Understanding how Testing Conditions Affect Hazard Quantification in Lithium-Ion Battery Abuse Tests

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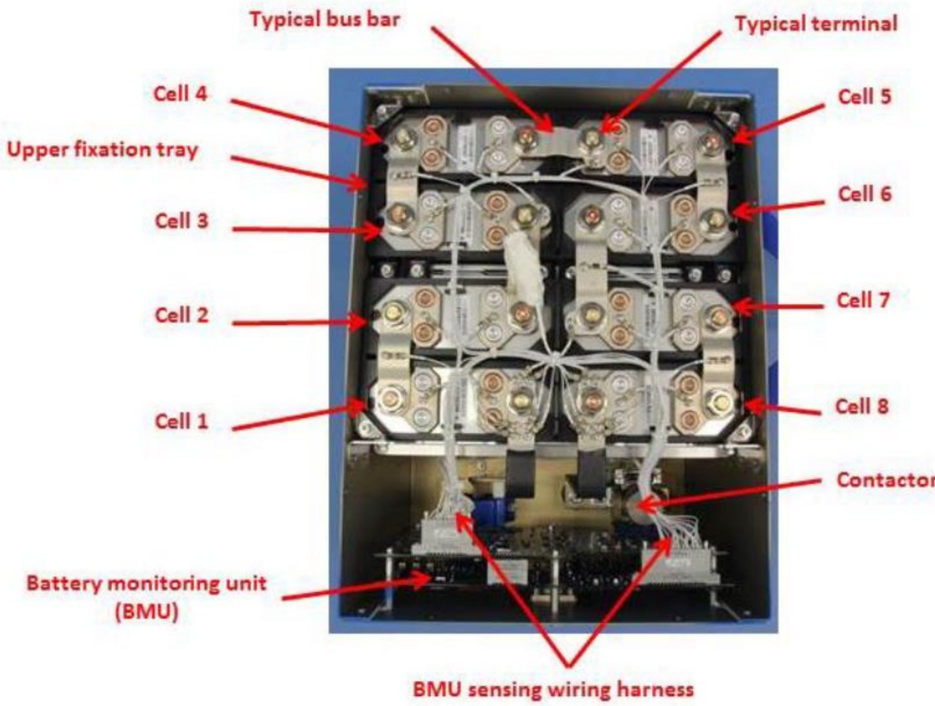
Motivation

- Critical battery systems require understanding and planning for conditions resulting from overheating, cell failure and/or propagation.
- For fire and explosion safety planning, there is a need to understand and quantify hazards if these batteries are involved in a fire. Quantities of interest include:
  - The rate and total volume of gas evolved
  - The composition of the gas evolved
- New commercial industry (non-space) standards allow these hazards to be quantified through abuse tests at the cell level. UL 9540A specifies an inert atmosphere for testing and generally is written for external heating but does allow for other abuse testing methods.
- It is unclear how well such standards will correlate to real world situations
  - Cells are packed into modules and devices which have a variety of volumes and geometries.
  - There are potential environmental differences (e.g. air or inert) in how batteries and systems are tested versus deployed.
  - The abuse conditions that the cell may face in the field may be different than the abuse condition tested (e.g. nail penetration abuse test, external heating field failure).



FreedomCAR Abuse Test Manual

SANDIA REPORT
SAND2005-3123
Unlimited Release
Printed August 2006

FreedomCAR
Electrical Energy Storage System
Abuse Test Manual for Electric and
Hybrid Electric Vehicle Applications

Daniel H. Doughty and Chris C. Crafts

2.2.2. Analysis of Released Gases

Gas, smoke and flames may be released from the test article during the abuse tests. While it is important to analyze these gases, gas analysis may not be desired on all tests, especially if the tests are repetitive in nature. Gas and particulate analysis may be qualitative or quantitative, depending on the test objective. Measurements of hazardous substances, when possible, should be referenced to the AIHA's ERPG-2 recommendations. Other similar standards may be substituted because the concentration levels recommended are for comparison purposes only. It is recommended that when such testing is conducted out of doors wind speed should be ≤3 mph. Multiple gas sample locations, spaced equally around the device under test, should be placed as close to the EESS as is practical during the test.

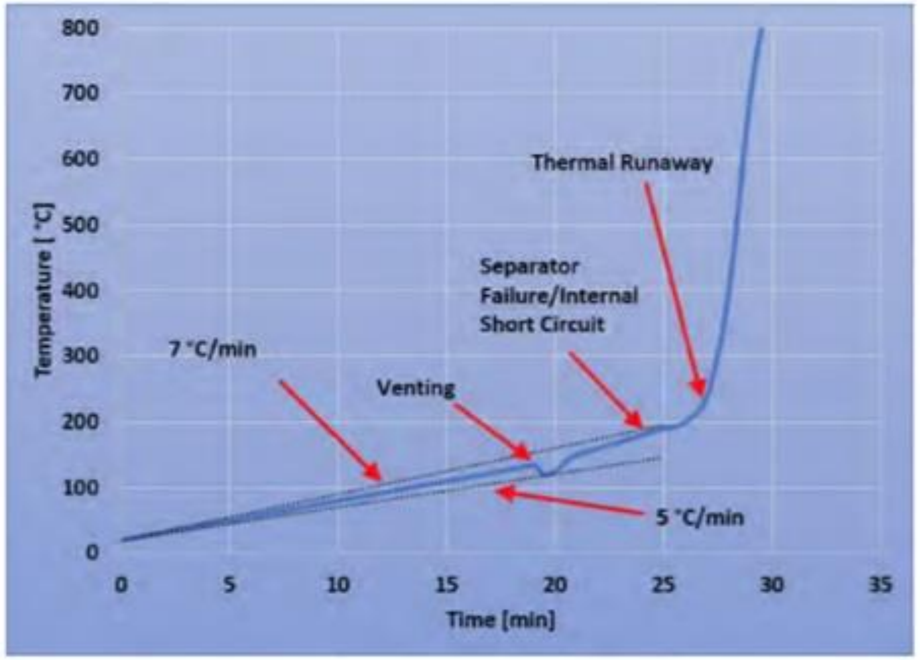
2.2.3. Flammability Analysis

The flammability of expelled materials should be determined. The lower limit of flammability in air is used for flammable gases and liquids. For example, the lower limit of flammability in air for H_2 is 4%. A spark source or other ignition source should be installed near the test article to accurately determine if the vented gas and smoke is flammable.

UL 9540A

CELL LEVEL TESTING

Purpose:
1. Cell thermal runaway methodology, instrumentation
2. Thermal runaway test parameters
3. Cell surface temp at venting and thermal runaway
4. Gas generation/composition; characterize gas flammability hazards (LFL)



Cell Level Testing Apparatus

Important Data

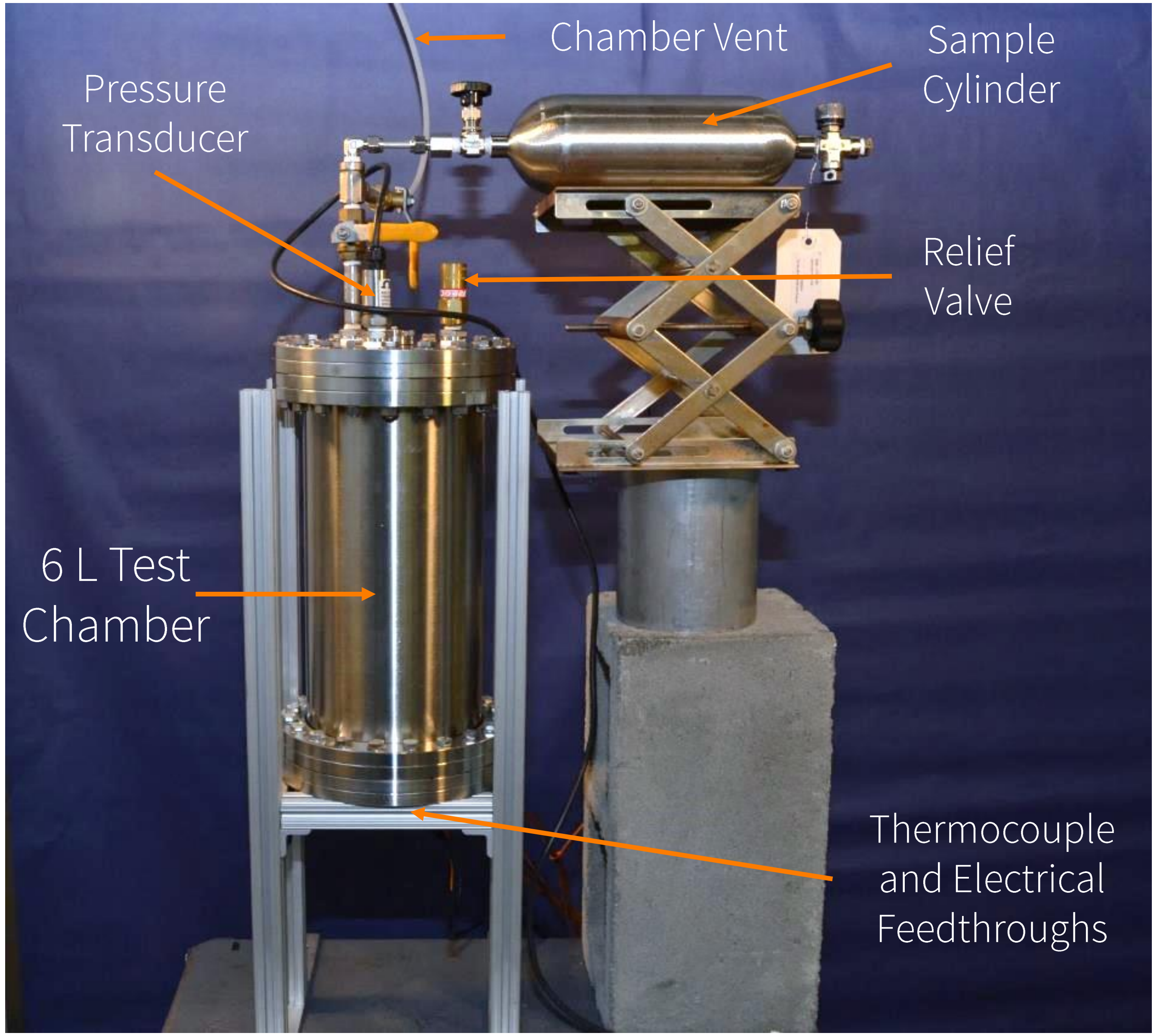
- Thermal runaway method and parameters
- Temperature at venting
- Temperature at thermal runaway initiation
- Cell vent gas measurements:
  - Composition
  - Volume
  - Lower Flammability Limit
  - Burning Velocity
  - P_{max}

Testing Methodology

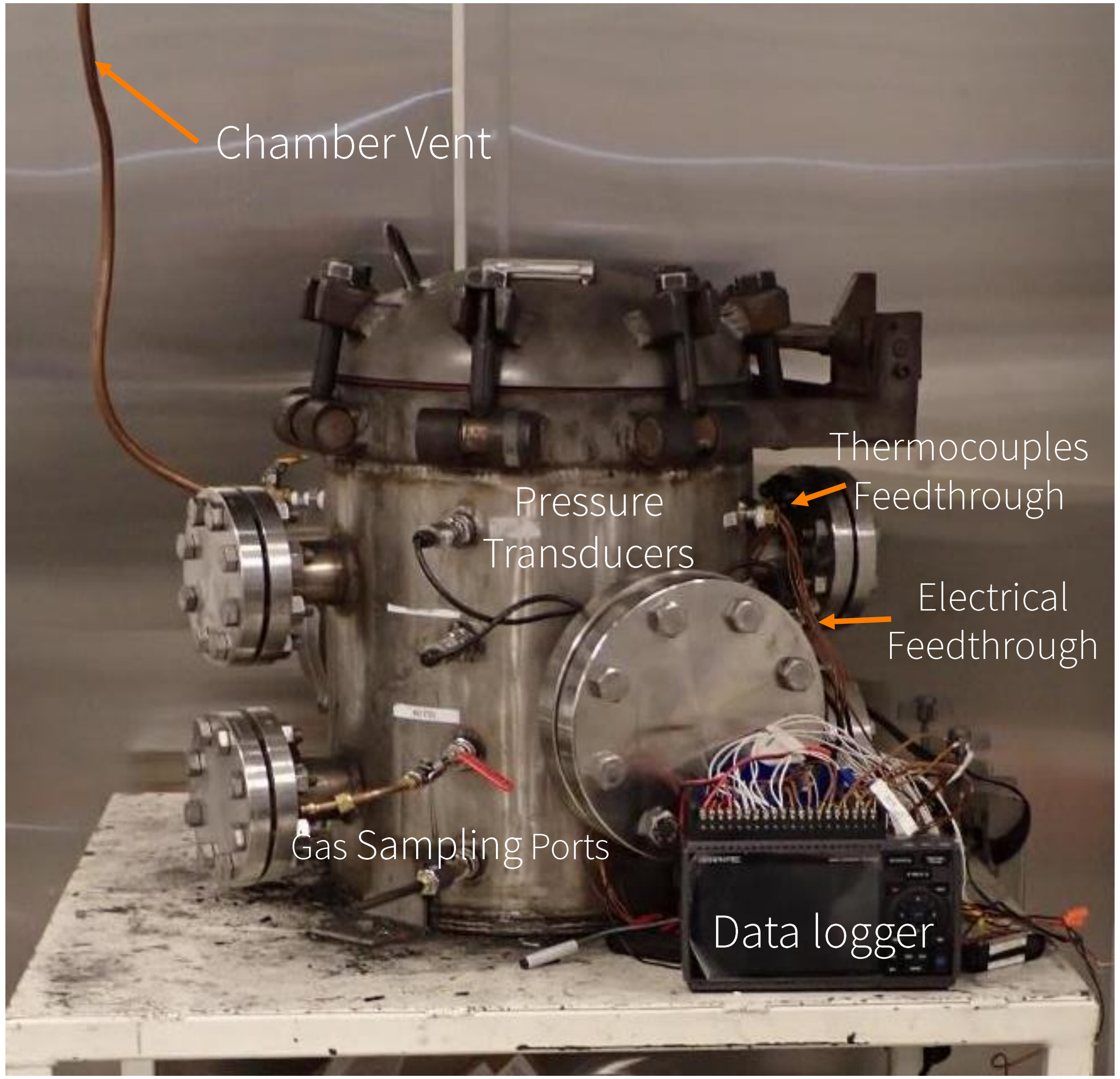
- Perform a variety of abuse tests on a single type of 18650 lithium-ion cell.
  - The 18650 format cell is used as a test system which can be scaled to larger formats
- Three different abuse conditions were tested
  - Case A: External heating in a 60-L chamber in air *(Baseline case)*
  - Case B: External heating in a 60-L chamber in N_2 *(Effect of Air vs. Inert atmosphere)*
  - Case C: External heating in a 6-L chamber in air *(Effect of testing chamber volume)*
- Temperature and pressure measurements within the chamber were used to determine the quantity of gas evolved during the test.
- Gas sampled from the chamber was analyzed using gas chromatography (GC) to determine the gas composition of non-condensable and hydrocarbon gases.

Testing Chambers: 6 L and 60 L

Outside view of the
6-L test chamber

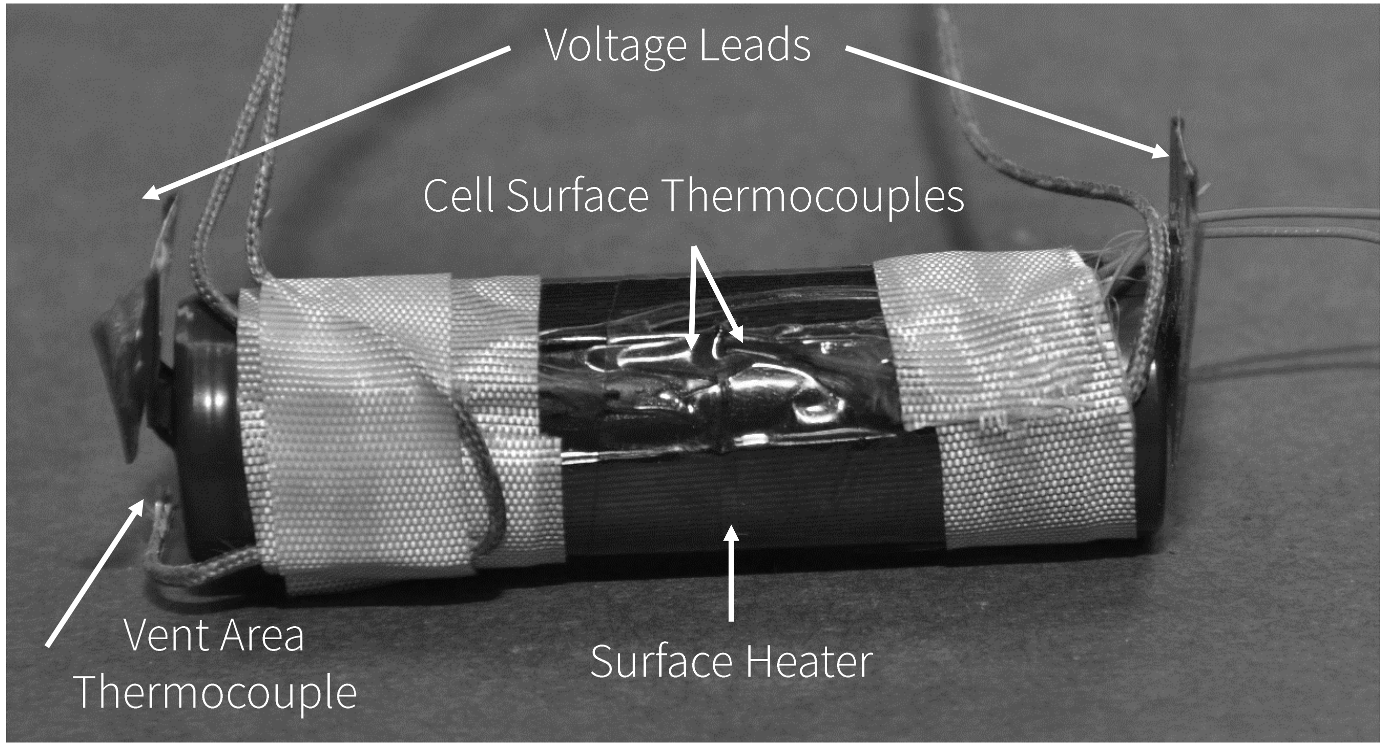


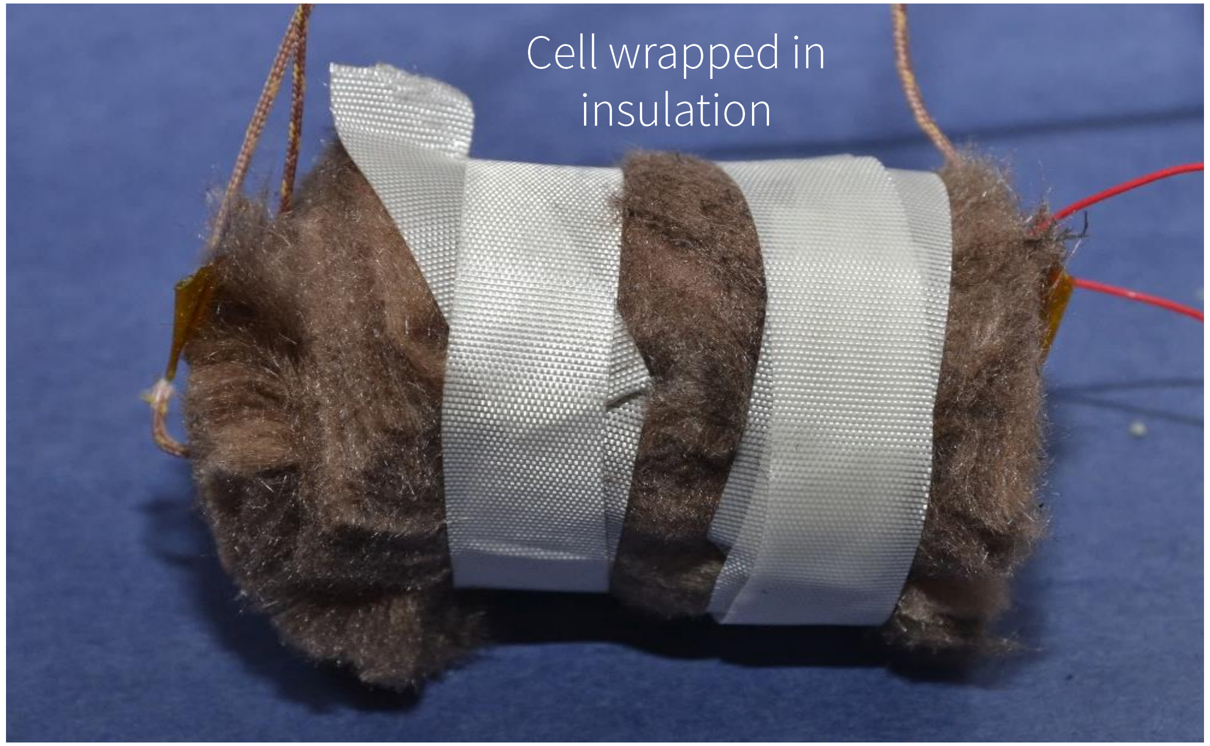
Outside view of the
60-L test chamber



Cell Instrumentation

- Surface heater is affixed to cell surface.
- Thermocouples are place on the cell surface and in the vicinity of the cell vent area.
- Cell in wrapped in insulation to control heating rate.

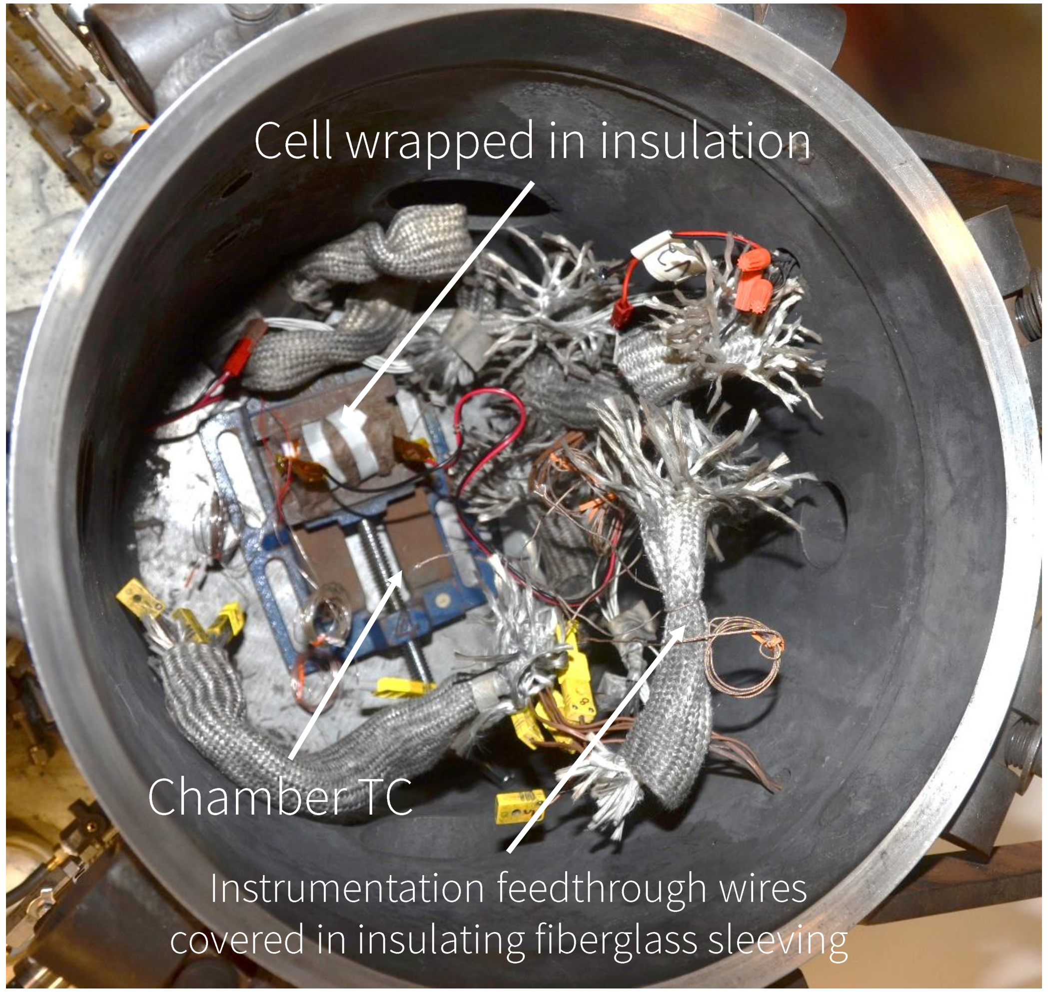




Experimental Details

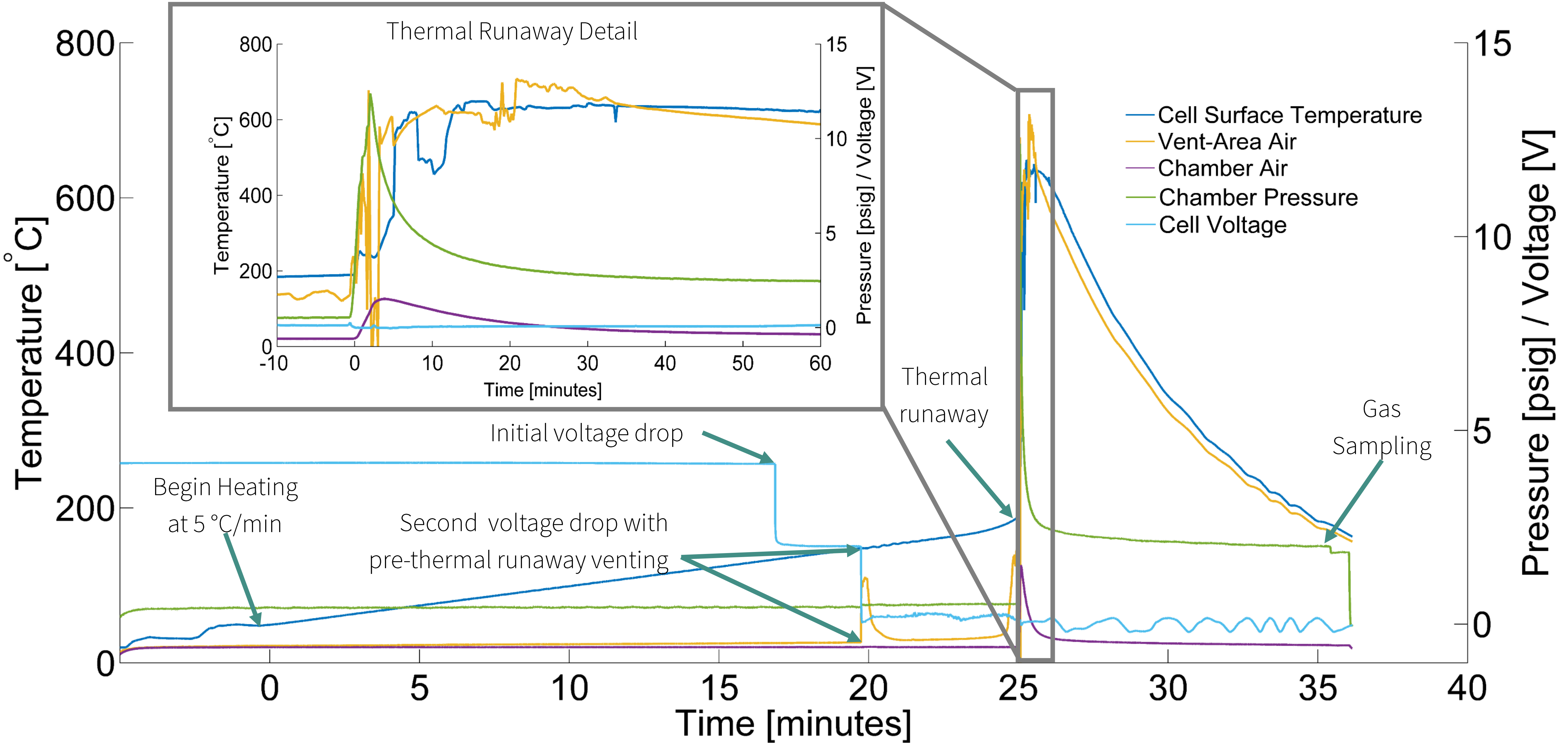
- Test Setup
  - The cell was charged to 100% SOC by a protocol provided by the manufacturer specification sheet.
  - A resistance heater (Rated at 40 W total at 115 V) was affixed to the surface of the cell, and the cell was wrapped in insulation.
  - The assembly was placed in the chamber, and the chamber was sealed.
  - The chamber was brought to ~1 psia and back-filled to ~30 psia with Nitrogen three times. **(Inert Testing Only)**
- Test Procedure
  1. The cell was heated from ~50 °C at a rate of 5 °C/min to thermal failure.[1]
  2. Gas was sampled directly ~10 minutes after the cell thermally failed.

Overhead view of 18650 cell in the 60 L chamber for an external heating test



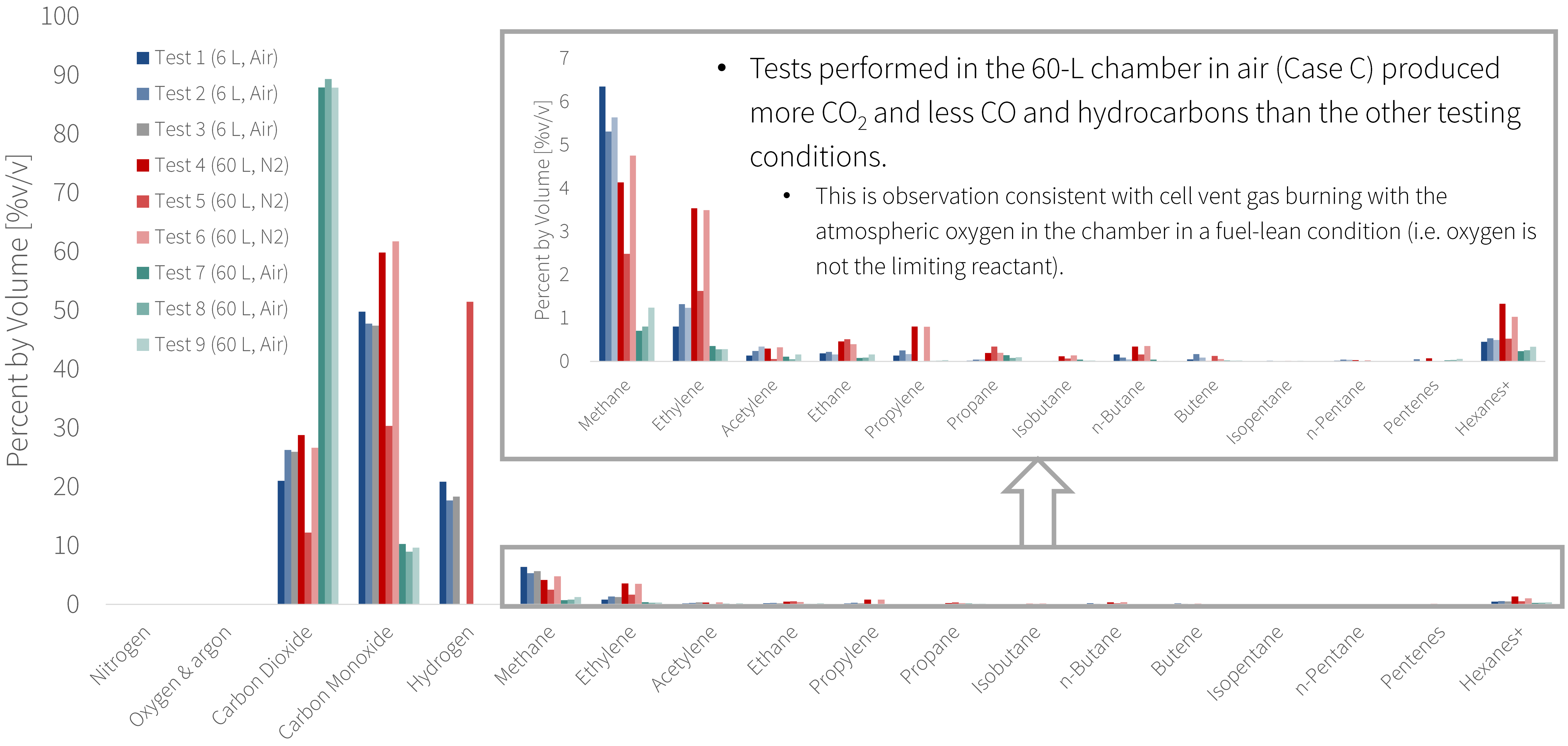
[1] Note that each cell is initially heated to 50 °C during the temperature controller's autotune procedure, where the controller assesses the thermal characteristics of the object.

Example Data



t = 0 corresponds with the beginning of the eating ramp

Gas Analysis of External Heating Tests (Normalized)



- Tests performed in the 60-L chamber in air (Case C) produced more CO_2 and less CO and hydrocarbons than the other testing conditions.
  - This is observation consistent with cell vent gas burning with the atmospheric oxygen in the chamber in a fuel-lean condition (i.e. oxygen is not the limiting reactant).

- The gas compositions reported here are normalized to exclude any contribution from nitrogen, oxygen and argon.

Vent Gas Amount (Flammable & Non-flammable Components)

	Case A			Case B			Case C		
Test #: Chamber Volume Chamber Atmosphere	Test 1 6 L Air	Test 2 6 L Air	Test 3 6 L Air	Test 4 60 L N_2	Test 5 60 L N_2	Test 6 60 L N_2	Test 7 60 L Air	Test 8 60 L Air	Test 9 60 L Air
Gas (Detection Limit)	[%v/v]	[%v/v]	[%v/v]	[%v/v]	[%v/v]	[%v/v]	[%v/v]	[%v/v]	[%v/v]
Nitrogen (0.01)	35.30	37.20	35.60	93.30	85.50	92.30	76.30	76.90	76.60
Oxygen & Argon (0.01)	0.00	0.00	0.00	0.00	0.36	0.74	9.48	12.10	10.60
Post-test Gas [L at STP]	6.6	5.9	6.4	5.2	5.9	5.2	2.2	2.0	2.0
Average		6.3			5.4			2.1	
Calculated Gas Evolved [L at STP]	7.9	7.2	7.7	4.0	8.5	4.2	8.0	6.2	7.2
Average		7.6			5.6			7.1	

- The amount of gas evolved was calculated using the ideal gas law. STP is taken as atmospheric pressure and 0 °C. The contribution of the chamber was removed by subtracting the average quantity of gas calculated in the chamber prior to testing.
- For Case A (6 L) and Case C (60 L), the chambers are initially filled with air, which contains oxygen. The gas analysis shows:
  - All of the oxygen was consumed in the 6-L testing chamber (i.e. oxygen deficient environment)
  - There was oxygen remaining in the 60-L testing chamber
- Case B (60 L, inert) on average produced:
  - ~2.6x (i.e. 160%) ***more*** gas than Case C (60 L, air)
  - ~13% ***Less*** gas than Case A (6 L, air)
- The gas evolved in Case B (60 L, inert) correlated more closely to Case A (6 L, air).

Compare Molecular Makeup of Vent Gas: C, H, and O

Test #: Abuse Method Chamber Volume Chamber Atmosphere	Test 1 External Heating 6 L Air	Test 2 External Heating 6 L Air	Test 3 External Heating 6 L Air	Test 4 External Heating 60 L N_2	Test 5 External Heating 60 L N_2	Test 6 External Heating 60 L N_2	Test 7 External Heating 60 L Air	Test 8 External Heating 60 L Air	Test 9 External Heating 60 L Air
Moles of C in vent gas [L@STP]	6.60	6.40	6.72	4.64	4.70	4.73	8.19	6.28	7.44
Moles of H in vent gas [L@STP]	6.43	5.54	5.89	2.63	11.60	2.62	0.88	0.63	1.05
Moles of O in vent gas [L@STP]	7.24	7.24	7.66	4.74	4.67	4.81	14.86	11.54	13.38
% of C in vent gas	32.54	33.38	33.14	38.62	22.41	38.90	34.22	34.06	34.01
% of H in vent gas	**31.73**	**28.89**	**29.05**	**21.89**	**55.35**	**21.57**	**3.70**	**3.41**	**4.79**
% of O in vent gas	35.73	37.73	37.81	39.49	22.25	39.54	62.09	62.53	61.20

- Hydrogen makes up a much smaller portion of the vent gas in the tests conducted in the 60-L chamber in air.
  - Hydrogen reacting with oxygen will produce water vapor, which may condense on chamber walls after the initial thermal runaway.

Summary of Results

- Oxygen availability increased the amount of vent gases coming from the cell.
- Oxygen consumption leads to a reduction in the net evolution of gas during the test in a closed chamber/system.
- The amount of atomic oxygen present in the gases in the chamber (i.e. O in O_2 , CO_2 , and CO) increased during the test (i.e. Oxygen was evolved from the cell).
  - Approximately twice as much oxygen was evolved in Cases A and B where the cell was in an oxygen deficient environment compared to Case C where there was environmental oxygen available.
- Gas analysis shows that CO and CO_2 are the dominant gases produced in systems with environmental oxygen, which is consistent with the cell vent gas burning in air.
- The highest amount of gas was produced with a limited amount of atmospheric oxygen initially in the chamber. This amount of oxygen may have supported combustion in a limited way but was eventually fully consumed. After that point in the reaction, the chamber was functionally inert (i.e. comparable to the tests with initially inert atmospheres).
  - Condensation of water vapor produced from this combustion process may be contributing to the lower estimates of gas production when compared to the inert or oxygen-limited testing conditions.

Conclusions

- The availability of environmental oxygen plays a large role in the gas evolved from the abuse test.
  - Gas analysis shows that CO_2 is the dominant gas produced in systems with excess environmental oxygen, which is consistent with the cell vent gas burning in air.
  - The highest amount of gas was produced with a limited amount of atmospheric oxygen initially in the chamber. This amount of oxygen may have supported combustion in a limited way but was eventually fully consumed. After that point in the reaction, the chamber was functionally inert (i.e. comparable to the tests with initially inert atmospheres).
- The effects of full, partial and no inert atmosphere can be demonstrated and will be important to understand as cell chemistries and applications evolve.

Thank you!

Questions?

Limitations

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