Li-ion 18650 Thermal Runaway Particulate Analysis

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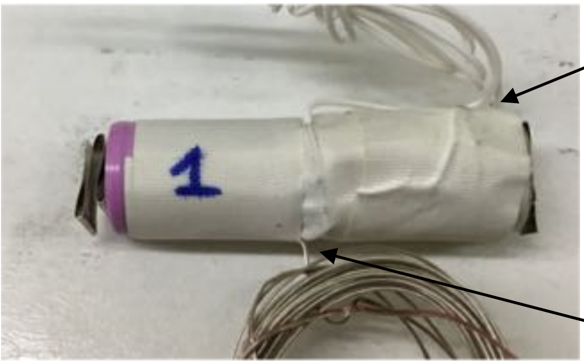
Particulate Analysis Thermal Runaway Testing

- Purpose: Generate and analyze particulates from the temperature induced thermal runaway of a Li-ion cell, simulating the atmospheres associated with International Space Station conditions.
  - The Extravehicular Activity (EVA) suit batteries use the Samsung ICR18650-26F lithium ion cell.

- The cells were sent into thermal runaway under three conditions, simulating three different environments:
  - Ambient atmosphere to simulate ground storage and test.
  - ISS atmosphere (23.5% O_2) to simulate an onboard (airlock) failure.
  - Vacuum to simulate failure during mission operation.

- These three atmospheres may influence the combustion products and residue generated from a thermal runaway event, and need to be evaluated independently.

Samsung 26F Overview



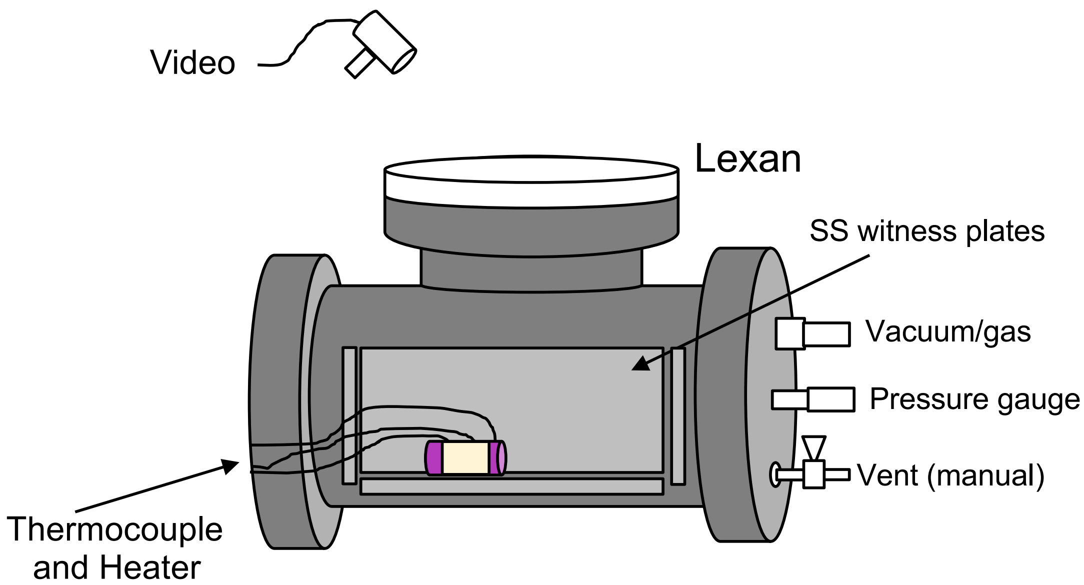
Manufacturer	Samsung
Name	ICR18650-26F
Capacity (Ah)	2.6
Chemistry	**$LiCoO_2$/NMC**

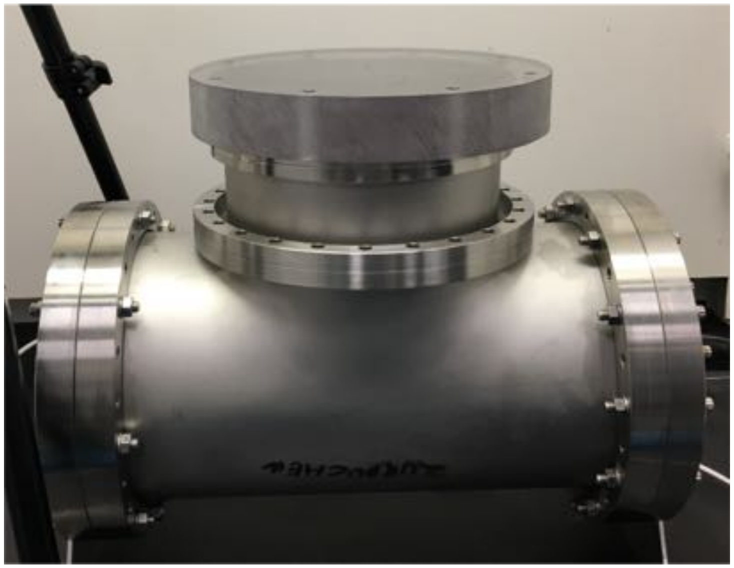
Test cells were wrapped in heater tape and sent into thermal runaway in a closed environment.

Thermal runaway was initiated through an overtemperature condition driven by heater tape.

Thermal Runaway Test Chamber

The test box was a vacuum tee, 2' on long axis with 10" ports, one of which was covered with 2" thick Lexan. The cell was placed in a witness box in the tee, and the Lexan cover closed. Overpressure protection was supplied by allowing the O-ring seal for the Lexan cover to blow out if needed. For vacuum and ISS gas test, the inlet ports were closed prior to testing and the atmosphere was static.





Test Conditions

All cells were charged prior to testing to 4.1 V at C/10, and tapered at 4.1V until a C/100 current was achieved.

Ambient
- Sample chamber was filled with laboratory ambient atmosphere.
- Test chamber ports were closed, but not sealed.
- Sample heated at up to 43 W. Sample went into thermal runaway at 6m 39s.

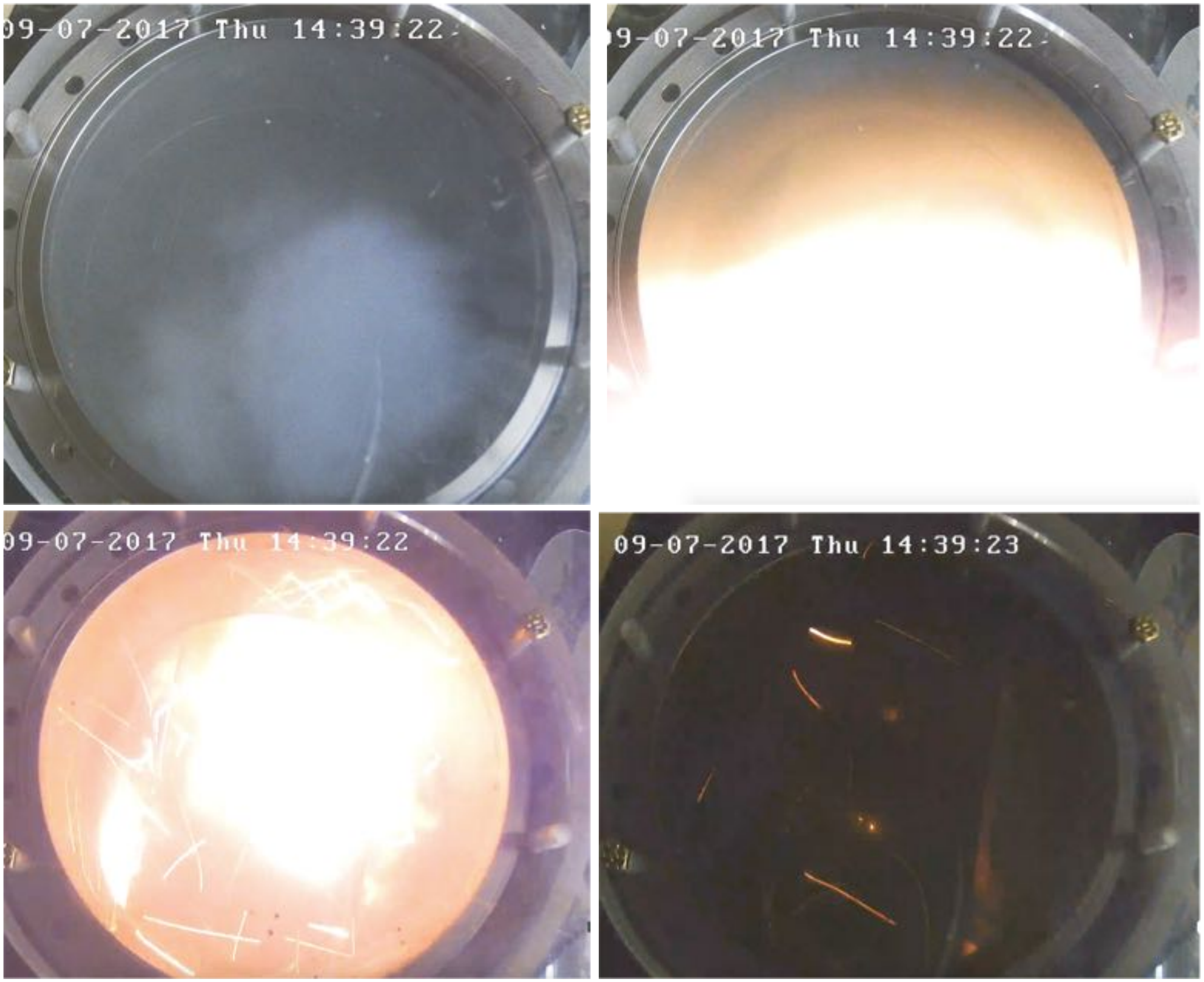
ISS
- Sample chamber was purged for 1 hour with 23.5% O_2/76.5% N_2 gas mixture.
- The test was conducted with the gas supply valves closed.
- Sample heated at 43 W. Sample went into thermal runaway at 4m 01s.

Vacuum
- Sample chamber was evacuated using a dry mechanical pump for 1 hour, then backfilled to 500 torr with N_2. Evacuated and refilled 3x, before final pump down to a pressure of 175 mtorr.
- Tested under a vacuum environment with valves to vacuum pump closed.
- Sample heated at 43 W. Sample went into thermal runaway at 4m 22s.

Thermal Runaway: Ambient Testing

Venting of electrolyte vapor.

Ignition of electrolyte vapor.



Hot particles ejected.

Cooldown of cell components.

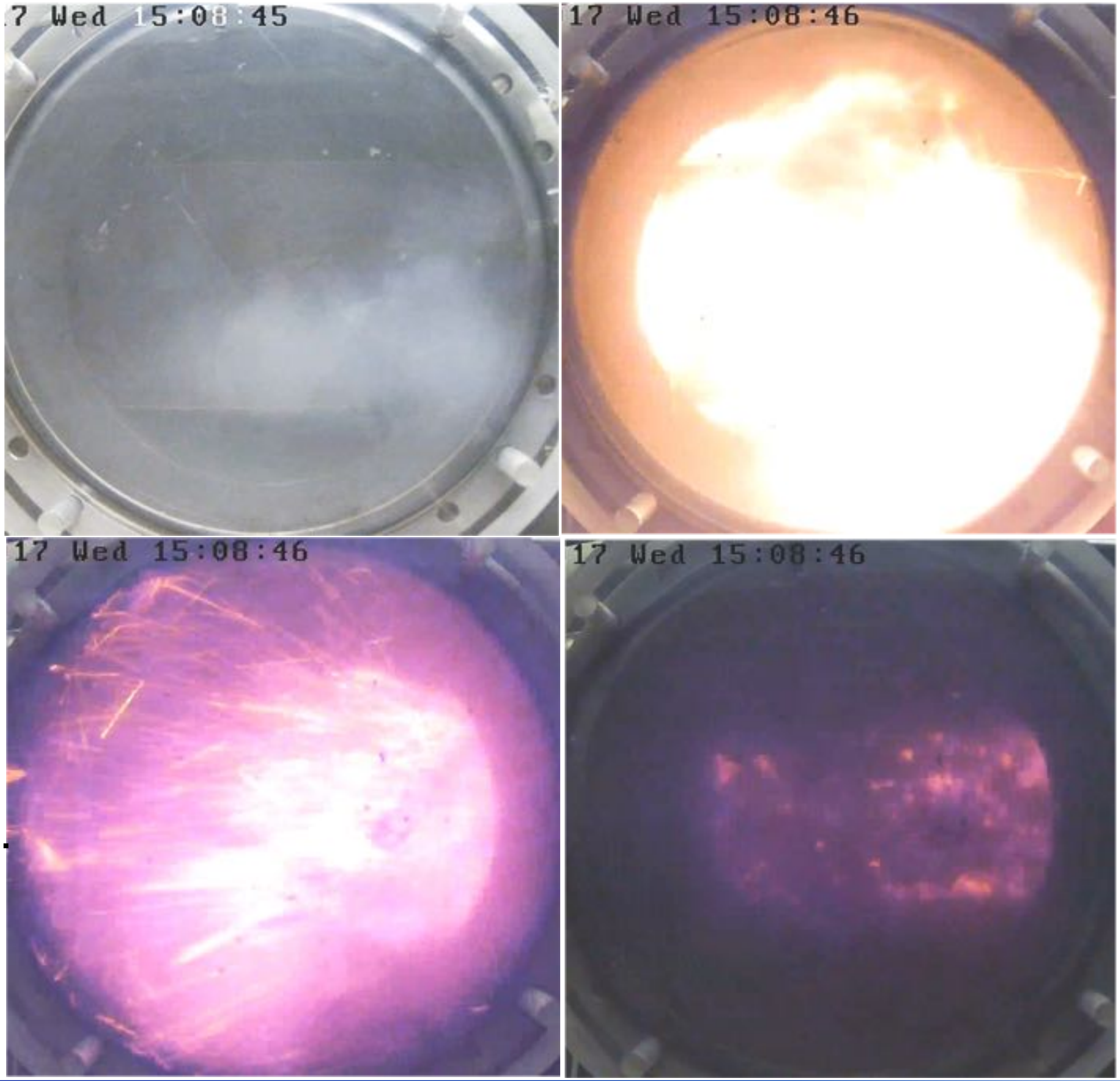
Ignition following the venting of the cell. Ignition event lasted ~1.5 s. After event, thick gray/black particulate obscured viewport.

Thermal Runaway: Ambient Testing

Thermal Runaway: ISS Testing

Venting of electrolyte vapor.

Ignition of vented vapor.

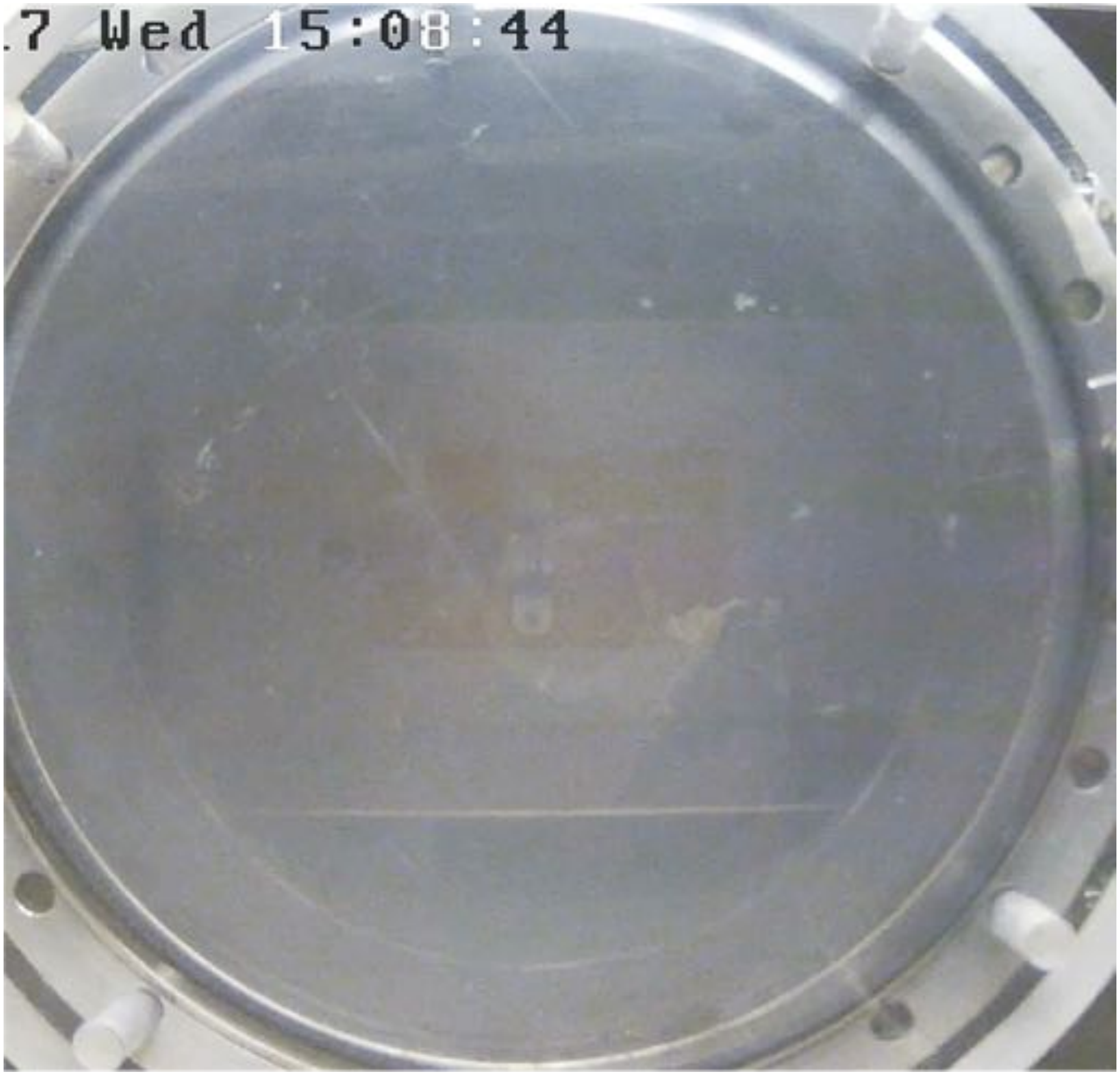


Ejection of entire cell components.

Cooldown of cell components.

The cell vented and quickly ignited with a bang. A second retort occurred when the cell contents were ejected.

Thermal Runaway: ISS Testing

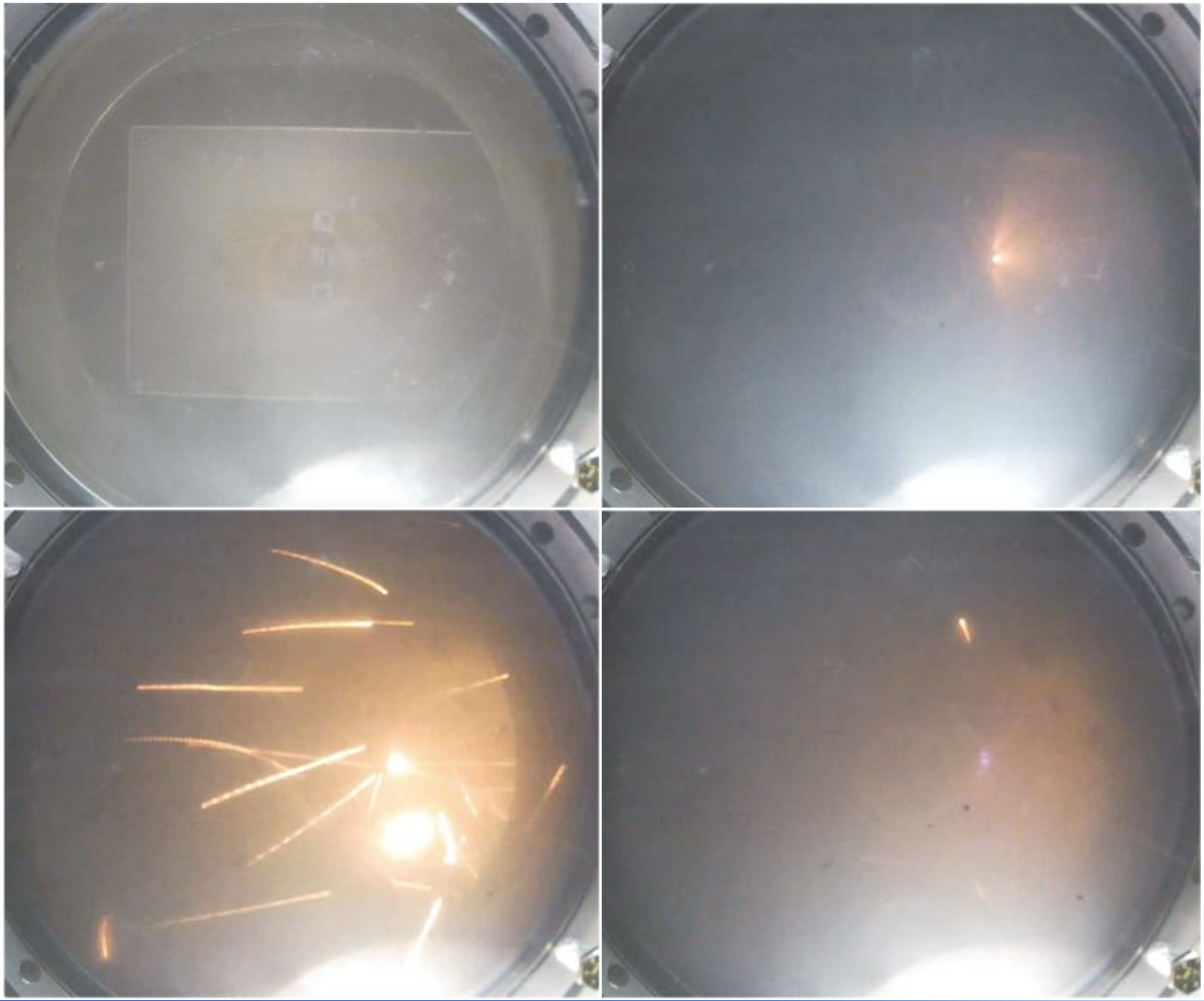


The cell vented and quickly ignited with a bang. A second retort occurred when the cell contents were ejected.

Thermal Runaway: Vacuum Testing

Vented vapor.

Spray of hot material from vent.



Hot particles ejected.

Cooldown of cell components.

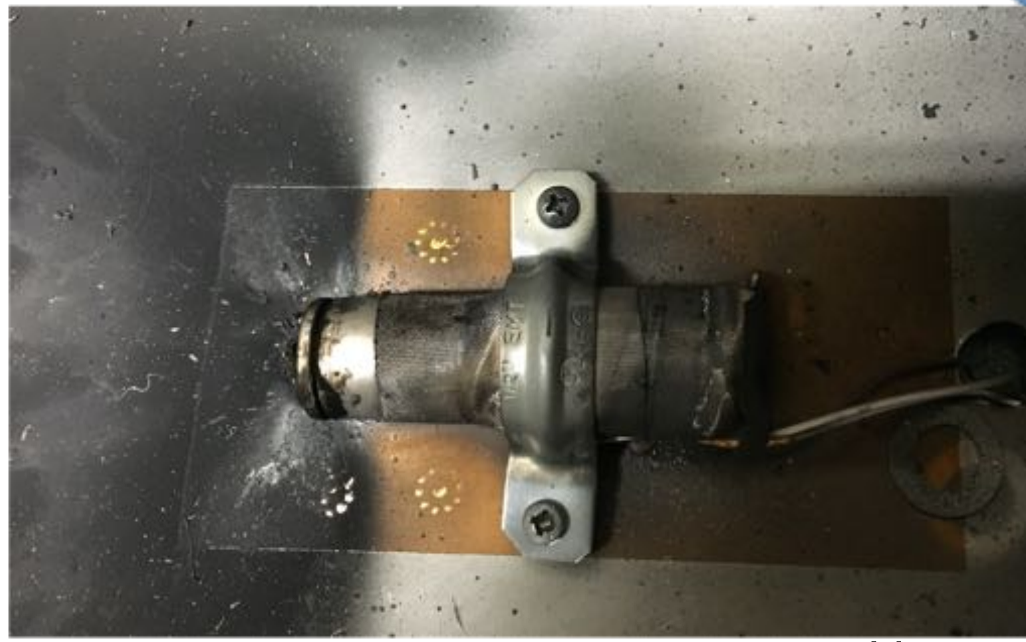
Vacuum thermal runaway did not have an ignition event of the vented electrolyte vapor.

Thermal Runaway: Vacuum Testing

Vacuum thermal runaway did not have an ignition event of the vented electrolyte vapor.

Post Testing

Ambient



Vacuum

ISS

Ambient thermal runaway first vented and then flared up leaving black residue.

ISS runaway first vented and flared, and a second retort expelled the full cell contents.

Vacuum thermal runaway was a hot spray of particles without flare up.

A thick layer of dense black material covered all open surfaces of the witness box. It is likely that the ISS expulsion of cell contents was caused by a vent failure rather than the specific atmosphere.

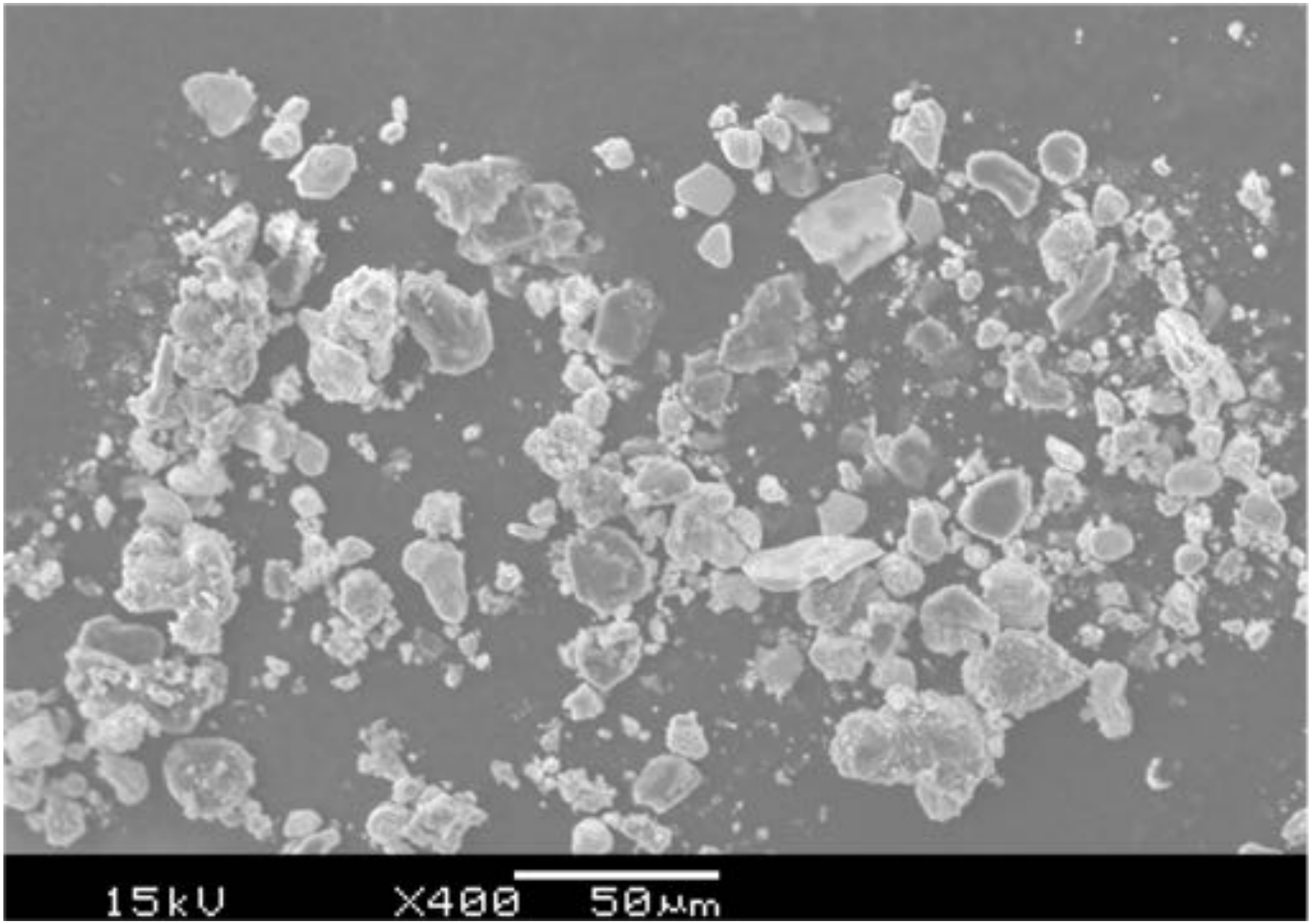
Typical Particles

Particles are fine black material. The particulates were fairly also fairly clumpy.

Particles demonstrate attraction to a strong magnet.

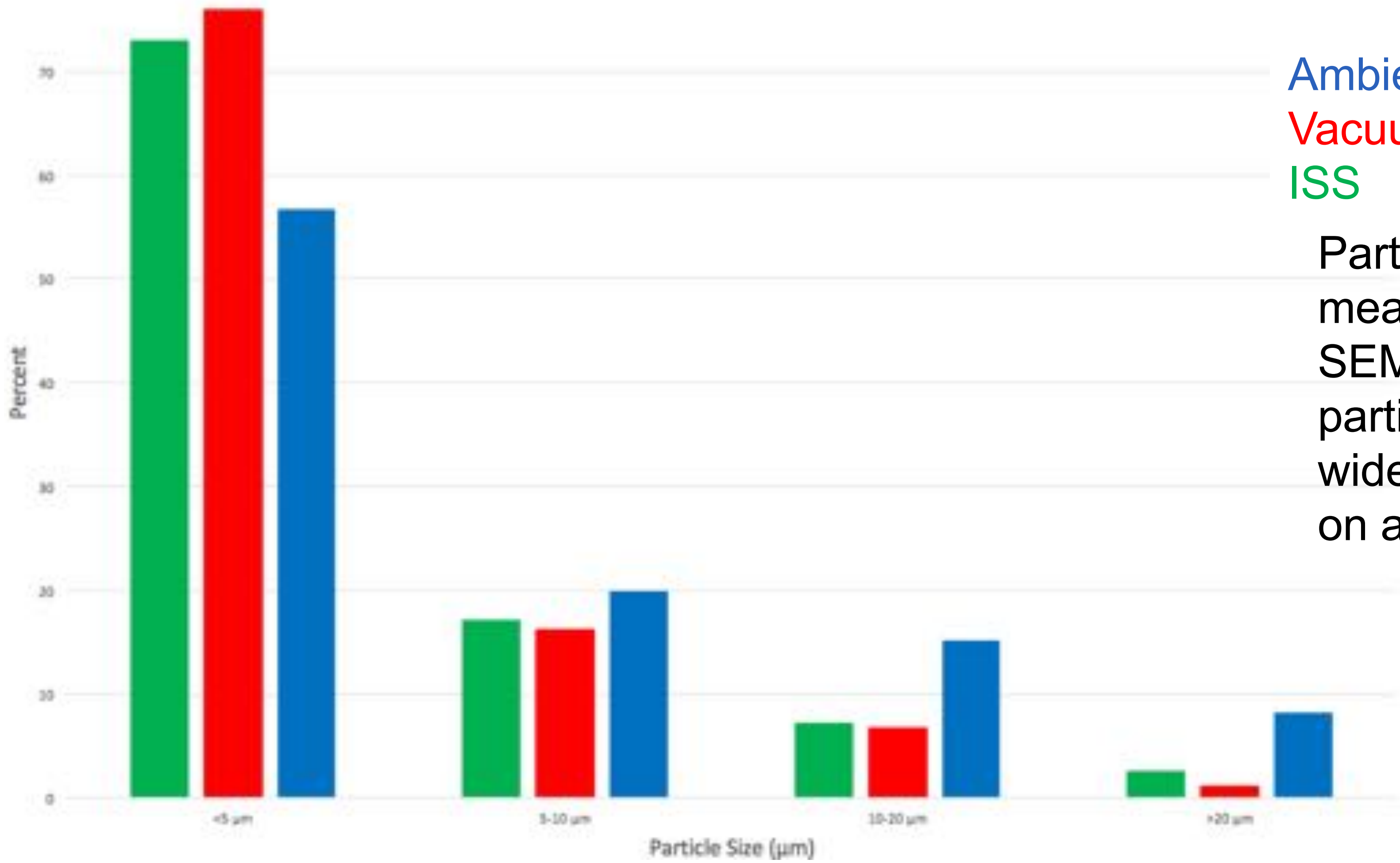
Magnetic separation did not separate out much material, indicating that the bulk of the particulates are either ferro- or paramagnetic.

Typical Size and Shapes of Particles



Particulates had a wide range of shapes and sizes. Particle appearances were similar across all three test conditions.

Particle Size Distribution



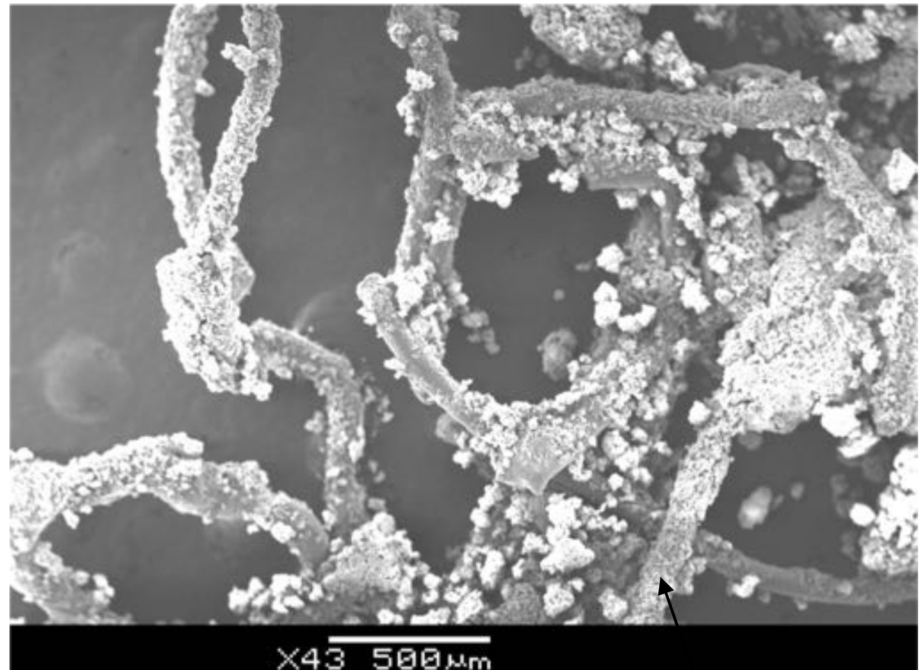
Ambient
Vacuum
ISS

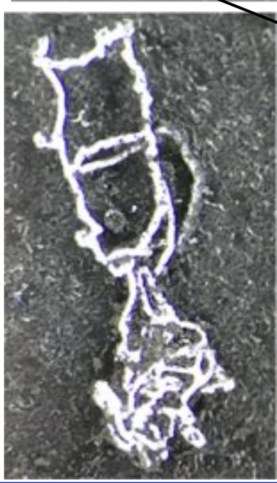
Particle size is measured from SEM images of particulates widely scattered on a surface.

Significant percent of the particle population is in the <2.5 µm size. Smaller particulate sizes are linked to inhalation health hazards.

Vacuum Testing-Aluminum Filaments

Vacuum venting





Aluminum filaments

Aluminum filament

Elemental Analysis

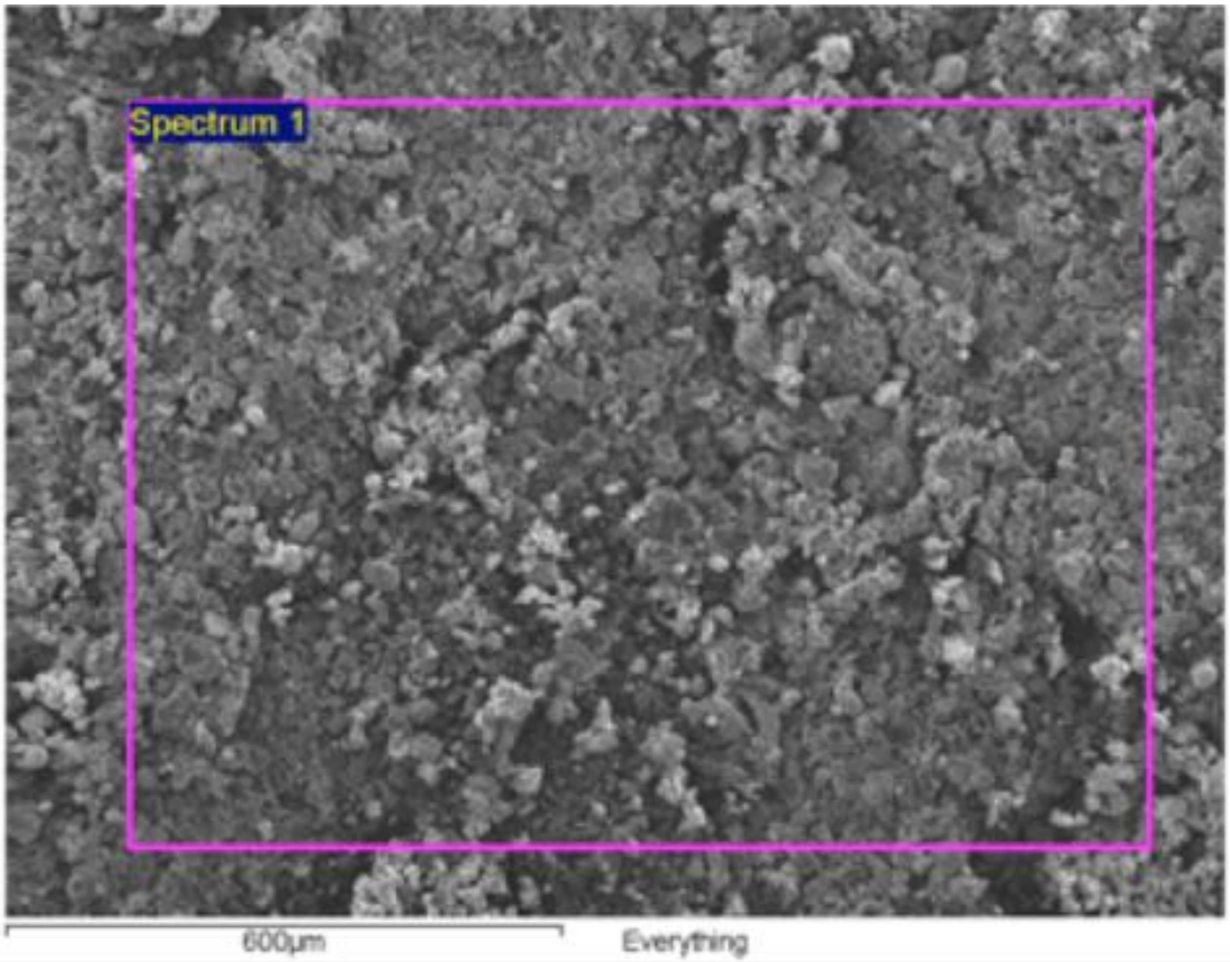
C	O	F	Al	P	Co
18.08	0.00	0.00	81.45	0.00	0.47

Vacuum thermal runaway had copious amounts of fine Al filaments spread over the vented area.

These filaments were not found in ambient/ISS atmospheres. Likely that molten Al combusted in O_2 atmospheres.

The long (many cm unwound) filaments may pose a shorting hazard to electrical components.

Particle Atomic Composition by EDX



Sample suspension pH tested:

Ambient:	10.14
ISS:	11.03
Vacuum:	6.94

Particulates for ambient and ISS may be very caustic in eyes and lungs.

	C	O	F	Al	P	Mn	Co	Ni	Cu	NMC
Ambient	64.63	10.62	6.35	4.17	1.01	1.14	8.64	2.35	1.09	12.13
ISS	63.39	11.99	6.78	4.24	1.26	1.31	7.97	2.78	0.27	12.06
Vacuum	55.48	11.67	8.21	6.71	1.25	2.43	9.07	4.87	0.27	16.37

Overall composition mirrors expected cell components. Only Cu is deficient, as it was left behind in the cell.

Particle Population Composition

Particle Identity	Ambient % Population	ISS % Population	Vacuum % Population
Carbon	40	43	17
Cobalt	29	30	45
NMC	13	13	6
Mixed Cathode	9	2	7
Al	4	3	13
Cu	3	1	0
Other	4	8	12

Individual particles were analyzed using SEM/EDX. The chemical composition as measured by EDX was used to assign an identity for the particle as follows:

Carbon: > 75% At.% C
Cobalt: > 45% At.% Co
NMC: > 45% At.% Ni, Mn, Co, ratio ~2:1:1
Mixed Cathode: other ratio of NMC
Al: > 20% At.% Al
Cu: > 20% At.% Cu

For particles determined to be either Cobalt, NMC, or Mixed Cathode, the average M_xO_y formula is (in the conservative assumption that all measured oxygen is with the metals):

Ambient: $MO_{0.16}$
ISS: $MO_{0.26}$
Vacuum: $MO_{0.57}$

This indicates that the metallic particulates contain significant amounts of pure metal.

Ambient and ISS populations appear similar, while Vacuum has relatively fewer carbon particles and more Al particles.

Thermal Separation GC-MS

- Added particle samples directly to thermal separation probe (TSP) vials.
  - Measured sample mass change before and after analysis.
  - *Heat TSP injector rapidly to 320 °C, hold for 1 min.*
  - *Ramp GC oven to 330 °C at 10 °C/min, hold for 5 min.*

- Sample mass data was collected before and after GC-MS runs to determine change in mass after heating to 320 °C under He flow.

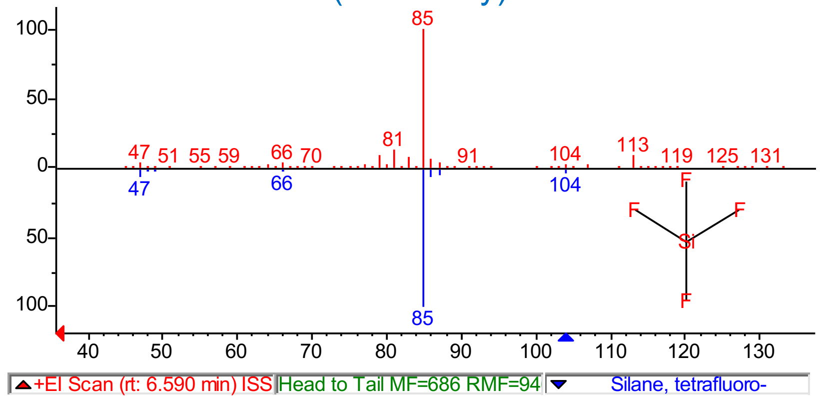
Sample	Initial mass (mg)	Final mass (mg)	Δ mass (mg)	% Δ mass
Vacuum	0.9507	0.8515	0.0992	10.43
Ambient	0.4844	0.4650	0.0194	4.00
ISS	0.3678	0.3467	0.0211	5.74

- The Vacuum sample produced the largest percent mass change of 10.43%. This mass loss likely results from a higher fraction of volatiles present in the sample.
- The Ambient and ISS samples exhibited lower mass change at 4.00% and 5.74%, respectively.
- Likely that without an O_2 atmosphere, vacuum runaway did not combust *vented* organics.
- However, components that remained within the cell until thermal runaway began were oxidized by the charged cathode.

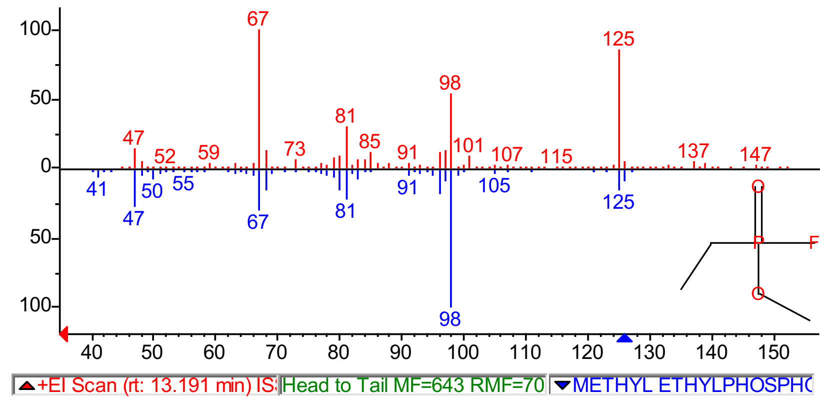
GCMS Analysis from Particulates

MS library best matches

RT = 6.59 min → detected in Vac and ISS only
Tetrafluorosilane (MS library)

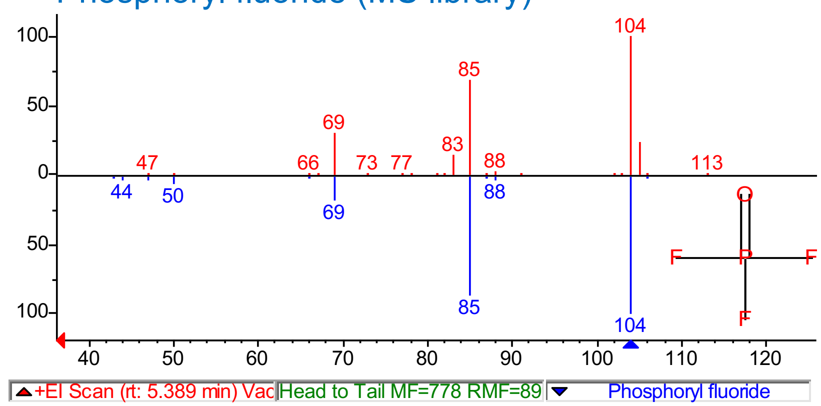


RT = 13.19 min → detected in Vac and ISS only
Methylethylphosphonofluoridoate (MS library)



Reactive F species will be detected as SiF_4 due to the silica separation column.

RT = 5.39 min → detected in all 3
Phosphoryl fluoride (MS library)



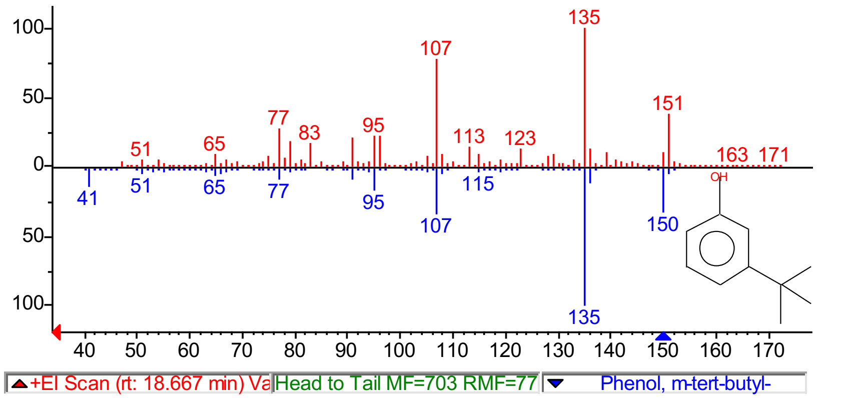
The oxy-phosphorous compounds were found in Vacuum as well, indicating that the O came from the cathode.

A collection of fluorinated and phosphine related compounds were detected, likely from partial combustion of electrolyte salts.

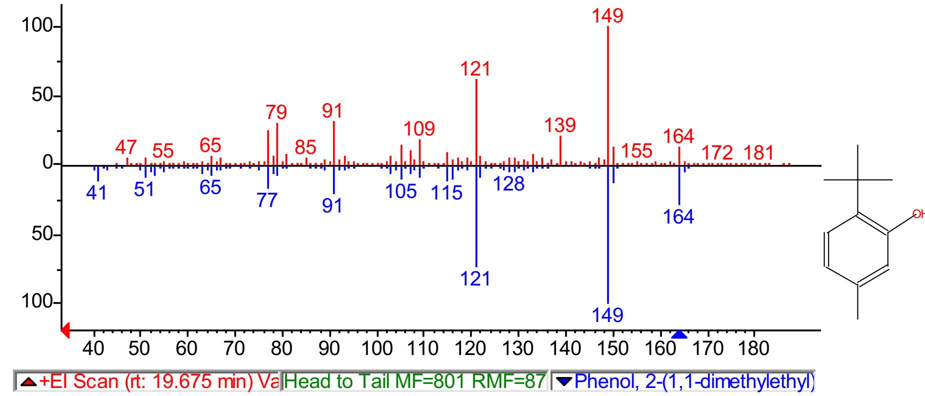
GCMS Analysis of Particulate Volatiles

MS library best matches

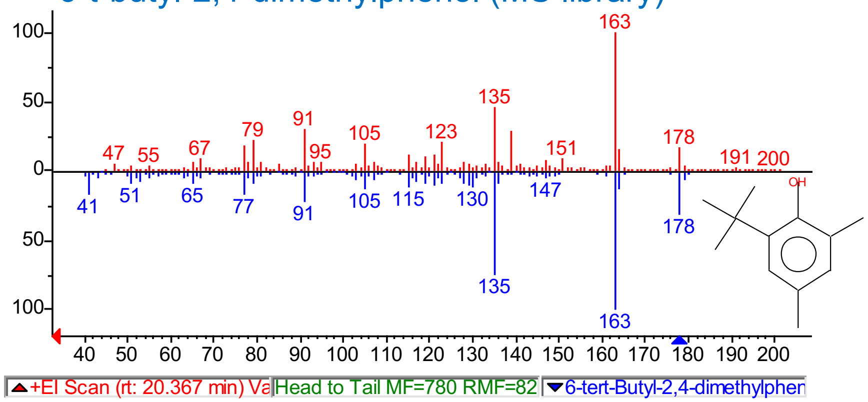
RT = 18.67 min → detected in all 3
3-t-butylphenol (MS library)



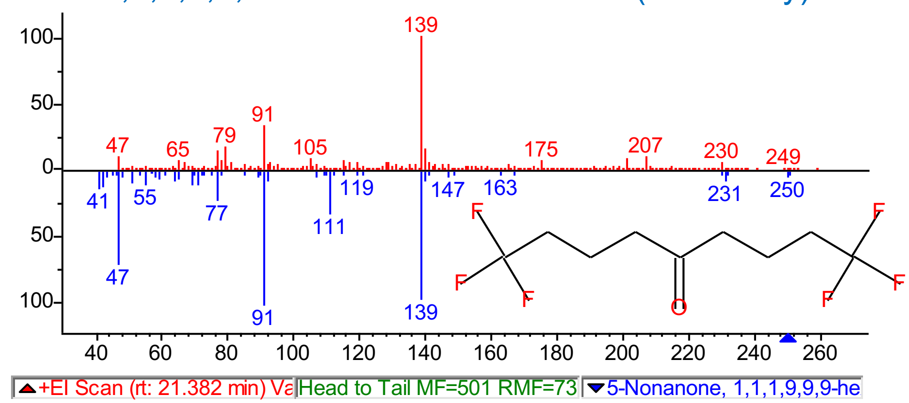
RT = 19.68 min → detected in all 3
2-t-butyl-5-methylphenol (MS library)



RT = 20.37 min → detected in all 3
6-t-butyl-2,4-dimethylphenol (MS library)



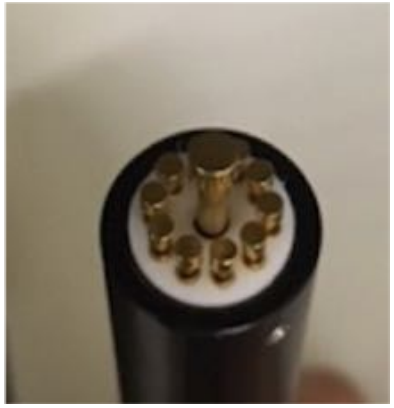
RT = 21.38 min → detected in Vac and ISS only
1,1,1,9,9,9-hexafluoro-5-nonanone (MS library)



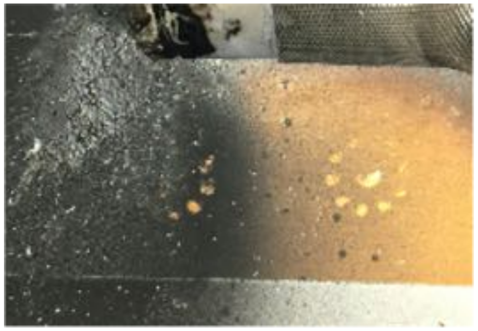
Various phenol and other aromatic materials detected, likely products of partial solvent combustion.

Particle Film Conductivity

Conductivity measurements through contact probe

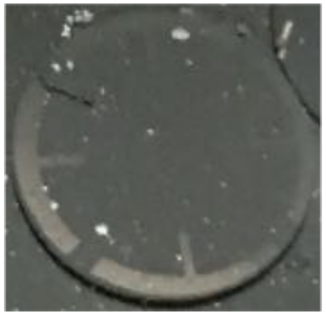


Spring-loaded Au probes



Particulate coating on Kapton

Conductivity through Van der Pauw measurements



Particulate coating on Au pads on sapphire

	Contact (Ω)	vDP (Ω/sq.)
Ambient	n.a.	n.a
ISS	$1.4\text{x}10^2$ to $1.5\text{x}10^5$	$8.7\text{x}10^{10}$
Vacuum	$1.8\text{x}10^5$ to $3.0\text{x}10^{11}$	$1.2\text{x}10^9$

Conductivity test was added after ambient test occurred.

Significant variation in contact probe measurements due to the variation in the particle coatings.

There was a wide range of conductivity, likely due to variations in film thickness and composition. However, sample films were not generally conductive.

Summary

- The three thermal runaway conditions tested, ambient atmosphere, ISS atmosphere, and vacuum produced thick coatings of fine-grained black particulates.
  - *These particulates were a combination of carbon particles from the anode and reduced metallic particles produced from the cathode.*
  - *The oxidation of the cell components (with the exception of vapor vented prior to thermal runaway) occurred even in vacuum, demonstrating that the cathode material is the primary oxidizer for the combustion process.*
  - *While having the appearance of common soot, the chemical composition is very different from soot, and thermal runaway material clean up and handling procedures need to be specifically tailored for this material.*

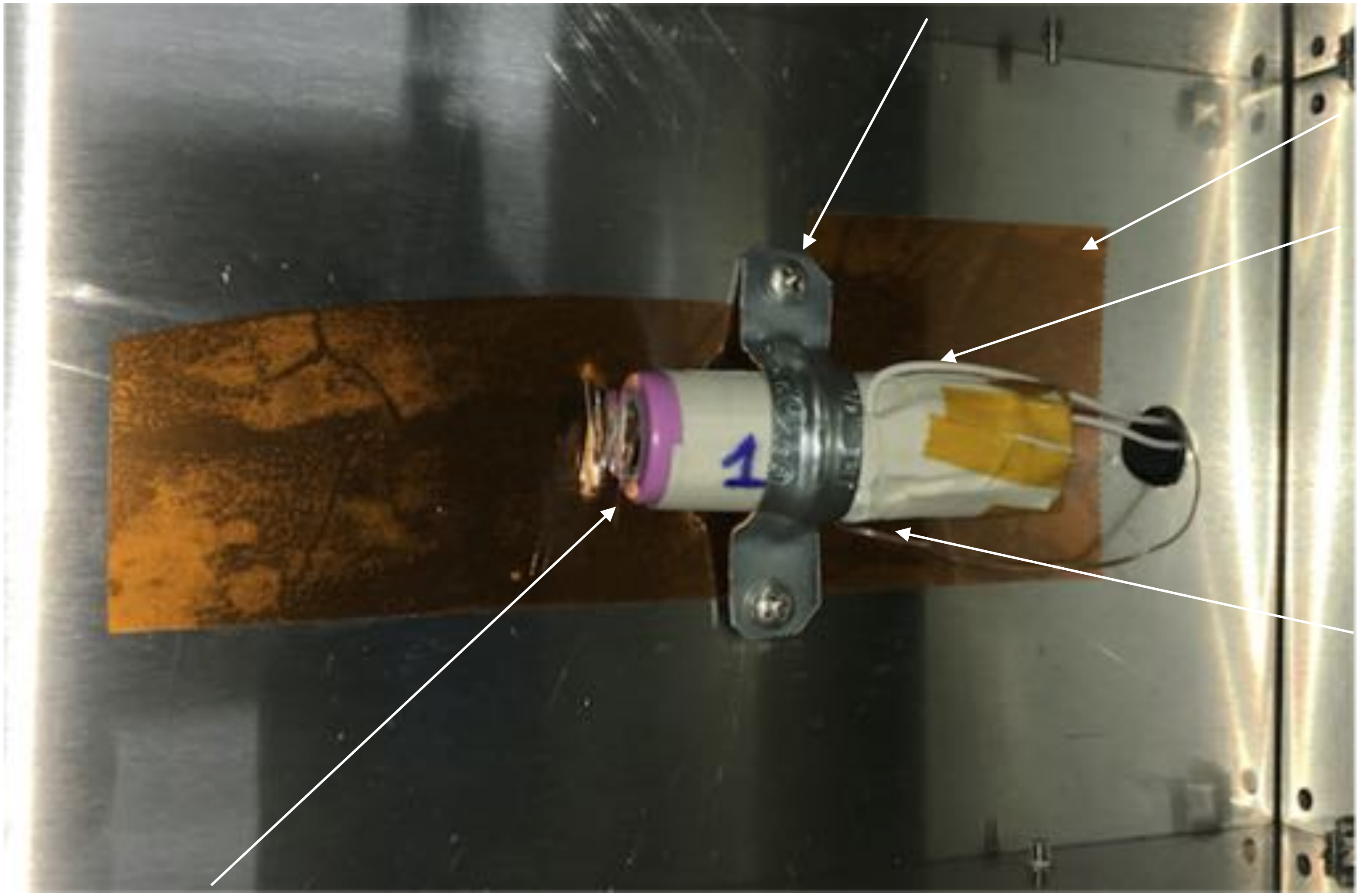
- The non-vacuum particulates were particularly alkaline (pH 10-11), and would be caustic if inhaled or exposed to eyes or other sensitive tissues.

- These particles were coated with the partial combustion products of the electrolyte. The identifiable $LiPF_6$ salt products are partially oxidized, as was the solvent residue.

- Particle films, while containing metallic and carbon particles, did not form conductive films, though individual large conductive particles may still pose a shorting risk to electrical components.
  - *The vacuum venting also produced long aluminum filaments which may pose an additional shorting risk depending on where they land.*

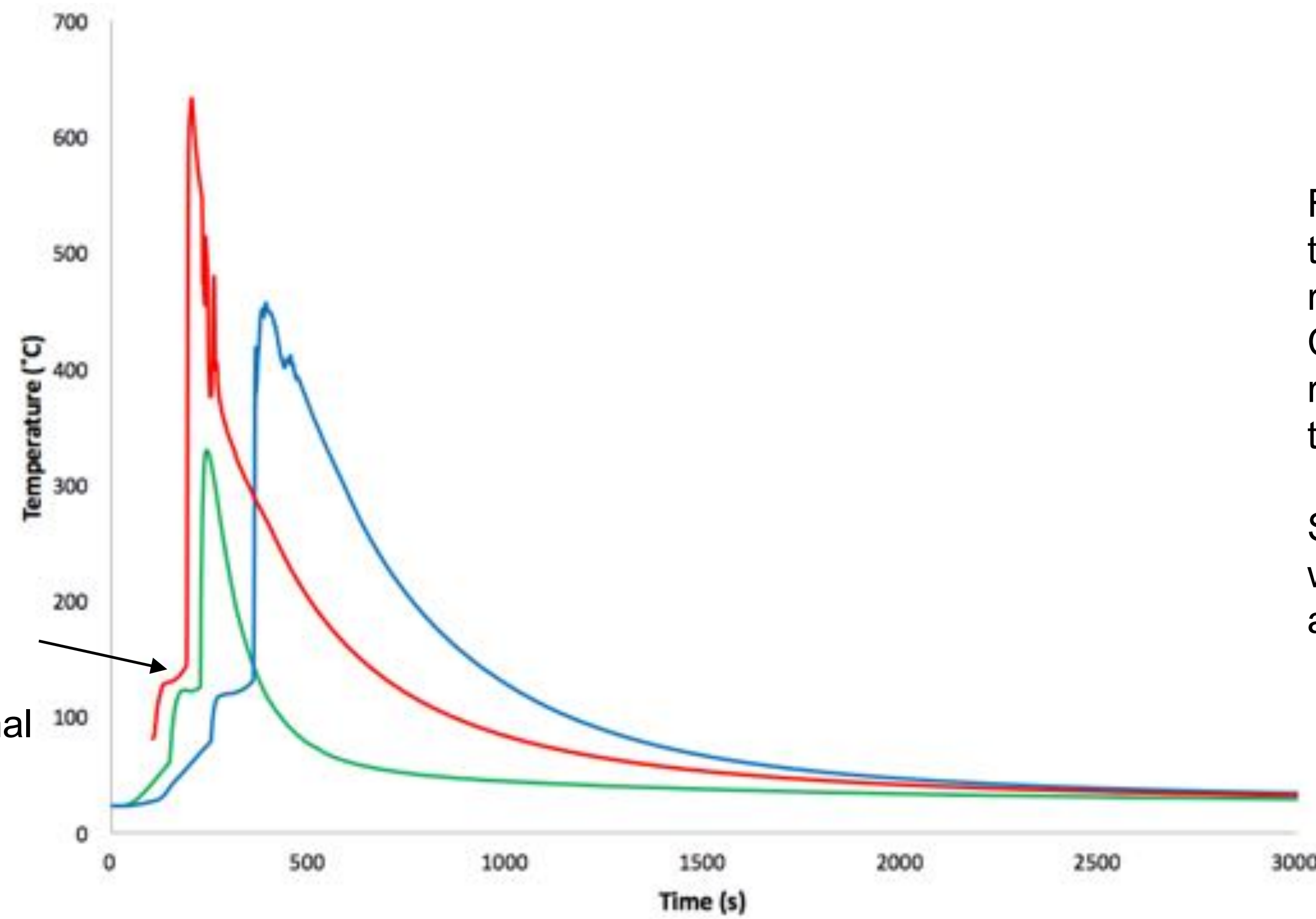
Supplementary Information

Cell Test Arrangement



Test setup showing the hold down clamp for the cell and the Kapton isolating tape.

Temperature Profiles



Ambient
Vacuum
ISS

For first (ambient) test power was ramped to 43W. Concern of thermal runaway occurring too quickly.

Successive tests were heated by direct application of 43W.

Plateau in heating immediately before thermal runaway.

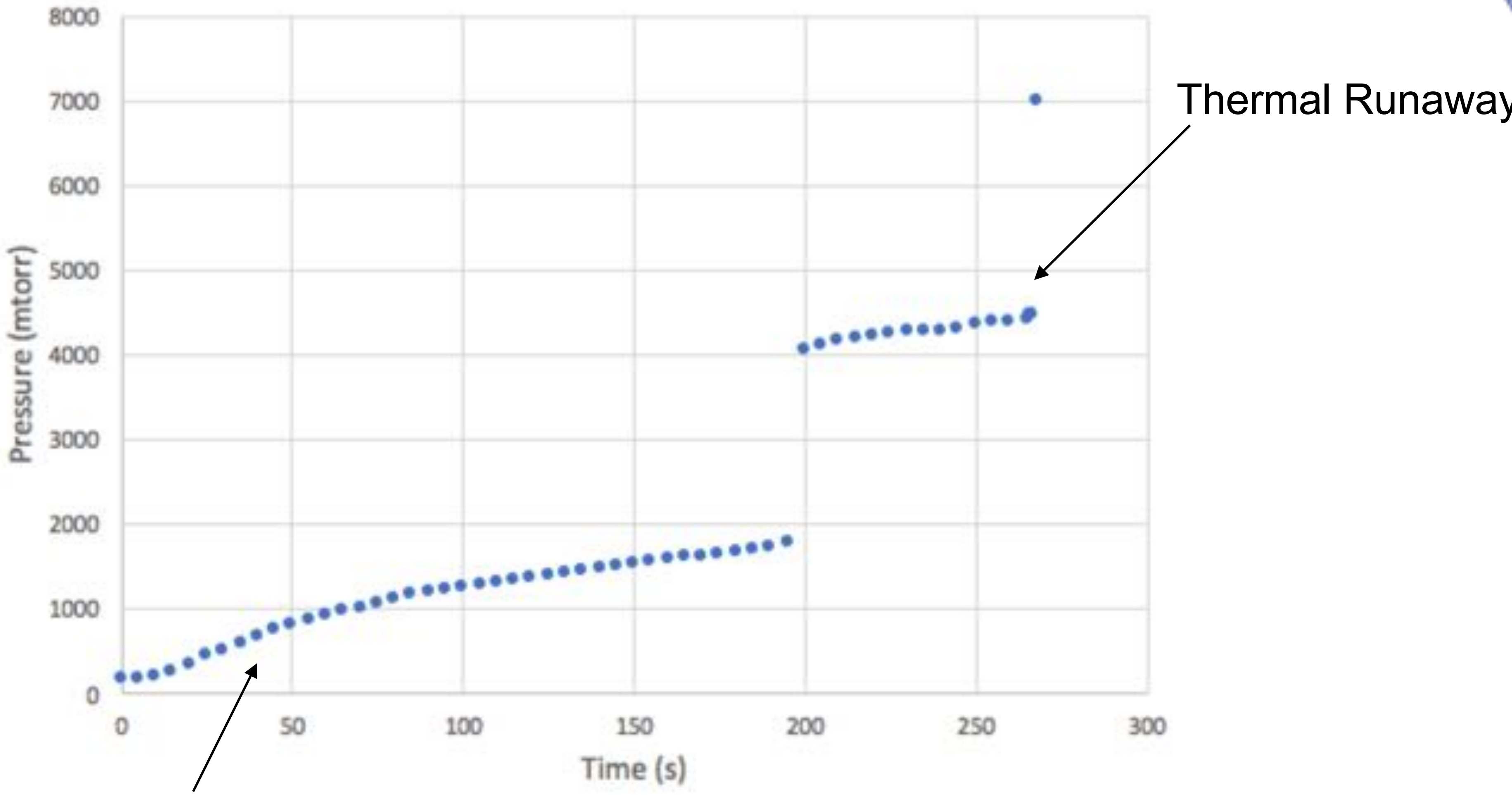
Large variation in the maximum measured cell skin temperature. This likely represents a minimum for the cell internal temperature.

Post Ambient Testing

Puddles of dried electrolyte.

Coating was thicker in front of vent, but coverage was total, and a thick layer of black material covered all open surfaces of the witness box.

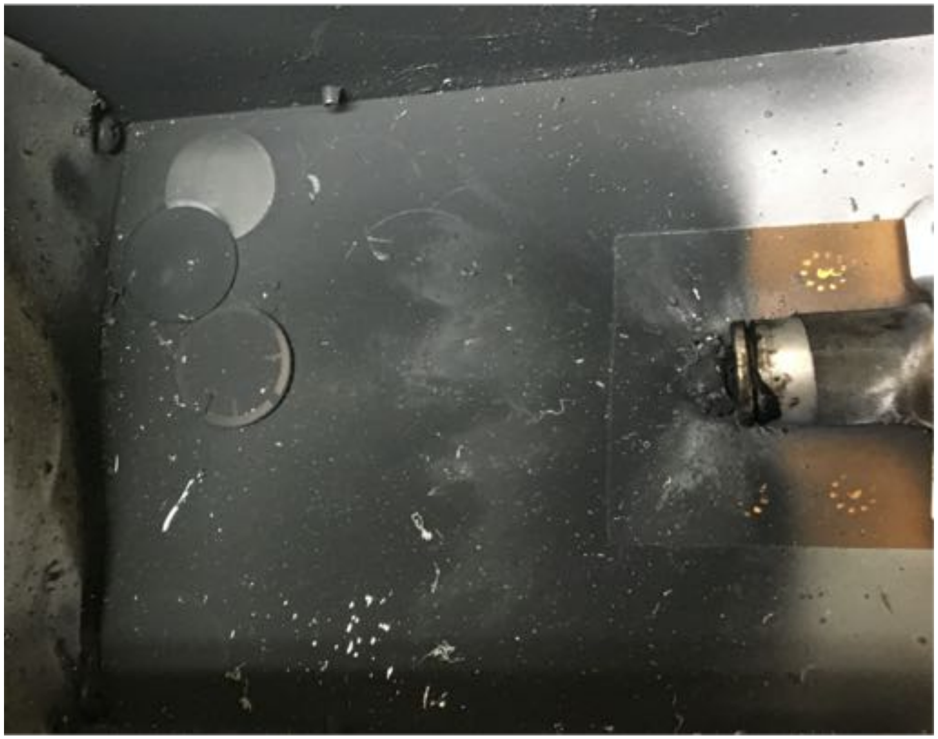
Vacuum Testing: Pressure



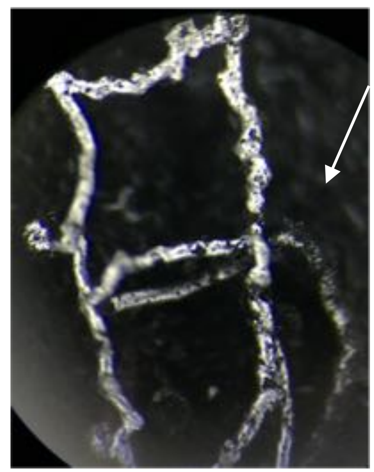
Initial pressure rise from outgassing of cell wrappings.

Pressure went off scale at onset of thermal runaway.

Post Vacuum Testing



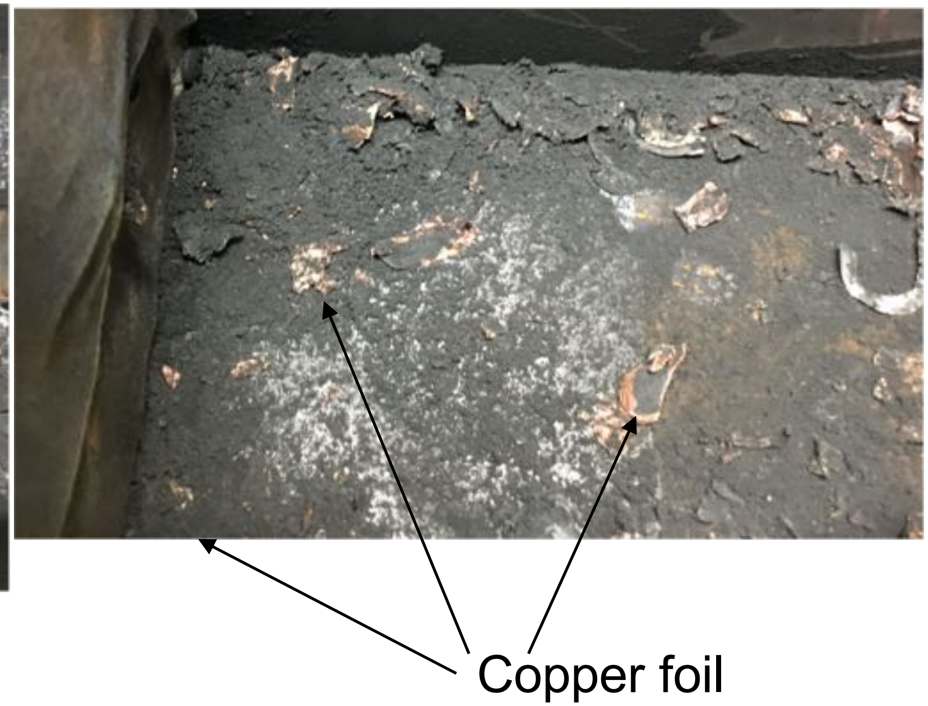
Significant difference between the ambient and vacuum testing: bright solidified aluminum filaments.



Aluminum filaments

Coating of particles was much denser in front of vent than for ambient. May be related to the violent expansion into a vacuum rather than a gas mass.

Post ISS Testing

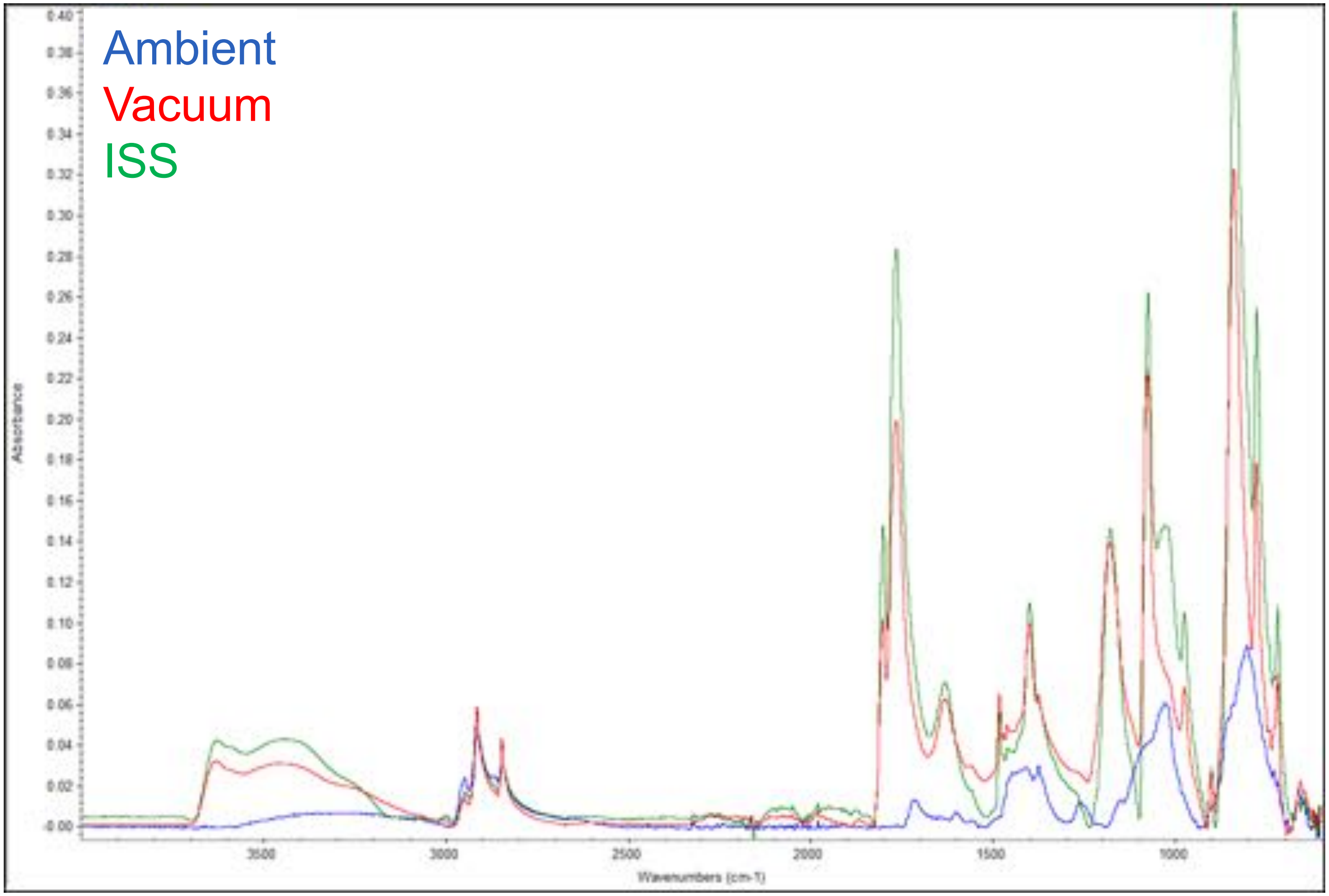


This cell did not cleanly vent material as seen in the other cells. The top of the cell failed and the full contents of the cell were expelled. It is unlikely that this is related to the atmosphere, but rather from the vent becoming clogged.

For sampling, all loose material was poured off and kept separately. The material that was adhered to the witness plates appeared similar to that observed in the other two tests. This is the material that was collected and analyzed.

FTIR Analysis of Particulates

Applied samples directly to ATR diamond crystal.

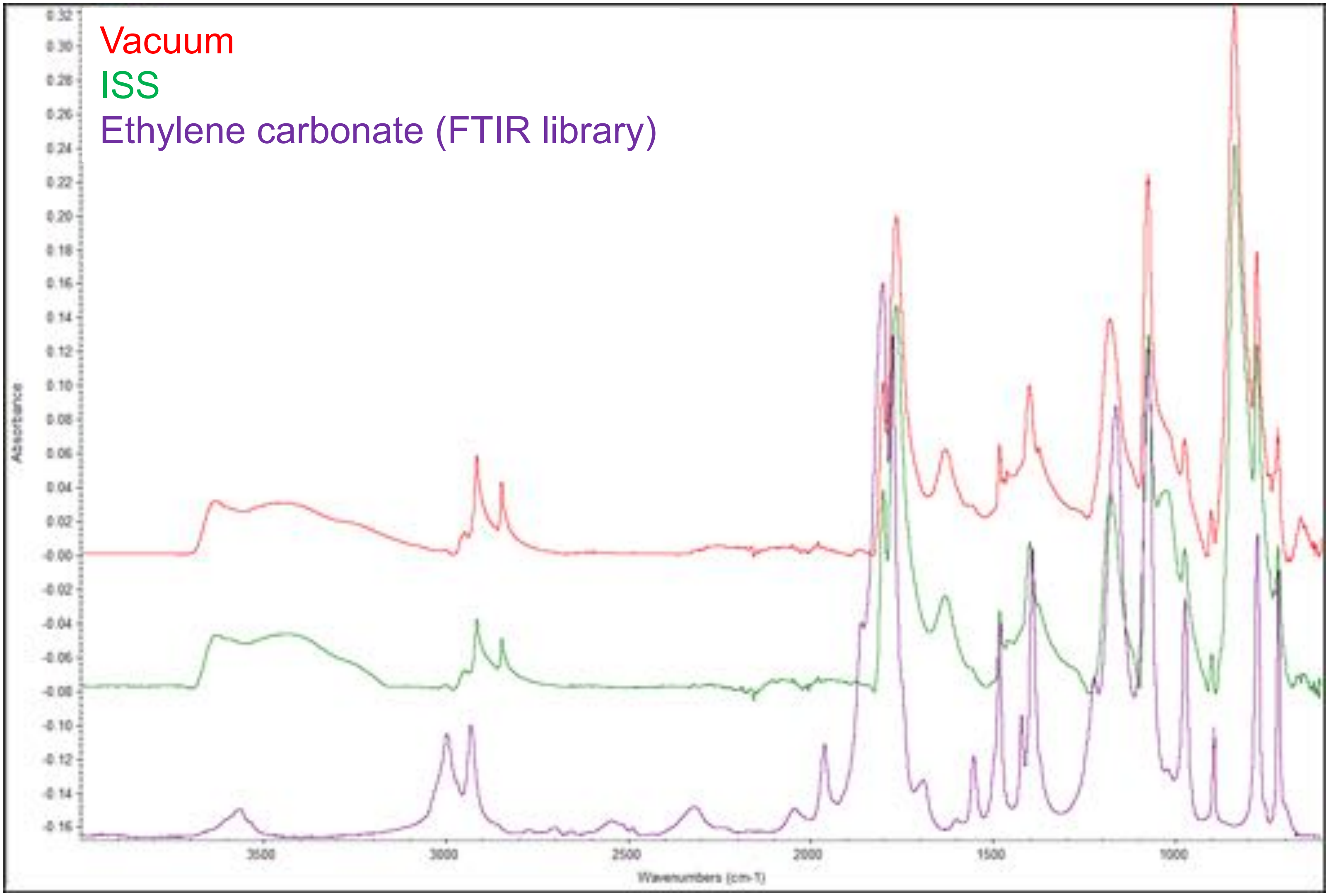


Particulate samples for ISS and vacuum were very clumpy, while the Ambient sample was loose.

The Vacuum and ISS produced much stronger IR signals relative to the ambient sample. This suggests additional material is present in this sample and could explain the observed clumpy powder.

FTIR spectra are baseline corrected.

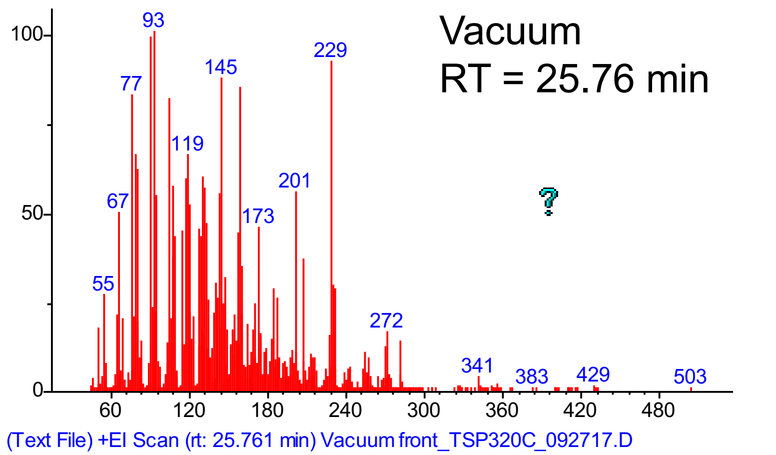
FTIR Analysis of Particulates

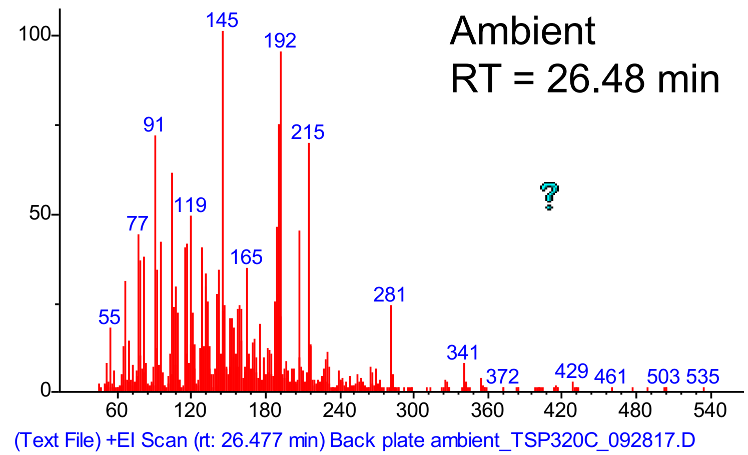


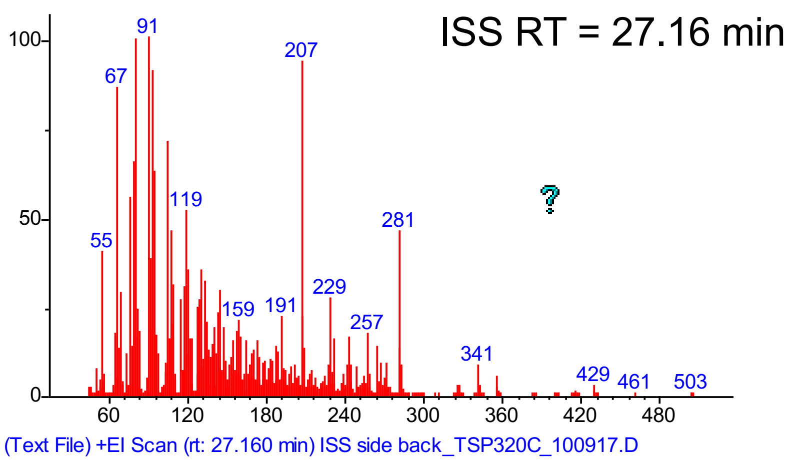
Ethylene carbonate (electrolyte) present in the ash samples.

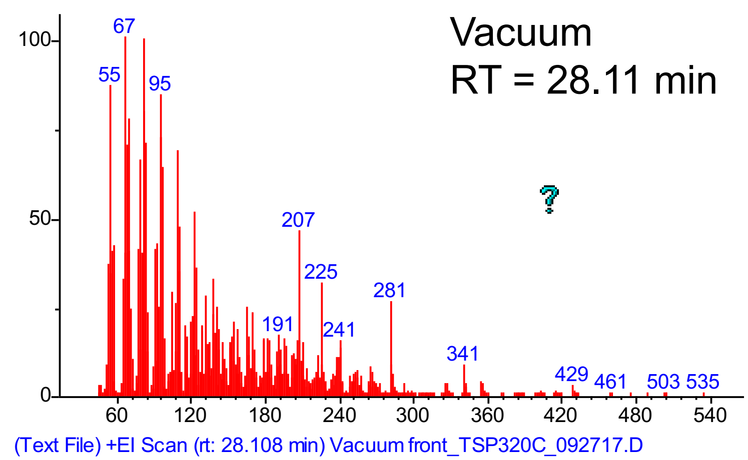
GC-MS High MW Components

- MS at high RT (> 25 min)







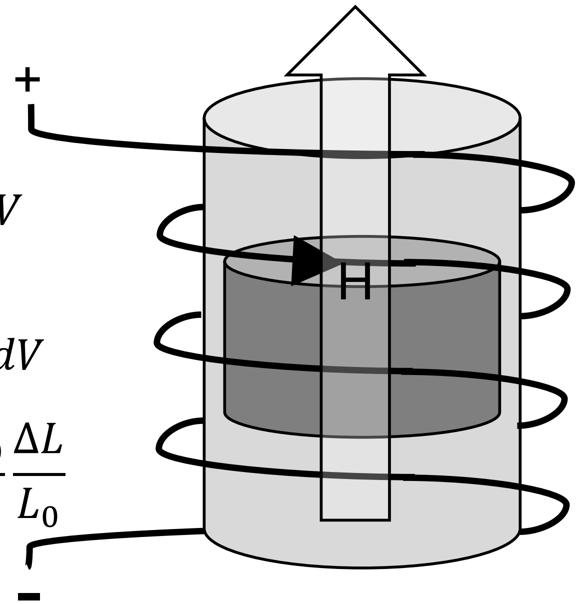


Note: masses 207, 281 are from the GC column as oven reaches max column temperature of 330 °C.

GC separation shows less resolution since the materials are similar in molecular structure as evidenced by MS. These appear to be significant amounts of large organics.

Particle Magnetic Susceptibility

Powder magnetic susceptibility through AC inductance measurements



$$L_0 \propto H \int dV$$

$$L \propto H \int \mu_r dV$$

$$\mu_r = 1 + \frac{V_0}{V_s}\frac{\Delta L}{L_0}$$

L_0 *is inductance of empty coil*
L *is inductance of sample in coil*
μ_r *is relative magnetic permeability*
V_0, V_S *are coil volume and sample volume*

Magnetic susceptibility is derived from permeability by reference to nickel powder.

Sample	Relative Permeability	Susceptibility (CGS) (*Ni powder reference value)
Ambient	1.017	0.349
Vacuum	1.028	0.371
ISS	1.061	1.251
Ni powder	3.360	48*
Air	1	0

The ambient and vacuum samples were paramagnetic, but not strongly so. The ISS sample was more paramagnetic, but not as strong as the ferromagnetic sample of nickel powder.