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NEXT GENERATION ANODES FOR LITHIUM-ION BATTERIES: THERMODYNAMIC UNDERSTANDING AND ABUSE PERFORMANCE

KYLE FENTON, ERIC ALLCORN, GANESAN NAGASUBRAMANIAN, CHRIS ORENDORFF

Silicon Deep Dive Program Informational Meeting
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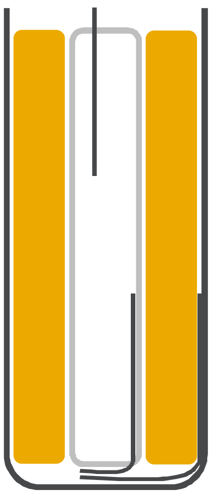
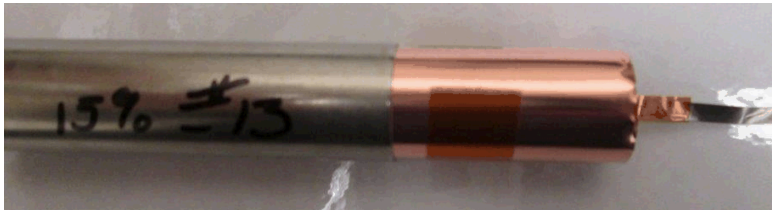
DESIGN AND ASSEMBLY OF NEW LOWER CAPACITY 18650 CELLS

Copper wrapping or sleeves to reduce jellyroll size and limit free volume in cell

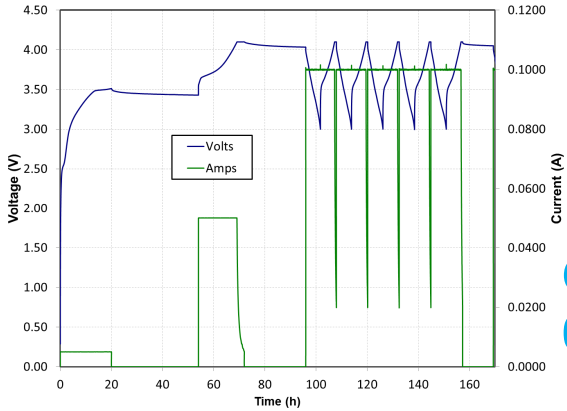


- Lower capacity should allow for safe operation of ARC to obtain quantitative data on runaway of Silicon anode



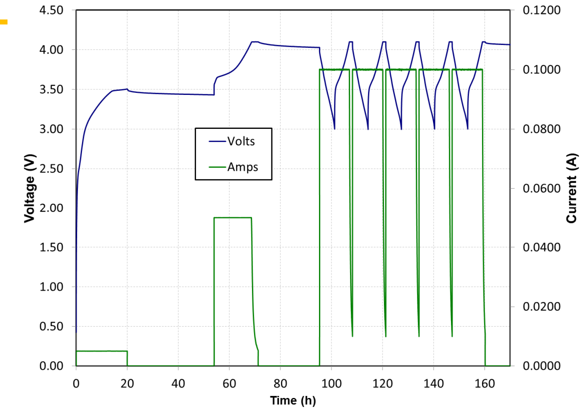
Electrode lengths ~ ½ of regular 18650s

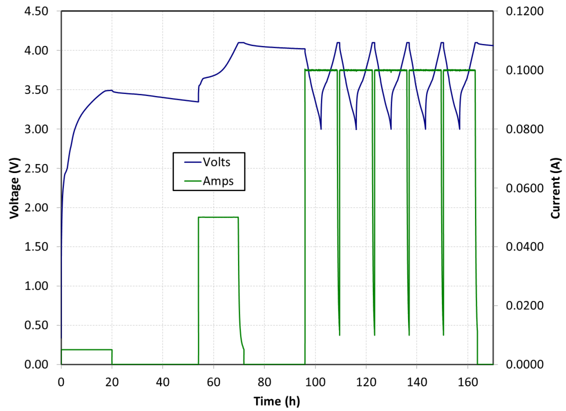
FORMATION COMPARISON BETWEEN ARC CELLS SHOWS MINIMAL VARIABILITY



Cell 13 – 0.59 Ah

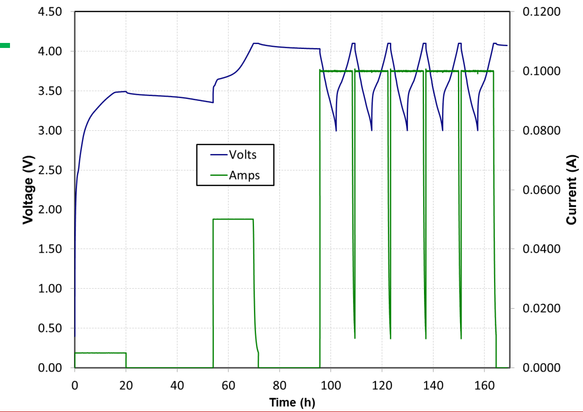
Cell 17 – 0.61 Ah





Cell 20 – 0.65 Ah

Cell 21 – 0.64 Ah



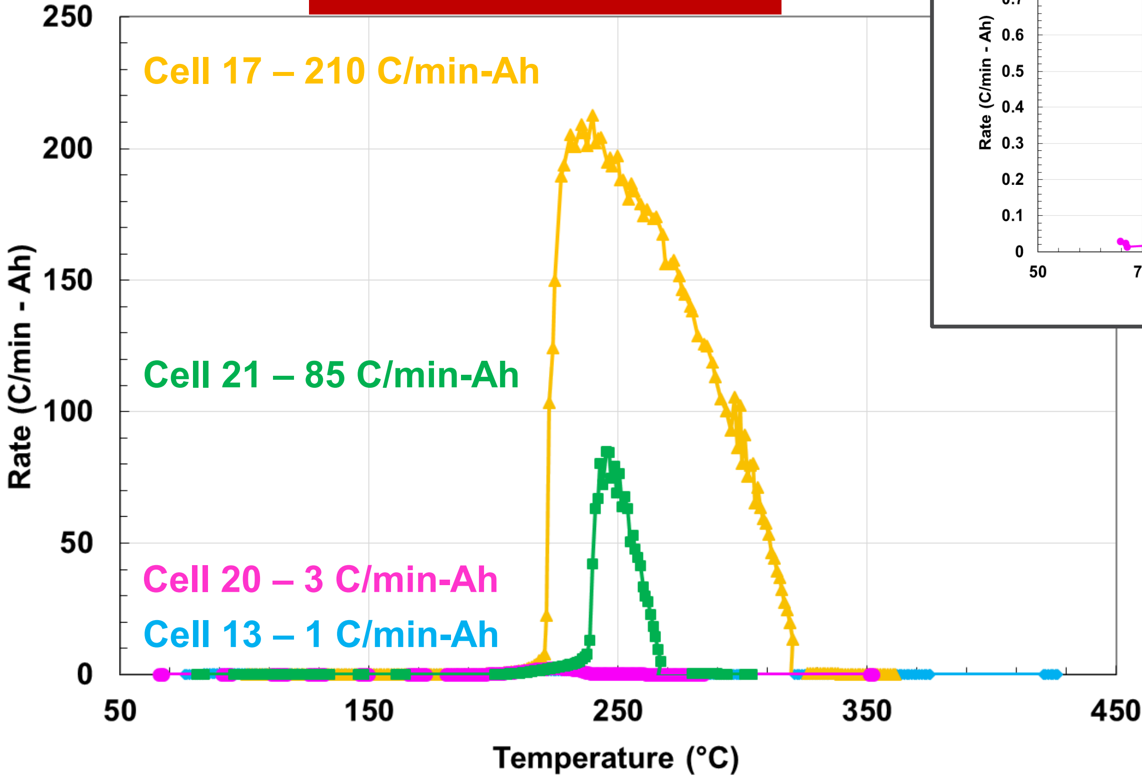
No significant difference in formation cycles between ARC 18650s to explain difference in runaway response

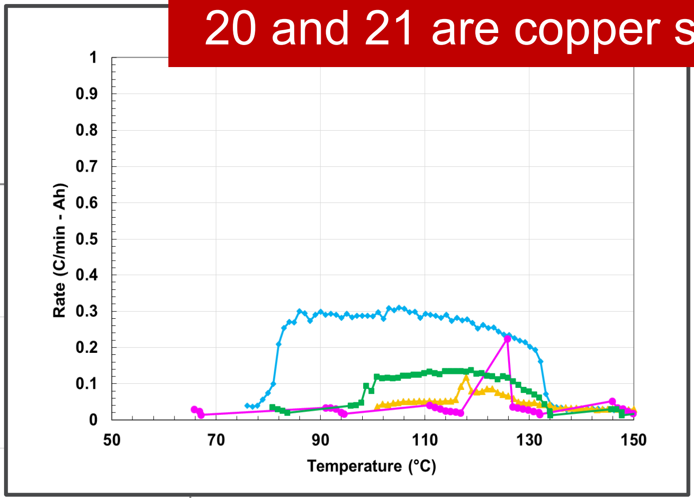
ARC TESTING OF LOW CAPACITY 18650 CELLS

15% silicon data for ~0.6 Ah cells

15% nSi v NMC @ 100% SOC
Gen2 + 10%FEC

13 and 17 are wound copper
20 and 21 are copper sleeve

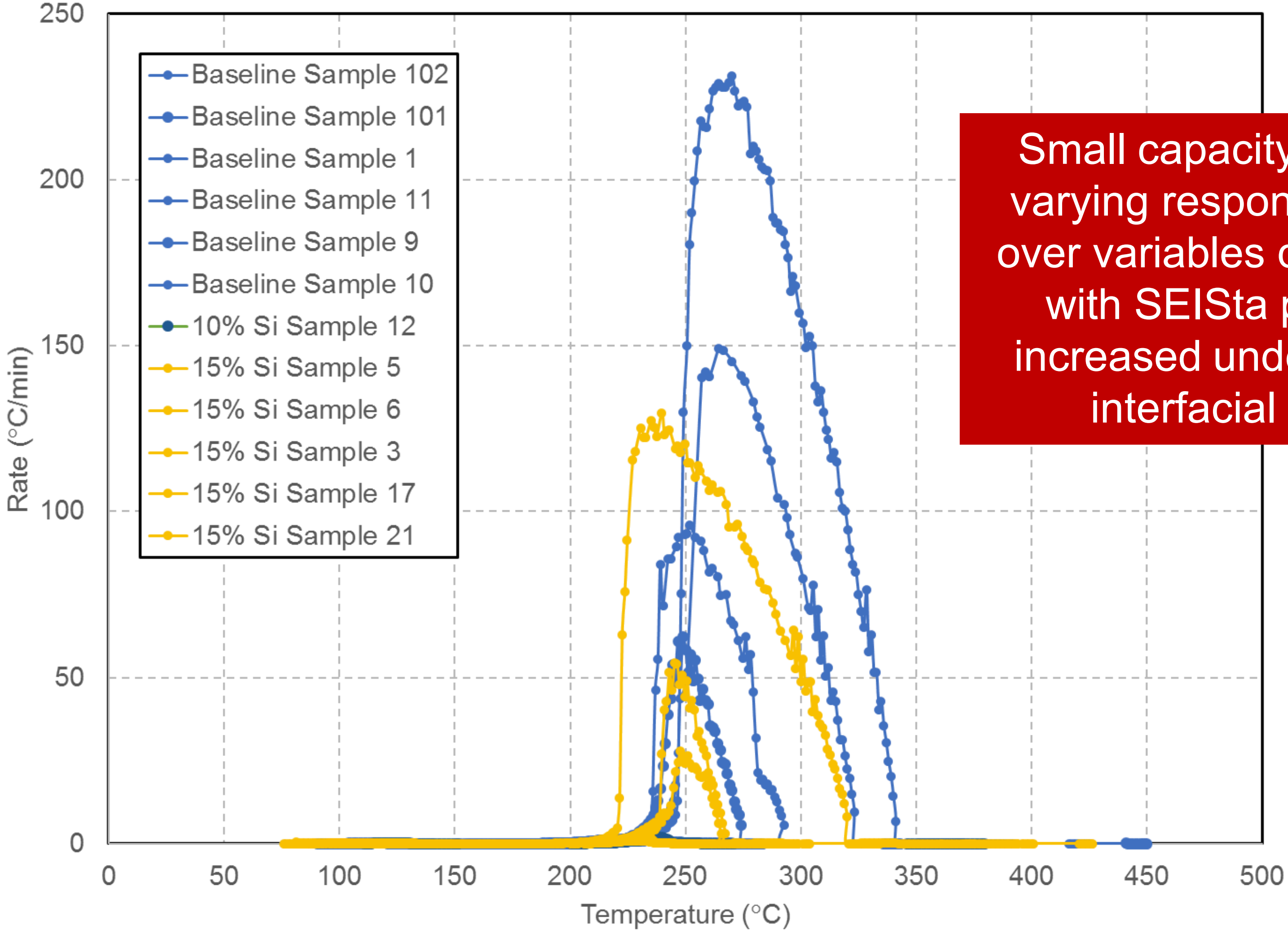




CAMP 50-70nm Nanoamor anodes
46 % coating porosity
15% nSi
78% MAG-E
2 % Timcal C45
10 % LiPAA

RECENT ARC RUNS

Not normalized to capacity!



Small capacity cells exhibit varying responses – control over variables difficult. Team with SEISta program for increased understanding of interfacial reactivity

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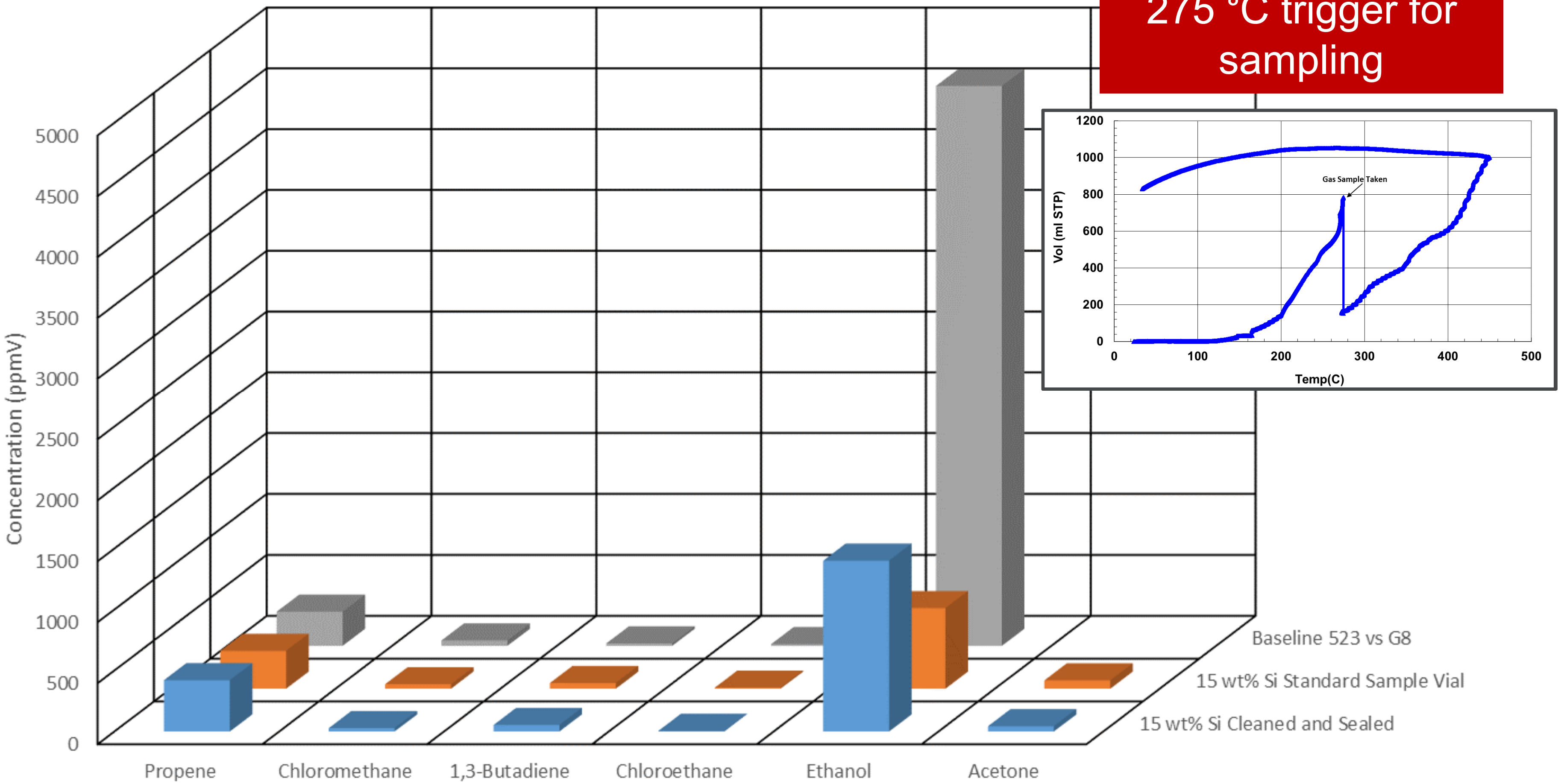
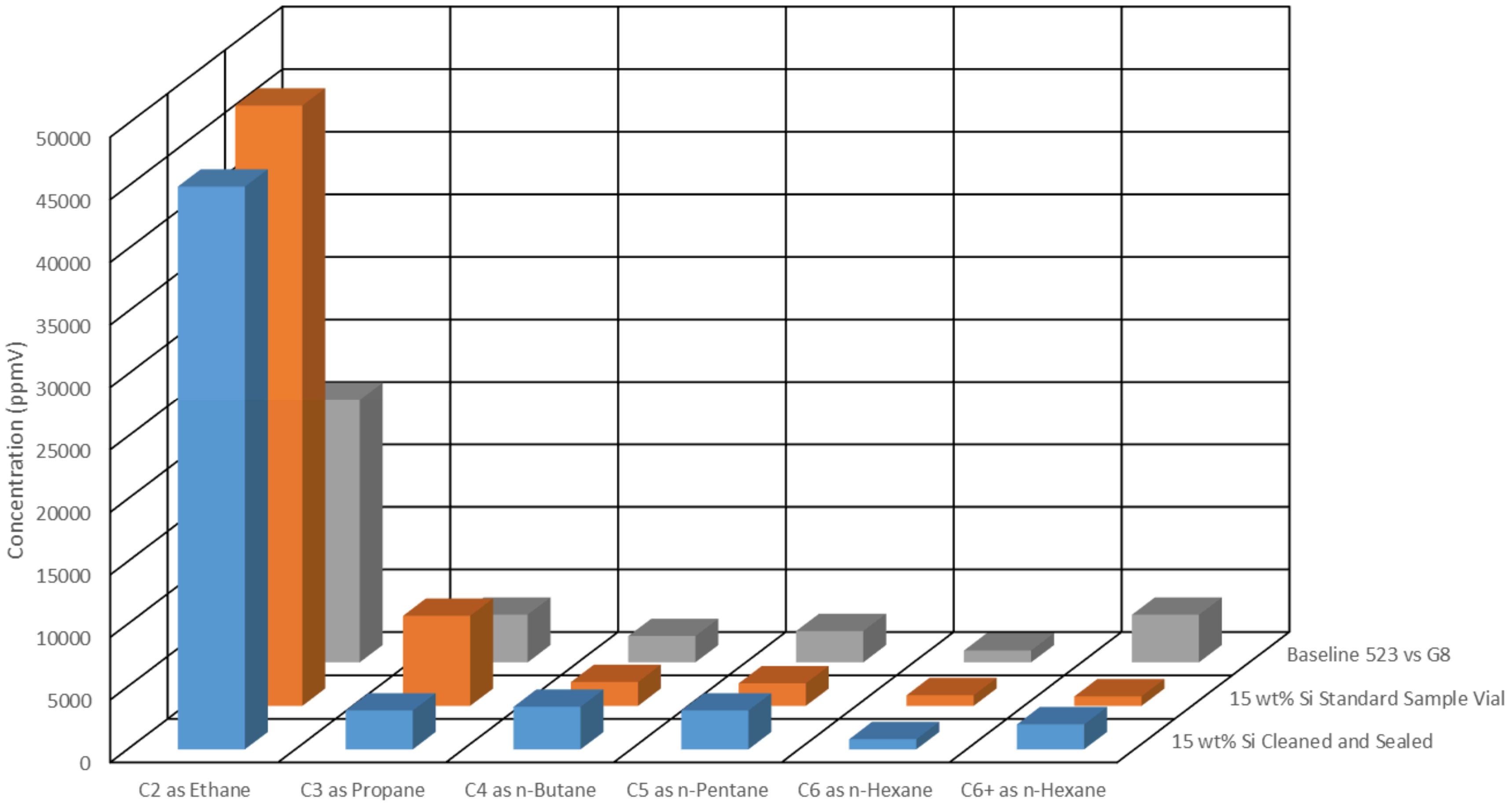
GAS SAMPLING – ORGANICS

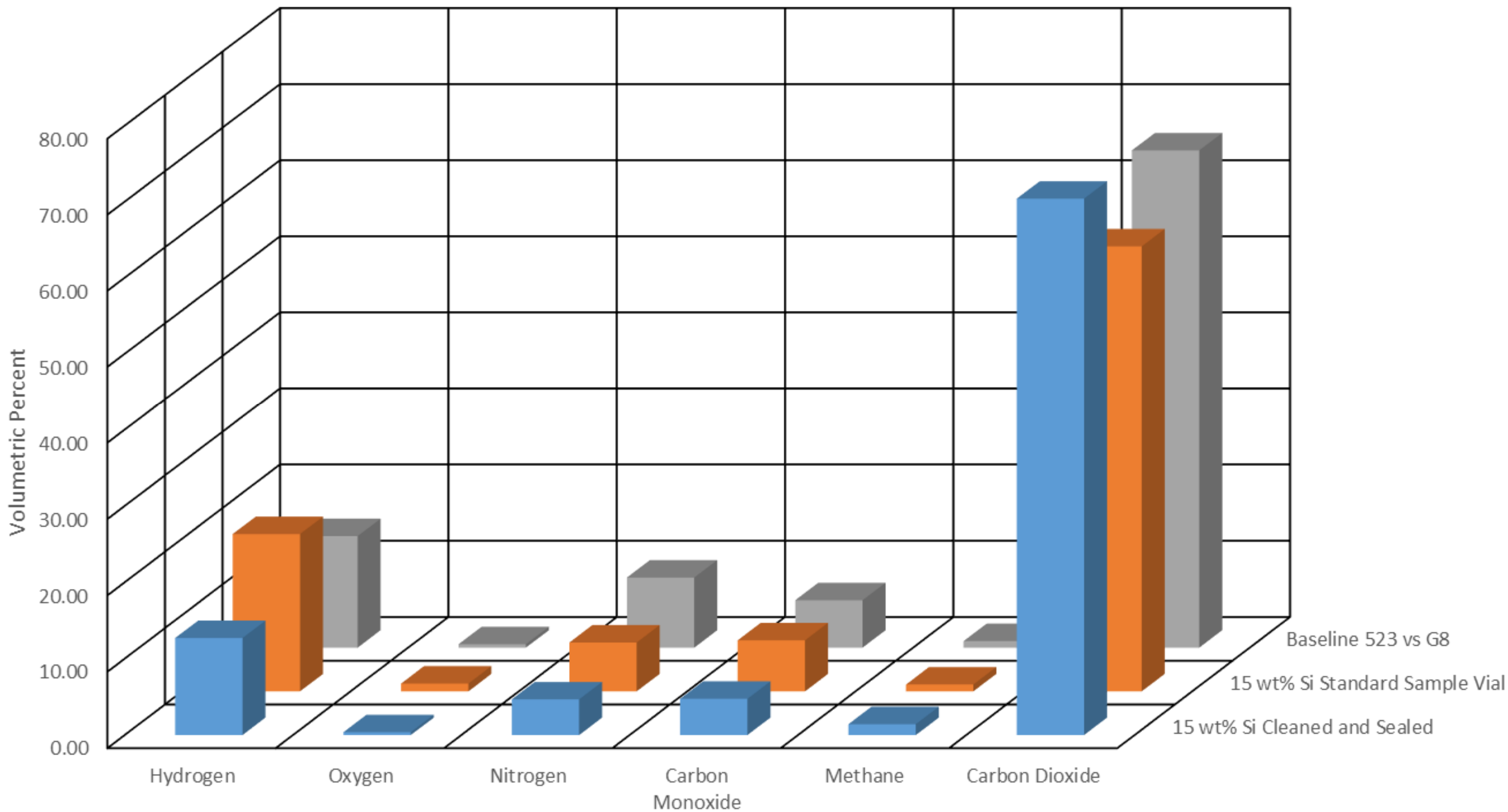
Grab samples taken during ARC runs – 275 °C trigger for sampling



GAS SAMPLING – HYDROCARBONS



GAS SAMPLING – GAS ANALYSIS

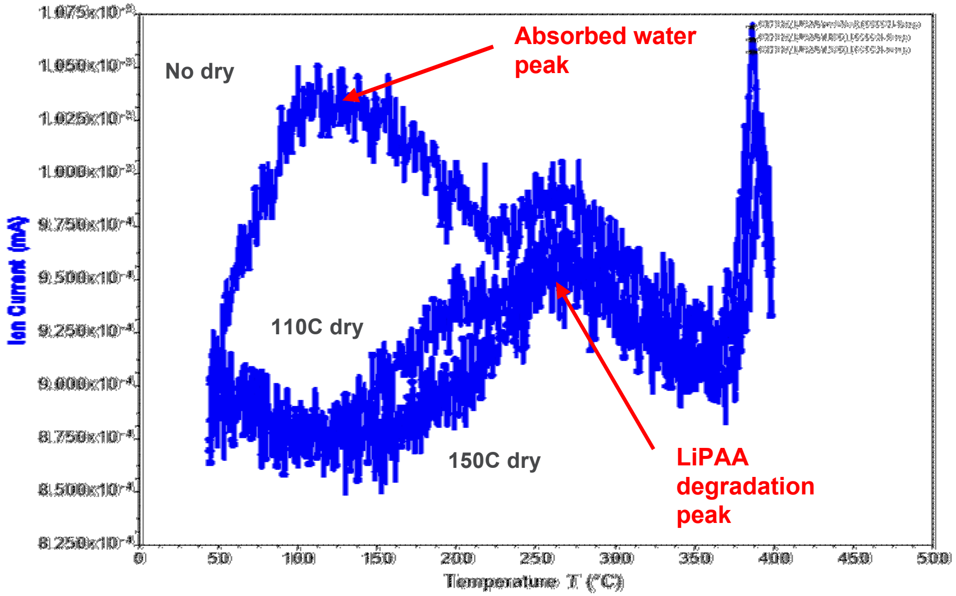


IMPACT OF BINDER MATERIAL ON ABUSE PERFORMANCE

- Contribution of binder water generation to observed abuse performance
  - Water processing (<150C)
  - Water from binder degradation (>170C) – relevant to abuse conditions
- Water + silicon interaction has been shown by ORNL and ANL during processing to produce H_2 gas and alter surface chemistry
- We are interested in the impacts at higher temperatures
  - Faster kinetics
  - Oxygen generating reactions (cathode)
  - Potential ignition sources

REACTIONS OF BINDERS AT ELEVATED TEMPERATURES

- High temperature drying of LiPAA films has shown to be effective in removing residual water from processing
- PAA degrades at >170°C to generate water (and CO_2)
  - LiPAA has been shown experimentally to perform similarly



- I.C. McNeill, S.M.T. Sadeghi. "Thermal Stability and Degradation Mechanisms of Poly(Acrylic Acid) and its Salts: Part 1 Poly(Acrylic Acid)" *Polymer Degradation and Stability* **29** (1990) 233-246.

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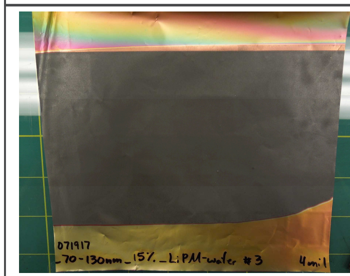
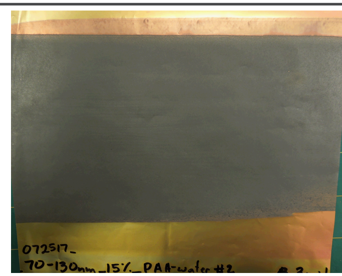
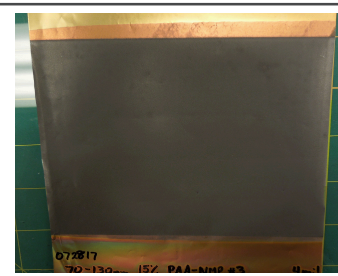
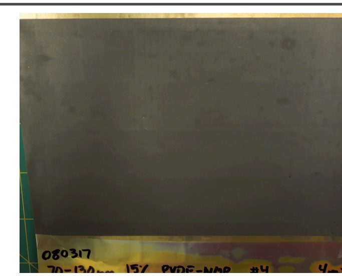
IMPACT OF EVOLVED WATER ON ABUSE PERFORMANCE

- For comparison purposes we need a binder that does not generate water upon degradation
  - CMC is another widely used Si binder but also degrades to generate water
  - PVDF degrades to form HF but is stable to >400C, not a great binder for Si systems
- In order to control for effects of solvent we fabricated a series of electrodes

LiPAA-water	PAA-water	PAA-NMP	PVDF-NMP
			
Water used in processing	Water used in processing		
Water generated by binder	Water generated by binder	Water generated by binder	

ELECTRODE FABRICATION

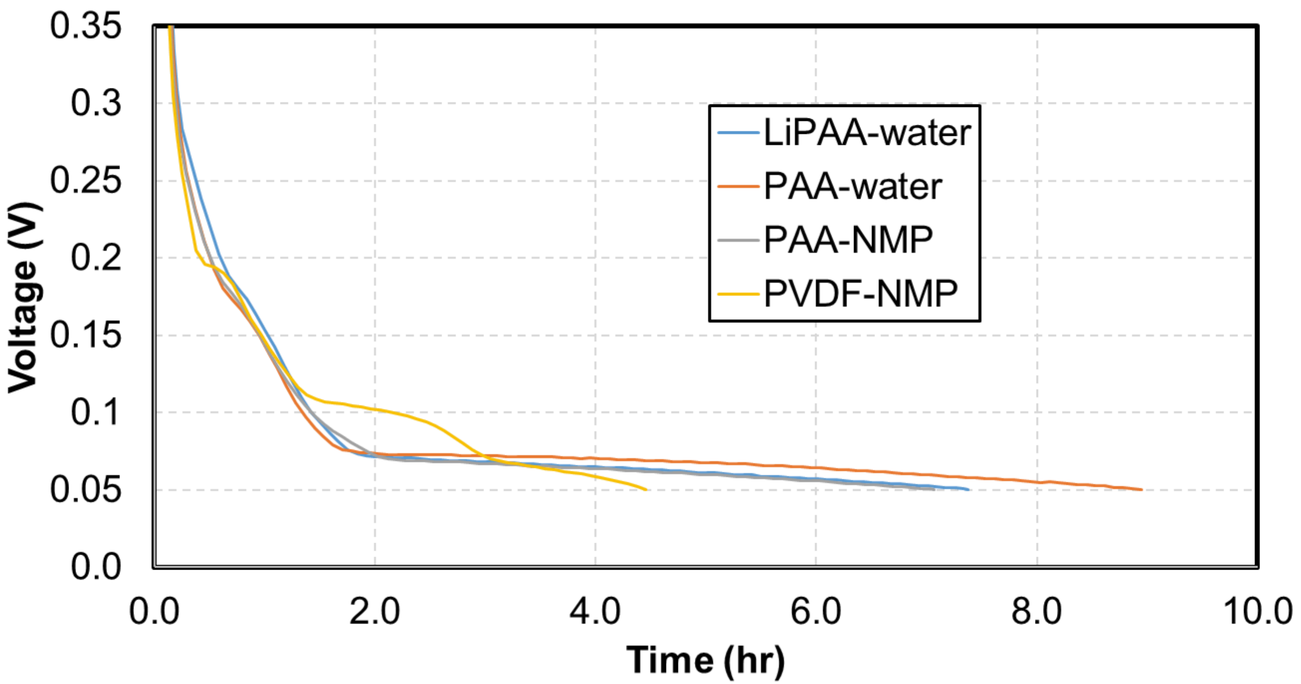
All electrodes were fabricated with roughly the parameters below

Silicon/Graphite/CB/Binder: 15/73/2/10
Silicon: Nanoamor 70-130nm
Graphite: Hitachi MAG-E
CB: Timcal C45

Coating thickness: ~45µm
Calendar porosity: ~47%
Areal Capacity: ~1.9 mAh/cm^2

FORMATION OF ELECTRODES

- Half cells assembled with Gen2 + 10% FEC electrolyte
- Cycled from 1.5V – 0.05V for 4 full cycles and held at the 5th lithiation (100% SOC) for disassembly and DSC testing



LiPAA and PAA systems perform similarly

PVDF shows reduced capacity

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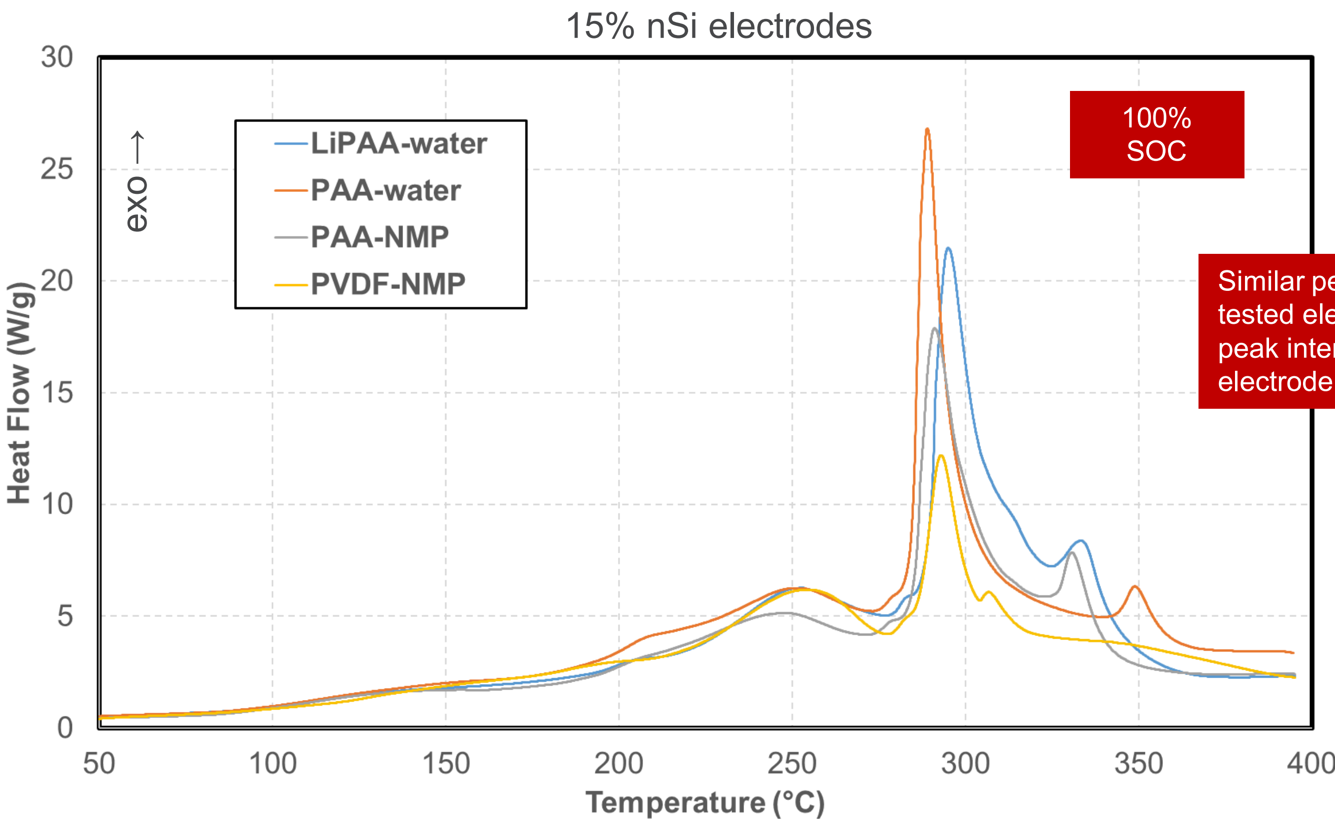
DSC RESULTS

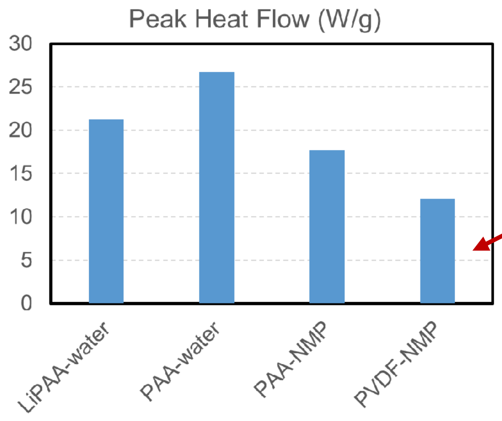
- Heated at 10°C/min to 400°C sealed under argon
- Active material to electrolyte ratio of 1:1



Similar peak locations for all tested electrodes and similar peak intensities with PVDF-NMP electrode showing weakest peak

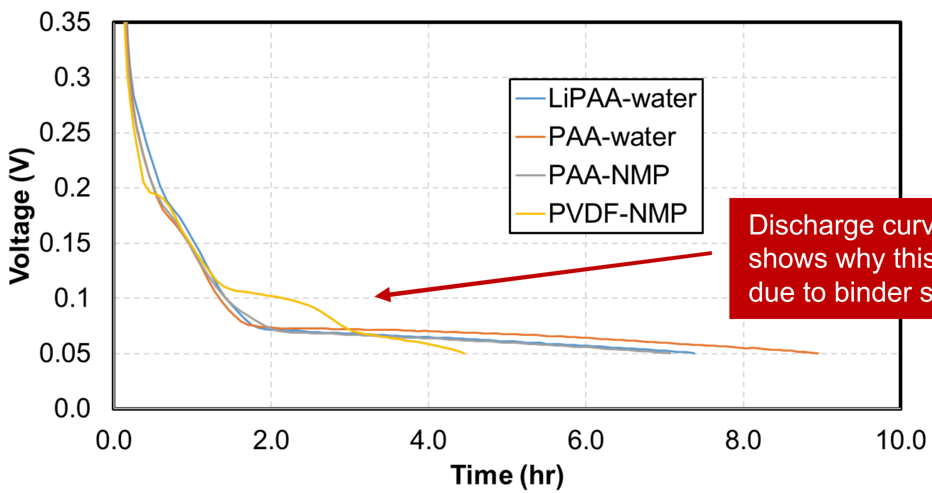
APPARENT TREND WITH BINDER SELECTION

- *PAA containing electrodes demonstrate a significantly greater peak heat rate and total heat generation*
  - This trend appears when normalized to **sample active mass**

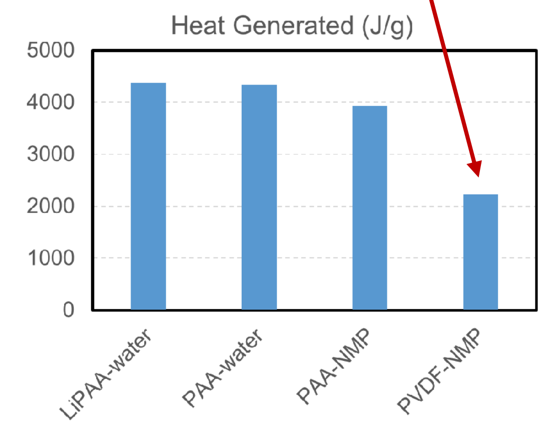


Not due to binder

Decrease in peak heat flow and heat generation for PVDF electrodes



Discharge curve for electrodes shows why this trend is not really due to binder selection



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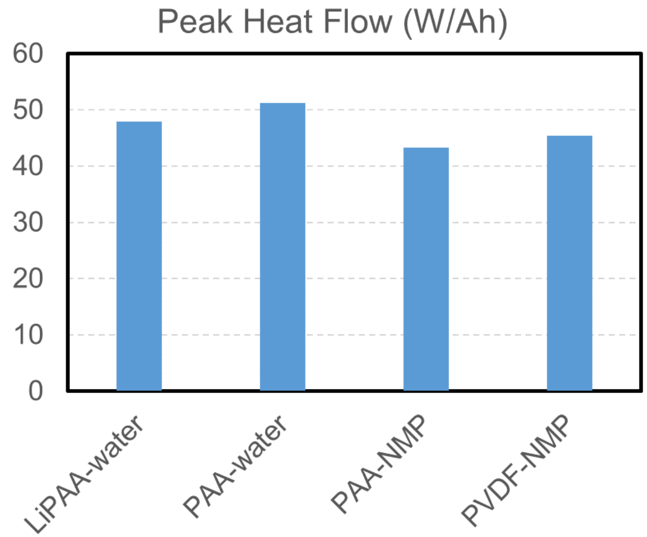
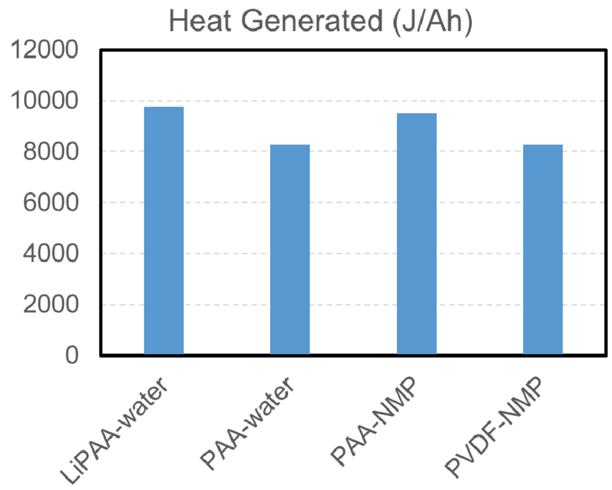
TREND DISAPPEARS WHEN NORMALIZED TO CAPACITY

- *PVDF binder anodes have a lower capacity than LiPAA/PAA anodes*
  - Because electrode masses are similar this must correspond to a lower effective SOC of the materials
  - When normalized to actual capacity, the trend disappears and binder choice does not appear to strongly influence anode thermal degradation





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SUMMARY

- ARC Performance
  - Smaller capacity 18650s allow for quantitative ARC measurement of silicon anode thermal runaway – consistency is difficult
  - Still significant variation in both peak heating rate and gas generation
- Gas Sampling shows similar off gassing (after transportation and testing) but silicon based samples have increased short chain hydrocarbon content
- Neither binder selection nor solvent selection appear to significantly impact materials thermal performance
  - At least not among binders and solvents tested
- Combined with previous results show that materials thermal performance is not affected by binder, solvent, coating thickness, or small N/P variations
- Performance is impacted by silicon content, SOC, and silicon particle size

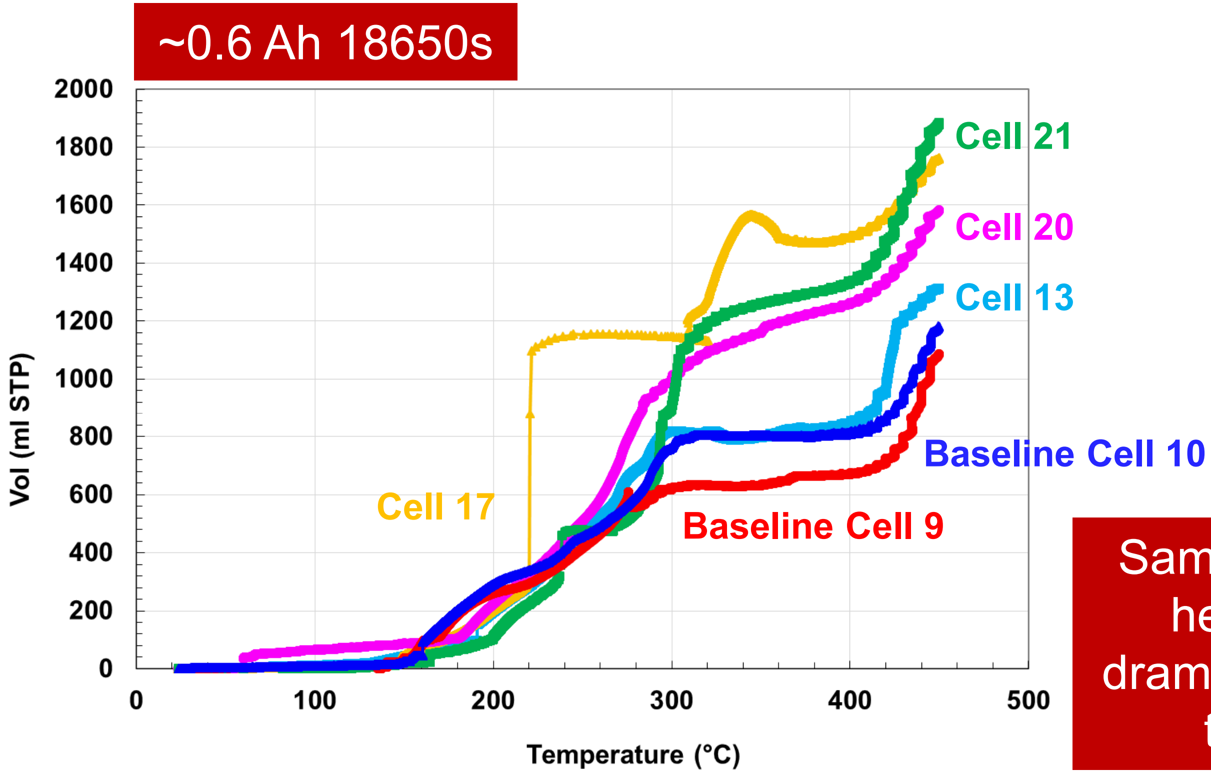
EXTRA SLIDES

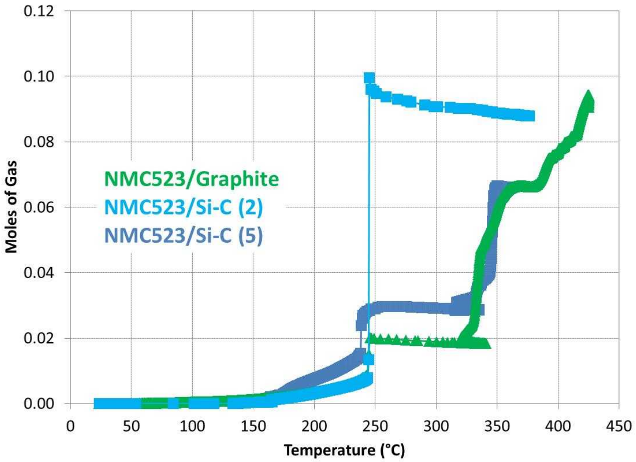
FUTURE WORK

- ARC testing
  - Testing of copper sleeve cells to improve consistency and reproducibility
  - Gas capture and analysis of evolved gases to determine composition of large gas production
- Water evolution from LiPAA
  - Test non-aqueous coatings or PVDF coatings for insight into contributions of LiPAA produced water on material energetics and cell runaway
  - Gas composition data can provide feedback into significance of water evolution from the binder on the actual abuse response
- Calorimetry measurements
  - Precise measurements of reactive heat produced by nanosilicon in contact with water

GAS GENERATION DURING ABUSE OF SILICON ANODES

Varies substantially between cells but in all cases higher than similar graphite only 18650s



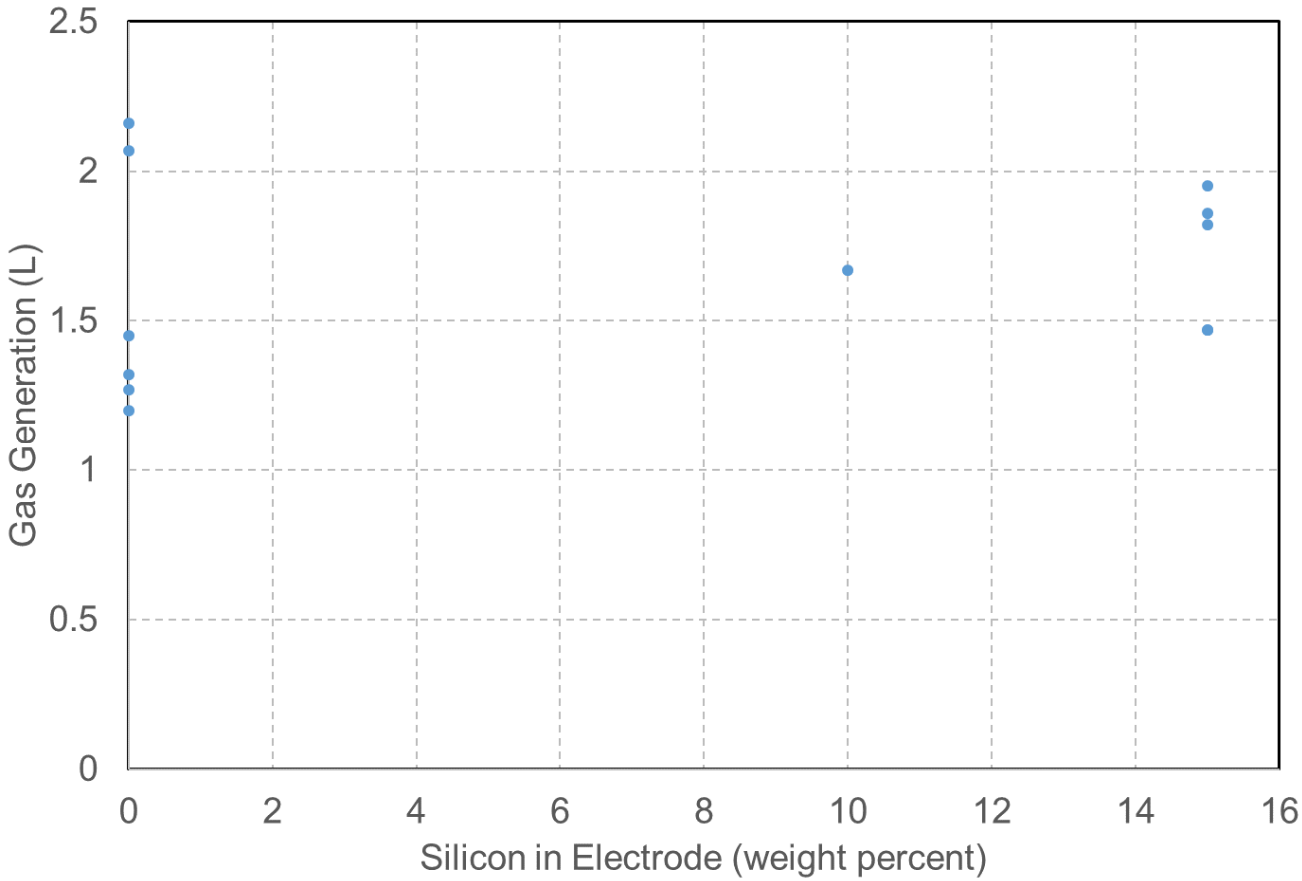


- Previous data from XG-Sciences Si/C testing showed sporadic occurrence of rapid gas generating event

Same occurrence can be seen here with Cell 17 showing dramatic gas generation relative to Cells 20, 21, and 13

Gas Volume also appears to be inconsistent

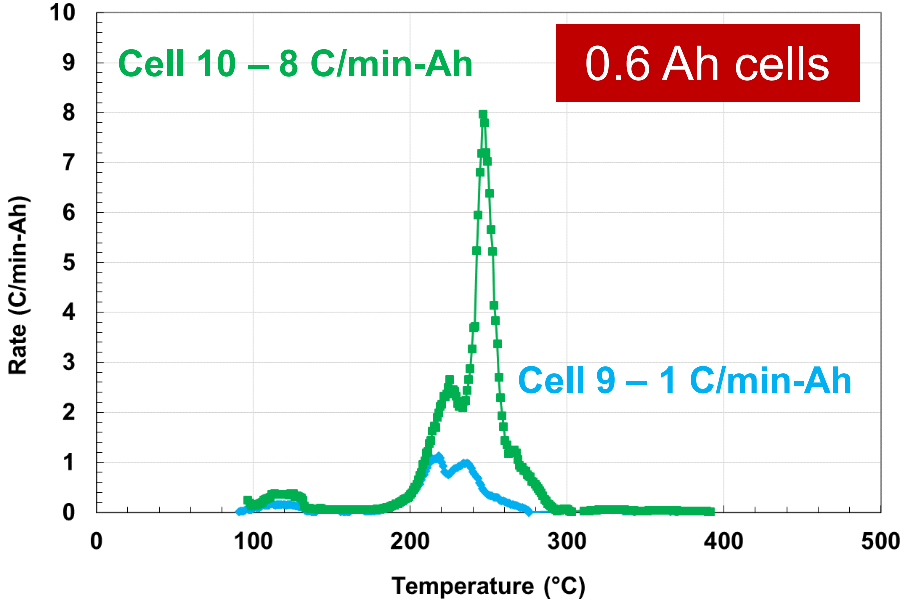
RECENT ARC RUNS

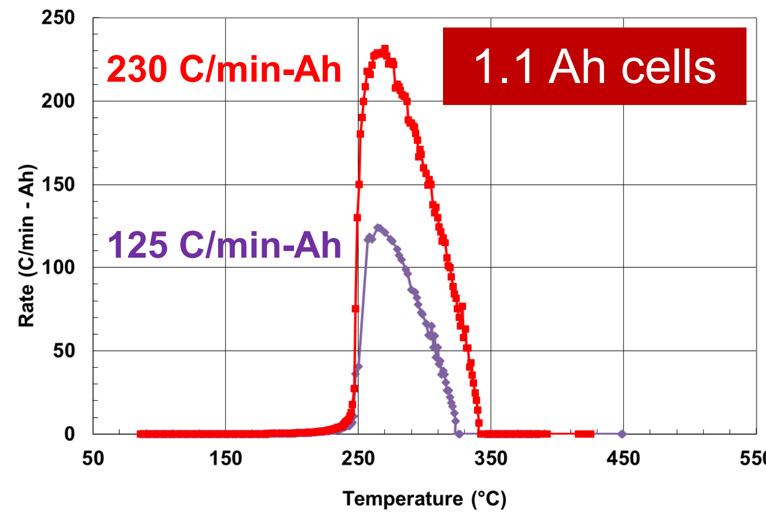


BASELINE ARC FOR 0% SI 18650’S

Lower capacity cells were below threshold for thermal runaway

0% nSi v NMC @
100% SOC
Gen2 + 10%FEC





Data comparison is difficult at this size because it is near the threshold for runaway to occur, size scaling is not simple to determine

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INCREASE IN GAS GENERATION OBSERVED WITH SILICON ANODES

Gas generation for half-capacity silicon cells nearly matches that of full-sized graphite-only cells

Cell	Capacity (Ah)	Gas Volume @ 400C (mL STP)	Normalized Gas Generation (mL STP/Ah)	
0% Si Cell 9	0.63	669	1062	
0% Si Cell 10	0.66	811	1229	
Graphite Baseline Cell 1	1	1716	1716	
Graphite Baseline Cell 2	1.2	1478	1232	
15% Silicon Cell 13	0.59	841	**1425**	
15% Silicon Cell 17	0.61	1486	**2436**	← Runaway
15% Silicon Cell 20	0.65	1246	**1917**	
15% Silicon Cell 21	0.64	1324	**2069**	← Runaway

Normalized gas generation for silicon anodes even without significant runaway event (see Cell 20) is higher than graphite

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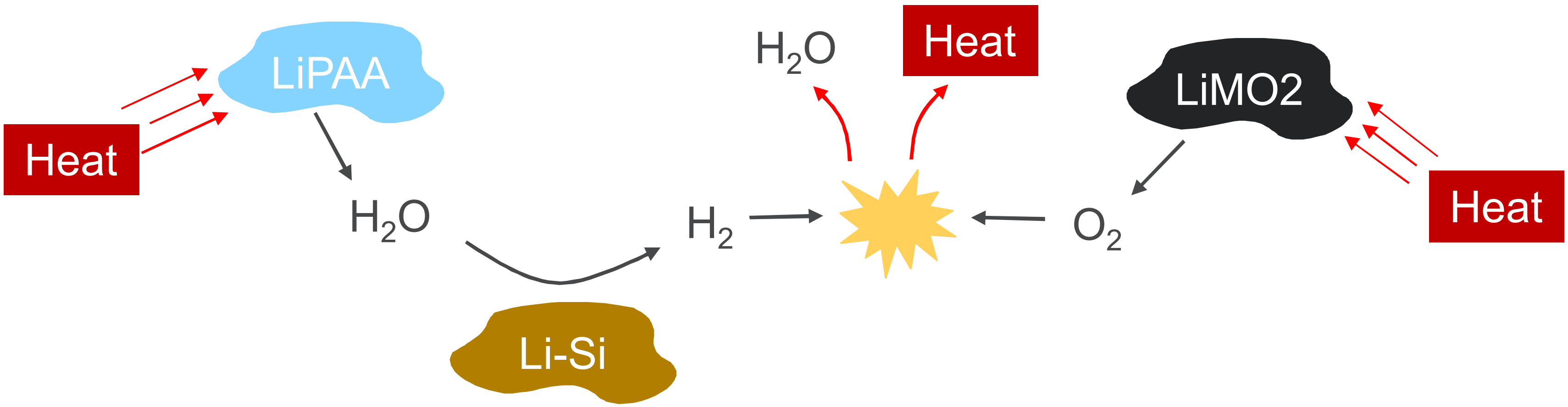
CONTRIBUTION OF WATER-PROCESSING TO RUNAWAY?

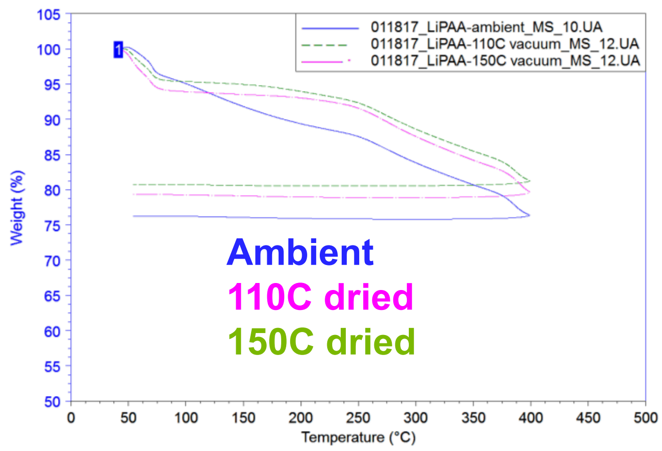
Generation of H_2 gas from nanosilicon / water interaction

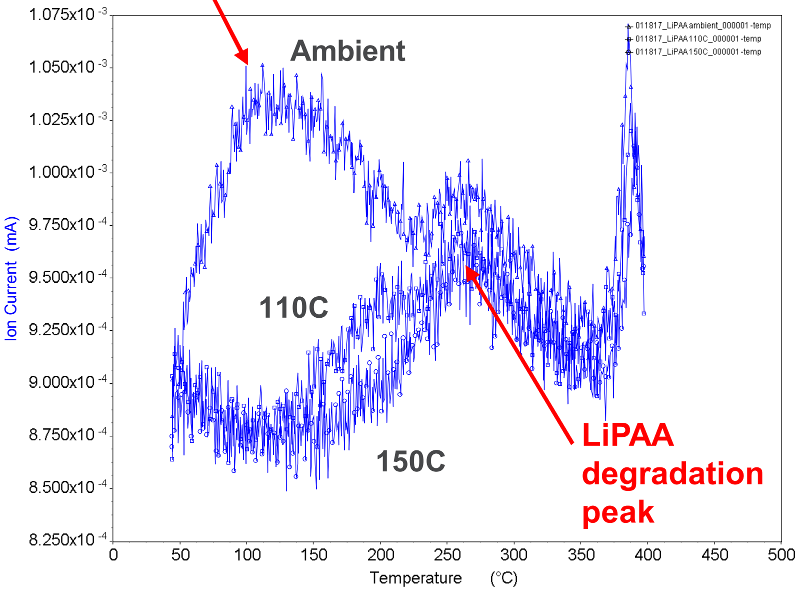
- ORNL and ANL slurry processing has demonstrated reactivity of nanosilicon to water
  - Oxidation of Si to SiO_2 generates gaseous hydrogen – contributor to violent abuse response of silicon cells? Lithiated silicon alloys known to be even more water-reactive
  - Could H_2O be released by water-processed LiPAA binder under elevated temperatures?



WATER EVOLUTION FROM LIPAA BINDER

TGA-MS shows water generation even under 150C drying





Even when adequately dried at 150°C for 12h there is still significant water evolution from LiPAA

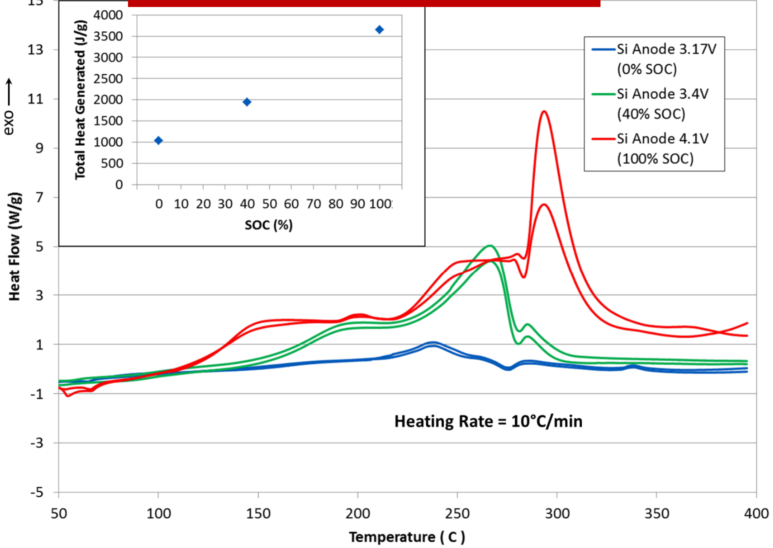
Literature shows thermal degradation of PAA involves water evolution as one of the primary products with onset at ~170C and peak at ~250C

- I.C. McNeill, S.M.T. Sadeghi. "Thermal Stability and Degradation Mechanisms of Poly(Acrylic Acid) and its Salts: Part 1 Poly(Acrylic Acid)" *Polymer Degradation and Stability* **29** (1990) 233-246.

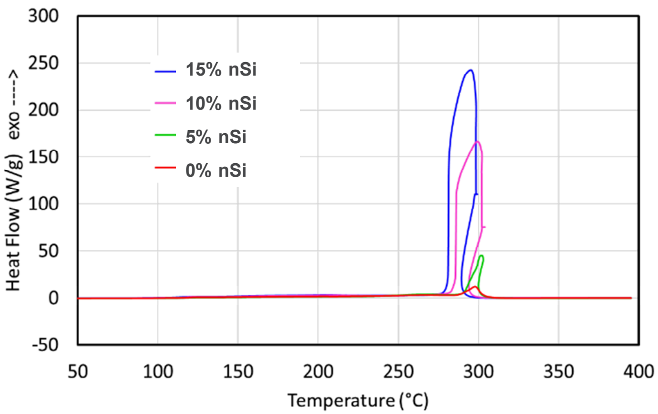
ABUSE CORRELATION WITH DSC TESTING

- Previous analysis showed a disconnect in DSC performance between ANL coating, which showed larger exotherms relative to SNL coatings and did not correlate to particle size
  - N/P variations resulting in different SOC?
  - Coating thickness effects?

SNL – 130nm



ANL – 50-70nm



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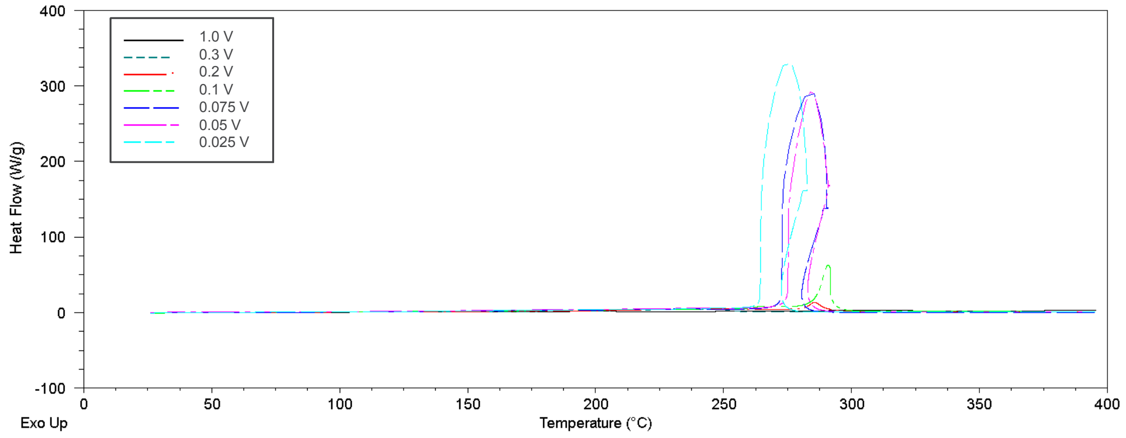
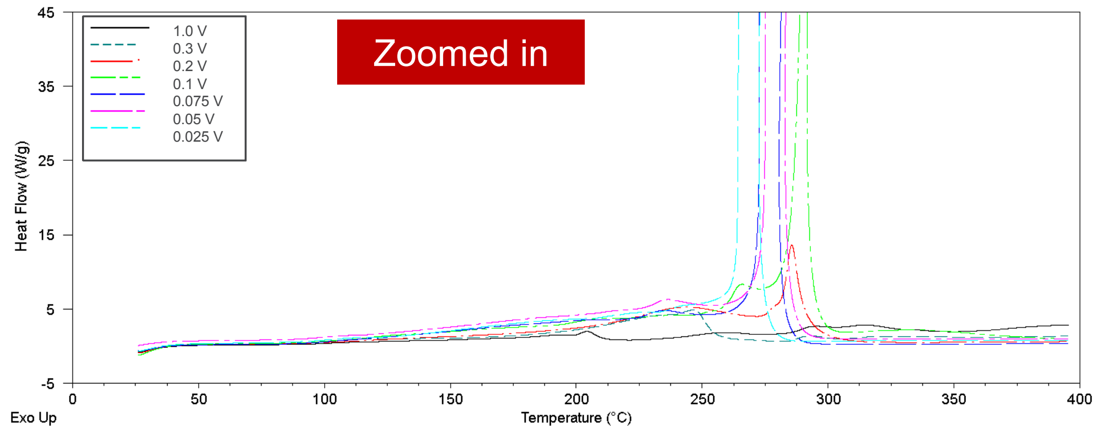
DSC DEPENDENCE ON HALF CELL SOC

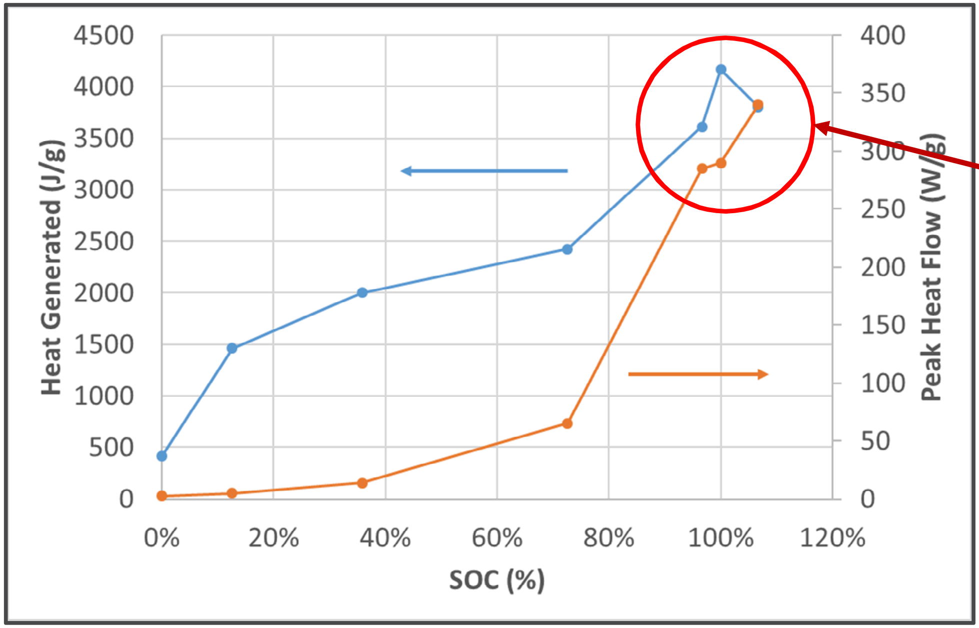




Half cell v lithium
50-70nm Nanoamor silicon
46 % coating porosity
15% nSi
78% MAG-E
2 % Timcal C45
10 % LiPAA

DSC DEPENDENCE ON HALF CELL SOC

Heat generation and peak heat flow all trend with SOC with a spike near 100% SOC



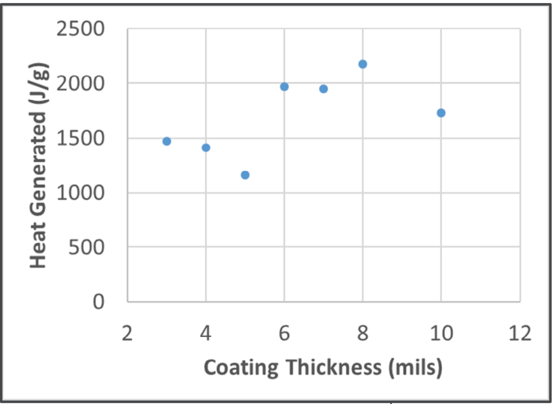
Small variations in SOC due to N/P ratios would not cause large DSC response change

MATERIAL ENERGETICS DEPENDENCE ON COATING THICKNESS

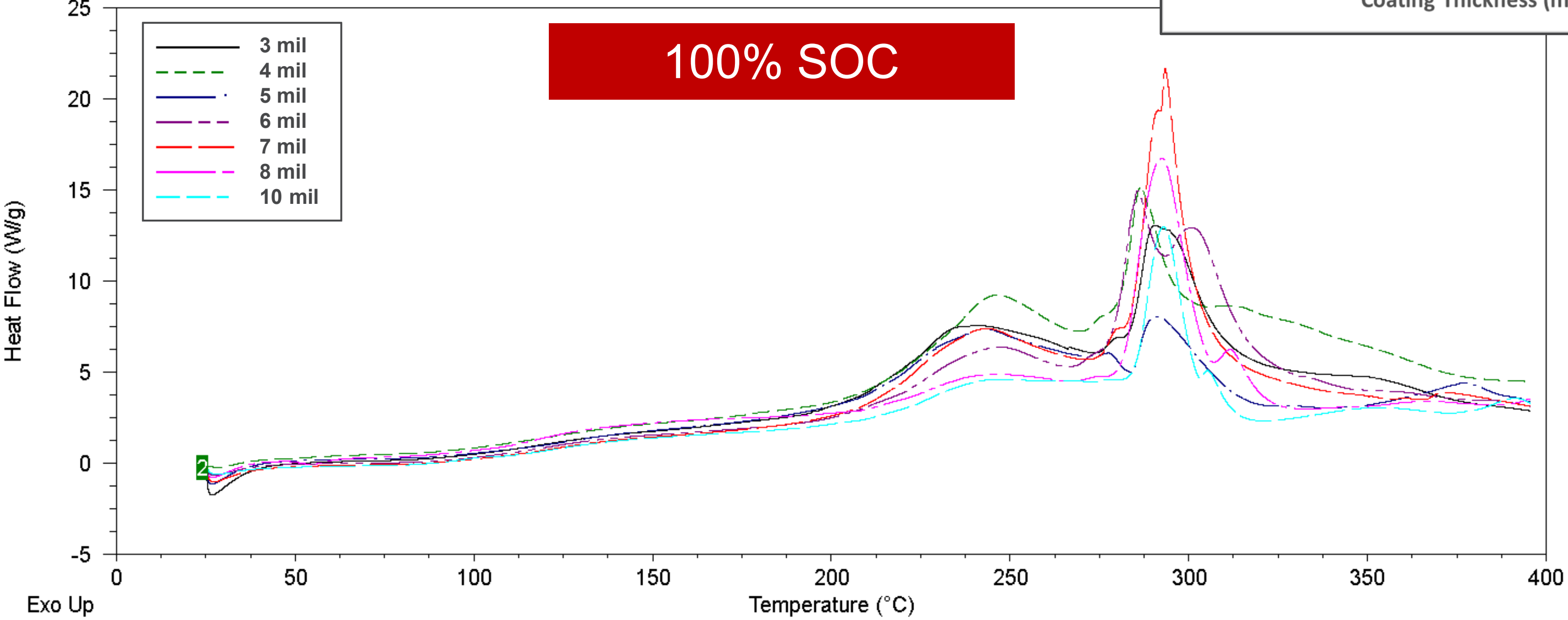
Minimal dependence on coating thickness

Half cell v lithium
70-130nm Nanoamor silicon
46 % coating porosity
15% nSi
78% MAG-E
2 % Timcal C45
10 % LiPAA

No strong correlation between coating thickness and DSC performance



100% SOC



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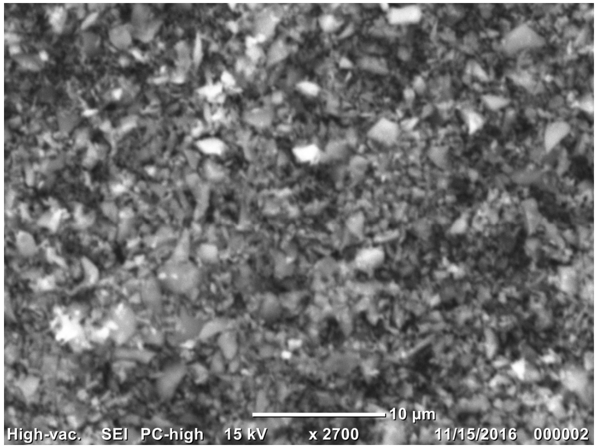
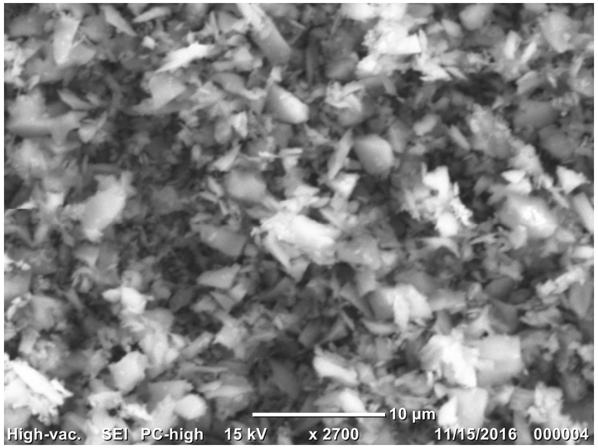
DIFFERENT PARTICLE SIZES FOR DSC TESTING

Wide range of particle sizes selected – many previously studied by ANL

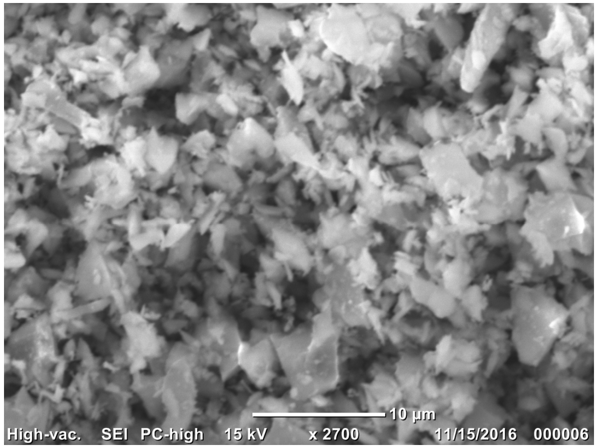
Previous analysis was restricted to small range of particle size:
30-50nm, 50-70nm, 70-130nm



Nanoamor, 70-130nm



American Elements, 500nm



Alfa Aesar, 1-5µm

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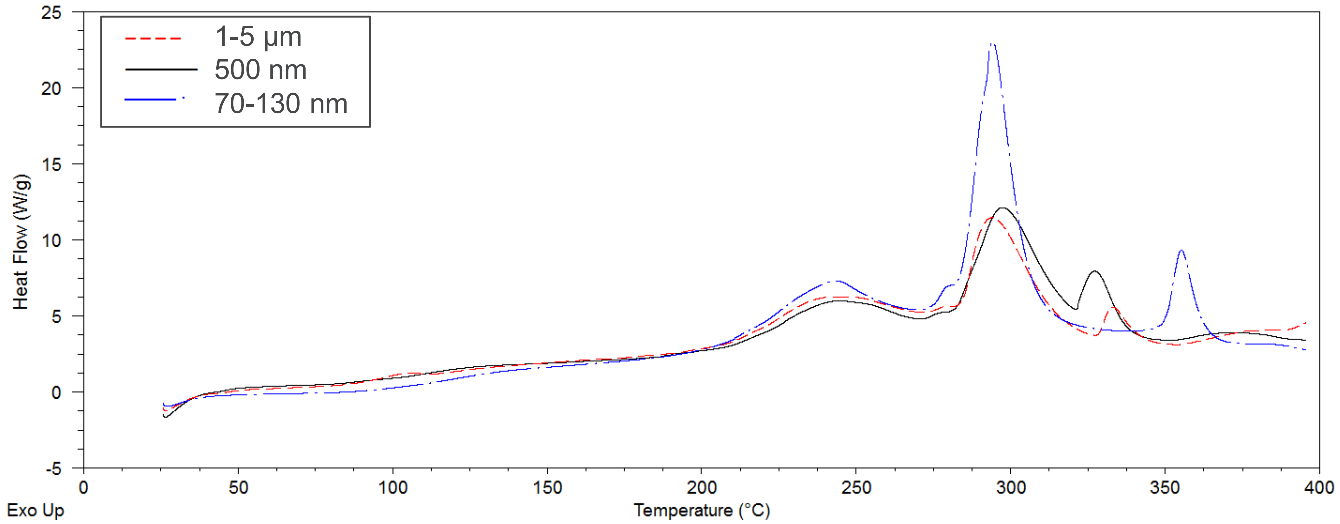
DSC DEPENDENCE ON SI PARTICLE SIZE

Greater heat generation and peak heating for smaller particle silicon



Particle Size	Heat Generation (J/g)	Peak Heat Flow (W/g)
1-5 µm	1364	11.4
500 nm	1430	12.1
70-130 nm	2377	23.0

~ 70% increase in heat generation and near doubling of peak heating rate for nanosilicon

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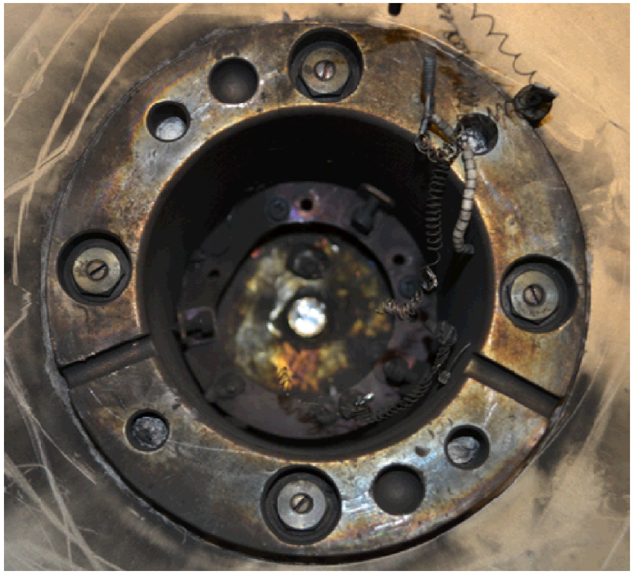
ABUSE RESPONSE OF SILICON ANODES

Previously presented data

Complete rupture for entire ARC system seen with nano silicon electrodes at both 10 and 15% Si (both ARCs same result) – only a few instances of this occurring in SNL abuse testing



DPA analysis for cells show no indication of manufacturing defects. Results suggest energetic runaway is attributed to chemical decomposition.

EFFECT OF NSI PARTICLE SIZE

- Electrolyte clearly participates in highly exothermic reaction, suggests that greater surface area (ie. Smaller particle size) will lead to greater reaction rates
  - Anticipated trends of greater peak heating rate / lower reaction onset with smaller particle size

Observed Trends

- High loading CAMP electrodes do not follow trends
  - Extreme exotherms may be associated with greater material loading
- In lower loading electrodes smaller particles show:
  - Stronger SEI peak, lower temperature peak onset, minimal change to peak heating rate and total heat generation
  - Conclusions are tentative due to limited data points, limited characterization of nSi particles