Heat Rate and Vent Gas Analysis

Thermal Runaway Vent Gas Analysis of 18650 and Pouch Cells

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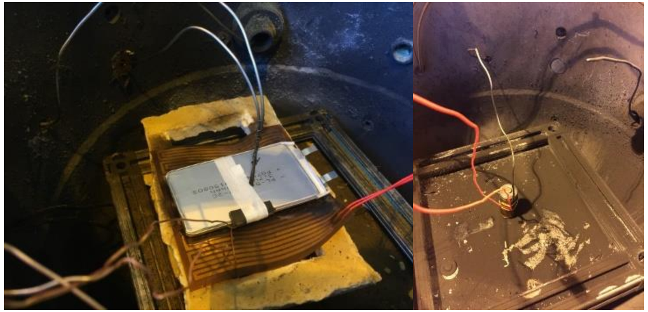
Objective

- The objective of the study is to determine if and how the heating rate affects the thermal runaway event

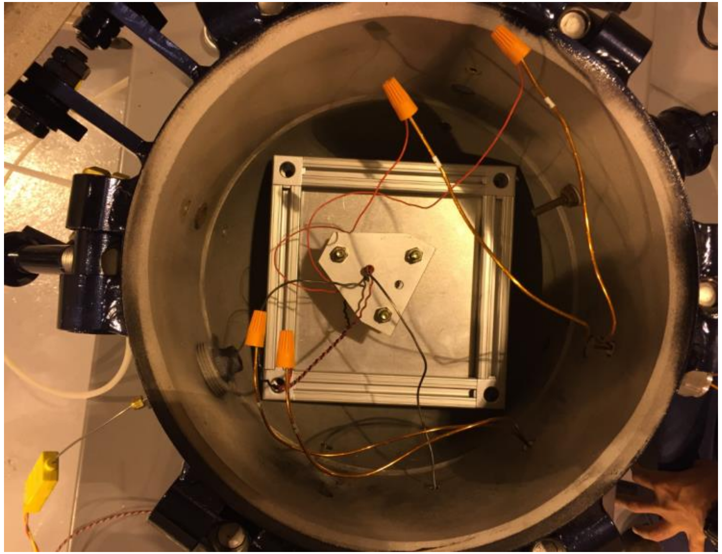
- The gases were collected and analyzed for percent hydrogen, carbon monoxide, carbon dioxide, oxygen, and total hydrocarbon content (THC)

- The maximum temperature rise and peak pressure rise were annotated



Scope of Test

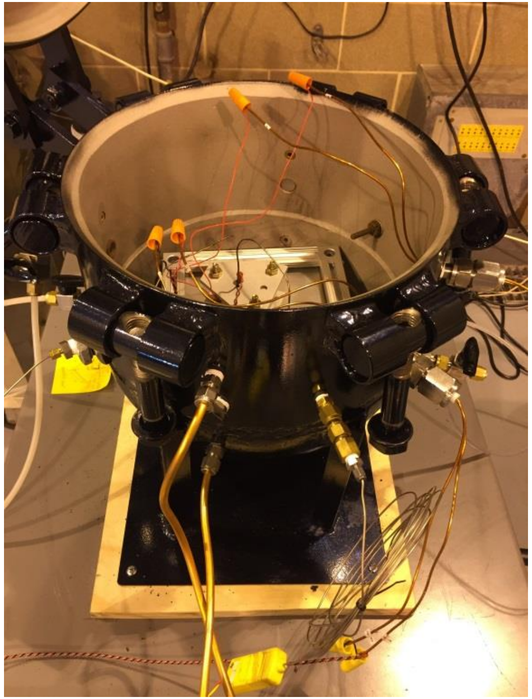
Heating Rate, °C/min	5	10	15	20
18650 $LiCoO_2$ 3.7V 2600mAh 30% SOC	x	x	x	x
Pouch Cell $LiCoO_2$ 3.7V 2500mAh 30% SOC	x	x	x	x



- 21.7L pressure vessel

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-dispersive infrared radiation (NDIR) to measure CO_2
- Flame ionization detector (FID) to measure total hydrocarbon content (THC)



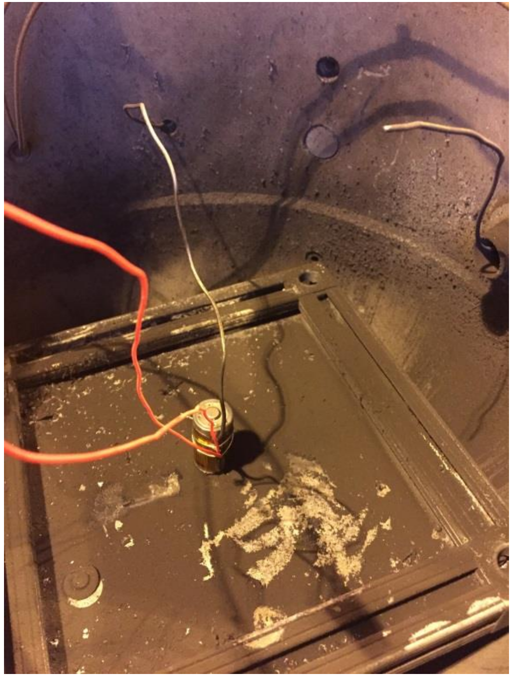
Test Apparatus

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

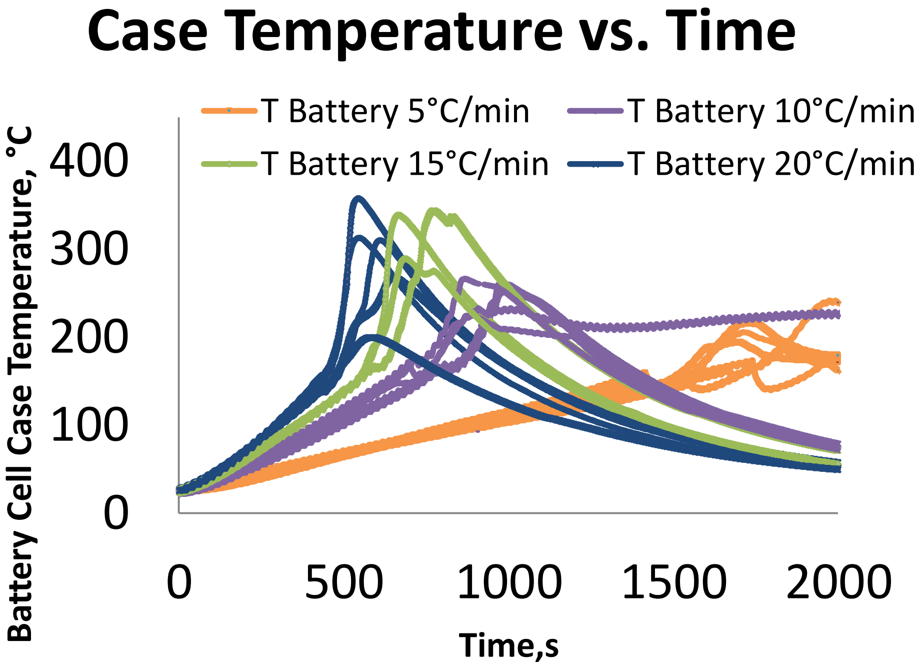
- The batteries were heated at various heating rates until the cell case reached 200°C and were held at 200°C for 180 minutes or until thermal runaway occurs
- The battery cells were wrapped in a flexible heater
- Temperature was measured at the vertical center of the cell case
- The temperature heating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



No battery holder setup

Heat Rate and Case Temperature

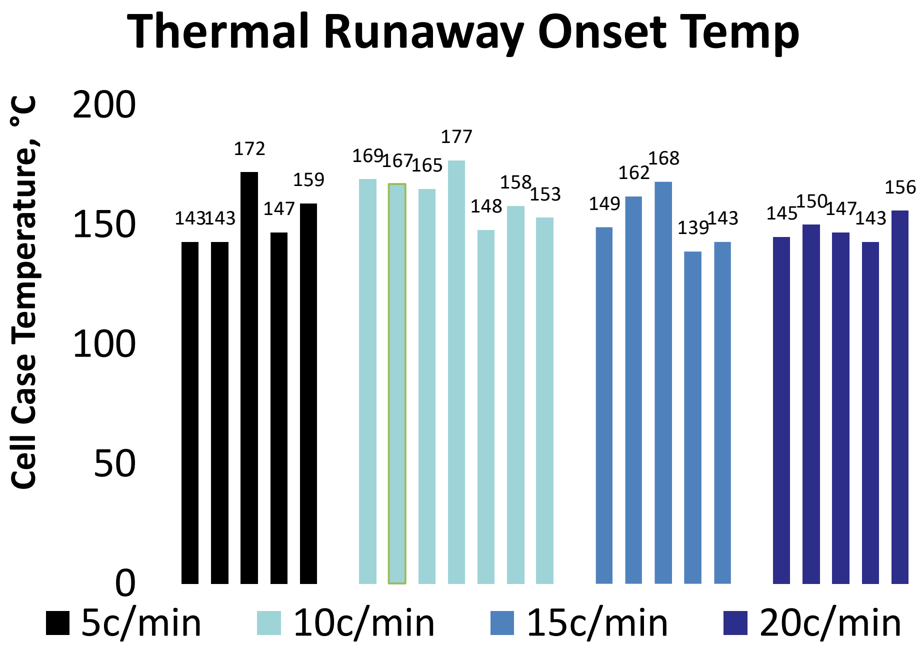
- The heating rate is controlled with a Proportional-Integral-Derivative (PID) controller
  - The heat rates were reproducible
  - Some degree of thermal lag
    - Analysis starts with assumption of perfect heat rate



Thermal Runaway Onset Temp

- There **was not a statistical difference in the thermal runaway onset temperature** for heating rates below 15°C/min (***M*=158**, *SD*=12) and heating rates at or above 15°C/min (***M*=150**, *SD*=9); t (20) =1.8, ***p* = 0.086**.

- These results suggest that heating rate do not have an effect on the thermal runaway onset temperature, *p* > 0.05.

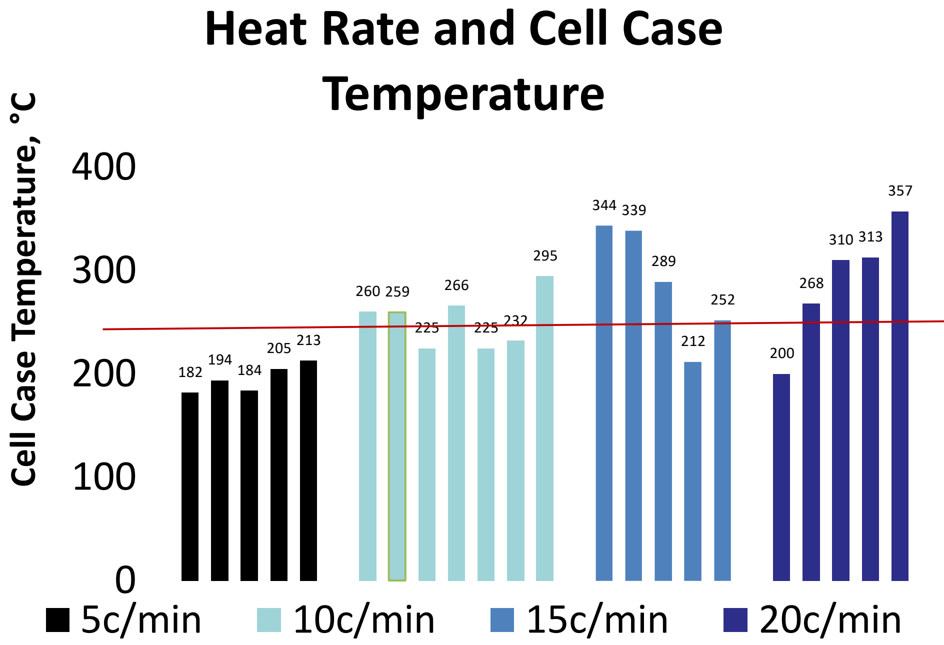


Heat Rate and Case Temperature

- There was a **significant difference in the maximum thermal runaway case temperature** for heating rates below 15°C/min (***M*=228**, *SD*=35) and heating rates at or above 15°C/min (***M*=288**, *SD*=54); *t* (20) =3.1, ***p* = 0.0053**

- **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

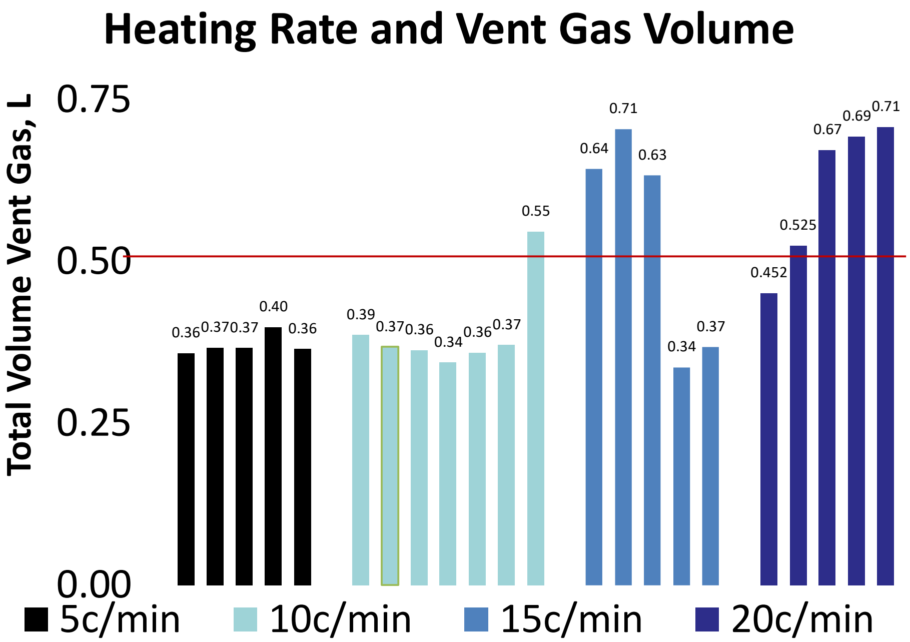


Heat Rate and Vent Gas Volume

- There was a **significant difference in the volume of the vent gas** for heating rates below 15°C/min (***M*=0.38**, *SD*=0.055) and heating rates at or above 15°C/min (***M*=0.57**, *SD*=0.14); *t* (20) =4.3, ***p* = 0.0003**.

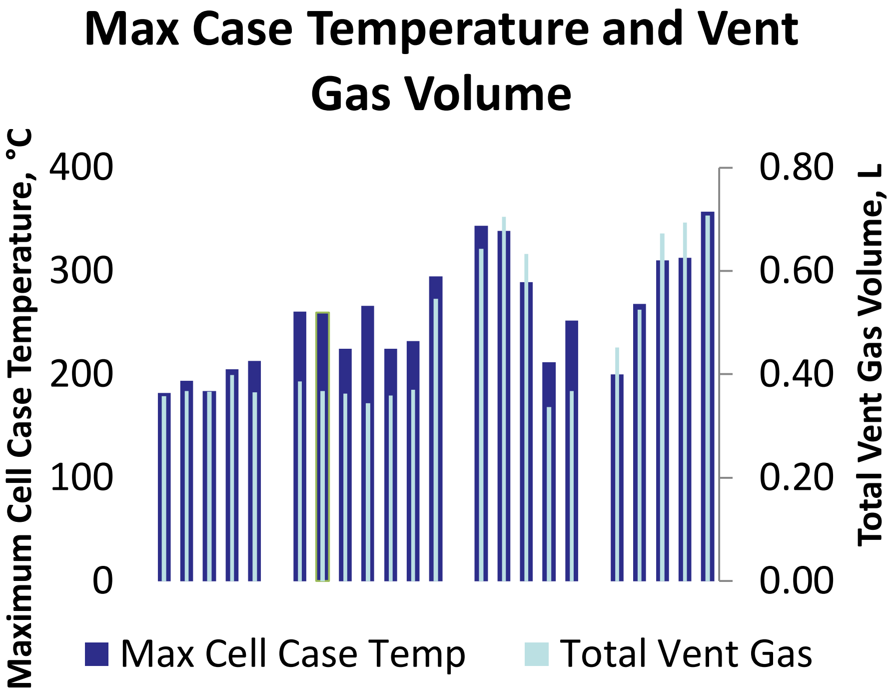
- **7/10 tests** (70%) at or above 15°C/min yielded greater than 0.5L of vent gas

- **1/12 tests** (8%) below 15°C/min yielded case temperatures above 0.5L of vent gas



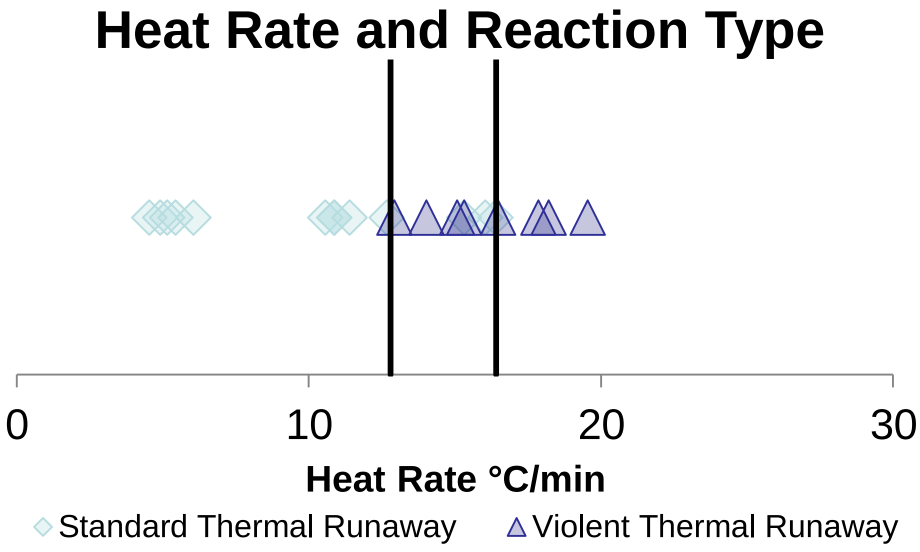
Heat Rate and Violent Reactions

- 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



Heat Rate and Violent Reactions

- Mix of standard and violent thermal runaway events with heat rates between 12.8 and 16.4°C/min
    - Testing above 16.4°C/min will yield a violent reaction (93%) of tests
    - Testing below 12.8°C/min will yield a standard reaction (93%) of tests
- The true heat rate was measured with the slope of a case temperature vs time graph from 30 to 140°C



Heat Rate and Violent Reactions

- The average heat rate for a standard thermal runaway reaction was 10.1°C/min (SD=4.2 °C/min)
  - High range of 1.5SD is 16.4°C/min
  - Testing above 16.4°C/min will yield a violent reaction (93%) of tests
- The average heat rate for a violent thermal runaway reaction was 16.2°C/min (SD=2.3°C/min)
  - Low range of 1.5SD is 12.8°C/min
  - Testing below 12.8°C/min will yield a standard reaction (93%) of tests
- Testing between 12.8 and 16.4°C/min will result in a mix of standard and violent thermal runaway reactions

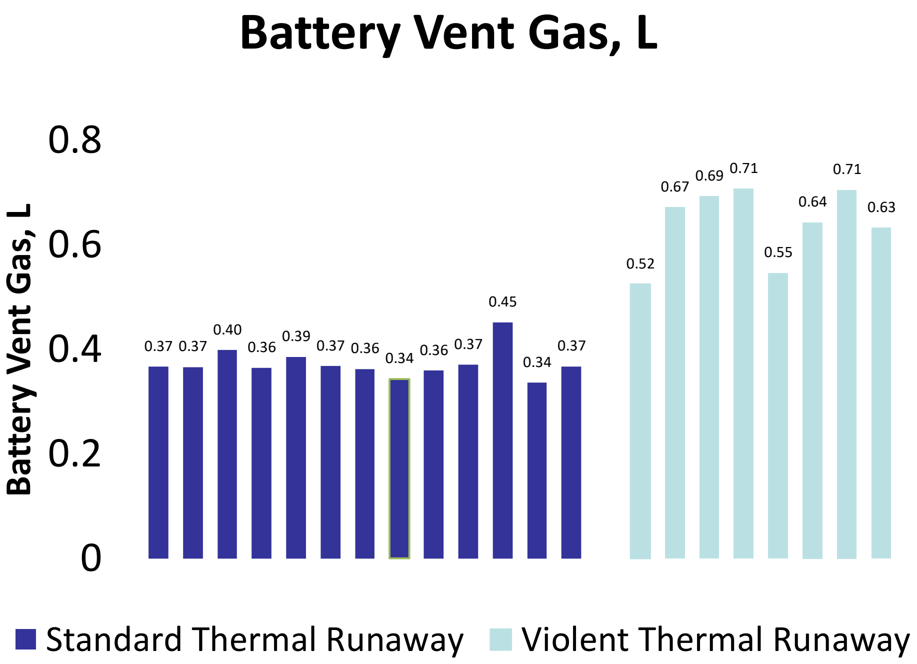
Theory

- 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

Battery Vent Gas

- The mean difference in vent gas volume was 0.27L (53.5%) with a 95% confidence interval ranging from 0.22 and 0.31L.

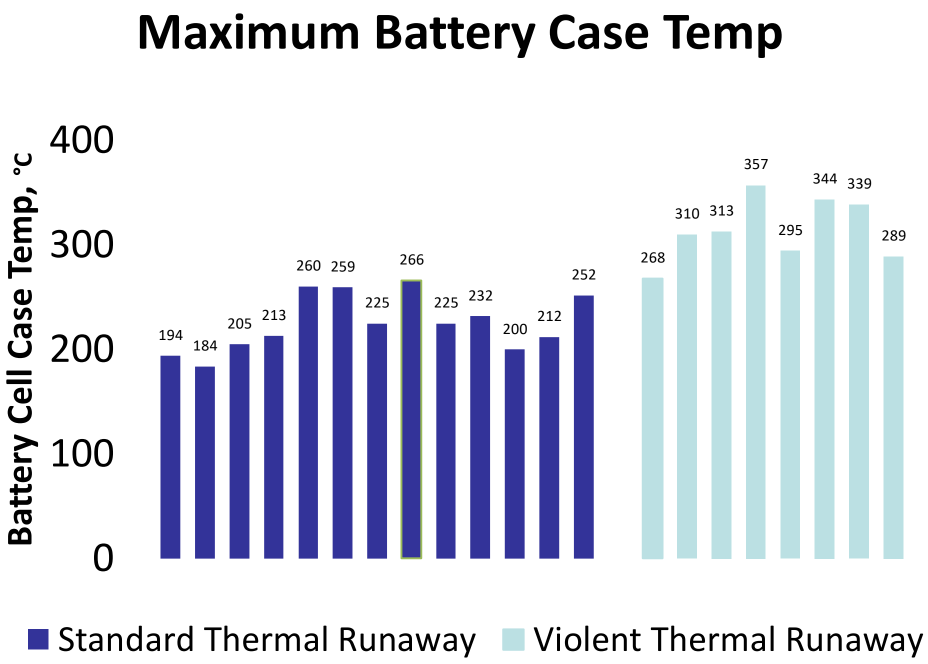
Reaction Type	n	Thermal Runaway Vent Gas Volume, L		
		Mean	SD	SEM
Standard	14	0.37	0.028	0.007
Violent	8	0.64	0.070	0.025



Max Battery Case Temperature

• The mean difference in the maximum battery cell case temperature was 92.0°C (34.3%) with a 95% confidence interval ranging from 64.9 and 119°C.

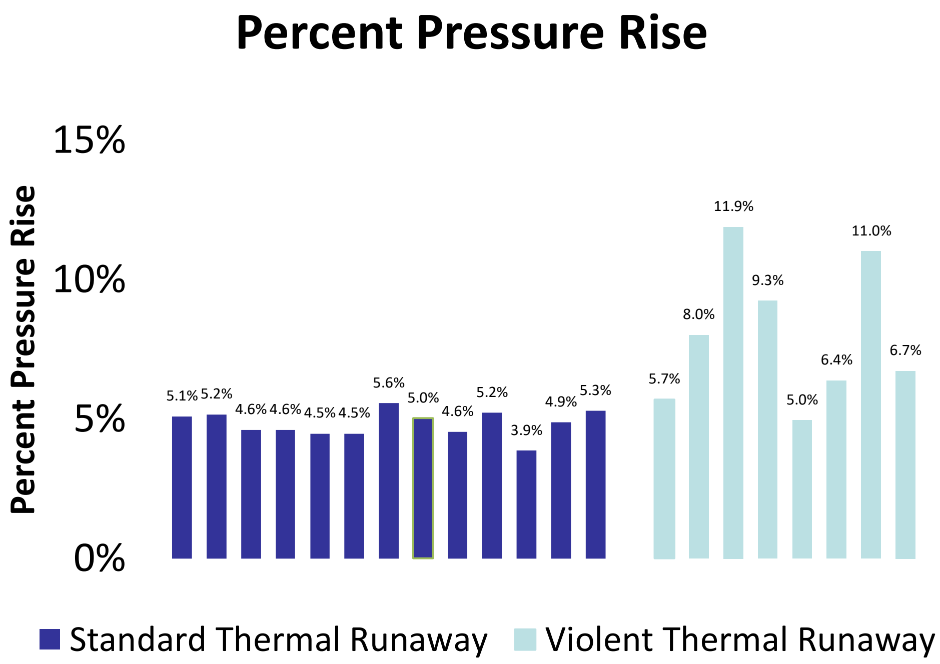
Reaction Type	n	Maximum Battery Cell Case Temperature, L		
		Mean	SD	SEM
Standard	14	222	28.6	7.64
Violent	8	314	30.5	10.8



Percent Pressure Rise, %

- The mean difference in percent pressure rise was 3.11% (48.4% difference) with a 95% confidence interval ranging from 1.69 and 4.54%

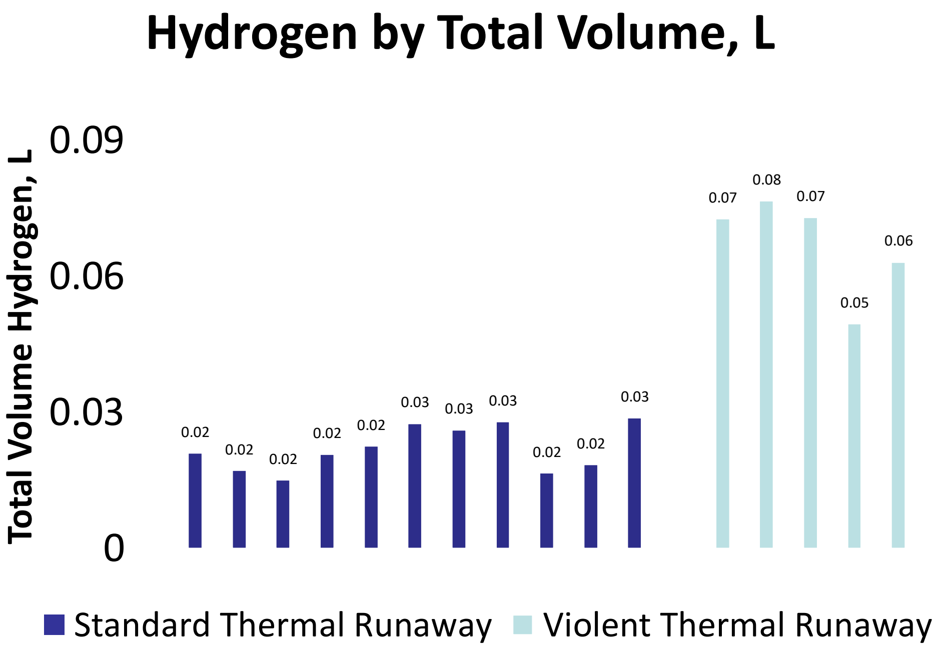
Reaction Type	n	Percent Pressure Rise,% Mean	SD	SEM
Standard	14	4.88	0.46	0.02
Violent	8	8.00	2.52	0.89



Total Volume of Hydrogen, L

- The mean difference in total volume of hydrogen was 0.045L (101%) with a 95% confidence interval ranging from 0.037 and 0.053L.

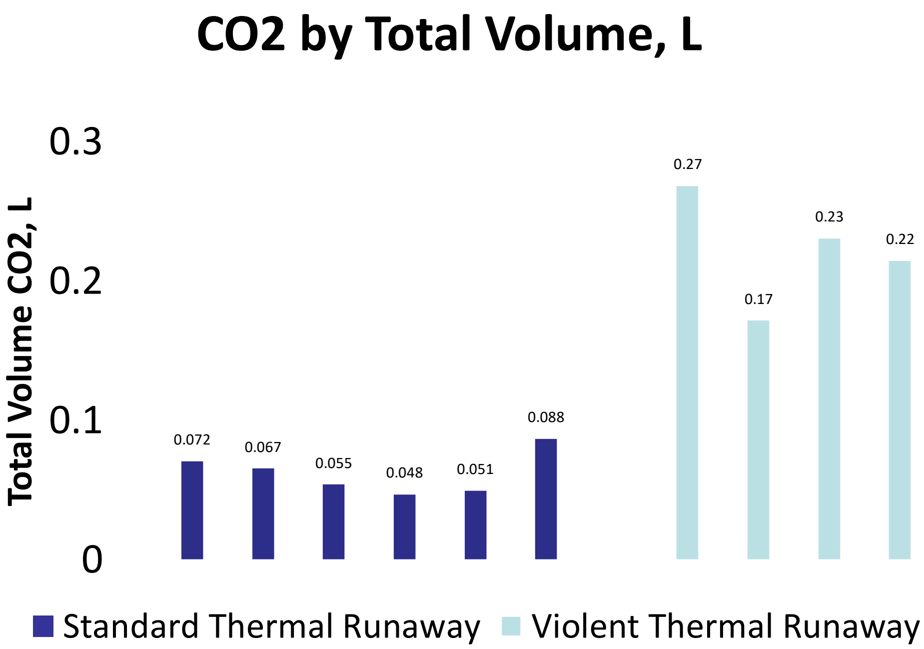
Reaction Type	n	Hydrogen Volume, L Mean	SD	SEM
Standard	11	0.022	0.005	0.001
Violent	5	0.067	0.011	0.005



Total Volume of Carbon Dioxide, L

- The mean difference in total volume of carbon dioxide was 0.16L (110%) with a 95% confidence interval ranging from 0.12 and 0.20L.

Reaction Type	n	Carbon Dioxide Volume, L Mean	SD	SEM
Standard	6	0.063	0.015	0.006
Violent	4	0.22	0.040	0.020



Le Chatelier’s Mixing Rule and LFL

- **Lower Flammability Limit (LFL)** is the minimum concentration of a fuel in an oxidizer that will ignite. *Less fuel will be too lean to ignite.*

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

Gas Specie	Standard Thermal Runaway, %vol	Violent Thermal Runaway, %vol
carbon dioxide	17.33±2.91	34.92±2.71
carbon monoxide	4.71±0.41	3.84±0.39
ethane	0.27±0.05	0.46±0.16
ethylene	2.16±0.45	1.67±0.24
hydrogen	5.98±0.86	10.25±0.70
methane	1.02±0.28	1.27±0.35
propane	0.10±0.01	0.14±0.07
propylene	0.07±0.01	0.26±0.18

± confidence intervals based off of a 95% confidence interval

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
- The violent thermal runaway vent gas is a more flammable mixture than the standard thermal runaway vent gas
- With the calculated LFL and the measured volume of vent gas, we can estimate the maximum volume that will become flammable during a thermal runaway event.

Reaction Type	Calculated LFL	Volume Vent Gas per Event, L	Max Potentially Flammable air mixture, L
Standard	27.7±0.67%	0.37±0.01	1.34±0.06
Violent	21.2±0.74%	0.64±0.05	3.02±0.24

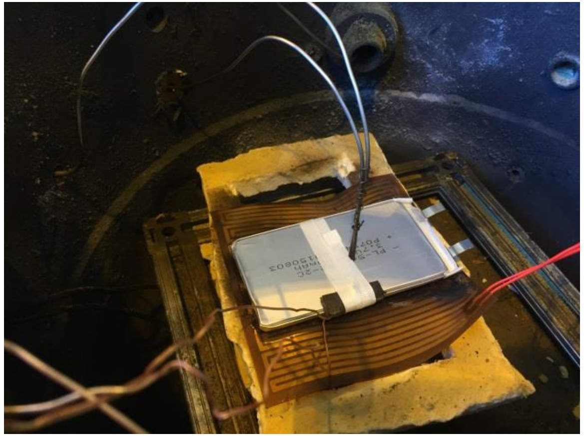
± confidence intervals based off of a 95% confidence interval

Conclusion

- Heat rates below 13°C/min were likely to cause a standard thermal runaway reaction while heat rates above 16°C/min were likely to cause a more violent thermal runaway reaction.
- A violent thermal runaway reaction is marked by:
  - Greater volume of vent gas (53% difference)
  - More flammable vent gas (27% difference)
  - Greater maximum cell case temperature (34% difference)
  - Greater percent pressure rise (48% difference).
- Whether or not a violent thermal runaway reaction occurs in an 18650 cell depends on how much electrolyte is boiled and vented prior to thermal runaway.
- The heat rate does not affect the thermal runaway onset temperature.

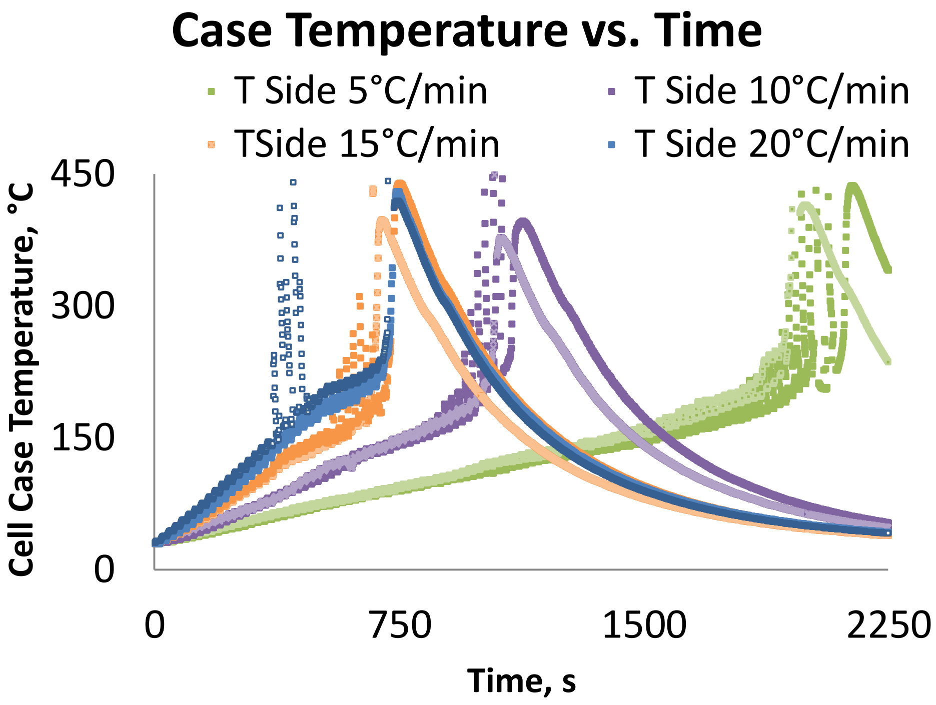
Test Procedure

- 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



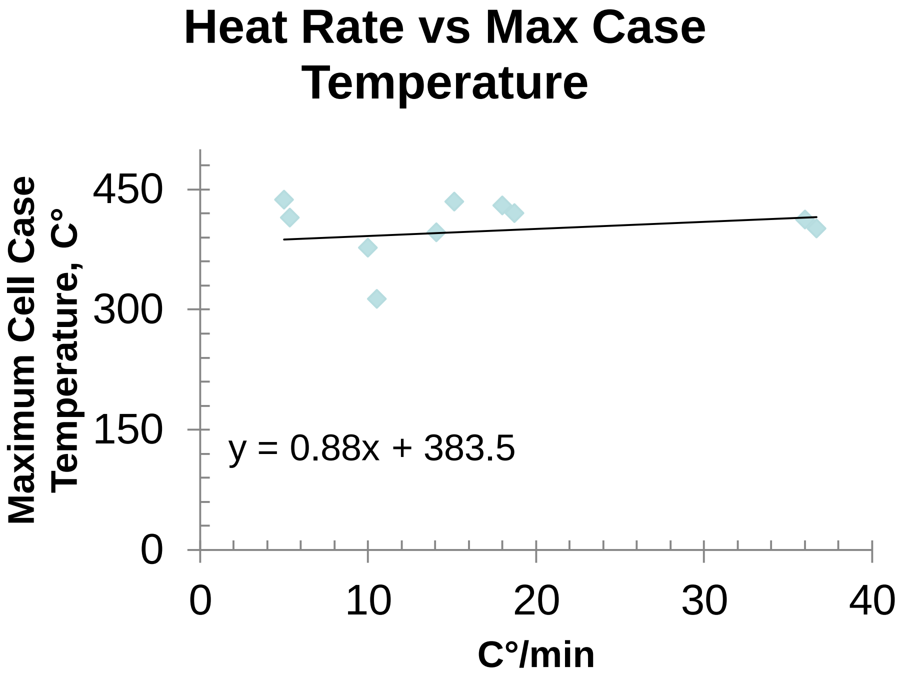
Heat Rate and Case Temperature

- The heating rate is controlled with a Proportional-Integral-Derivative (PID) controller
- Although the PID controller yielded mostly reproducible results, there were slight variances in the actual heat rate.
- This is especially true at high heat rates because of thermal lag. The actual heat rate was measured with the slope of the cell case temperature vs time graph from 30 to 140°C.



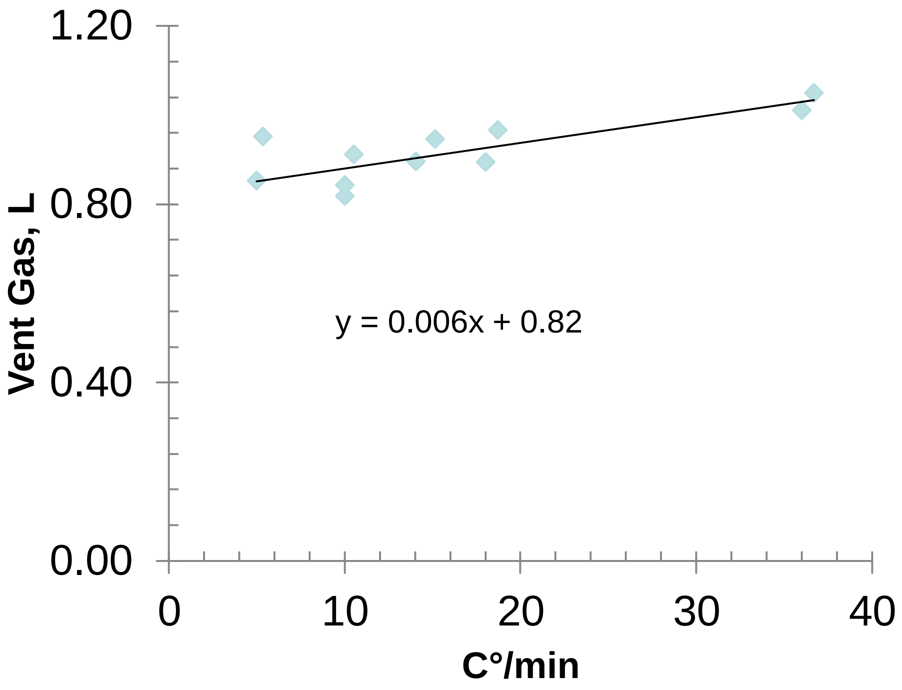
Heat Rate and Case Temperature

- A simple linear regression was calculated to predict maximum cell case temperature based on heat rate.
- A non-significant regression equation was found ($F(1,9)=0.56$, $p=0.47$), with a R^2 of 0.06



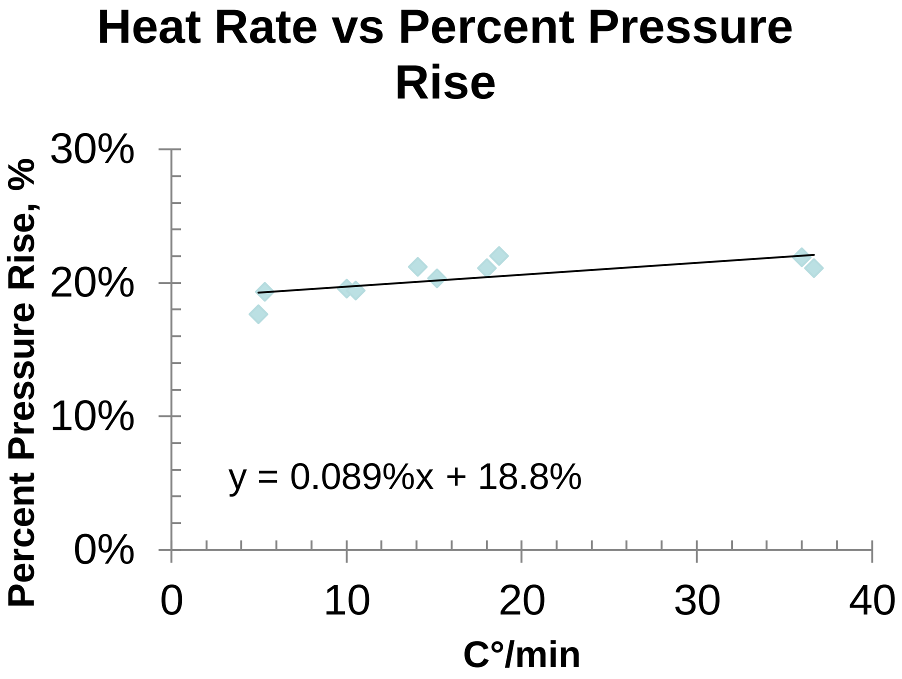
Heat Rate and Gas Volume

- A simple linear regression was calculated to predict vent gas volume based on heat rate.
- A significant regression equation was found ($F(1,10)=18.24$, $p=0.0016$), with a R^2 of 0.65.
- The vent gas volume increased 0.057L for every 10 C°/min increase



Heat Rate and Percent Pressure Rise

- A simple linear regression was calculated to predict percent pressure rise based on heat rate.
- A significant regression equation was found ($F(1,8)=9.24$, $p=0.016$), with a R^2 of 0.54
- The percent pressure rise increased 0.89% for every 10 C°/min increase



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

Gas Specie	Averaged Gas Concentration, %vol	LFL, %vol
carbon dioxide	41.2±2.05	0
carbon monoxide	3.82±0.35	12.5
ethane	1.35±0.08	3.00
ethylene	3.72±0.11	3.10
hydrogen	17.0±1.19	4.95
methane	2.58±0.09	5.30
propane	0.34±0.02	2.10
propylene	3.75±0.29	2.40

± confidence intervals based off of a 95% confidence interval

Le Chatelier's Mixing Rule, LFL

- The LFL is calculated to be **9.10%**
- 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 **10.2L** of vent gas and air mixture flammable

	Calculated LFL, %vol	Volume Vent Gas per Event, L	Max Potentially Flammable Vent and Air Mixture, L
Pouch Thermal Runaway	9.10±0.75	0.92±0.08	10.2±1.21

Conclusion

- Heat rate does have a measurable effect on
  - Vent gas total volume (*M*=0.94L, *SD*=0.17L, *SEM*=0.04L)
  - Percent pressure rise (*M*=20.6% *SD*=2.74% *SEM*=0.73%)
  - Carbon dioxide concentration
- Heat rate does not have a significant effect on
  - Cell case temperature (*M*=404°C, *SD*=36.9°C *SEM*=11.7°C)
  - The majority of vent gas constituent's concentrations and volumes
- The calculated LFL of the gas mixture is 9.10%

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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