30V
  - Increasing the charge by 6V, starting from 6V to 30V, with 30 minutes hold on/off increments
  - Increasing the charge by 15V, starting from 15V to 30V, with 30 minutes hold on/off increments, followed by 1 day rest, then charge to 30V

DC Overcharge Method

- The most effective DC overcharge method in forcing the CR123a 3V LiMnO2 batteries into thermal runaway is utilizing on/off cycles and extended rest periods.
    - Spike in temperature and pressure
    - Release of thermal runaway vent gases

DC overcharge post thermal runaway

DC Overcharge Method

- What did not work
  - Thermal runaway was not able to be forced by increasing the voltage from 1.5x nominal voltage to 10x nominal voltage in 1, 5, and 10 minute increments with varying steps in between.
  - Thermal runaway was not able to be induced by maintaining a constant charge rate of 1C nor at 3C.

DC Overcharge Method

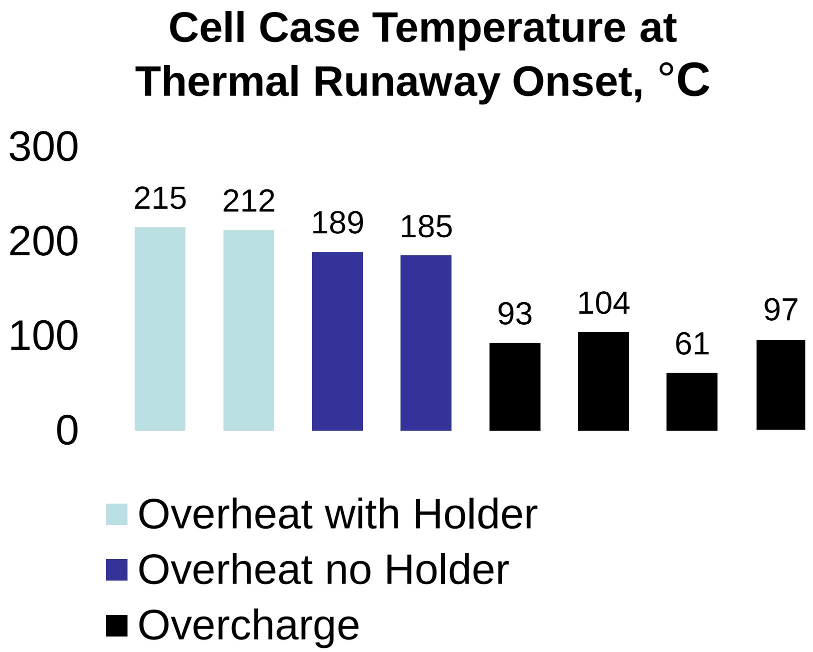
•With these methods of testing the PTC switch activated and eventually led to a non energetic failure

- Battery deformed
- Vented
- No rapid rise in temperature nor pressure

DC overcharge no thermal runaway

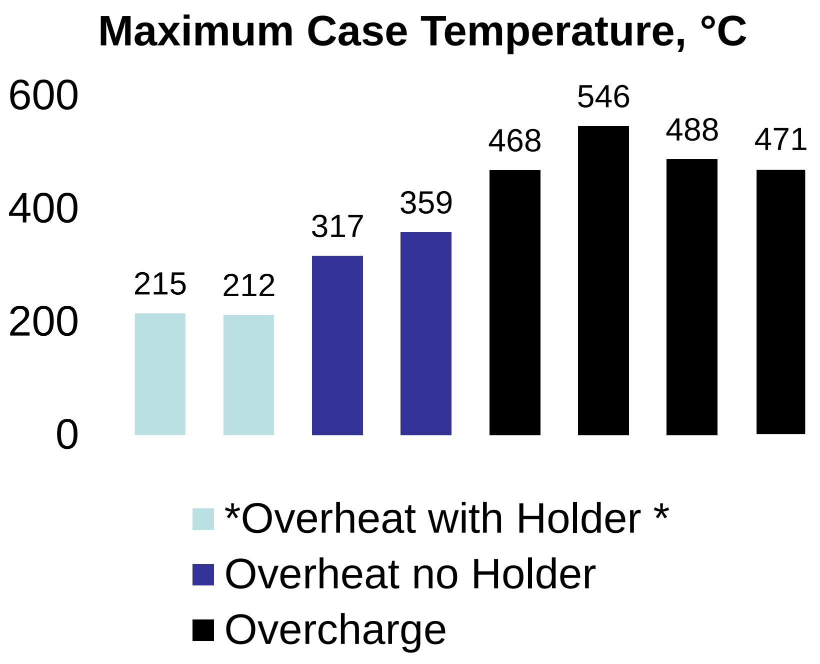
Results, Cell Case Temperature at Onset of Thermal Runaway

- The overcharge method brought the cell into thermal runaway with the lowest case temperature
- The average case temperature at thermal runaway was **213°C** for the overheating with battery holder method, **187°C** for the overheating without battery holder method, and **89°C** for the overcharge method
- The overcharge method yielded the lowest case temperature at the onset on thermal runaway because it is heated from within



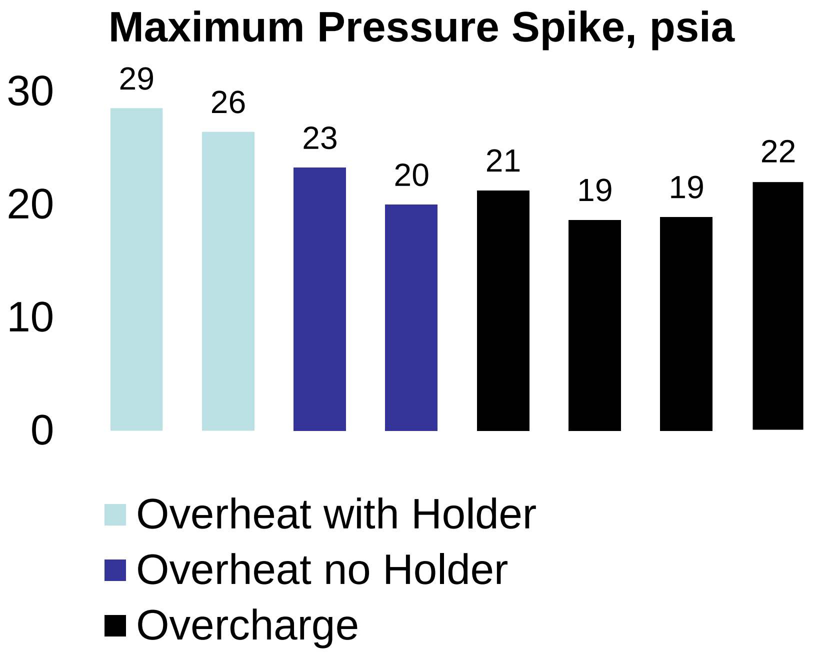
Results, Max Case Temperature

- The overcharge method produced the maximum measurable case temperature
- The average maximum case temperature was **213°C** for the overheating with battery holder method, **338°C** for the overheating without battery holder method, and **493°C** for the overcharge method
- *The maximum case temperature for the overheat with battery holder method was not measurable because the cell fragmented upon thermal runaway*



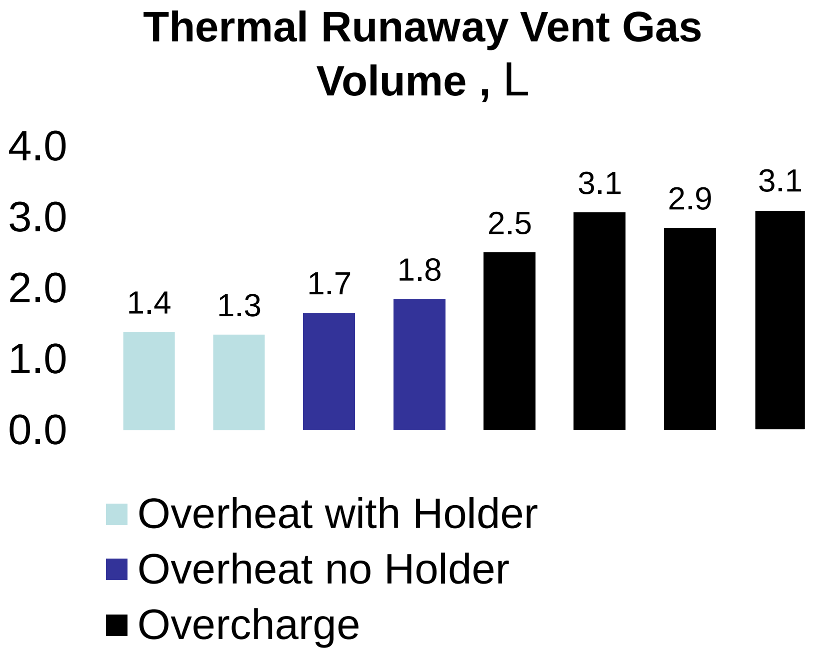
Results, Max Pressure Rise

- The overheat with battery holder method produced the maximum pressure spike
    - This is because the battery holder prevented the venting mechanism from activating
- The average maximum pressure spike was **28 psia** for the overheating with battery holder method, **22 psia** for the overheating without battery holder method, and **20 psia** for the overcharge method



Results, Thermal Runaway Vent Gas Volume, L

- The overcharge method produced the highest volume of thermal runaway vent gas
- The average volume of vent gas was **1.4L** for the overheating with battery holder method, **1.8L** for the overheating without battery holder method, and **2.9L** for the overcharge method



Tabulated Averaged Results

	Maximum Case Temperature, °C	Case Temperature at Thermal Runaway Onset, °C	Maximum Pressure Rise, psia	Thermal Runaway Vent Gas Volume, L
Overheat with Holder Method	213	213	27.5	1.4
Overheat no Holder Method	338	187	21.6	1.8
Overcharge Method	493	89	20.2	2.9

Conclusion

- The overheat method is the most consistent in forcing the CR123a 3V LiMnO2 cell into thermal runaway
- Applying pressure to the top and bottom of the cell while overheating causes the vent mechanism to fail. This creates the highest pressure rise as the battery explodes
- The overcharge method is inconsistent in forcing the cell into thermal runaway
- The overcharge method produces the highest measureable cell case temperature and the highest volume of vent gases

Heat Rate and Vent Gas

Thermal Runaway Vent Gas Analysis of 18650 Cells at Various Heat Rates

Presented to: <Audience>

By: Matthew Karp

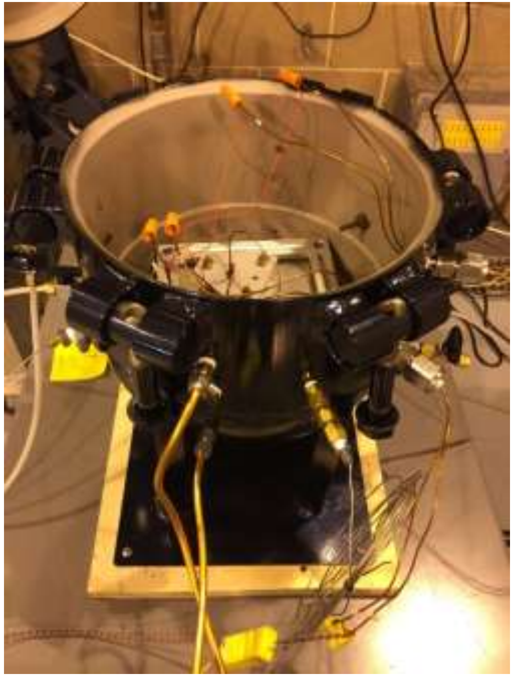
Date: April 27, 2017

Scope of Test

- All tests were conducted with 18650 sized 3.7V 2600mAh lithium ion rechargeable cells at 30% state of charge (SOC)
- The cells were forced into thermal runaway using the overheat method at various heat rates
- Tests were conducted in a 21.7L pressure vessel where a pressure transducer and thermocouple were used to quantify the gas release from each lithium battery cell
- The gases were collected and analyzed for percent hydrogen, carbon monoxide, carbon dioxide, oxygen, and total hydrocarbon content (THC)
- The maximum temperature rise and peak pressure rise were annotated

Test Equipment

- Experiments were conducted in a 21.7 liter stainless steel pressure vessel
- Gas chromatography (GC) with thermal conductivity detector (TCD) to measure H_2
- Paramagnetic sensor (pO_2) to measure CO/O_2
- Non-destructive infrared radiation to measure CO_2
- Flame ionization detector (FID) to measure THC



Test Apparatus

Test Procedure

- The pressure vessel is vacuumed to less than 0.1 psia
- The pressure vessel is filled to 14.7 psia with nitrogen gas
- Nitrogen gas is used because of its inert properties and to prevent interference with the gas analyzers
- The battery is forced into thermal runaway by overheating and the vent gases are released
- More nitrogen is added to the pressure vessel until the pressure reaches 18 psia, this creates a positive pressure to feed into gas analyzers
- The samples are analyzed for gas composition

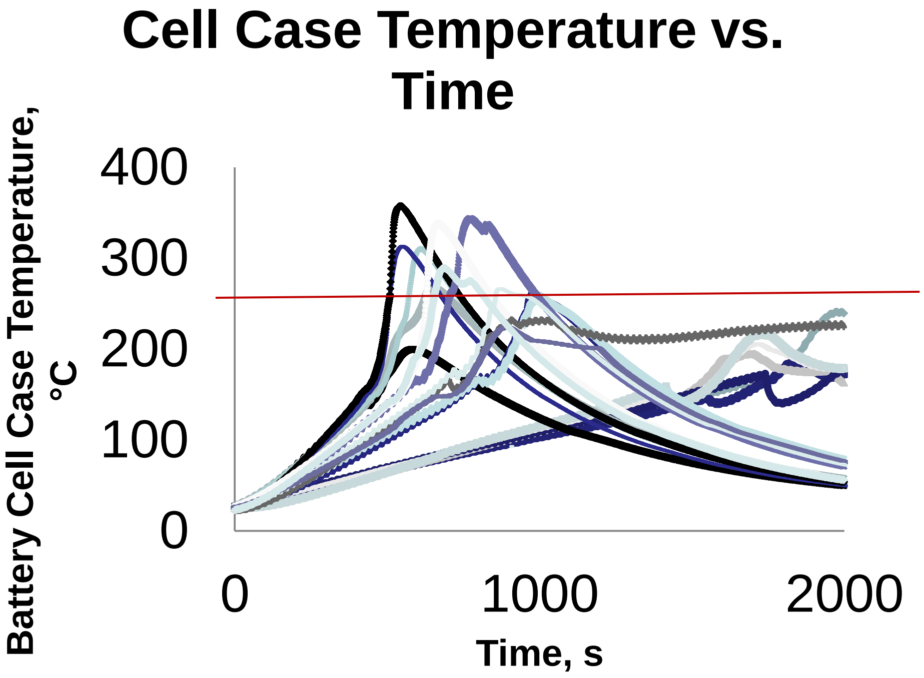
Test Procedure

- The batteries were heated at various heating rates until the cell case reached 200°C and were held at 200°C for 180 minutes or until thermal runaway occurs
- The battery cells were wrapped in a flexible heater
- Temperature was measured at the vertical center of the cell case
- The temperature heating rate was controlled by a Proportional-Integral-Derivative (PID) controller

No battery holder setup

Heat Rate and Case Temperature

- The heating rate is controlled with a Proportional-Integral-Derivative (PID) controller
    - The heat rates were reproducible
- Heating rates at or above 15°C/min were more likely to cause a more violent thermal runaway reaction
    - Marked by higher volume of vent gas and higher temperatures

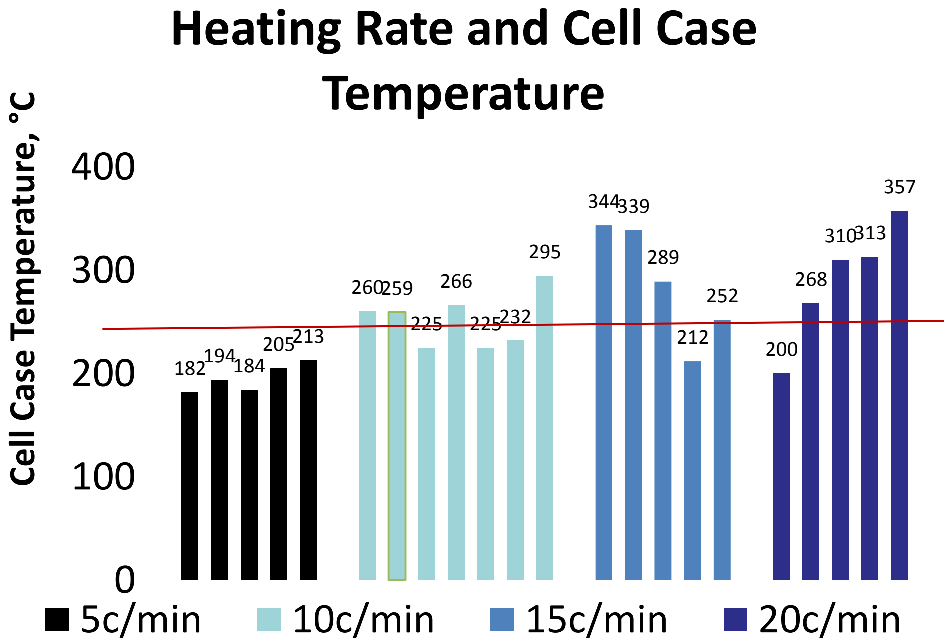


Heat Rate and Case Temperature

- Heating rates at or above 15°C/min were more likely to cause the cell case temperature to heat in excess of 250°C than heating rates below 15°C/min

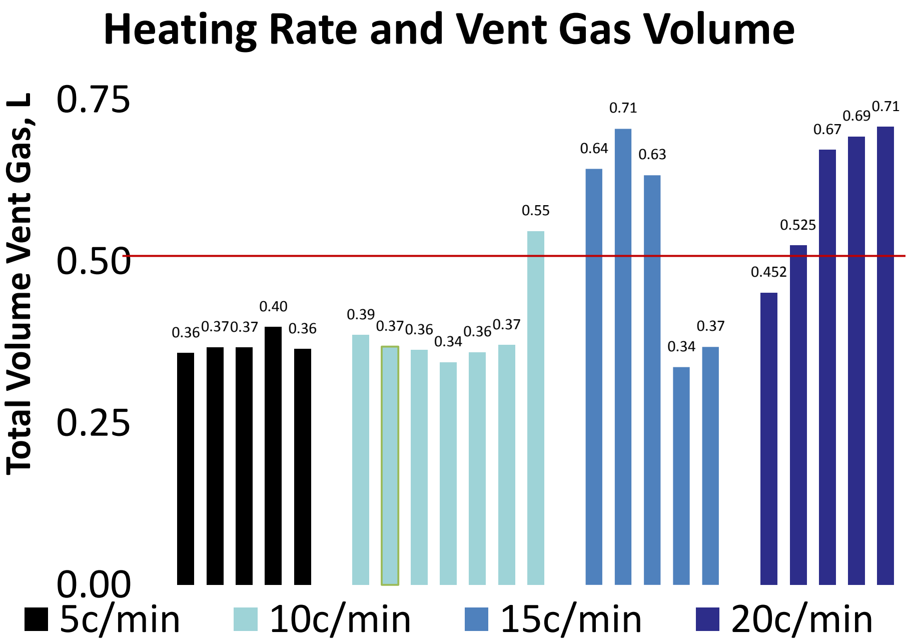
- **8/10 tests** (80%) at or above 15°C/min yielded case temperatures above 250°C

- **5/12 tests** (42%) below 15°C/min yielded case temperatures above 250°C



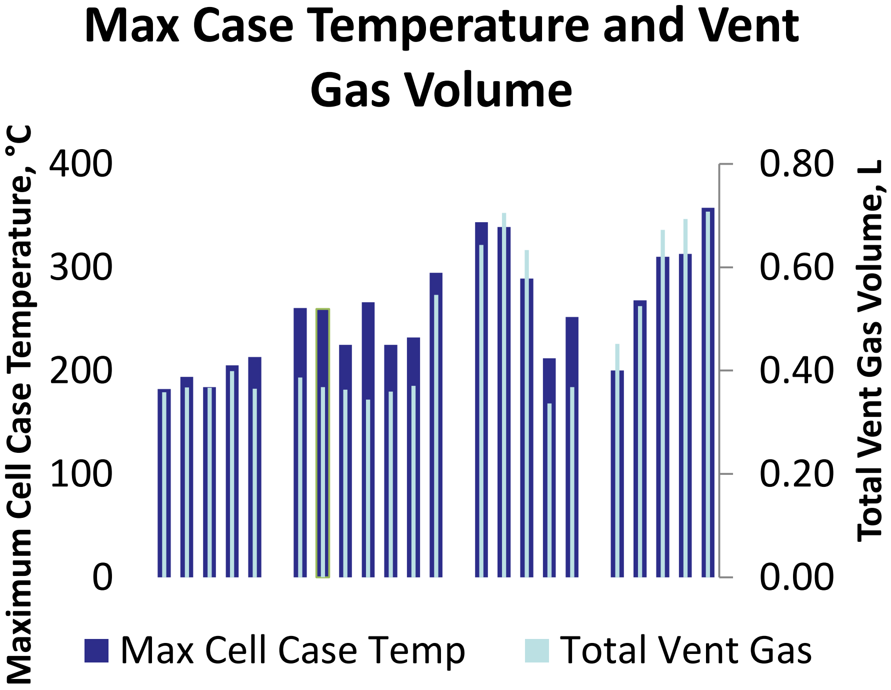
Heat Rate and Vent Gas Volume

- Heating rates at or above 15°C/min were more likely to produce greater than 0.5L of vent gas than heating rates below 15°C/min
- **7/10 tests** (70%) at or above 15°C/min yielded greater than 0.5L of vent gas
- **1/12 tests** (8%) below 15°C/min yielded case temperatures above 250°C



Heat Rate and Violent Reactions

- A **violent reaction** is defined as maximum temperature **above 250°C** and **over 0.5L** of vent gas release
- **0/5 tests (0%) at 5°C/min** had a violent reaction
- **1/7 tests (14%) at 10°C/min** had a violent reaction
- **3/5 tests (60%) at 15°C/min** had a violent reaction
- **4/5 tests (80%) at 20°C/min** had a violent reaction



Theory

•The slower heating rate allows more time for the electrolyte inside of the cell to boil and vent

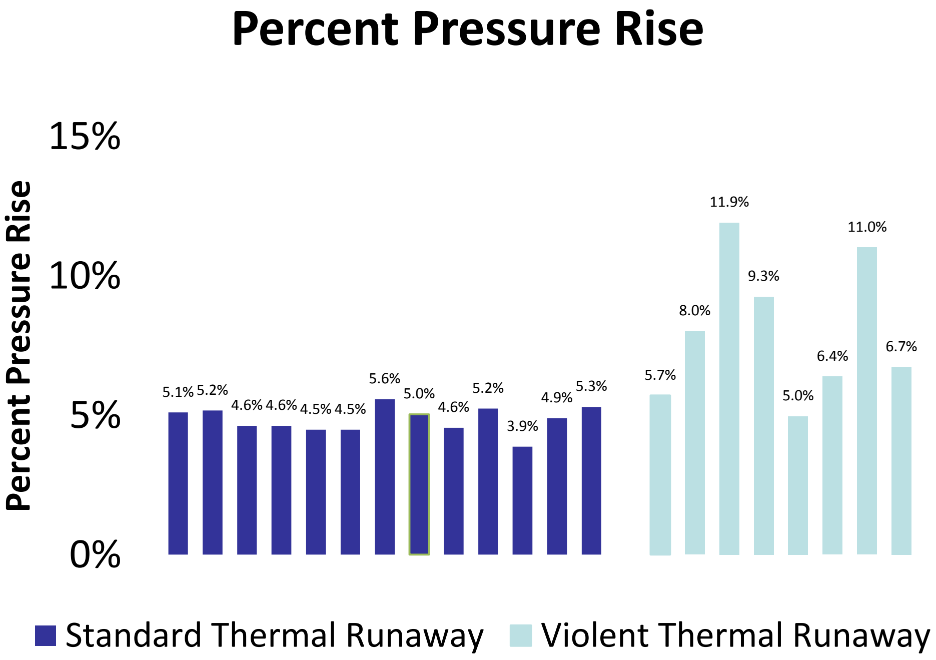
•The faster heating rate brings the battery cell into thermal runaway at a faster rate.

- •Therefore, more of the electrolyte remains to be used as a form of potential energy

Percent Pressure Rise, %

- The violent thermal runaway reactions produce a higher pressure rise over original pressure than the standard thermal runaway reaction

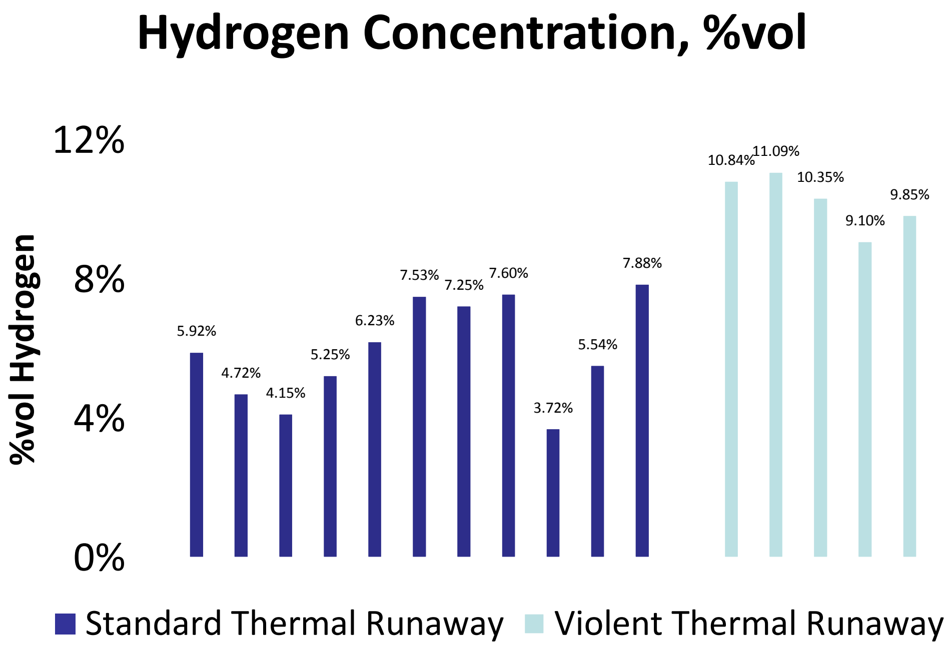
- The violent thermal runaway reaction has an average of **8.0%** and a maximum of **11.9% pressure rise** compared to an average of **4.9%** and a maximum of **5.6% pressure rise** in a standard thermal runaway reaction



Hydrogen Concentration, %vol

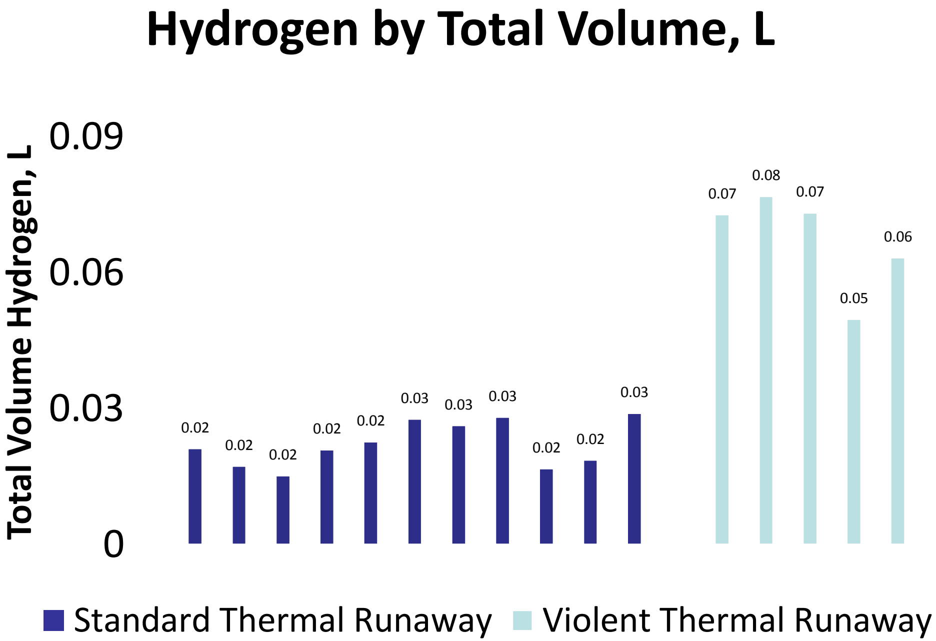
- The violent thermal runaway reactions produce a higher concentration of hydrogen by volume than the standard thermal runaway reaction

- The violent thermal runaway reaction has an average of **10.25%vol hydrogen** compared to **5.98%vol hydrogen** in a standard thermal runaway reaction



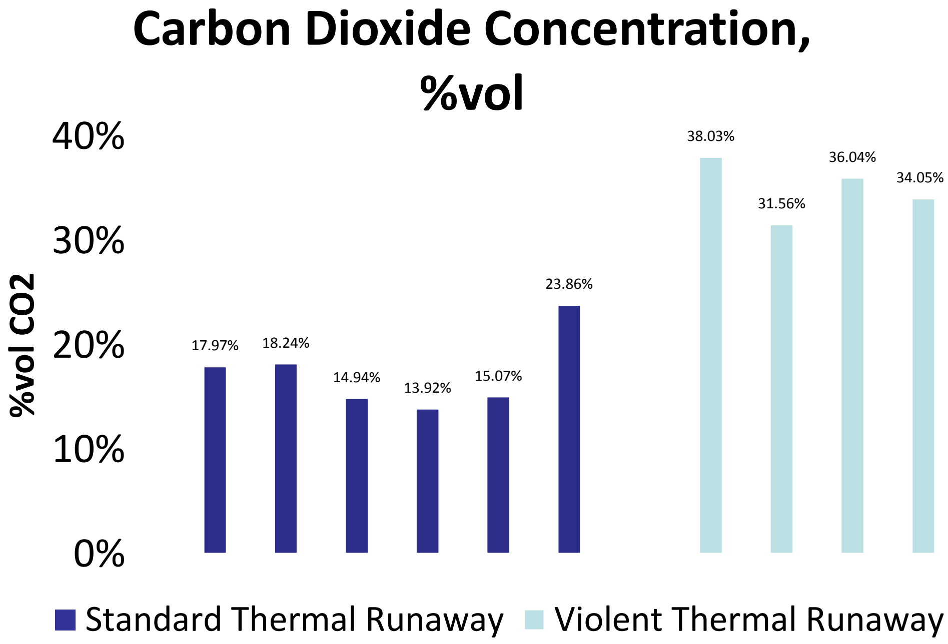
Total Volume of Hydrogen, L

- The violent thermal runaway reactions produce a greater total volume of hydrogen than the standard thermal runaway reaction
- The violent thermal runaway reaction has an average of **0.067L hydrogen** compared to **0.022L hydrogen** in a standard thermal runaway reaction



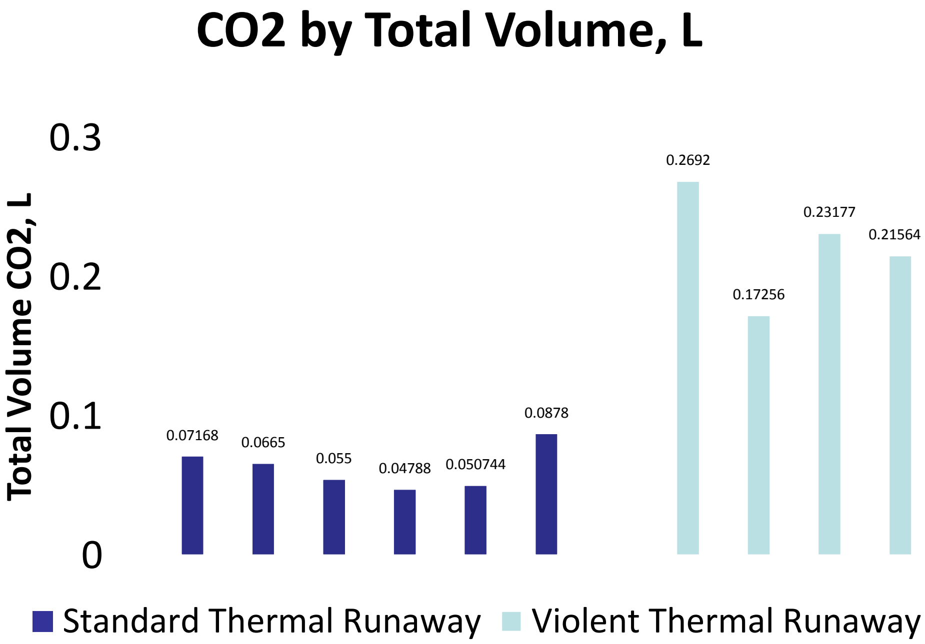
Carbon Dioxide Concentration, %vol

- The violent thermal runaway reactions produce a higher concentration of carbon dioxide by volume than the standard thermal runaway reaction
- The violent thermal runaway reaction has an average of **34.92%vol carbon dioxide** compared to **17.33%vol carbon dioxide** in a standard thermal runaway reaction



Total Volume of Carbon Dioxide, L

- The violent thermal runaway reactions produce a greater total volume of carbon dioxide than the standard thermal runaway reaction
- The violent thermal runaway reaction has an average of **0.063L hydrogen** compared to **0.22L hydrogen** in a standard thermal runaway reaction



Le Chatelier's Mixing Rule [1]

1. Calculate the constituents of the mixed gas neglecting the presence of air.
2. Create binary gases by combining part of or all of a nonflammable gas with one or more flammable gas and recalculate gas constituents.
3. Record the flammability limits of the mixtures constituents from tables or curves.
4. Calculate the flammability limits of the mixed gas using Le Chatelier's mixing rule equation

$$L = \frac{100}{\frac{p_1}{N_1} + \frac{p_2}{N_2} + \frac{p_3}{N_3} + \cdots}$$

Where L is either the LFL or the UFL of the gas mixture, p_1, p_2, p_3 … are the percentages of the mixtures constituents, and N_1, N_2, N_3 … are either the LFL or UFL of the individual constituents [1].

*Note that if the constituents do not add up to 100 percent, one could substitute the actual total percentage.

Le Chatelier's Mixing Rule

- The gas concentrations used for the calculation of the lower flammability limit were measured and averaged. The results are tabulated
- The lower flammability limit (LFL) can be calculated using Le Chatelier's Mixing Rule

	Violent Thermal Runaway	Standard Thermal Runaway
carbon dioxide	17.33%	34.92%
carbon monoxide	4.71%	3.84%
ethane	0.56%	1.11%
ethylene	2.16%	1.67%
hydrogen	5.98%	10.25%
methane	1.02%	1.27%
propane	0.08%	0.12%
propylene	0.13%	0.43%

Le Chatelier’s Mixing Rule, LFL

- The LFL is calculated to be **21.2%** for a violent thermal runaway and **27.7%** for a standard thermal runaway event
- With the LFL and the total volume of vent gas, we can calculate the total volume of vent gas and air mixture that will become flammable per single thermal runaway event
- The violent thermal runaway vent gas is a more flammable mixture than the standard thermal runaway vent gas

	Calculated LFL	Average Total Volume of Measured Vent Gas, L	Total Volume of Potentially Flammable Mixture with Air, L
Violent Thermal Runaway	21.2%	0.64	3.02
Standard Thermal Runaway	27.7%	0.37	1.34

Conclusion

- Heating rates at or above 15°C/min were more likely to cause a more violent thermal runaway reaction and is marked by:
    - Greater volume of vent gas
    - More flammable vent gas
    - Greater cell case temperature
    - Greater percent pressure rise
- The amount of vent gas released from an 18650 cell depends on how much electrolyte is boiled and vented prior to thermal runaway

References

[1] Coward, Hubert Frank, and George William Jones. *Limits of flammability of gases and vapors*. No. BM-BULL-503. Bureau of Mines Washington DC, 1952.

Contact Information

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Heat Rate and Vent Gas

Thermal Runaway Vent Gas Analysis of Pouch Cells at Various Heat Rates

Presented to: <Audience>

By: Matthew Karp

Date: April 27, 2017

Scope of Test

- All tests were conducted with 3.7V 2500mAh polymer lithium ion rechargeable pouch cells at 30% state of charge (SOC)
- The cells were forced into thermal runaway using the overheat method at various heating rates
- Tests were conducted in a 21.7L pressure vessel where a pressure transducer and thermocouple were used to quantify the gas release from each lithium battery cell
- The gases were collected and analyzed for percent hydrogen, carbon monoxide, carbon dioxide, oxygen, and total hydrocarbon content (THC)
- The maximum temperature rise and peak pressure rise were annotated

Test Equipment

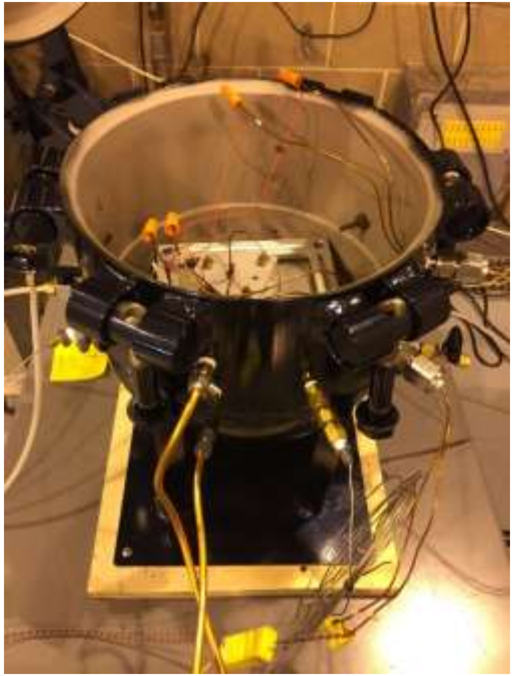
•Experiments were conducted in a 21.7 liter stainless steel pressure vessel

•Gas chromatography (GC) with thermal conductivity detector (TCD) to measure H_2

•Paramagnetic sensor (pO_2) to measure CO/O_2

•Non-destructive infrared radiation to measure CO_2

•Flame ionization detector (FID) to measure THC

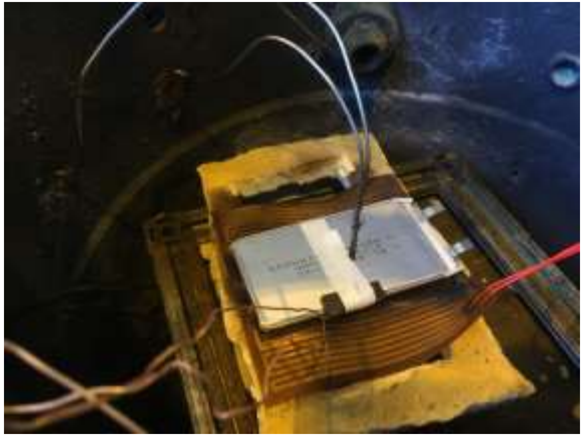


Test Apparatus

Test Procedure

- The pressure vessel is vacuumed to less than 0.1 psia
- The pressure vessel is filled to 14.7 psia with nitrogen gas
- Nitrogen gas is used because of its inert properties and to prevent interference with the gas analyzers
- The battery is forced into thermal runaway by overheating and the vent gases are released
- More nitrogen is added to the pressure vessel until the pressure reaches 18 psia, this creates a positive pressure to feed into gas analyzers
- The samples are analyzed for gas composition

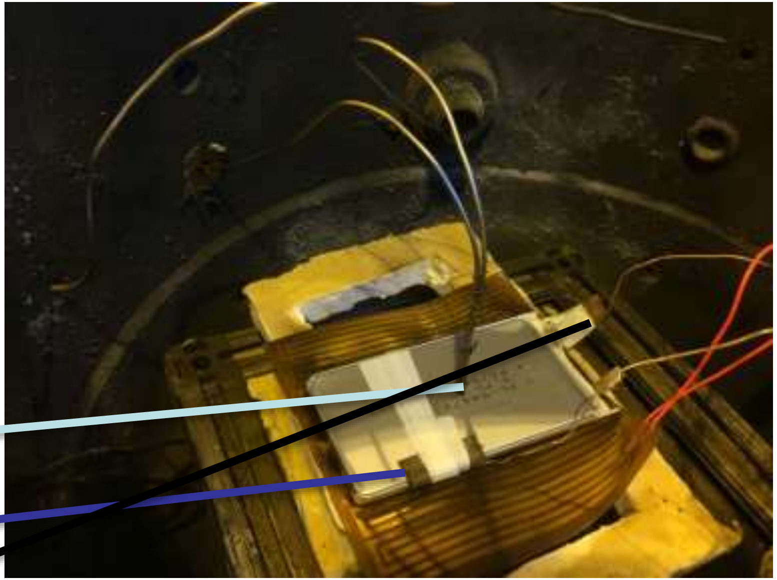
Test Procedure



- The batteries were heated at various heating rates until the cell reached 200°C and held at 200°C for 180 minutes or until thermal runaway is induced
- The battery cells were placed on top of a flexible heater
- Temperature was measured at the various locations
- The temperature heating rate was controlled by a Proportional-Integral-Derivative (PID) controller

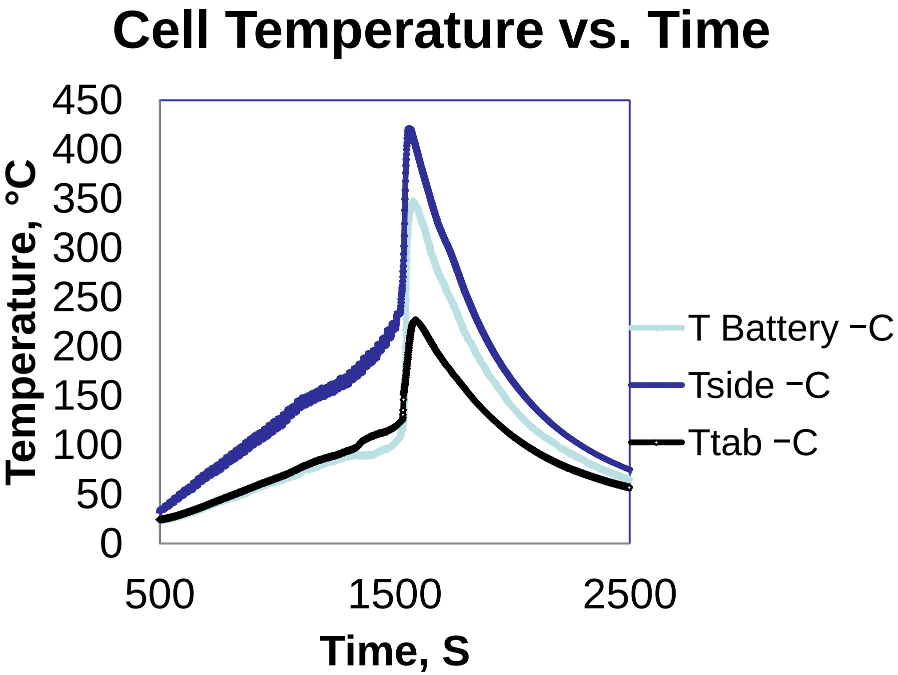
Thermocouple Location

- Thermocouples where placed at three separate locations
- The goal was to find which location yields the greatest temperatures
- The locations where
    - On top (T Battery)
    - On the side (Tside)
    - On the charging tab (Ttab)



Results, Thermocouple Location

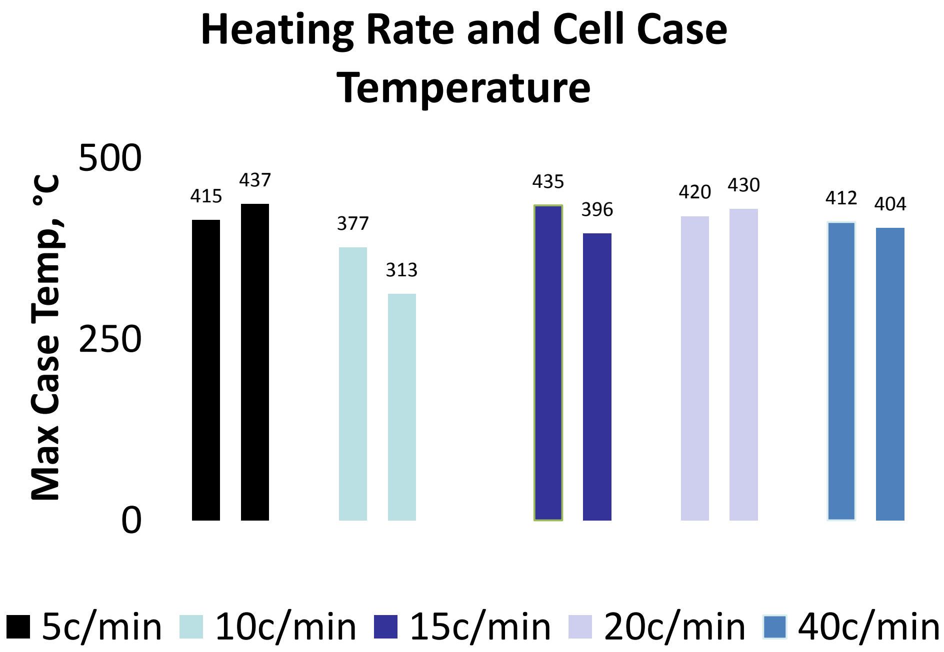
- The thermocouple on the side (Tside) heats at the fastest rate and yields the greatest maximum temperature.
- The thermocouple on top (T Battery) and the thermocouple on the tab (Ttab) heat at approximately the same rate. However, the top thermocouple yielded a greater maximum temperature.
- For the rest of the tests, the side thermocouple location is used.



Heat Rate and Case Temperature

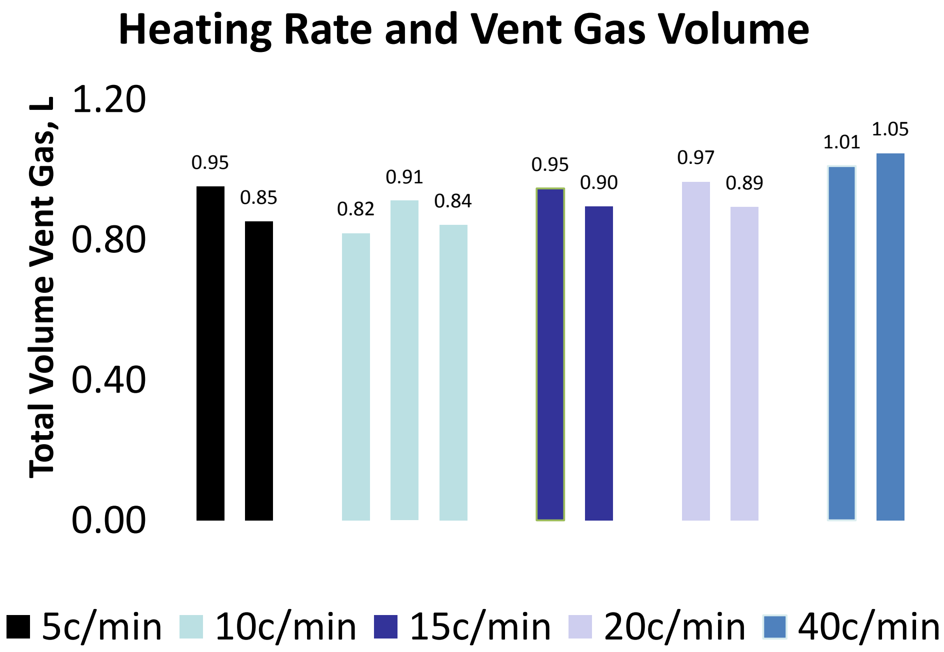
- Heat rate does not have a significant effect on the maximum case temperature

- Averages are:
    - **426°C** for 5°C/min
    - **345°C** for 10°C/min
    - **416°C** for 15°C/min
    - **425°C** for 20°C/min
    - **408°C** for 40°C/min



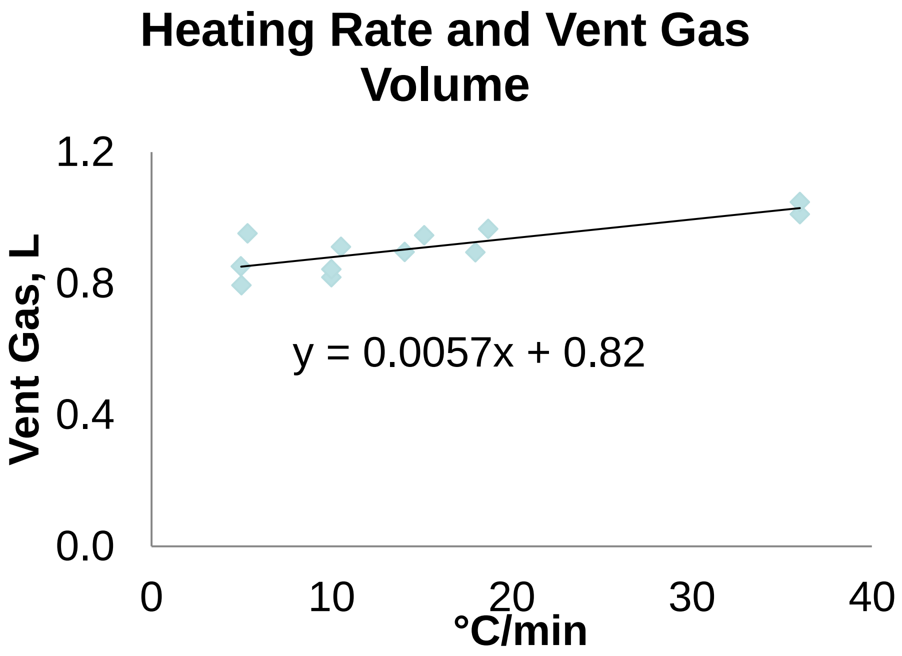
Heat Rate and Vent Gas Volume

- Heat rate does have a minor effect on the total vent gas volume
- As the heat rate increases, the total vent gas increases
- The amount of total vent gas increase in insignificant
- Averages are **0.9L** for 5°C/min, **0.86L** for 10°C/min, **0.93L** for 15°C/min, **0.93L** for 20°C/min, and **1.03L** for 40°C/min



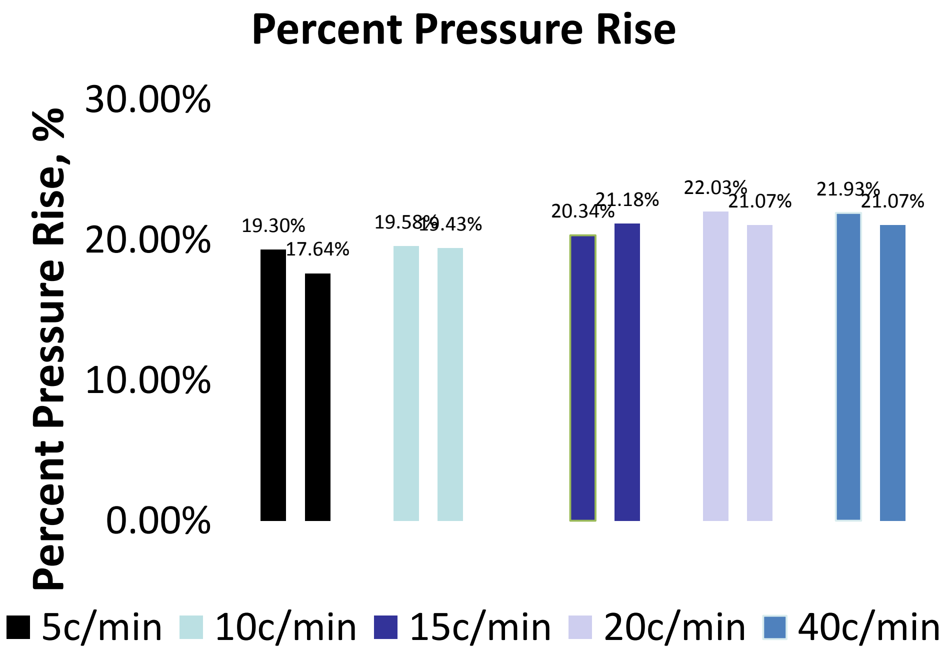
Heat Rate and Vent Gas Volume

- The slope of the temperature and time from 30°C to 140°C is measured to determine the actual heat rate in °C/min.
- It is found that for every 1°C/min the heat rate increases, there is an increase of 0.0057L of vent gas.

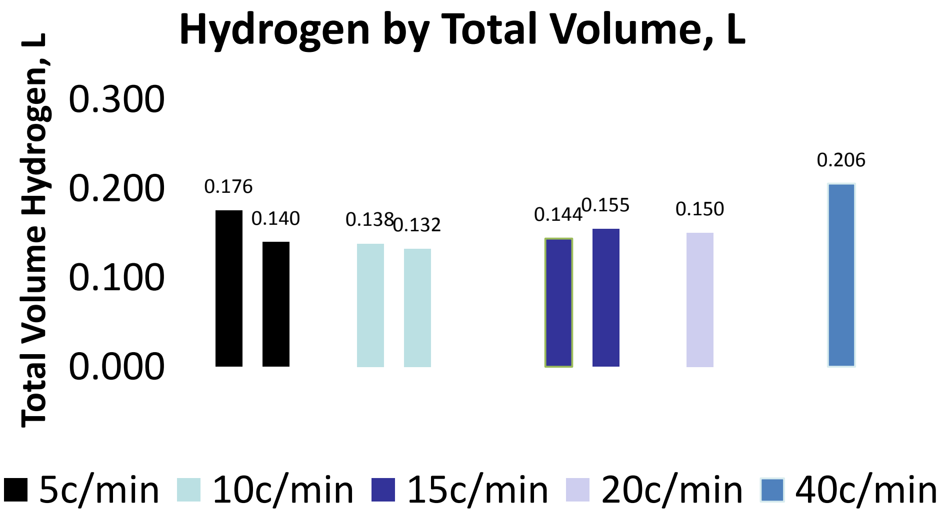


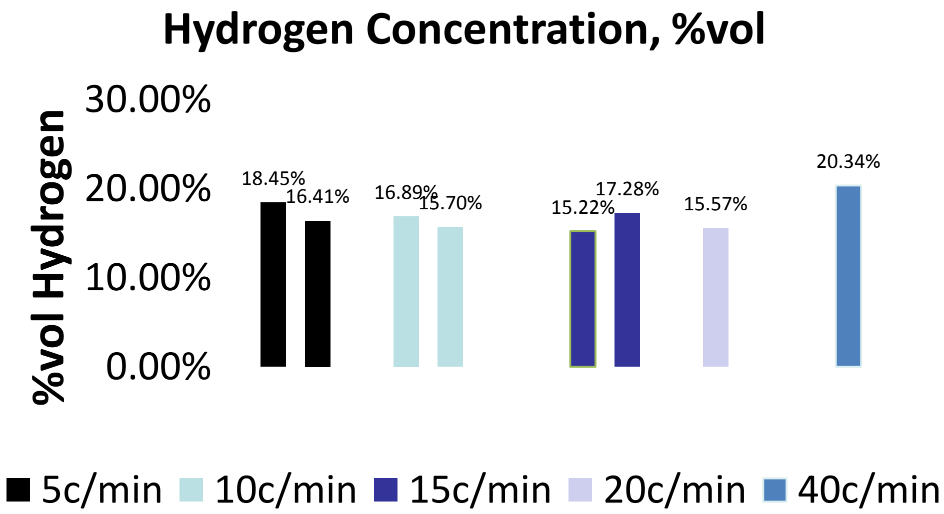
Percent Pressure Rise, %

- Heat rate does not have a significant effect on the percent pressure rise over original pressure
- Averages are:
    - **18.47%** for 5°C/min
    - **19.64%** for 10°C/min
    - **20.76%** for 15°C/min
    - **21.58%** for 20°C/min
    - **21.50%** for 40°C/min



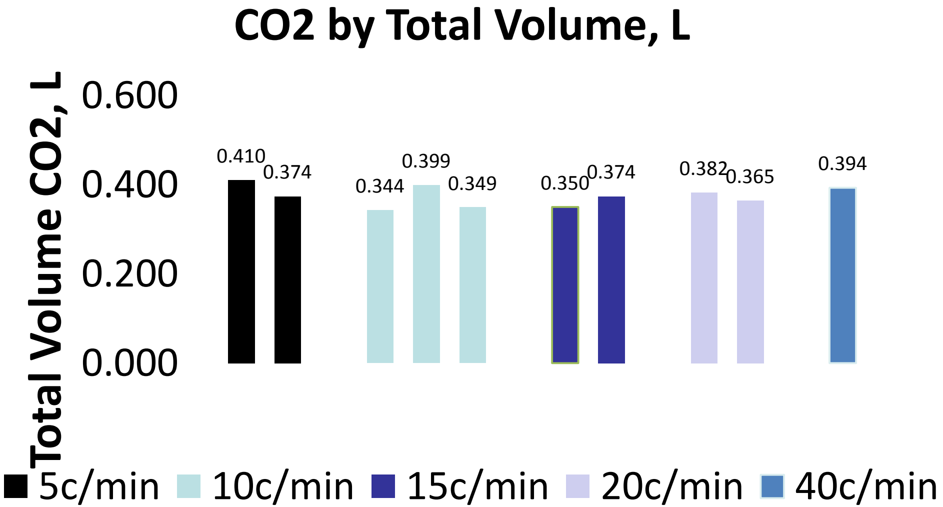
Hydrogen Concentration and Volume

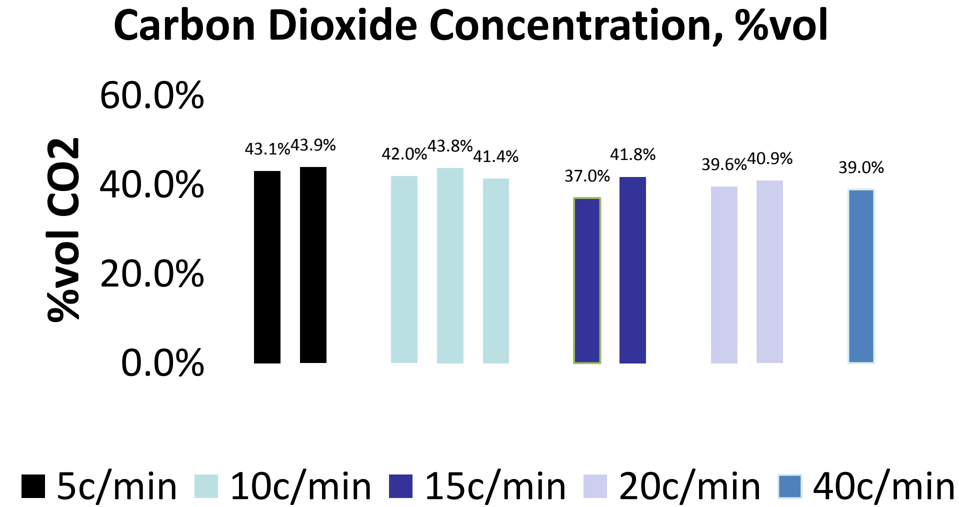




•Heat rate does not have a significant effect on the hydrogen concentration nor the total volume per thermal runaway event

Carbon Dioxide Concentration and Volume





•Heat rate does have a significant effect on the carbon dioxide concentration nor the total volume per thermal runaway event

Le Chatelier's Mixing Rule [1]

1. Calculate the constituents of the mixed gas neglecting the presence of air.
2. Create binary gases by combining part of or all of a nonflammable gas with one or more flammable gas and recalculate gas constituents.
3. Record the flammability limits of the mixtures constituents from tables or curves.
4. Calculate the flammability limits of the mixed gas using Le Chatelier's mixing rule equation

$$L = \frac{100}{\frac{p_1}{N_1} + \frac{p_2}{N_2} + \frac{p_3}{N_3} + \cdots}$$

Where L is either the LFL or the UFL of the gas mixture, p_1, p_2, p_3 … are the percentages of the mixtures constituents, and N_1, N_2, N_3 … are either the LFL or UFL of the individual constituents [1].

*Note that if the constituents do not add up to 100 percent, one could substitute the actual total percentage.

Le Chatelier's Mixing Rule

- Heat rate does not have a significant effect on the measured gas concentrations
- The gas concentrations used for the calculation of the lower flammability limit (LFL) were measured and averaged. The results are tabulated
- The LFL can be calculated using Le Chatelier's Mixing Rule

	Averaged Gas Concentration, %vol
carbon dioxide	41.24%
carbon monoxide	3.82%
ethane	1.35%
ethylene	3.72%
hydrogen	16.98%
methane	2.58%
propane	0.34%
propylene	3.75%

Le Chatelier's Mixing Rule, LFL

- The LFL is calculated to be **9.1%** for a thermal runaway event from a single 3.7V 2500mAh polymer lithium ion rechargeable pouch cells at 30% SOC
- With the LFL and the total volume of vent gas, we can calculate the total volume of vent gas and air mixture that will become flammable per single thermal runaway event
- A single cell can make **9.2L** of vent gas and air mixture flammable

	Calculated LFL	Average Total Volume of Measured Vent Gas, L	Total Volume of Potentially Flammable Mixture with air, L
Pouch Thermal Runaway	9.1%	0.92	9.23

Conclusion

- Heat rate does not have a significant effect on the thermal runaway event
    - No significant effect on the total volume of vent gas
    - No significant effect on the case temperature
    - No significant effect on the percent pressure rise
    - No significant effect on the measured gas concentrations nor volumes
- The average measured total vent gas volume is 0.92L
- The calculated LFL of the gas mixture is 9.1%

References

[1] Coward, Hubert Frank, and George William Jones. *Limits of flammability of gases and vapors*. No. BM-BULL-503. Bureau of Mines Washington DC, 1952.

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