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

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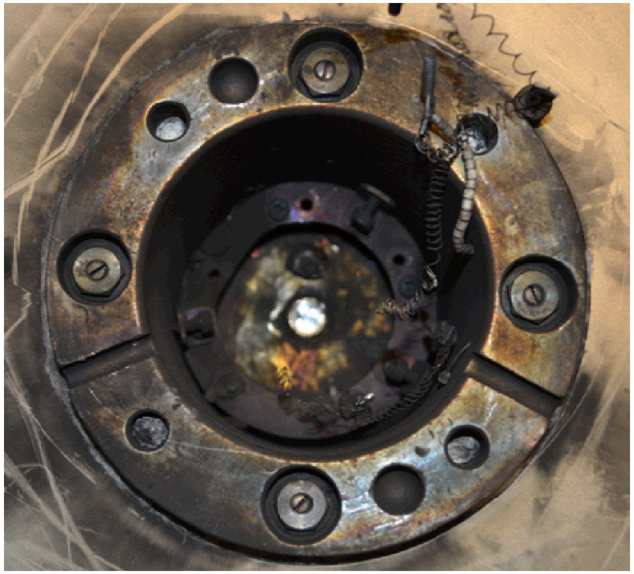
ABUSE RESPONSE OF SILICON ANODES

Previously presented data

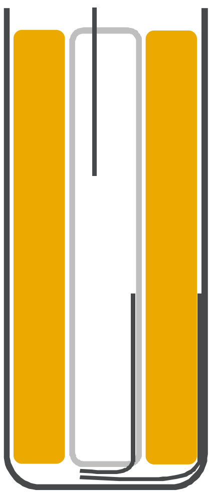
Complete rupture for entire ARC system seen with nano silicon electrodes at both 10 and 15% Si (both ARCs same result) – only a few instances of this occurring in SNL abuse testing



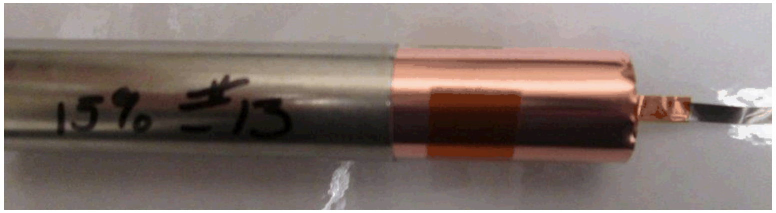
DPA analysis for cells show no indication of manufacturing defects. Results suggest energetic runaway is attributed to chemical decomposition.

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

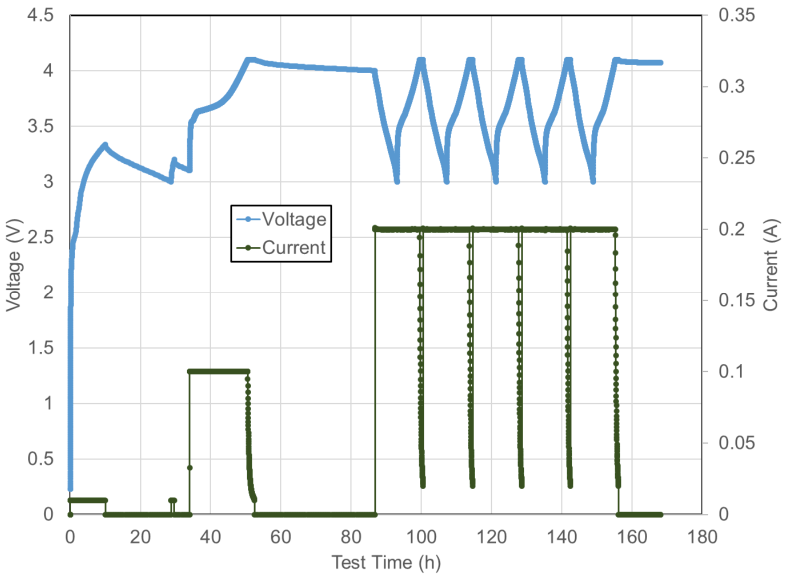


Electrode lengths ~ ½ of regular 18650s

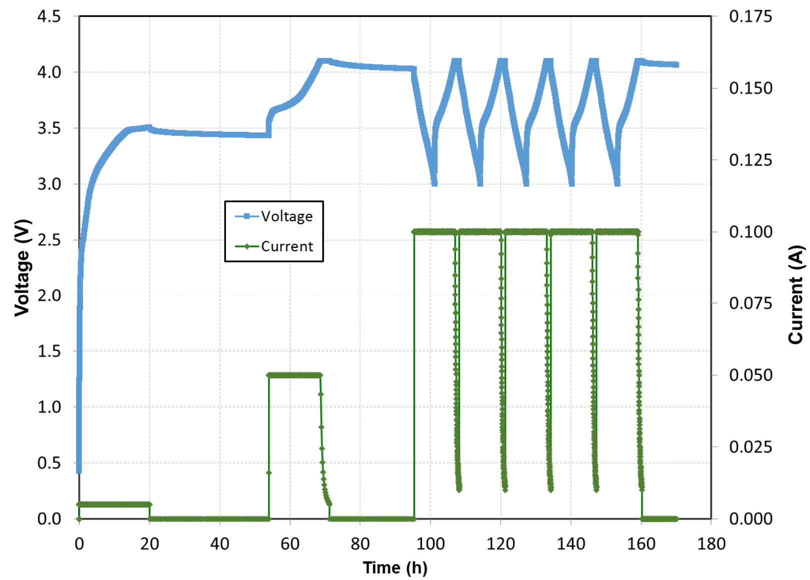
CYCLING PERFORMANCE OF LOW-CAPACITY 18650'S

Subjected to the same formation as previous cells

- No notable differences in performance of lower capacity 18650s during formation



Capacity – 1.3 Ah



Capacity – 0.64 Ah

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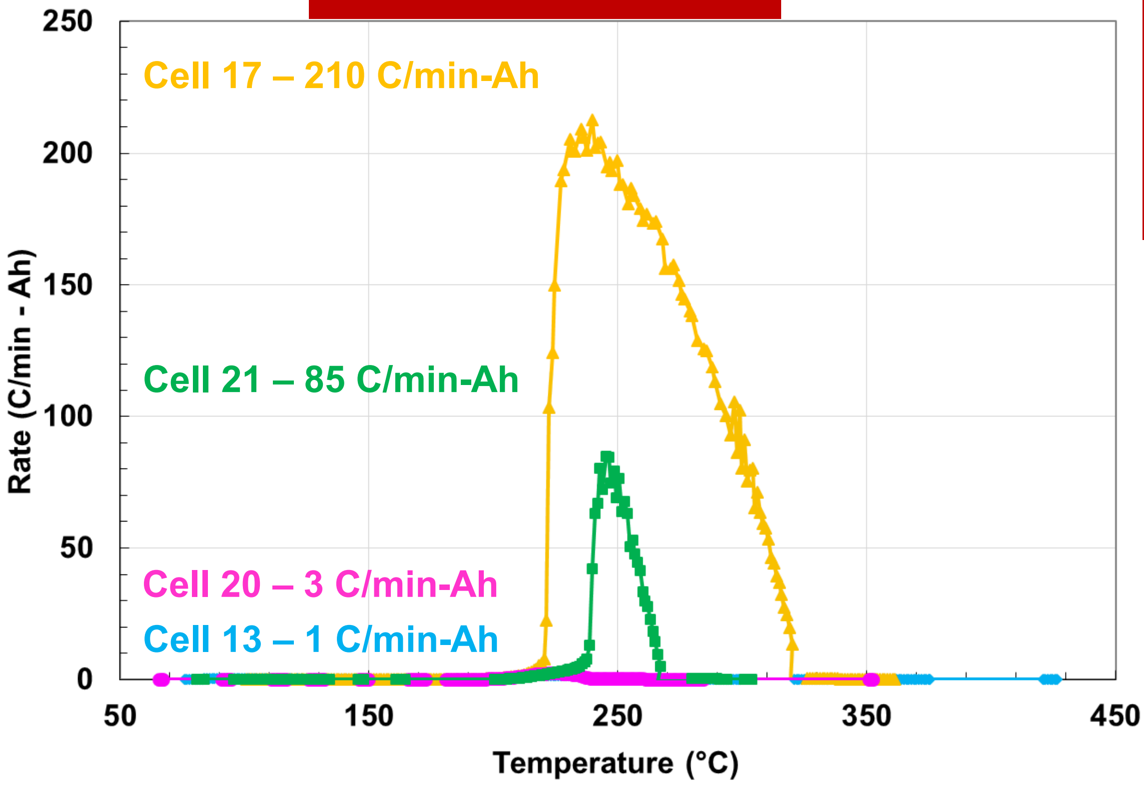
ARC TESTING OF LOW CAPACITY 18650 CELLS

15% silicon data for ~0.6 Ah cells

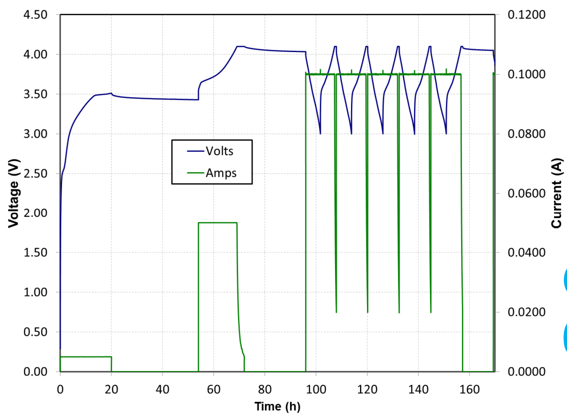
15% nSi v NMC @ 100% SOC Gen2 + 10%FEC



Four 15% silicon 18650s have been subjected to ARC with wide variability in performance

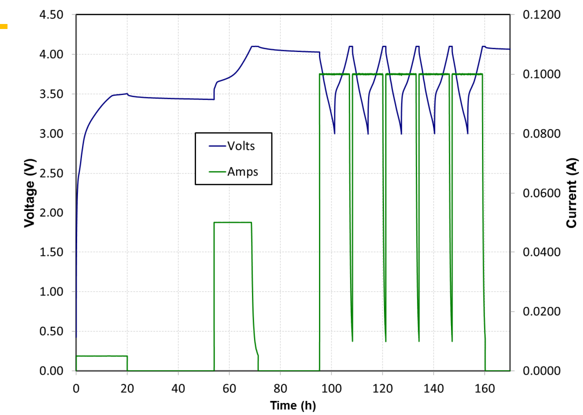
CAMP 50-70nm Nanoamor anodes
46 % coating porosity
15% nSi
78% MAG-E
2 % Timcal C45
10 % LiPAA

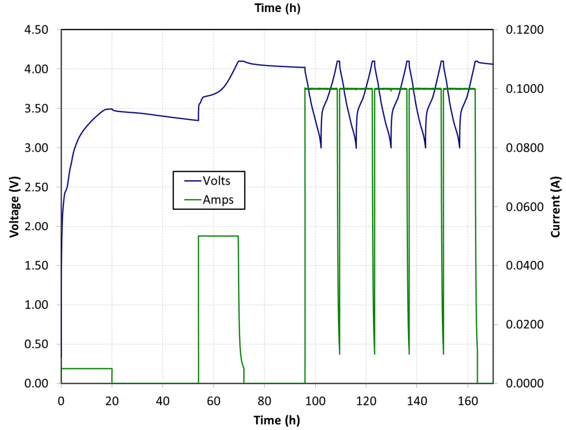
FORMATION COMPARISON BETWEEN ARC CELLS SHOWS MINIMAL VARIABILITY



Cell 13 – 0.59 Ah

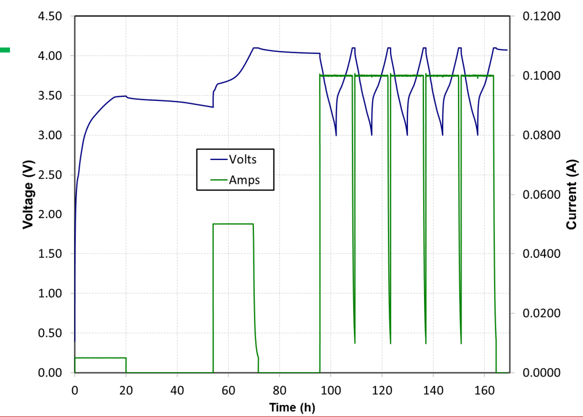
Cell 17 – 0.61 Ah





Cell 20 – 0.65 Ah

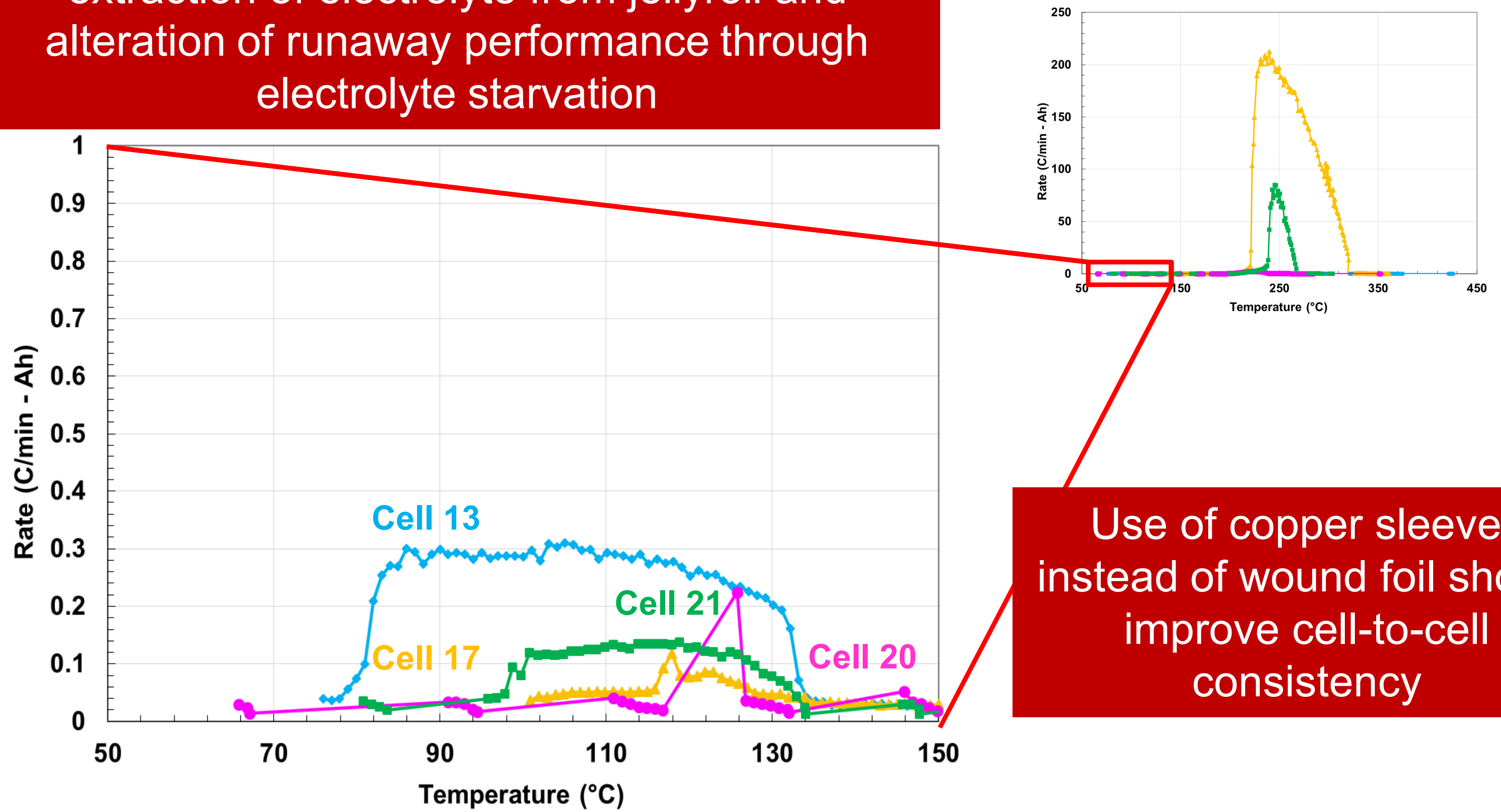
Cell 21 – 0.64 Ah



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

LOW TEMPERATURE EXOTHERM AND BOIL-OFF OF FREE ELECTROLYTE

Hand winding of copper can allow for capillary extraction of electrolyte from jellyroll and alteration of runaway performance through electrolyte starvation

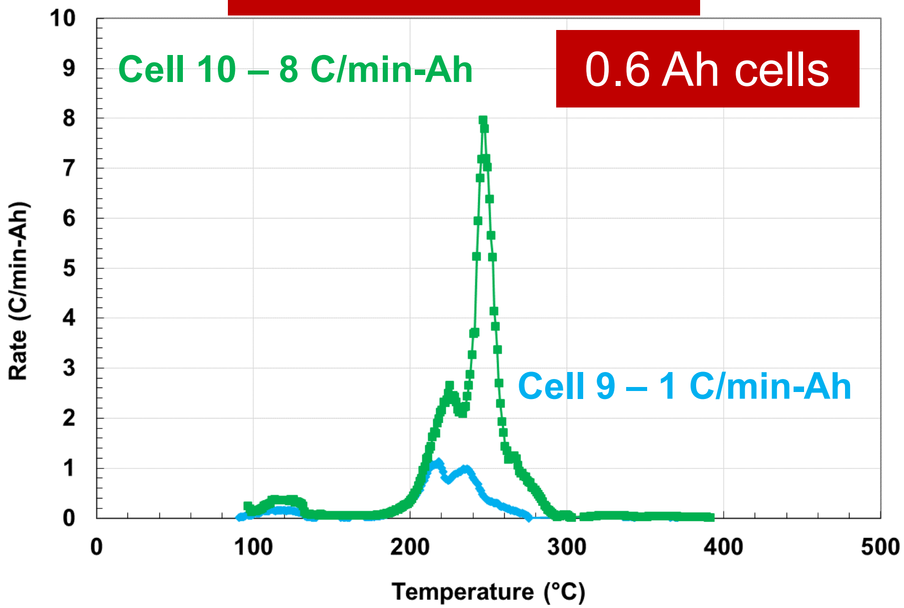


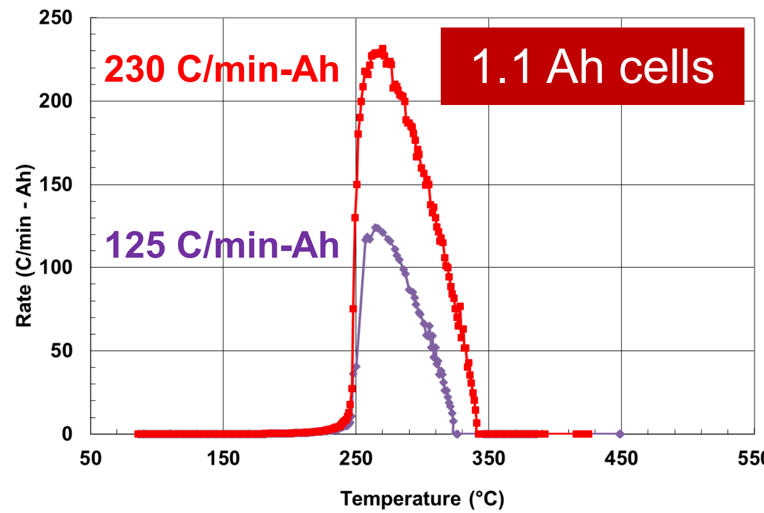
Use of copper sleeves instead of wound foil should improve cell-to-cell consistency

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

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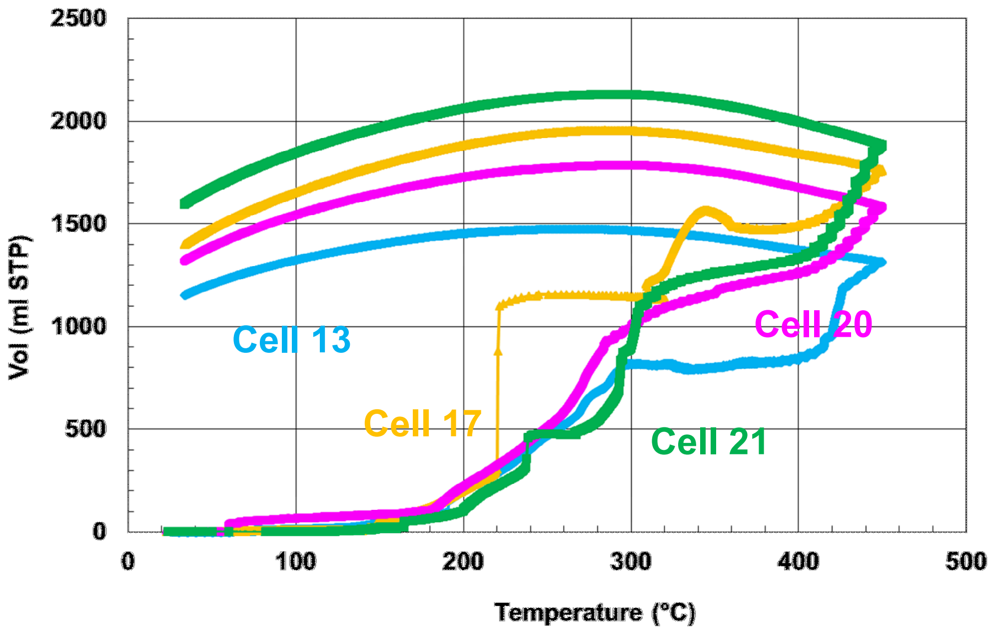
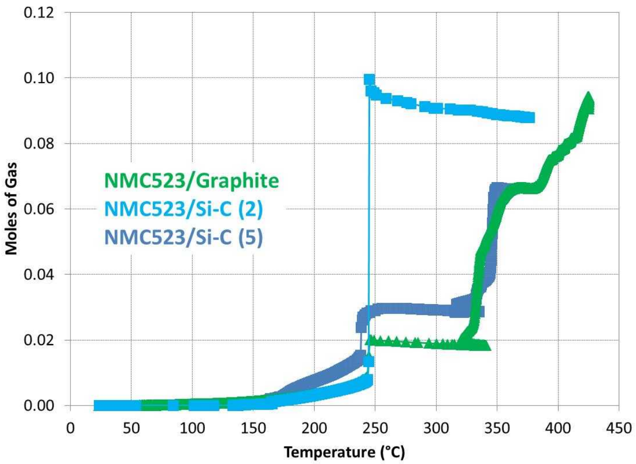
GAS GENERATION DURING ABUSE OF SILICON ANODES

Varies substantially between cells





- 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 Cell 21 and Cell 13

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INCREASE IN GAS GENERATION OBSERVED WITH SILICON ANODES

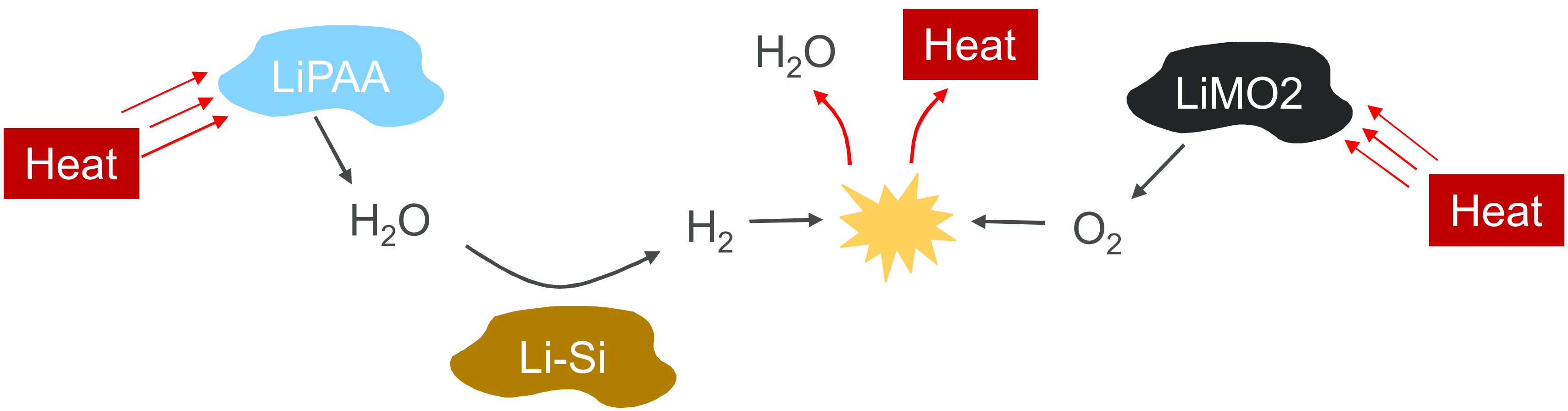
Cell	Capacity (Ah)	Gas Volume @ 400C (mL STP)	Normalized Gas Generation (mL STP/Ah)
0% Si Cell 9	0.63	669	1062
0% Si Cell 10	0.66	811	1229
Graphite Baseline Cell 1	1	1716	1716
Graphite Baseline Cell 2	1.2	1478	1232
15% Silicon Cell 13	0.59	841	**1425**
15% Silicon Cell 17	0.61	1486	**2436** ← Runaway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

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

CONTRIBUTION OF WATER-PROCESSING TO RUNAWAY?

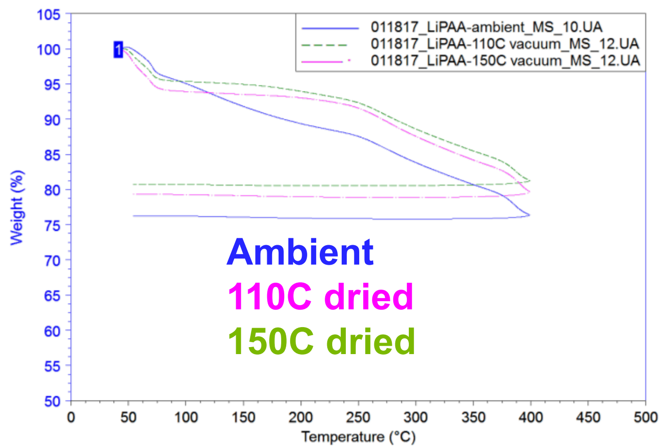
Generation of H_2 gas from nanosilicon / water interaction

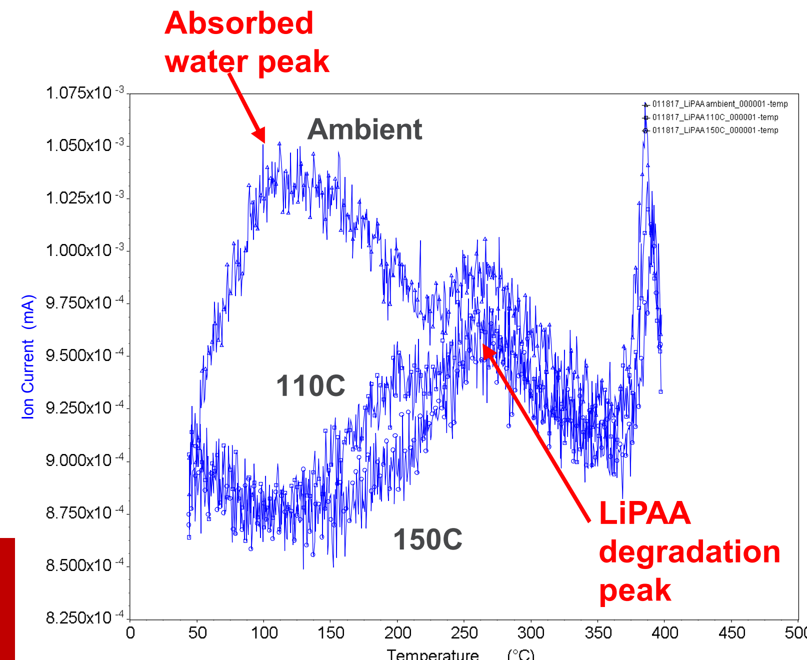
- ORNL and ANL slurry processing has demonstrated reactivity of nanosilicon to water
  - Oxidation of Si to SiO_2 generates gaseous hydrogen – contributor to violent abuse response of silicon cells? Lithiated silicon alloys known to be even more water-reactive
  - Could H_2O be released by water-processed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

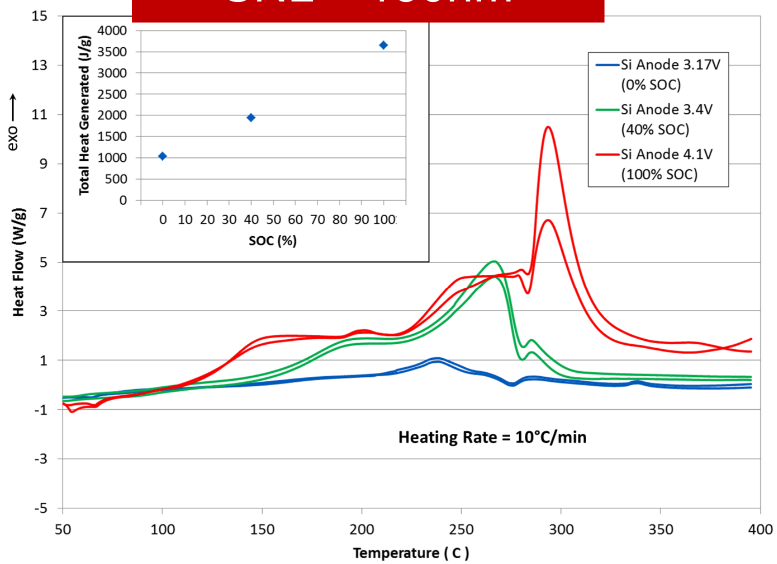
Literature search shows thermal degradation of LiPAA involves water evolution as one of the primary products with onset at ~190C and peak at ~250C

- 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.

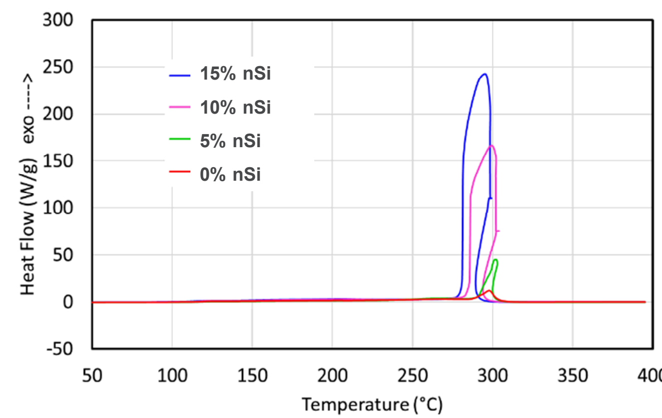
ABUSE CORRELATION WITH DSC TESTING

- 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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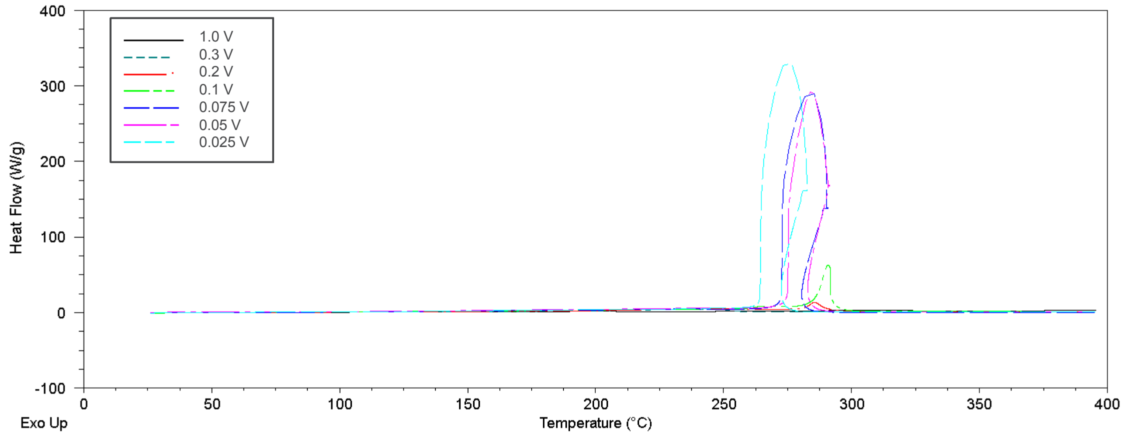
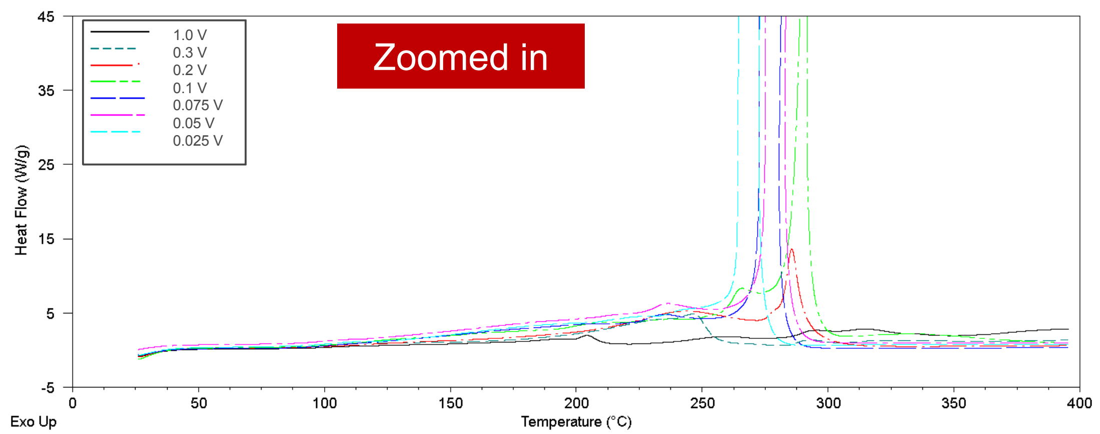
DSC DEPENDENCE ON HALF CELL SOC

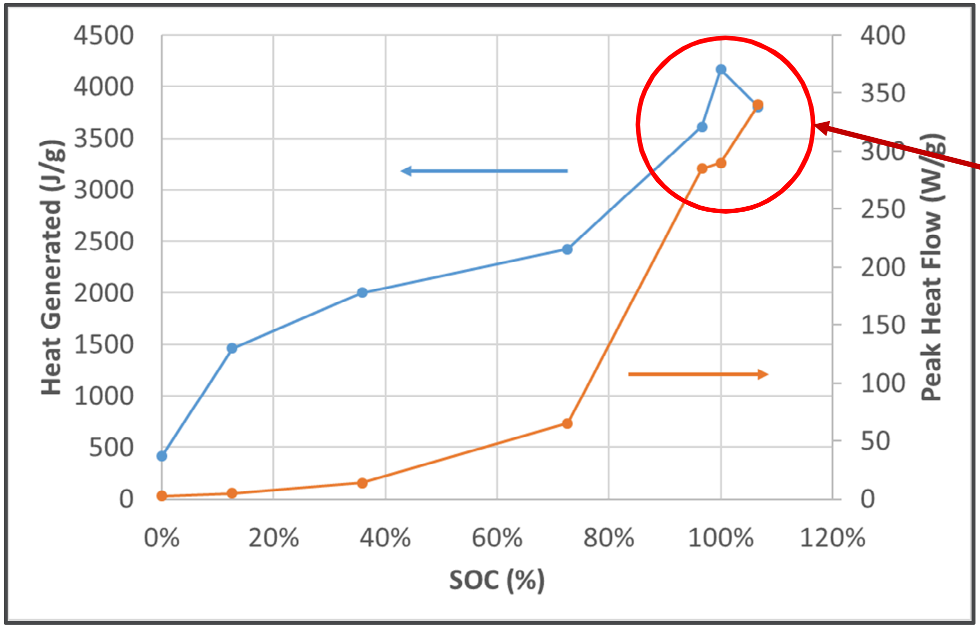




Half cell v lithium
50-70nm Nanoamor silicon
46 % coating porosity
15% nSi
78% MAG-E
2 % Timcal C45
10 % LiPAA

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

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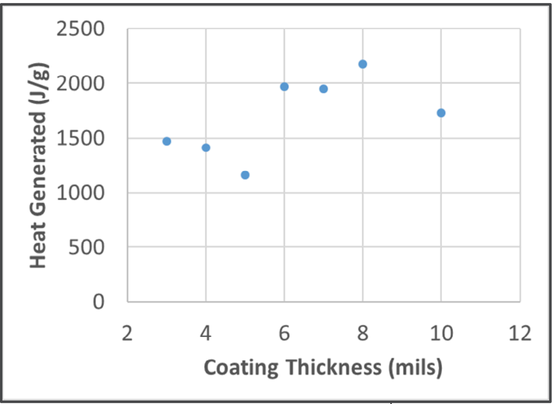
MATERIAL ENERGETICS DEPENDENCE ON COATING THICKNESS

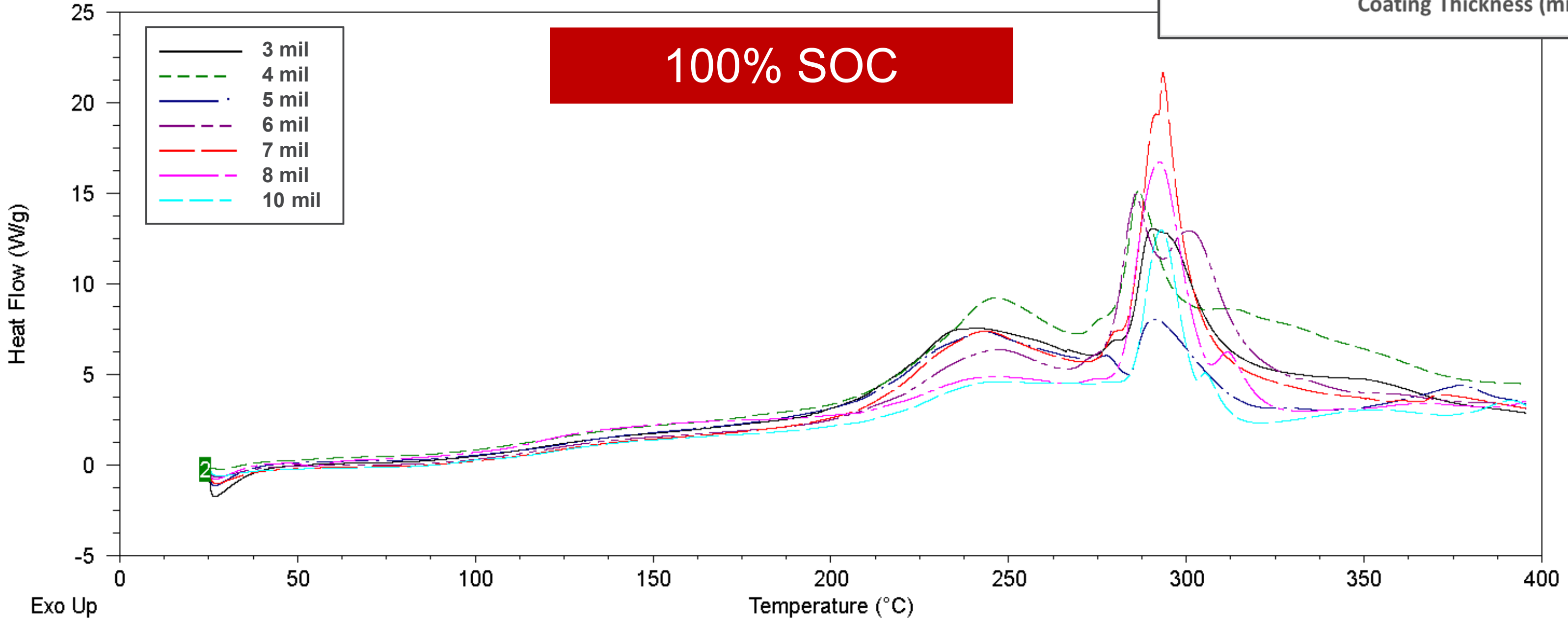
Minimal dependence on coating thickness

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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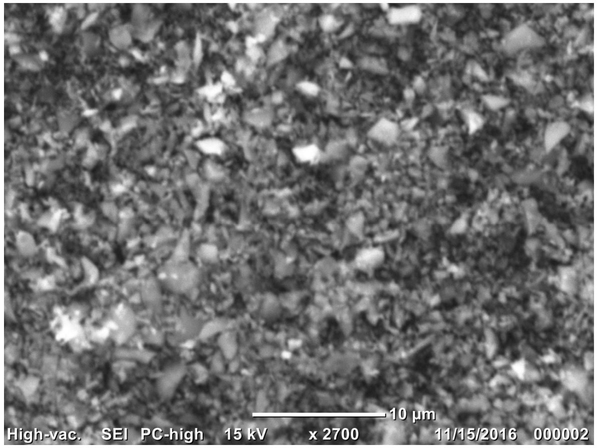
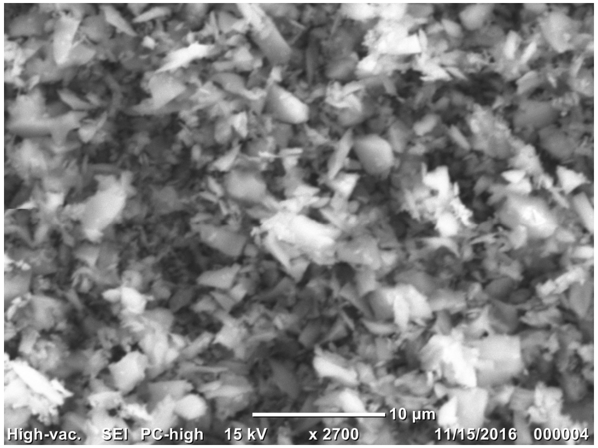
DIFFERENT PARTICLE SIZES FOR DSC TESTING

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

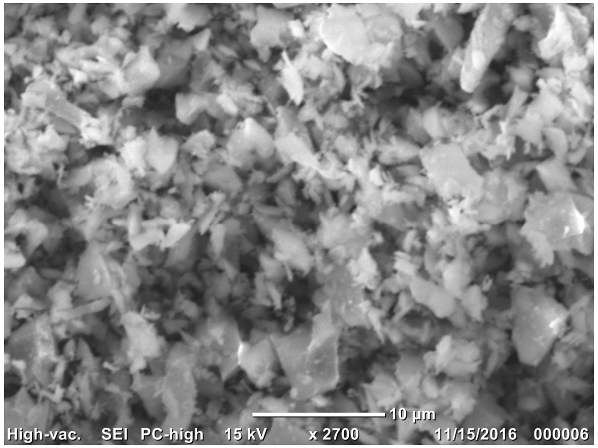
Previous analysis was restricted to small range of particle size: 30-50nm, 50-70nm, 70-130nm



Nanoamor, 70-130nm



American Elements, 500nm



Alfa Aesar, 1-5µm

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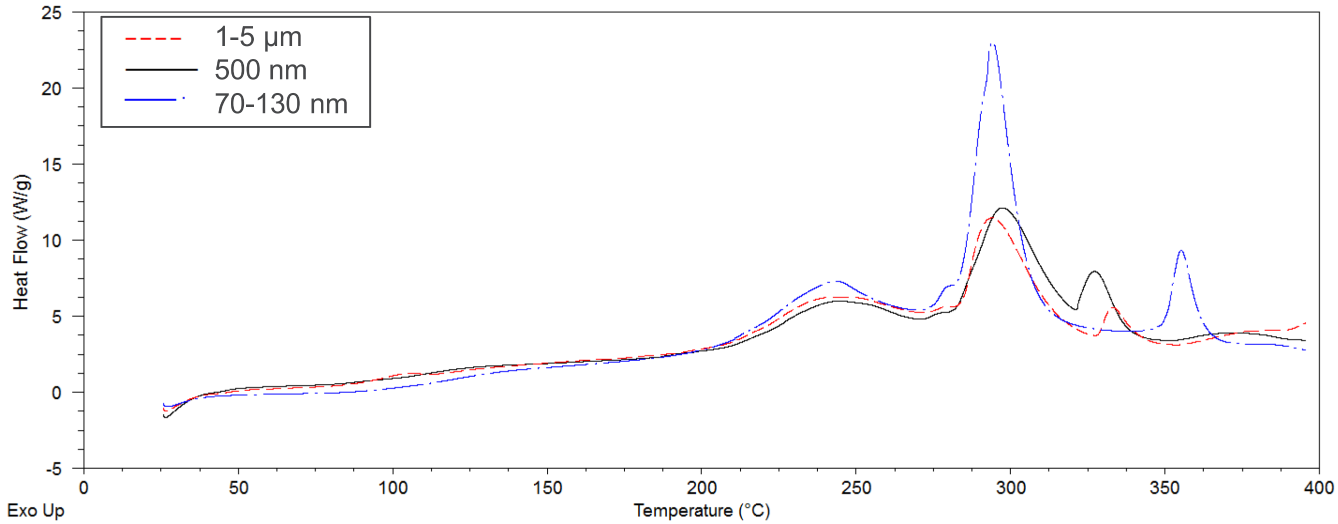
DSC DEPENDENCE ON SI PARTICLE SIZE

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

SUMMARY

- ARC Performance
  - Smaller capacity 18650s allow for quantitative ARC measurement of silicon anode thermal runaway
  - Still significant variation in both peak heating rate and gas generation but much more reactive than graphite anodes
- Water evolution from LiPAA is still significant even after 150C drying schedule
  - Could be contributing factor to energetic runaway of silicon anodes
- DSC testing shows N/P variations and coating thickness are likely not responsible for difference between SNL and ANL silicon electrode DSC responses
  - Reduction of particle size from ~1 μm to ~100 nm causes significant increase in heat generation and peak heating rates

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

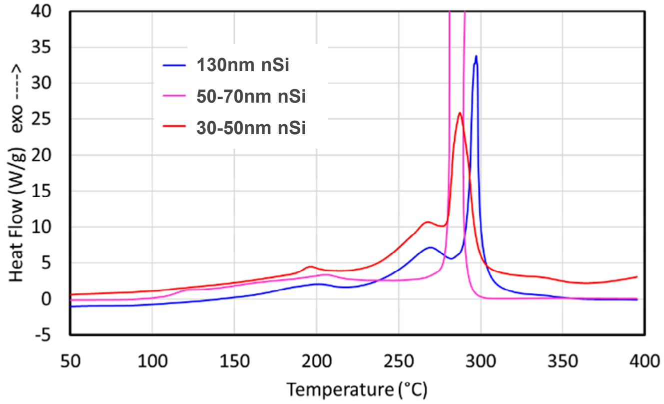
EXTRA SLIDES

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



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