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

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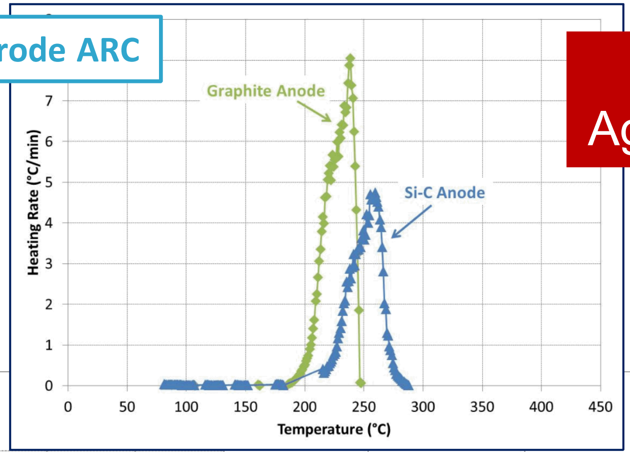
USDrive Electrochemical Energy Storage Tech Team
Applied Battery Research for Transportation (ABR)
Silicon Deep Dive Program Informational Meeting
Argonne National Laboratory
October 18, 2016

FOR ANDY AND DENNIS:

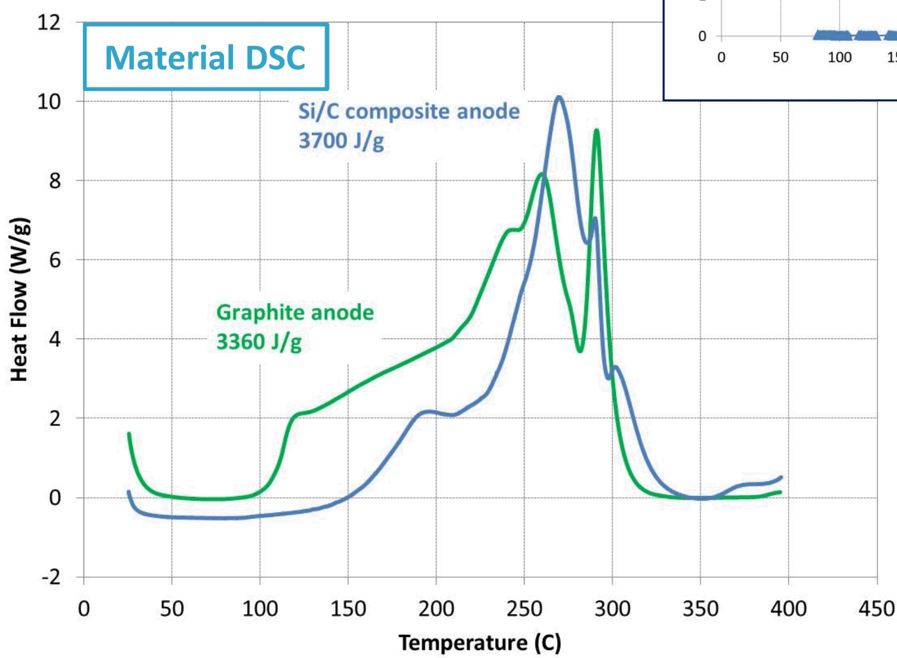
ABUSE RESPONSE OF SILICON ANODES

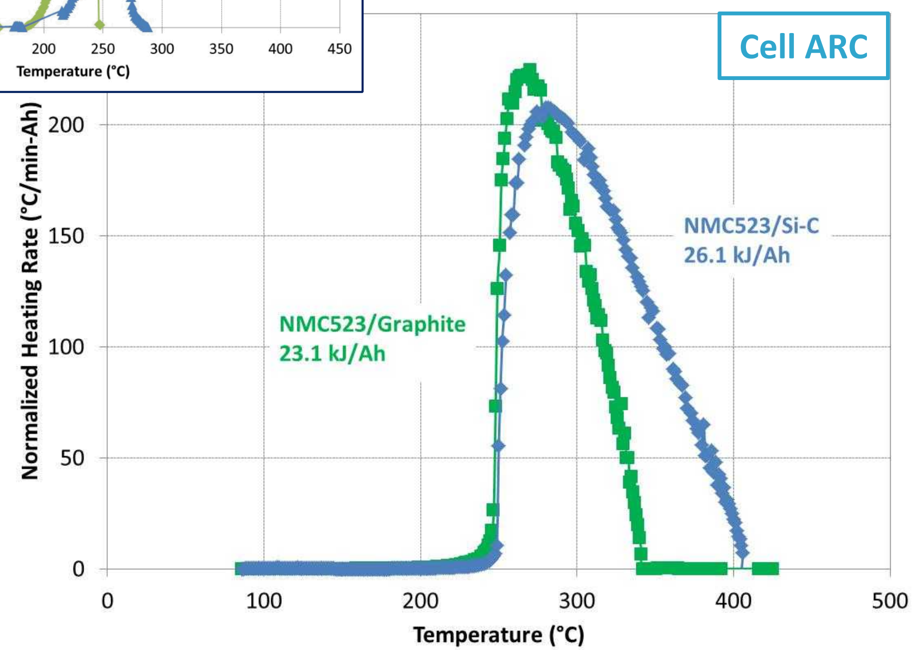
Approach for next generation of materials



ARC and DSC
Agree on Si/C differences

Si/C
~5% Si





Understanding thermal runaway from materials interactions to full scale response

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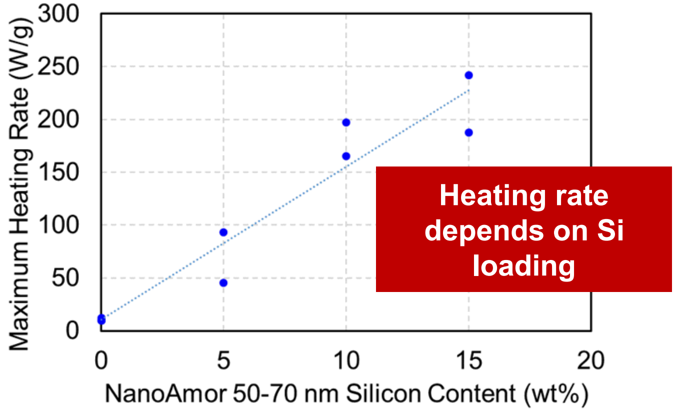
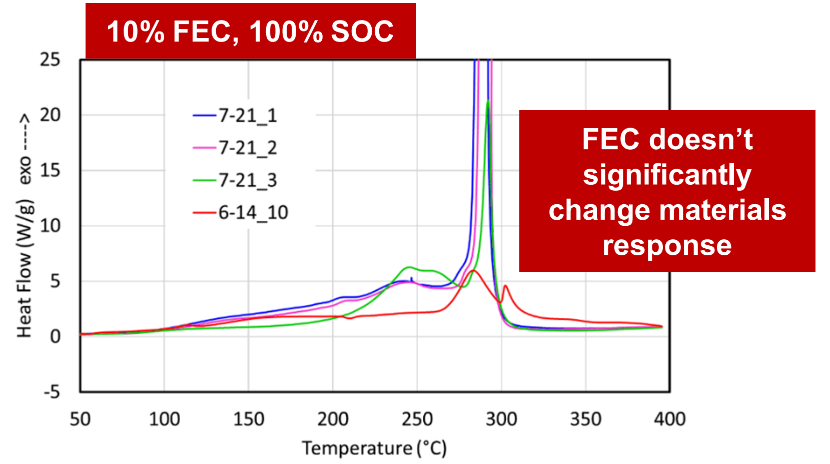
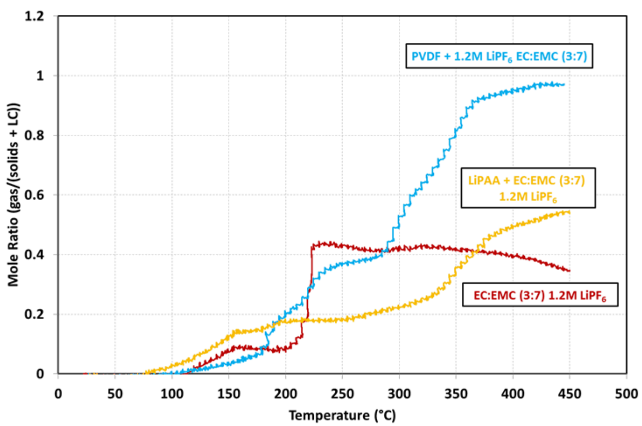
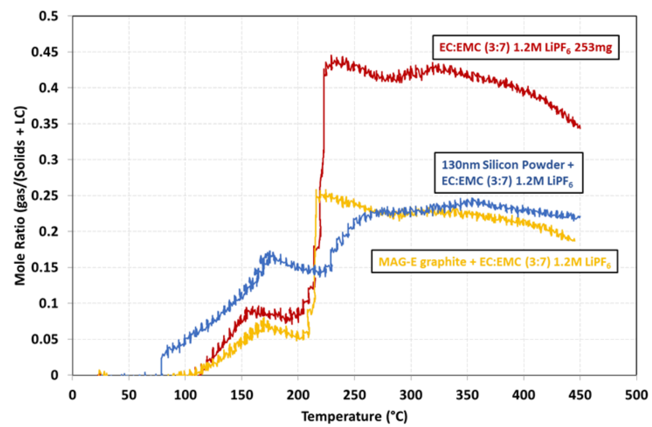
MATERIALS LEVEL EVALUATION FOR ABUSE RESPONSE









Additional gas generation from both PVDF and LiPAA

Almost no contribution from graphite or silicon at without interactions from charge/discharge

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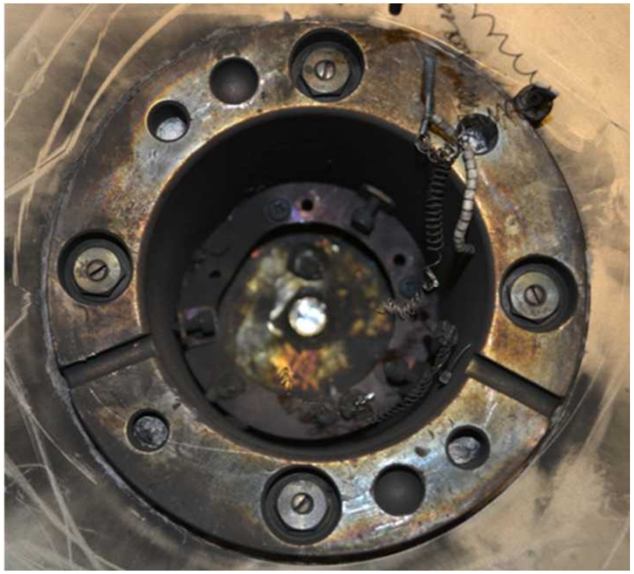
ARC EVALUATIONS OF FULL CELLS

ARC evaluation attempted for 10% and 15% Si anodes from CAMP vs NCM523



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

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FUTURE WORK

Understanding link between materials properties and abuse response of silicon materials

- **Materials Characterization – Determination of influence on overall thermal runaway enthalpy and/or electrode reactivity**
  - % Si Loading (starting with baseline)
  - Electrolyte effects (FEC, VC, etc.)
  - Particle Size Effects
  - Coating Efficacy (Collaboration with NREL)
  - Binder Effects – Polysiloxane based, Ion-conductive binders, etc.
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  - 18650 ARC understanding and path forward
  - ANL baseline Si electrodes
  - Candidate materials from materials characterization and CAMP
- **Post Abuse Tear Down Evaluations**
  - Program electrodes (Collaboration with Post Test Facility)
- **SiO and Si_xSn_y Alloys – Potential for future PYs**

DSC

Determine correlation between material level and full cell level

ARC

TELECON UPDATE SLIDES

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~5% Si

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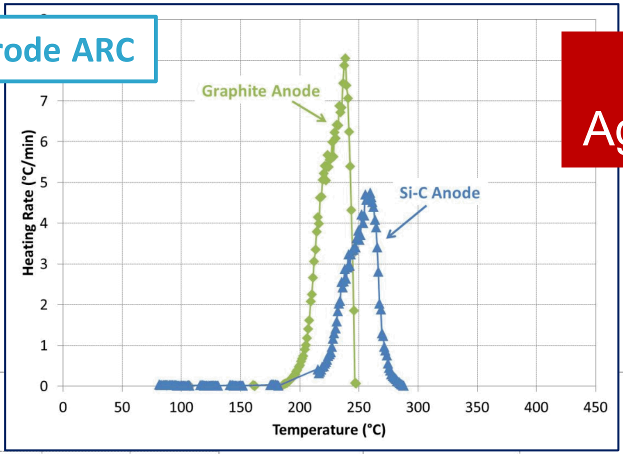

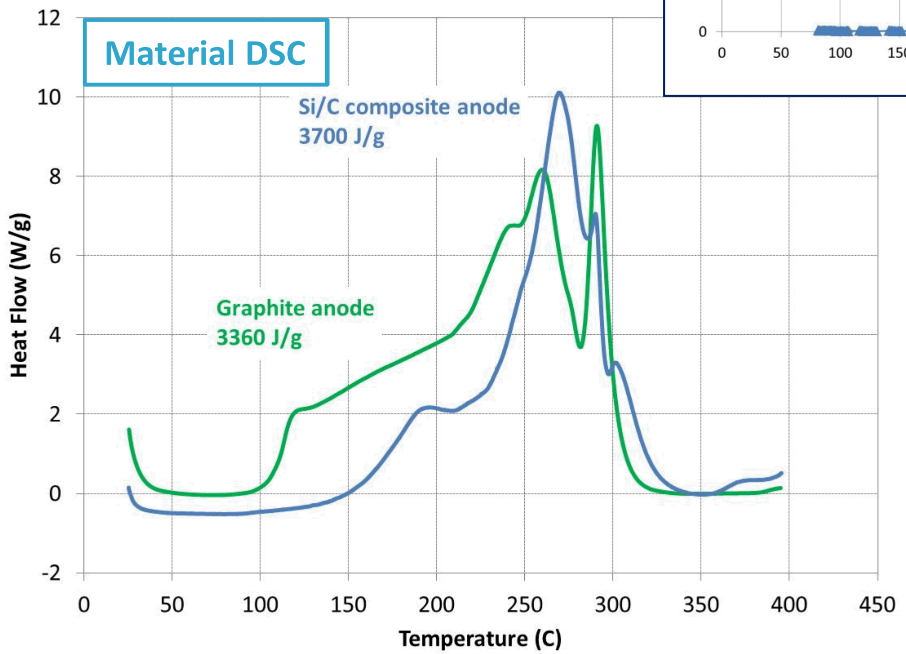

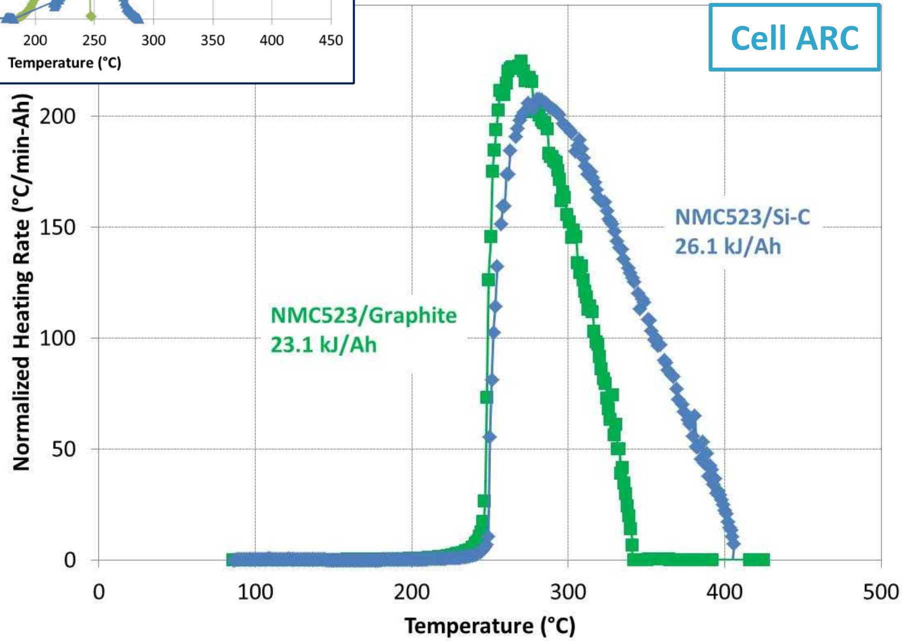

Understanding thermal runaway from materials interactions to full scale response

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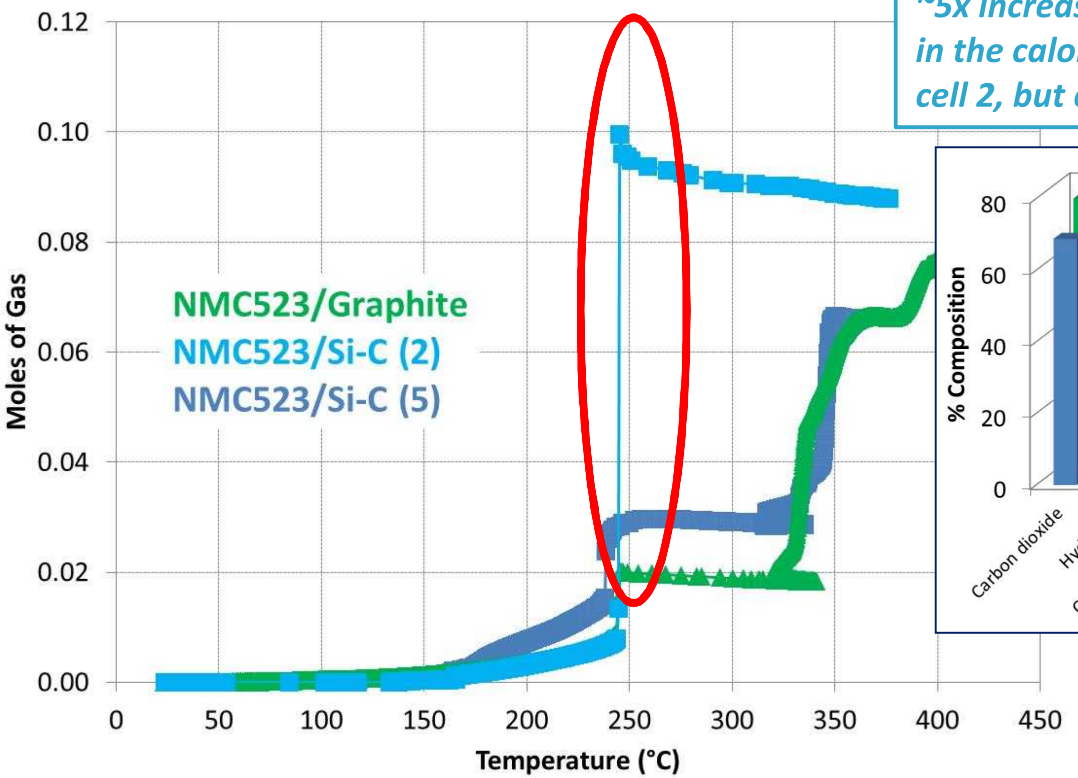
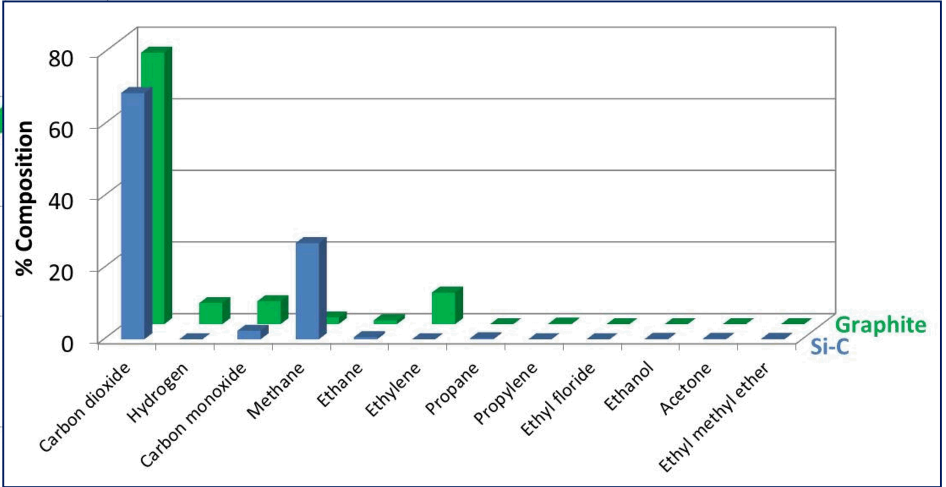
ABUSE RESPONSE OF SILICON ANODES

XG Sciences Material – Previous Evaluations

~5x increase in the amount of gas generated in the calorimeter during thermal runaway of cell 2, but comparable gas generation for cell 5





Difference in gas generation attributed to the differences in surface reactivity and surface products generated at the anode/electrolyte interface

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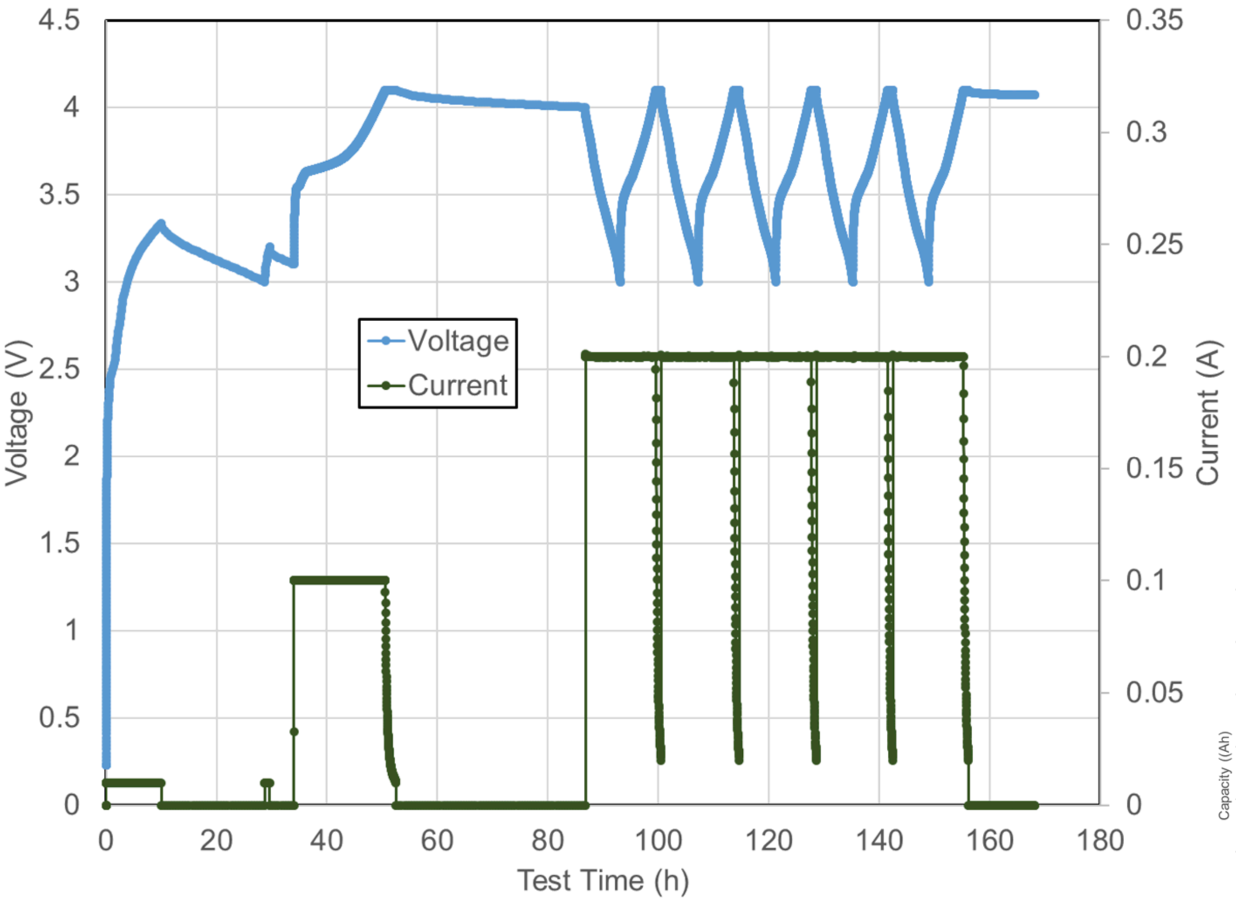
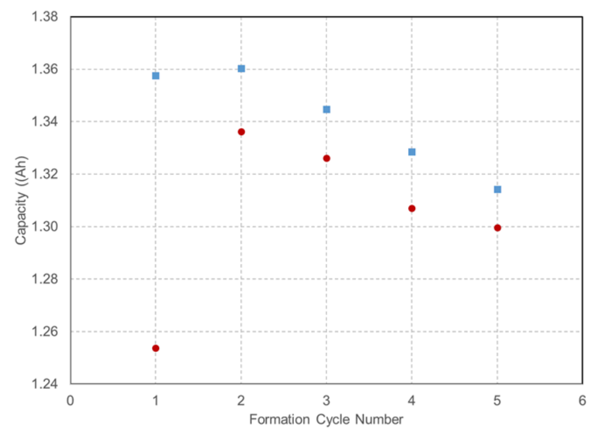
CYLINDRICAL CELL EVALUATIONS



Capacity – 1.3 Ah



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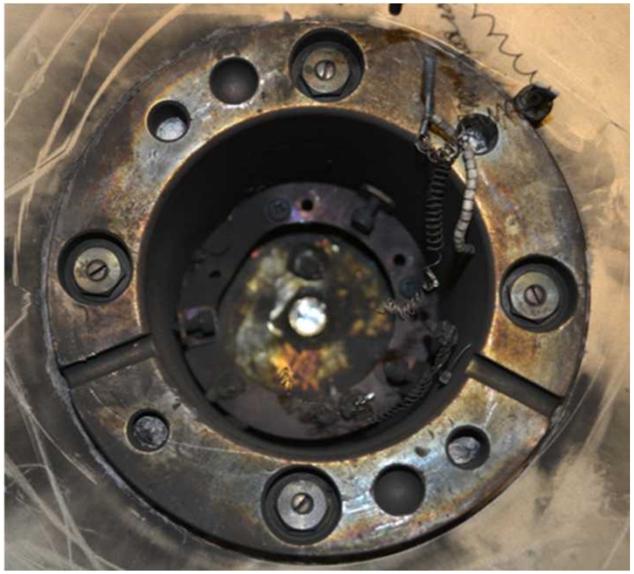
ARC EVALUATIONS OF FULL CELLS

ARC evaluation attempted for 10% and 15% Si anodes from CAMP vs NCM523

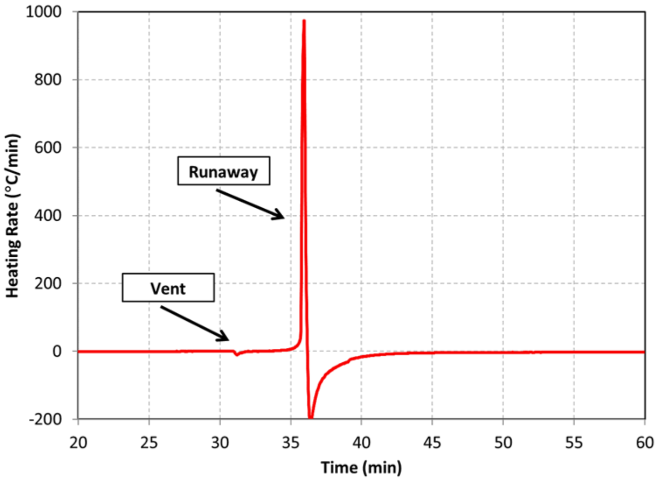


Complete rupture for entire ARC system seen with nano silicon electrodes at both 10 and 15% Si (both ARCs same result) – only a few instances of this occurring in SNL abuse testing

SINGLE CELL RESPONSE

Thermal ramp –
Runaway onset ~213 °C

Narrow angle runaway video



Peak heating rates observed indicate significant kinetics during decomposition

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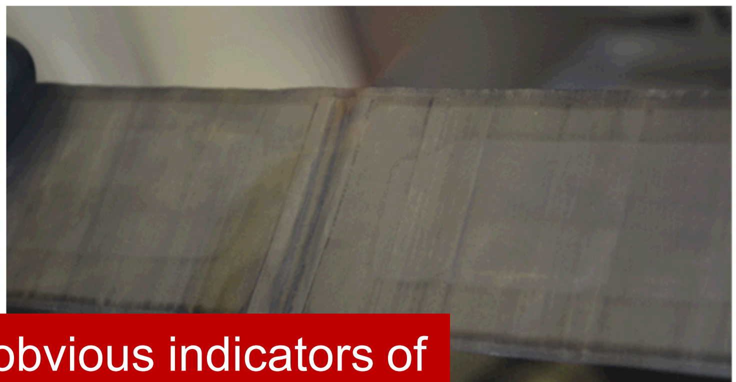
CELL TEARDOWN AND INSPECTION

- Evaluation of cells after formation cycling performed – investigate if there are indicators that lead to high enthalpy runaways or some failures during formation?



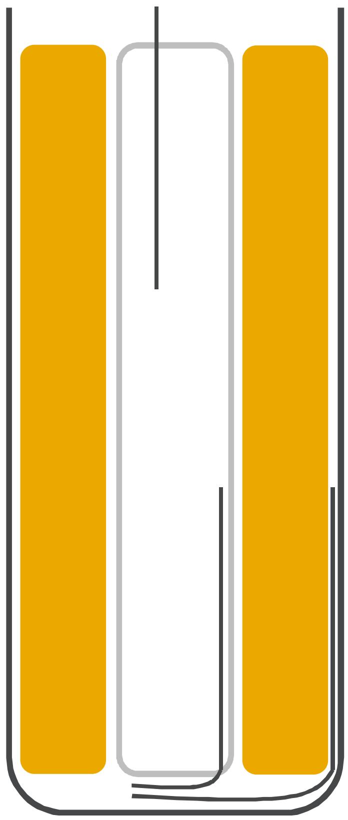
No obvious indicators of damage or irregularities

Some slight discolorations observed

18650 FABRICATION WITH LOWER MATERIAL LOADINGS

New method for ARC evaluations being developed

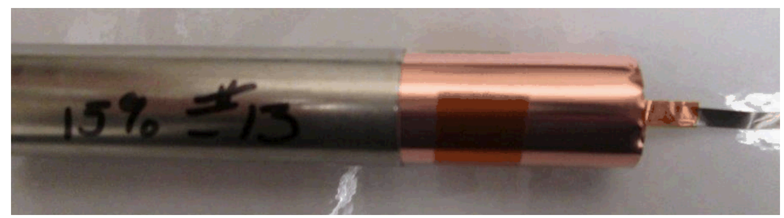
- Use of a cylindrical insert to minimize available volume for jelly roll.
  - Extra contact and welds required
  - Void space for liquid electrolyte to reside
  - Thermal transfer requirements for ARC evaluation
  - Fit must be tailored for each jelly roll - standardization



18650 FABRICATION WITH LOWER MATERIAL LOADINGS

New method for ARC evaluations being developed

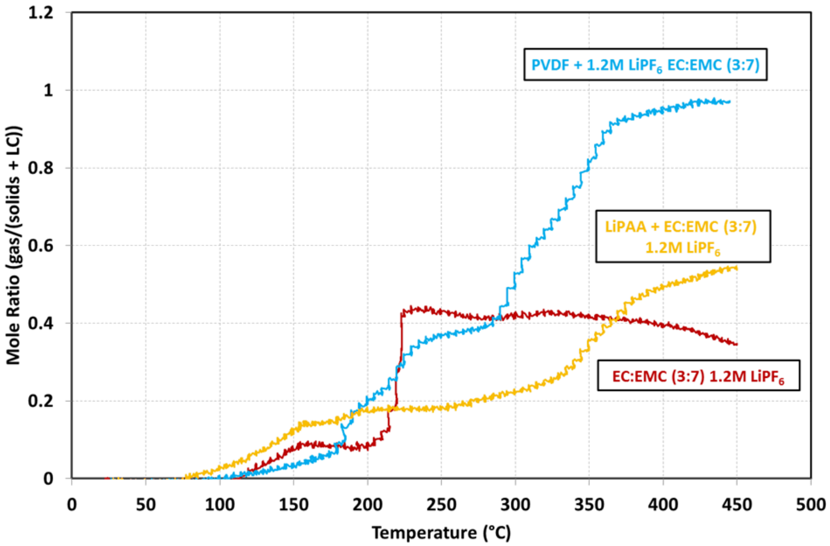
- **Difficulties with fit and welding required alternative method.**
  - **Use of copper current collector to take up dead space**
  - **Hand rolled operation – drift of wind likely**
  - **Allows for more open volume – potential for dry cell when filled**



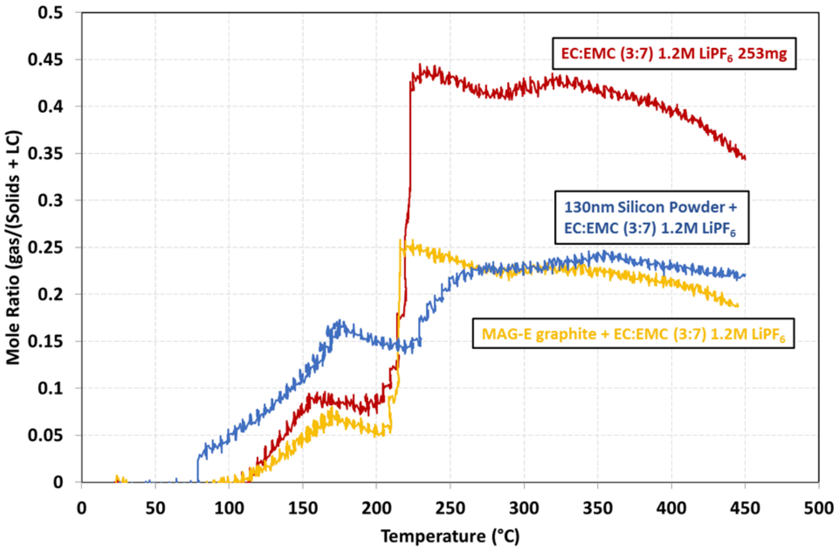
ARC BOMB CONTRIBUTION EVALUATION

- Gas generation of individual electrode components combined with electrolyte – NO SOC OR INTERACTION EFFECTS
  - Effect of shift to LiPAA from baseline PVDF
  - Effect of inclusion of nSi in place of graphite

250 mg solids + 250 mg electrolyte



Additional gas generation from both PVDF and LiPAA



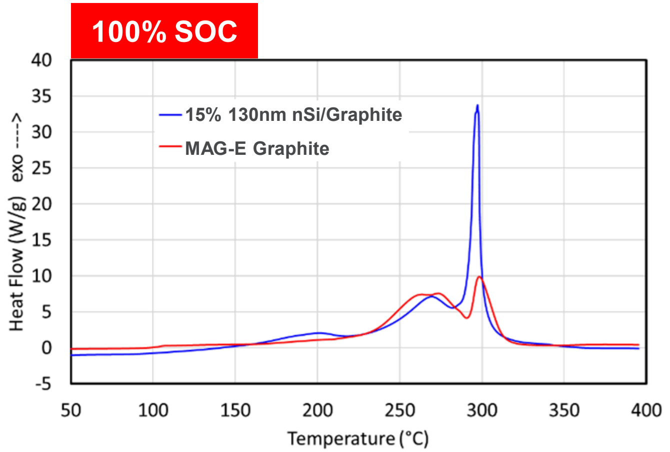
Almost no contribution from graphite or silicon

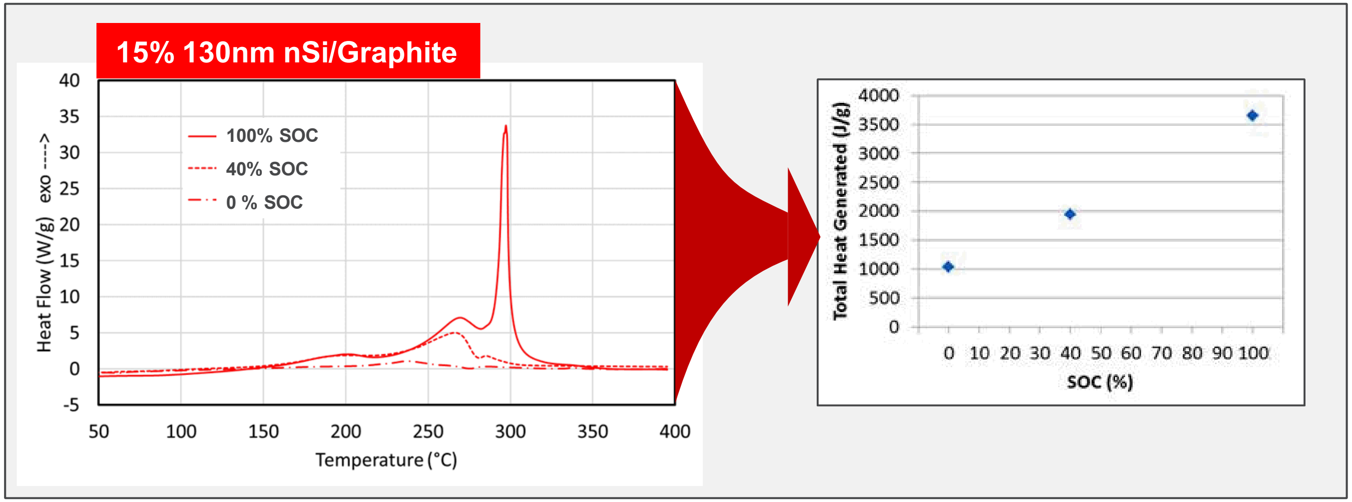
DSC OF NSI ELECTRODES

Cells undergo 4 formation cycles from 3.0-4.1V at C/10 followed by topoff or discharge to desired SOC, testing performed with 1:1 mass ratio of active material to electrolyte

- Similar peak locations, higher heat generation and significant exotherm present in silicon containing anodes at 100% SOC – **3800** J/g vs. **2300** J/g
- Large exotherm is only present at full SOC – reaction of $Li_{15}Si_4$?

* Y.S. Park, S.M. Lee. *Bull. Korean Chem. Soc.* **32**, 145-148 (2011).

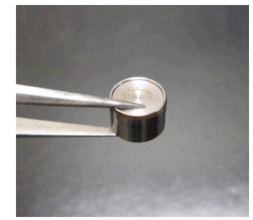




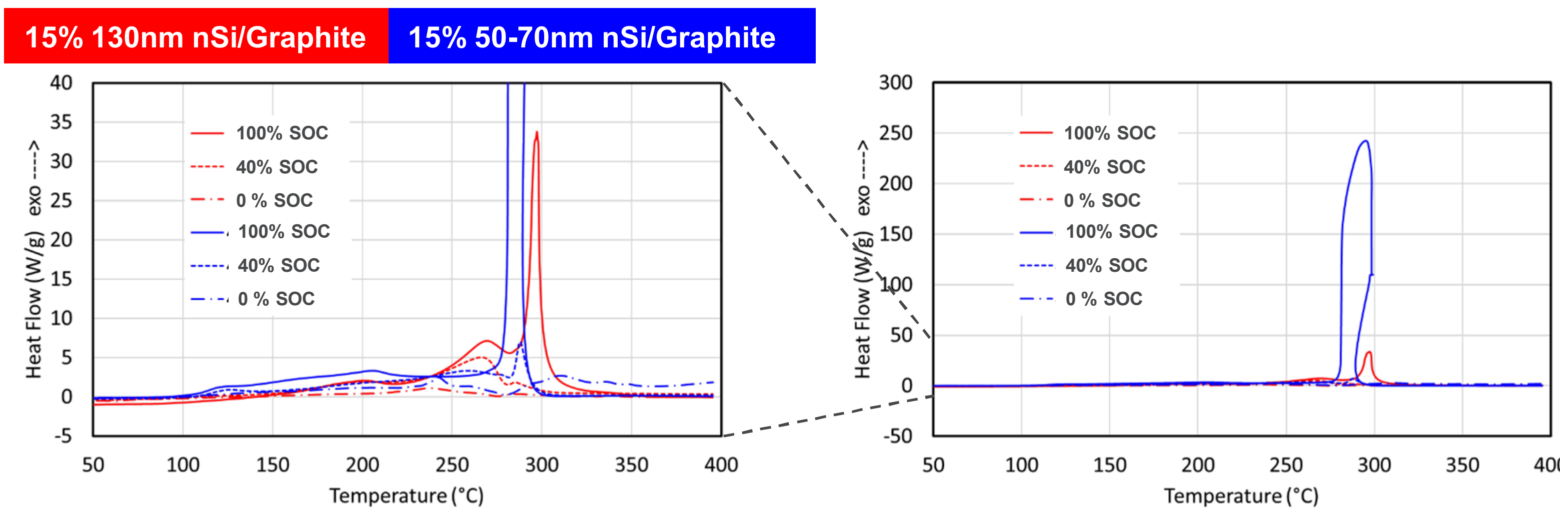
M. Klett, J.A. Gilbert, S.E. Trask, B.J. Polzin, A.N. Jansen, D.W. Dees, D.P. Abraham. *J. Electrochem. Soc.* **163,** A875-A887 (2016).

EXTREME EXOTHERMIC REACTIONS OBSERVED

- Testing of CAMP produced electrodes with higher loading and smaller particle sizes resulted in dramatic exothermic peaks, very high kinetics in 100% SOC electrodes
  - Surpassed equipment capability to accurately record heat flow with no observable leakage
- Smaller particle size lowers initiation temperature of large exotherm



No observed pan leakage



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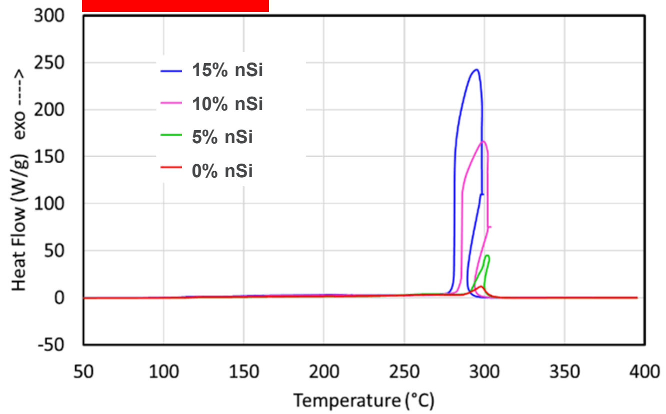
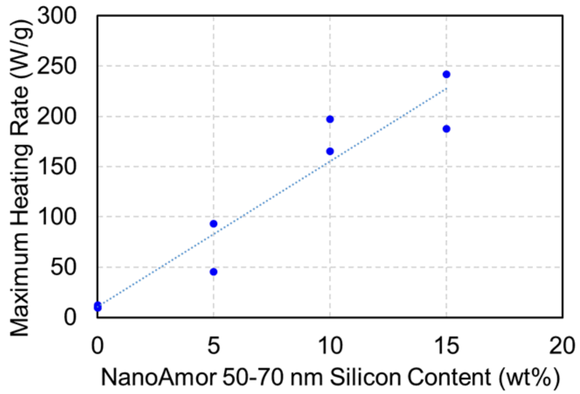
HEAT GENERATION VS SILICON LOADING AND ELECTROLYTE MITIGATION

100% SOC

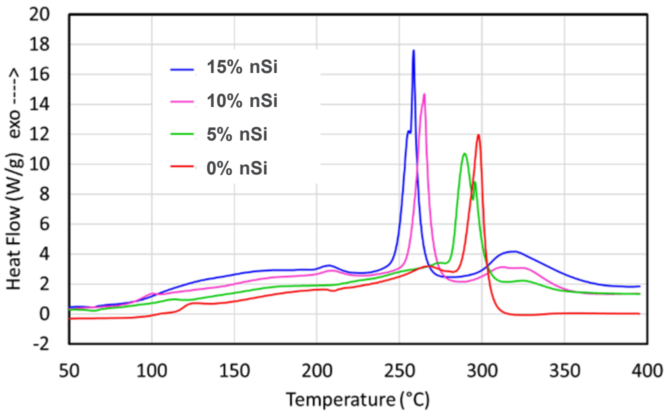


- Large exotherms are repeatable and trend with silicon content
  - Greater peak heating rate
  - Lower exotherm onset temperature
- Exotherm can be mitigated by reducing electrolyte ratio
  - Trends hold in this case but reaction peaks are quite altered

Exotherm values aren't true but qualitative comparison shows trending with silicon content



Testing with reduced electrolyte ratio



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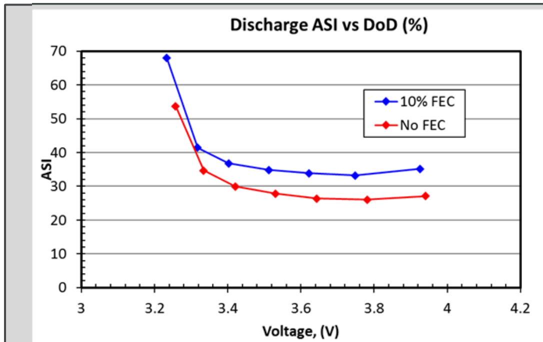
EFFECT OF FEC ON ELECTRODE PERFORMANCE

- FEC is widely demonstrated to improve capacity and cycle life of Si electrodes
  - Formed SEI is more passivating / robust

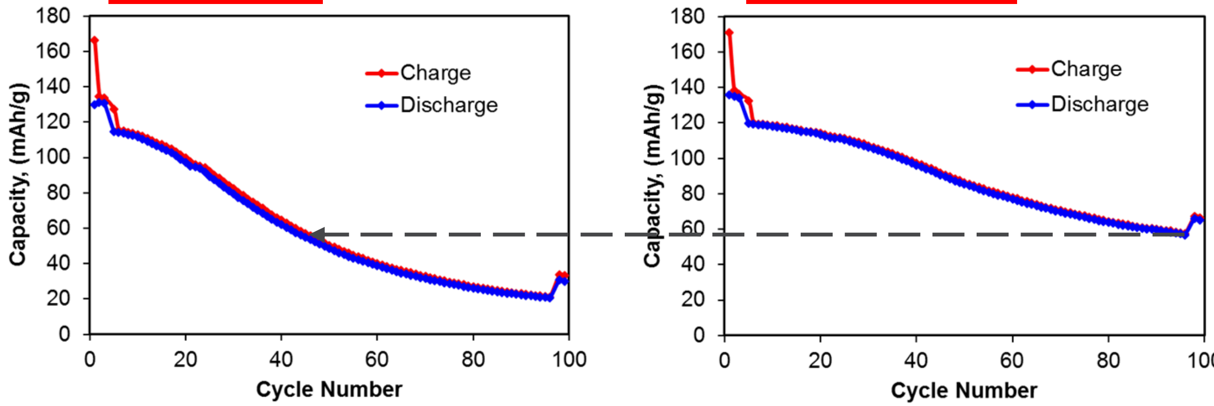
* N.S. Choi, K.H. Yew, K.Y. Lee, M. Sung, H. Kim, S.S. Kim. *J. Power Sources* **161**, 1254-1259 (2006).



HPPC shows higher ASI – more resistive SEI

No FEC

10% FEC



Addition of 10% FEC to electrolyte more than doubles cycle life at a given capacity

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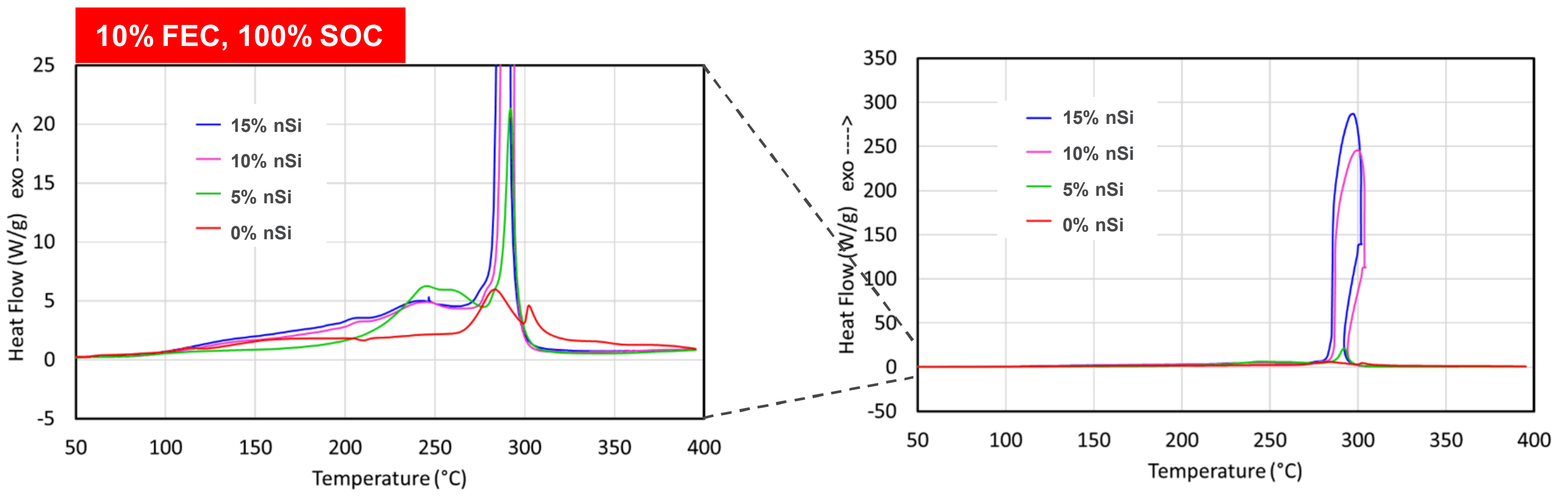
EFFECT OF FEC ON THERMAL PERFORMANCE

- Testing after cycling with and in the presence of 10% FEC shows thermal performance is not significantly affected by FEC addition
  - Extreme exotherms still present and still trend with nSi content



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DSC

Determine correlation between material level and full cell level

ARC

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CONCLUSIONS

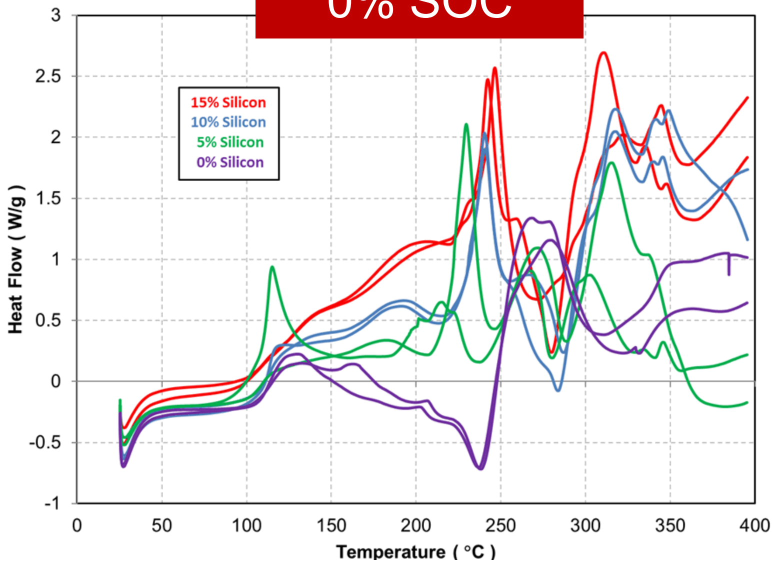
- Electrochemical Performance
  - Silicon anodes offer good capacity increases over graphite
  - For electrode processing, silicon loading remains low – similar cell level capacity to graphite
  - Lifetime remains problematic
- Thermal / Abuse Performance
  - Range of overall enthalpy release and runaway kinetics
  - Gas generation still unclear due to intermittent high volume releases
  - Depends on silicon morphology and composition
  - Generally see higher heating rates and increased peak runaway temperatures
  - > 10% increase in overall response – potentially much higher for new materials
  - Potential catalytic decomposition depending on alloy formation

EXTRA SLIDES

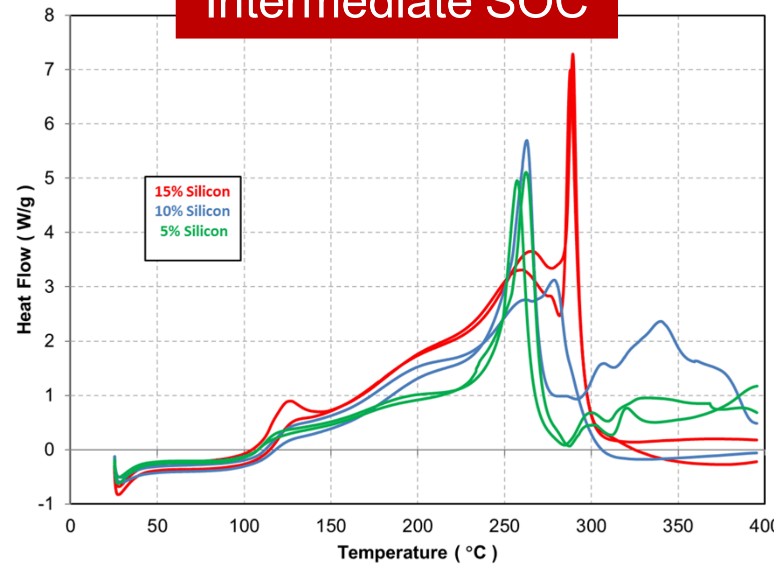
CALORIMETRY EVALUATION

Full Cell Evaluation After Formation 50-70 nm Si

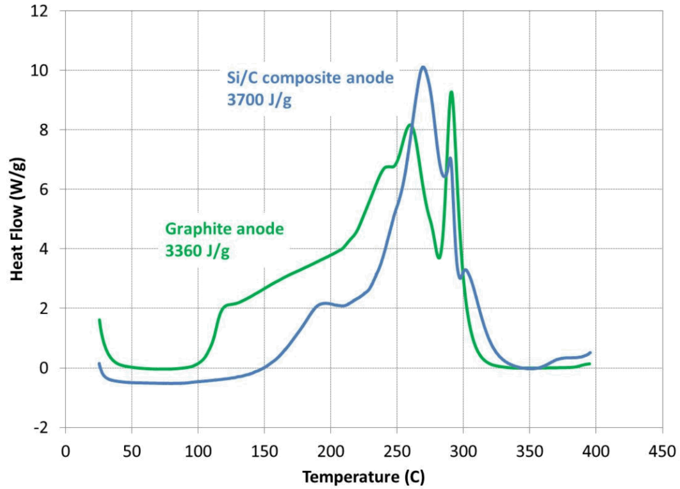
0% SOC



Intermediate SOC



Previous Data on Graphene 100% SOC



- SEI degradation peaks ~ 100 °C are clear with graphitic materials
- Similar heating rates and runaway temperatures to previous systems

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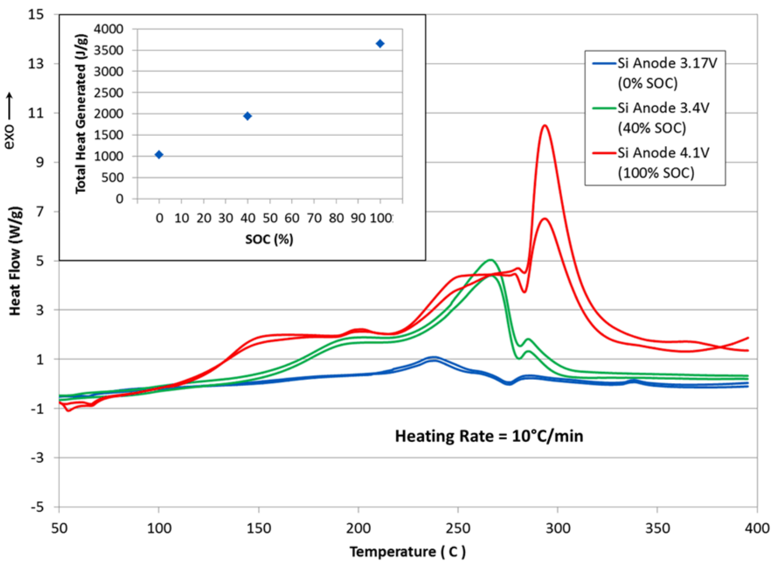
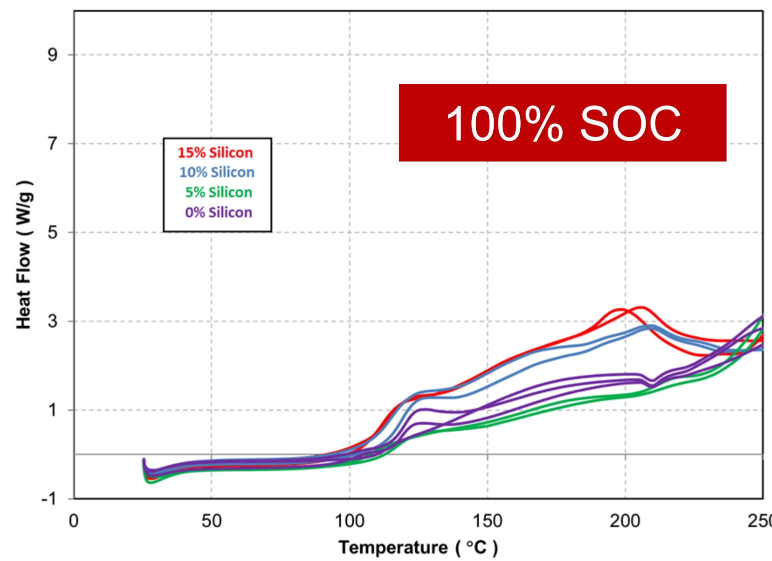
CALORIMETRY EVALUATION

Full Cell Evaluation After Formation 50-70 nm Si

130 nm
NanoAmor Si



50-70 nm
NanoAmor



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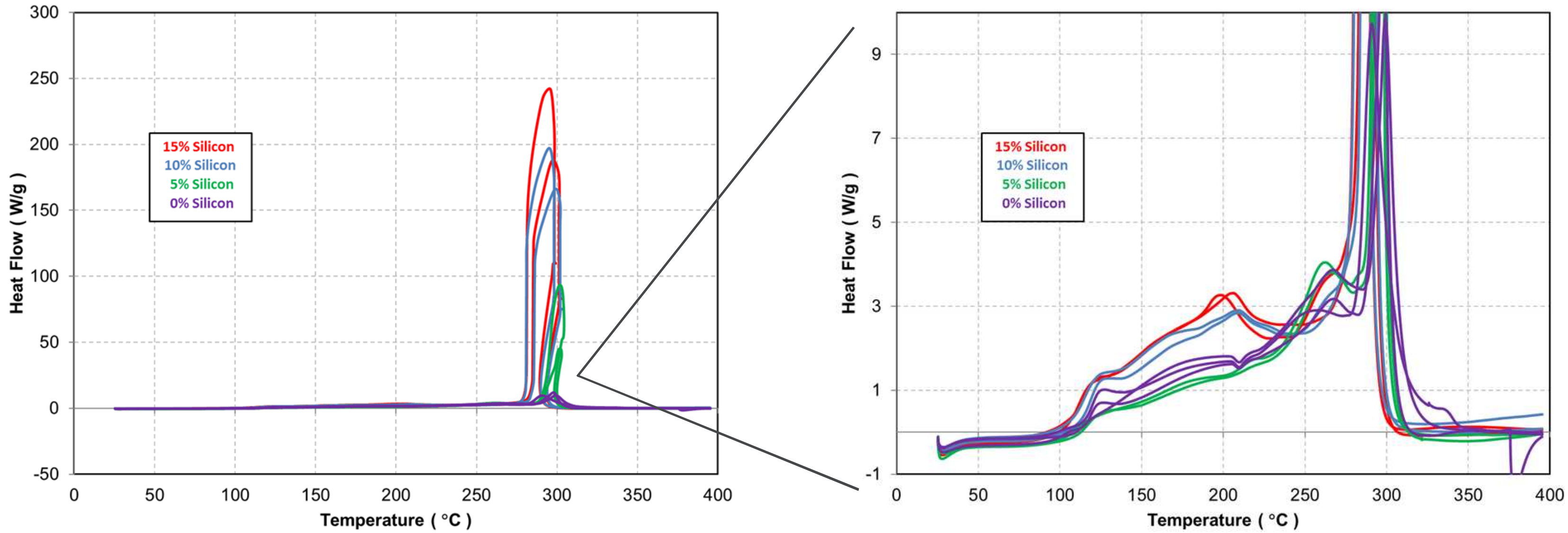
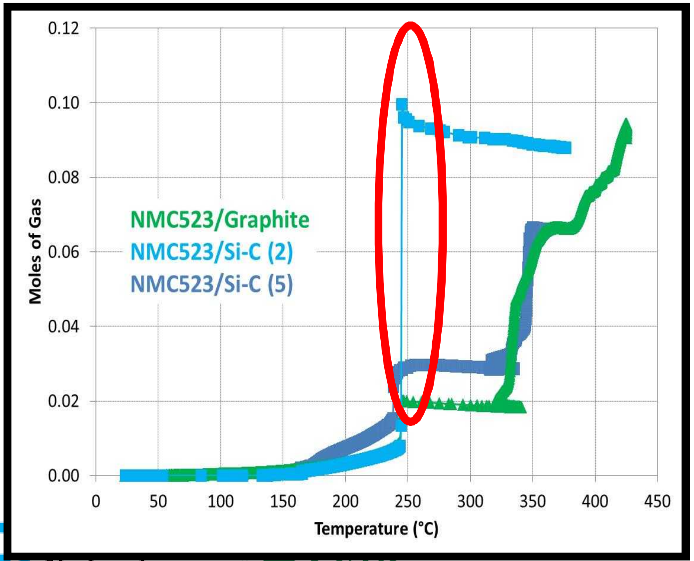
UNEXPECTED DSC PERFORMANCE

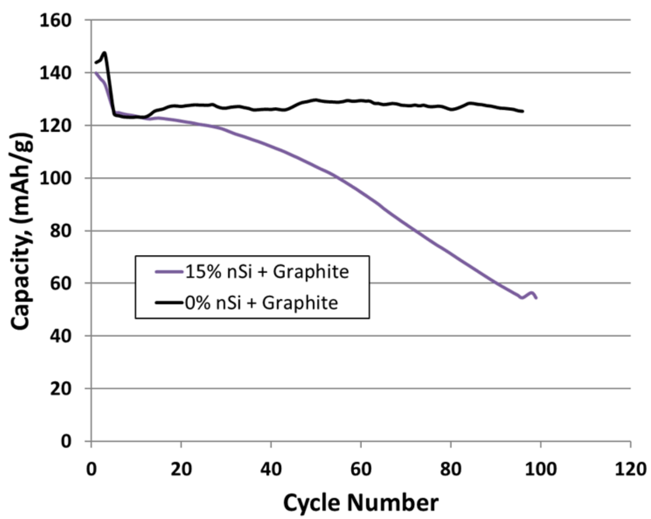


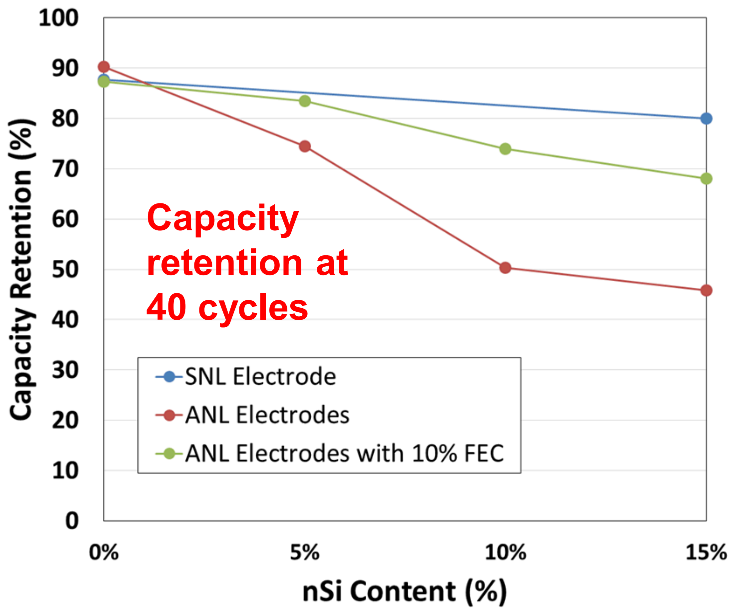


- Unclear behavior at full charge on the 50-70 nm materials
- No apparent sample leakage, no movement within instrument
- Resemblance to odd gas generation behavior previously seen in 18650 Si/graphene nanocomposites?

FULL CELL CYCLE LIFE

SNL electrodes cycled without FEC





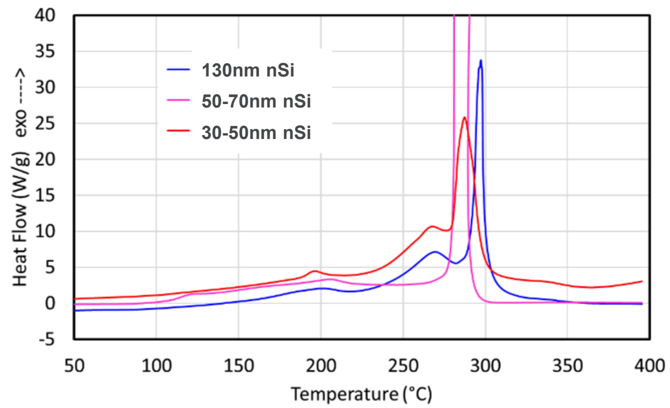
- Capacity retention of ANL electrodes improves significantly with 10% FEC addition
- SNL electrodes show high capacity retention but also have lower areal loading and higher porosity

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

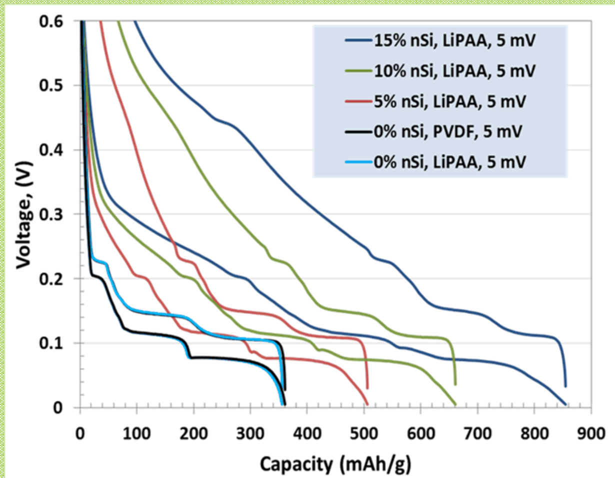
Observed Trends

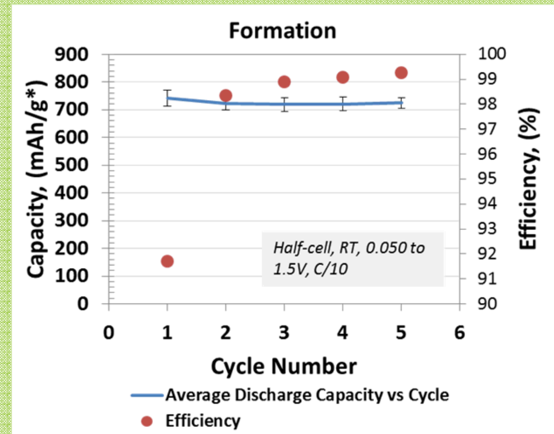
- High loading CAMP electrodes do not follow trends
  - Extreme exotherms may be associated with greater material loading
- In lower loading electrodes smaller particles show:
  - Stronger SEI peak, lower temperature peak onset, minimal change to peak heating rate and total heat generation
  - Conclusions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



NANOAMOR MATERIAL EVALUATION

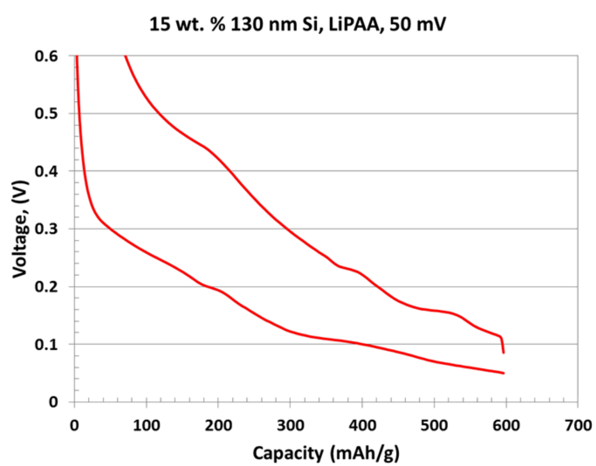
Electrode comparison and baseline

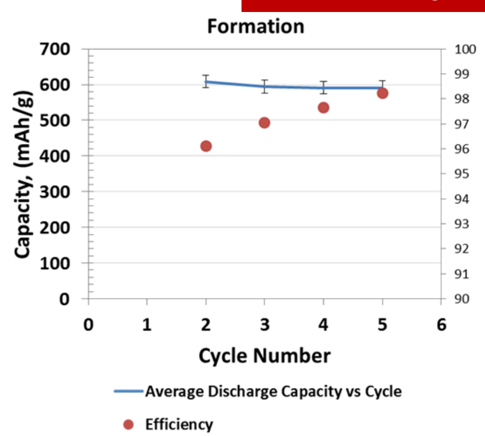




- Data from ANL using 50-70 nm NanoAmor silicon with 10 % FEC in electrolyte
- Charge / discharge profiles to 5mV
- Observed specific capacity upon discharge to 50 mV

Comparison with baseline CAMP cells comparable performance for SNL

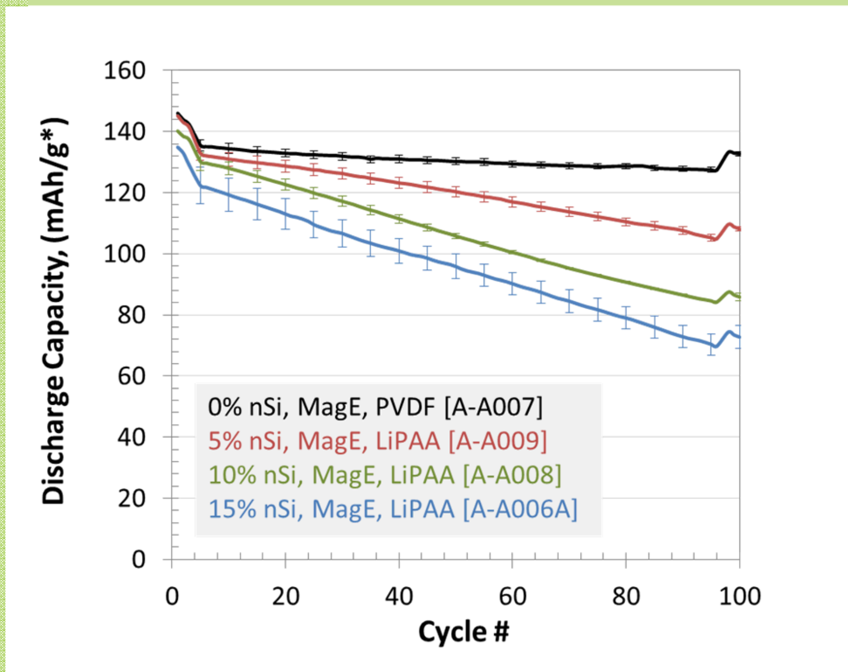




- Electrodes prepared at SNL using 130 nm NanoAmor silicon, all other aspects prepared in accordance with ANL processes, **no FEC**
- Only 15 wt. % nSi tested thus far
  - Areal Loading ~ 4.75 mg/cm^2 active material (Gr + Si)
  - Areal capacity ~ 1.6 mAh/cm^2
- Lower specific capacity and CE

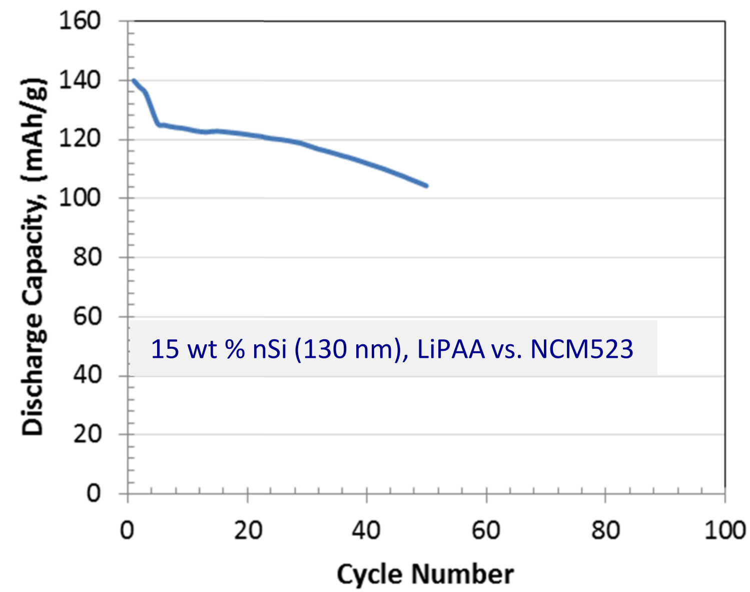
NANOAMOR MATERIAL EVALUATION

Electrode comparison and baseline



- Data from ANL using 50-70 nm NanoAmor silicon with 10 % FEC in electrolyte
- Voltage window of 4.1 – 3.0 V

Good agreement between electrodes – baseline electrochemical evaluations, thermodynamic evaluations ongoing



- Electrodes prepared at SNL using 130 nm NanoAmor silicon, all other aspects prepared in accordance with ANL processes using NCM cathodes from ANL, **no FEC**
- Voltage window of 4.1 – 3.0 V
- N/P = 1.13
- Shows slightly higher capacity than ANL data to 50 cycles

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