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

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2016 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING

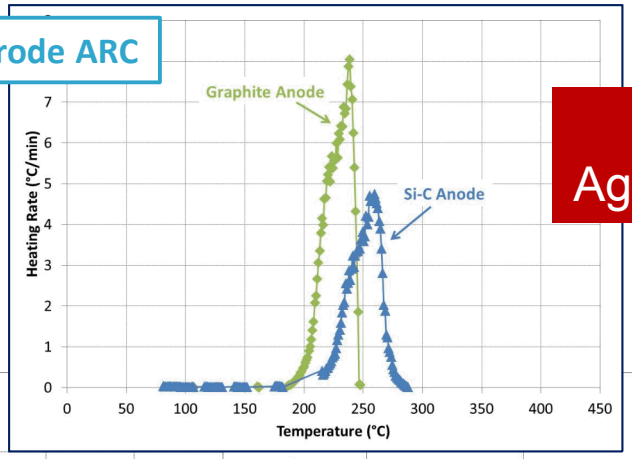
ABUSE RESPONSE OF SILICON ANODES

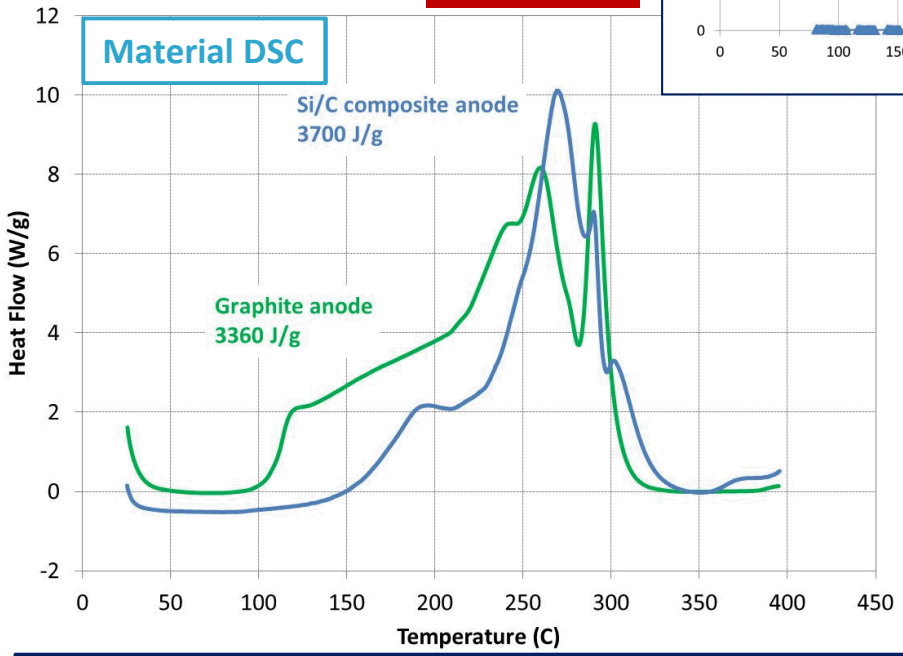
XG Sciences Material – Previous Evaluations

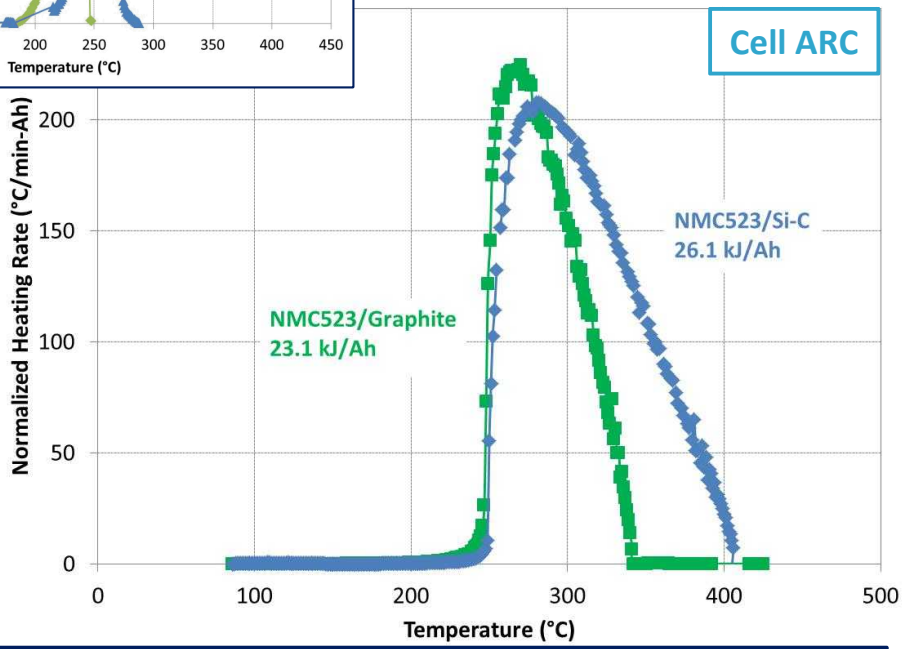
ES036 2014 AMR

XG Si/C ~5% Si

ARC and DSC Agree on Si/C differences







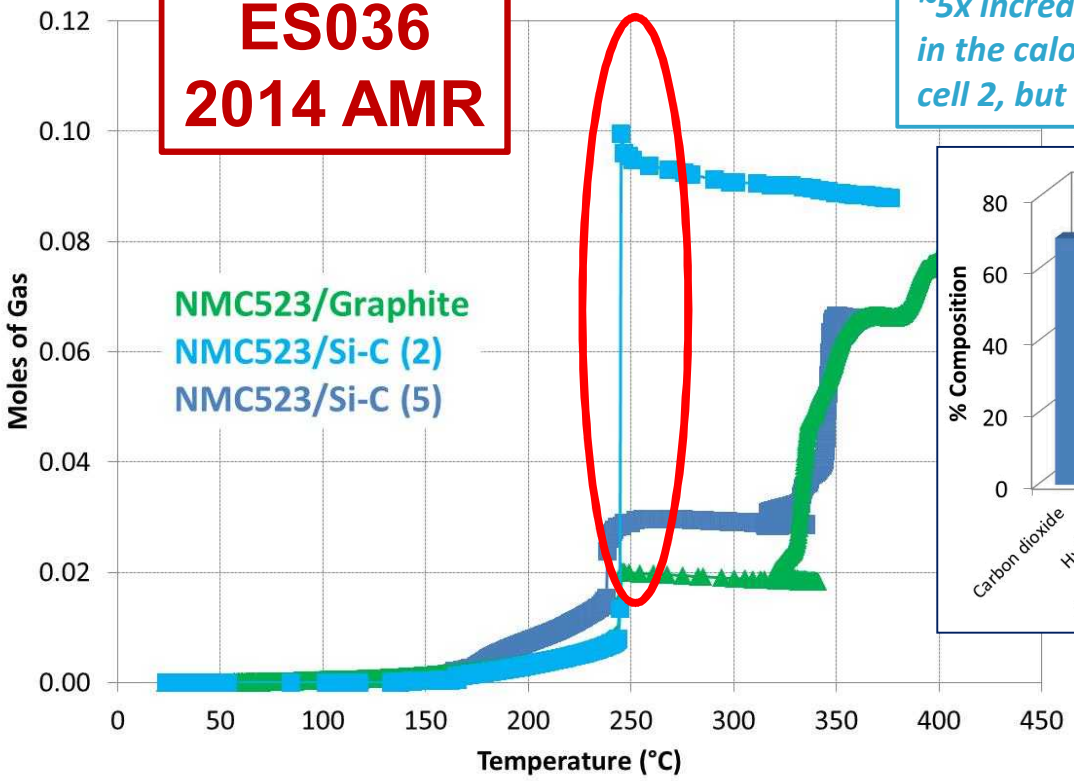
Thermal runaway enthalpy of NMC/Si-C cells is ~10% greater than NMC/Graphite cells

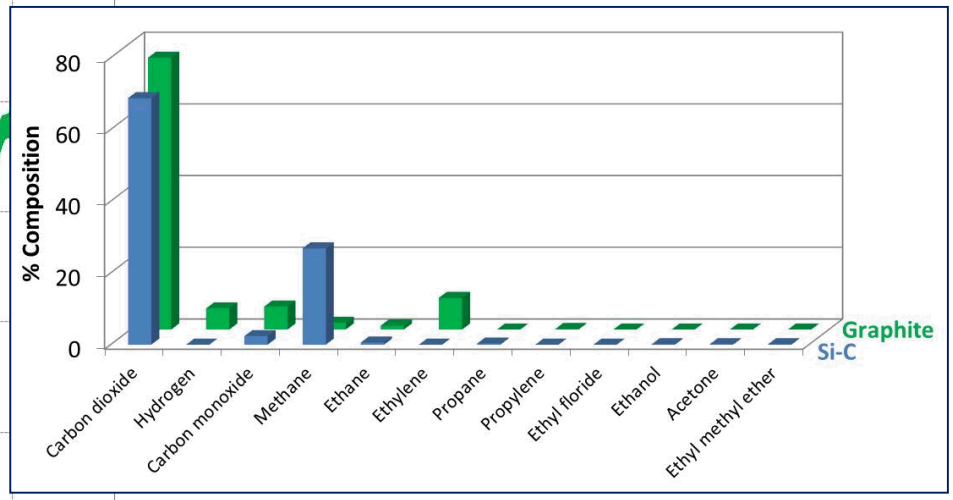
ABUSE RESPONSE OF SILICON ANODES

XG Sciences Material – Previous Evaluations

ES036
2014 AMR

~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

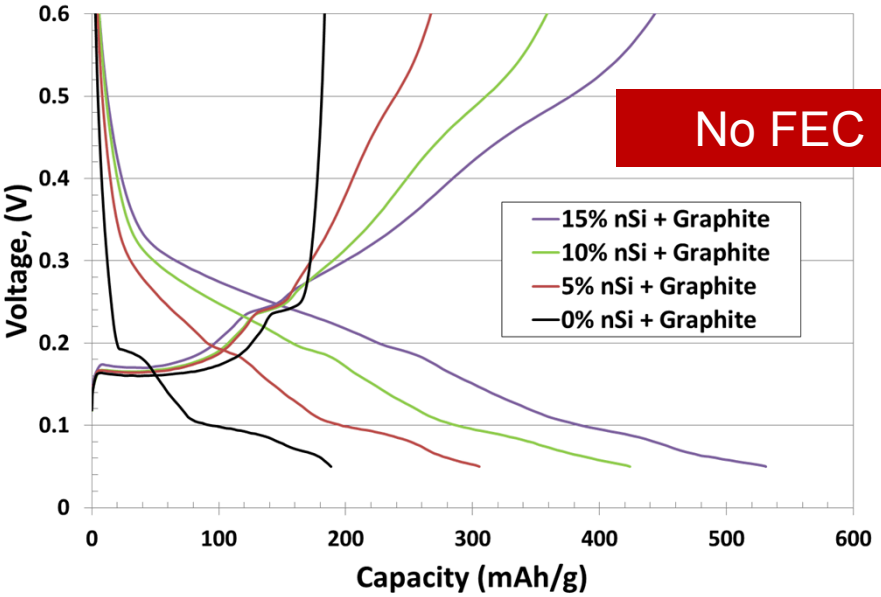
PERFORMANCE EVALUATIONS / COMPARISONS

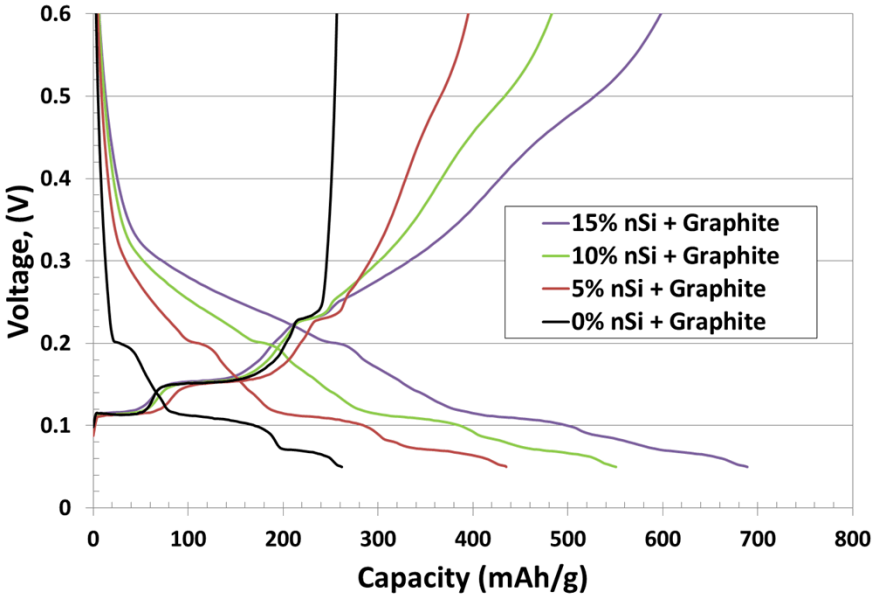
SNL Early materials and ANL/SNL made materials

- **Early testing (prior to ANL electrode delivery)**
  - nSI + Graphite prepared at SNL
  - Lower areal loadings of ~ 1.0 mA/cm^2
  - Using 130 nm nSi from NanoAmor
  - 88% Active Material, 10% LiPAA, 2% Timcal C45
- **CAMP 18650 Electrode Coating**
  - 10 – 15 m length coatings for cylindrical cells
  - Issues with coating/curling of current collectors for lower Si content electrodes and exposed current collectors
  - Areal Loadings > 2.5 mA/cm^2
  - 50 – 70 nm nSi from NanoAmor
  - 88% Active Material, 10% LiPAA, 2% Timcal C45
  - 0% nSi was prepared using PVDF with 92% active loadings
- **Electrolyte – 3:7 EC:EMC wt% 1.2 M LiPF6 with and without 10% FEC**
- **Performance comparison to ensure comparable data (similar to previous round robin efforts)**

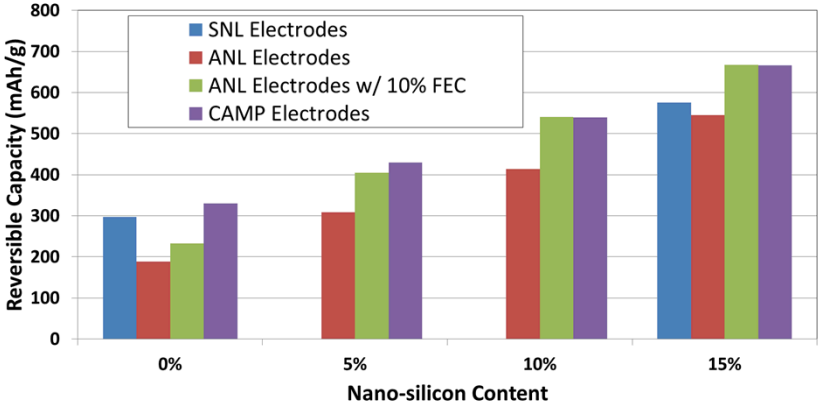
PERFORMANCE EVALUATIONS / COMPARISON

Half Cell Performance





- Significant increase in capacity performance with 10% FEC addition to Gen 2 electrolyte
- Upon FEC addition capacity values align well for all electrodes used



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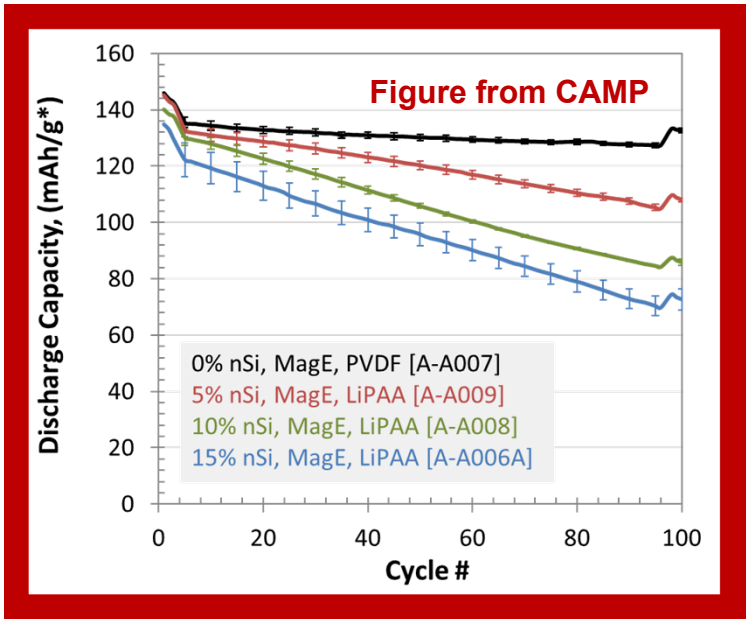
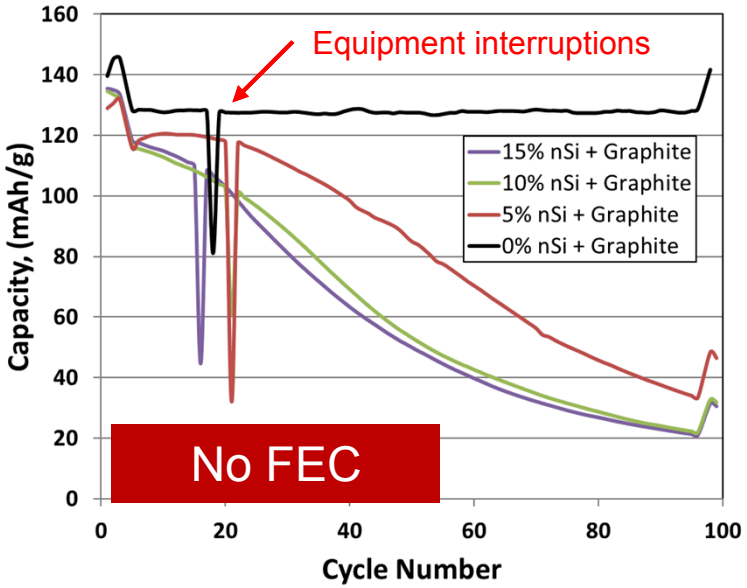
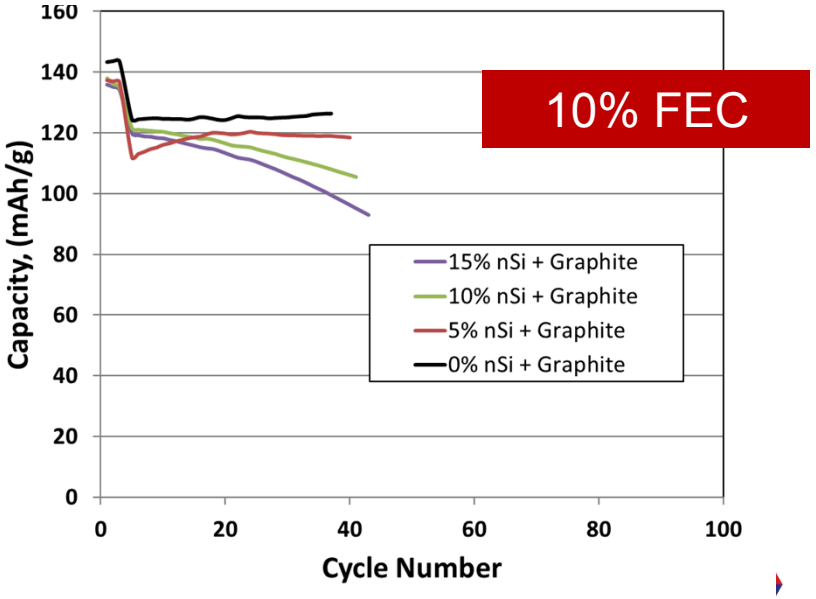
PERFORMANCE EVALUATIONS / COMPARISON

Full Cell Evaluations





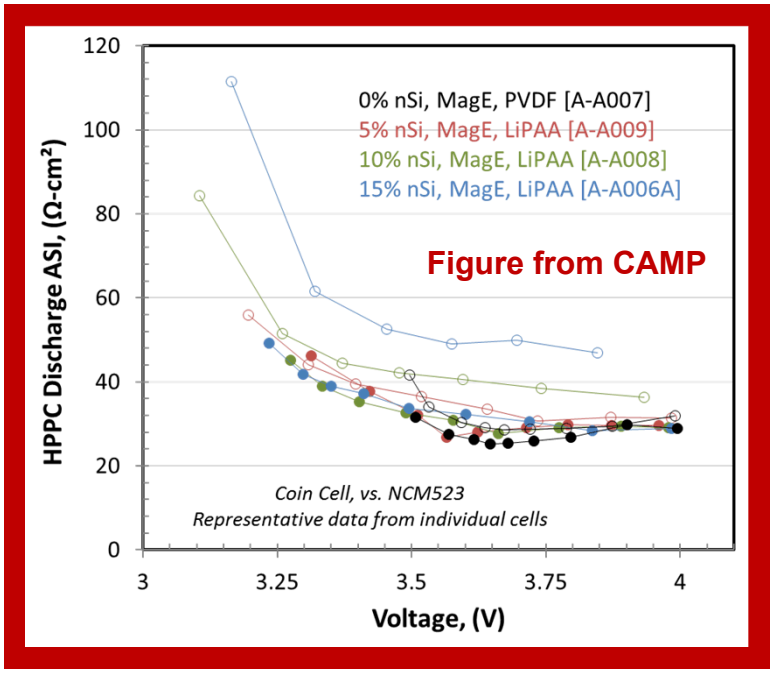


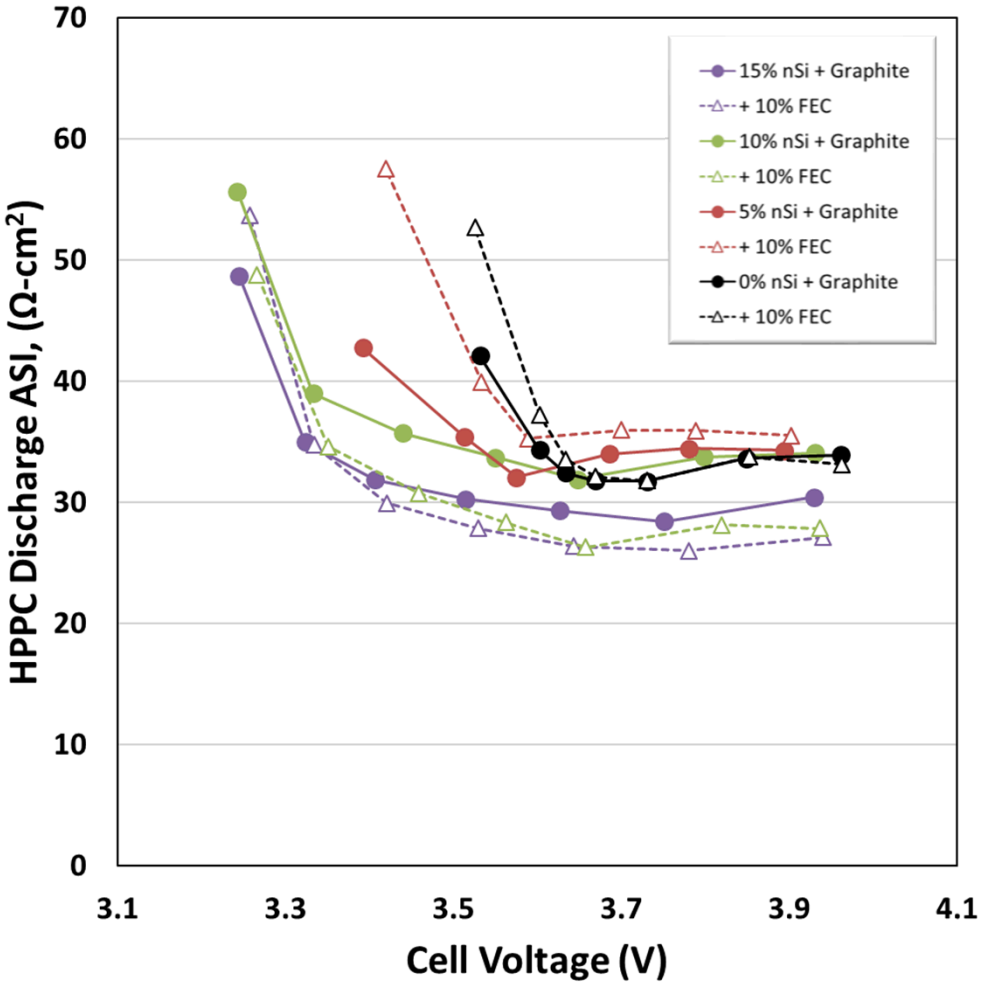
- Full cell capacity shown by cathode mass
- All electrodes show similar performance when FEC is used
  - Significantly higher rate of capacity loss without

PERFORMANCE EVALUATIONS / COMPARISON

Full Cell Impedance

Consistent ASI values across tested electrodes



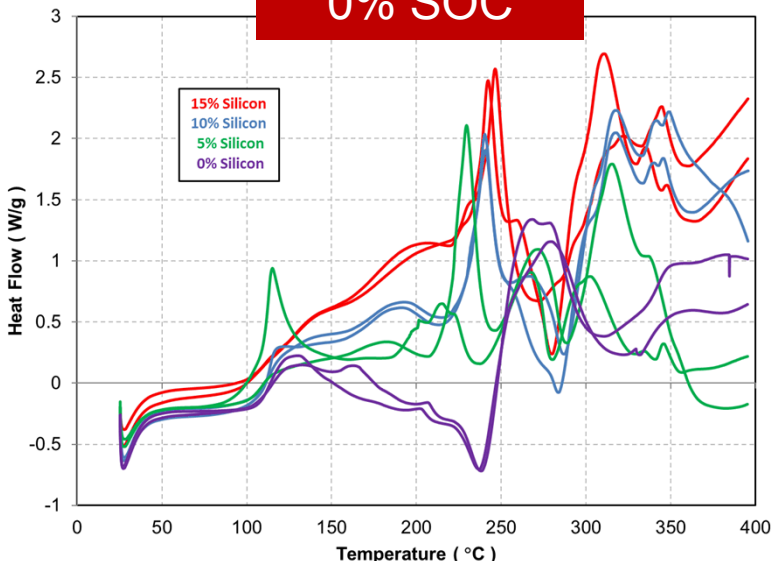


Lower nSi content electrodes demonstrate elevated ASI, reflecting issues experienced during coating process

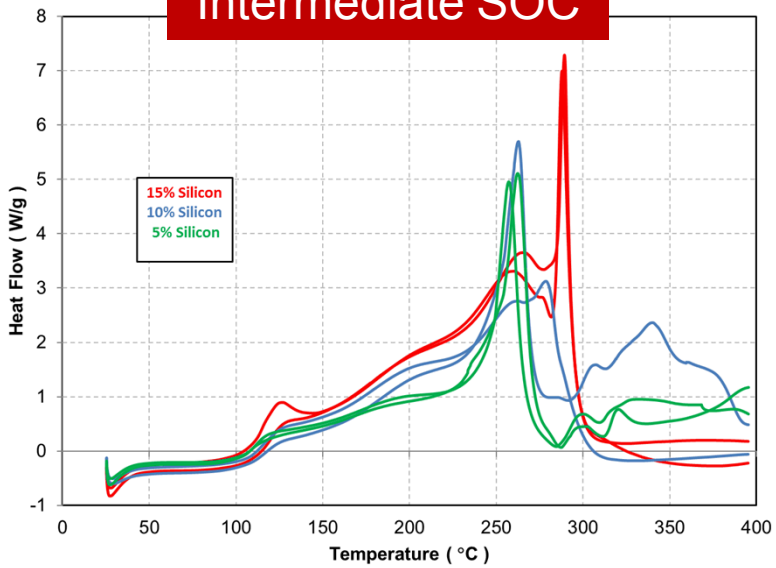
CALORIMETRY EVALUATION

Full Cell Evaluation After Formation 50-70 nm Si

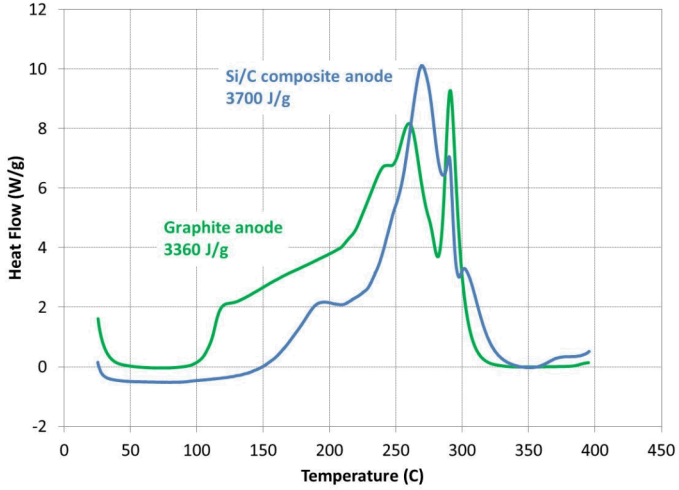
0% SOC



Intermediate SOC



Previous Data on Graphene 100% SOC



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

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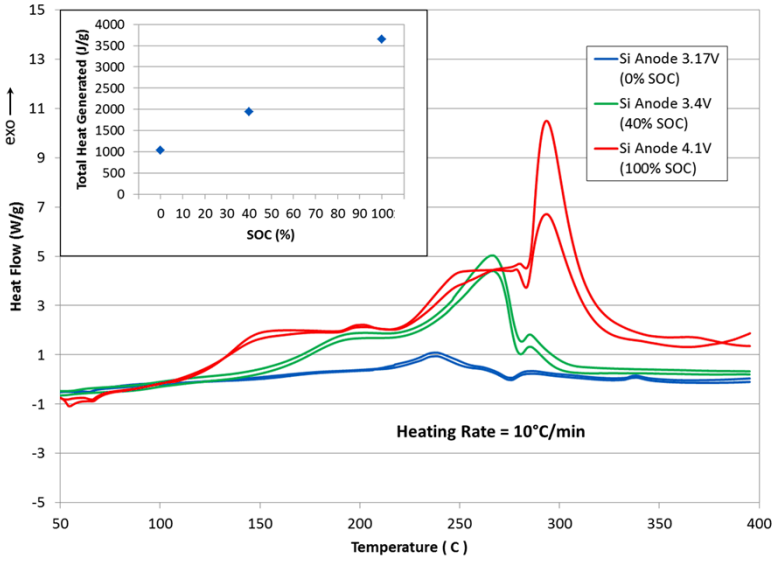
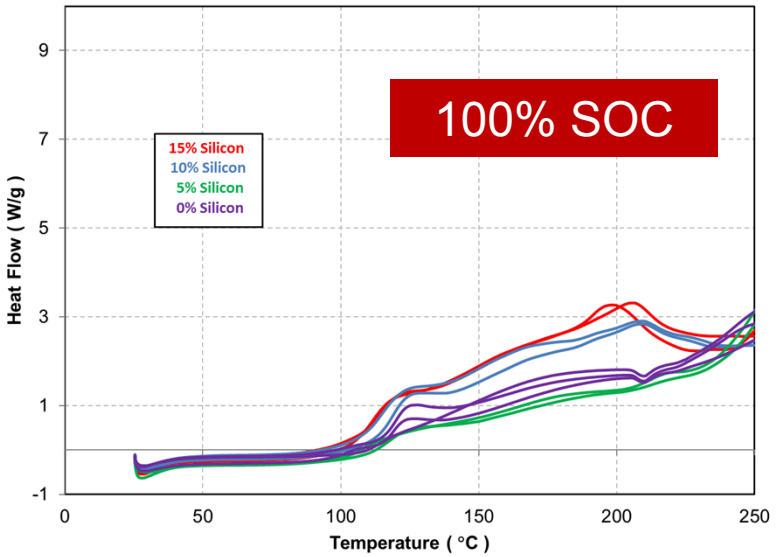
CALORIMETRY EVALUATION

Full Cell Evaluation After Formation 50-70 nm Si

130 nm NanoAmor Si



50-70 nm NanoAmor



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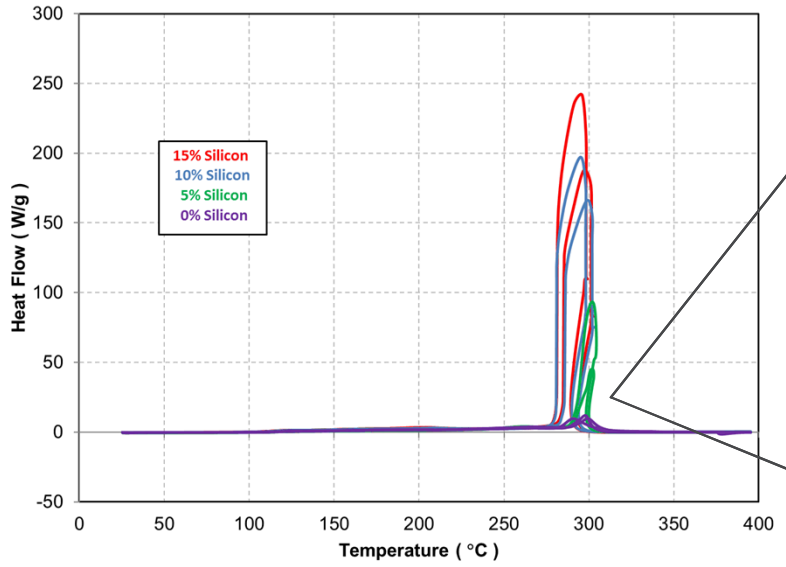
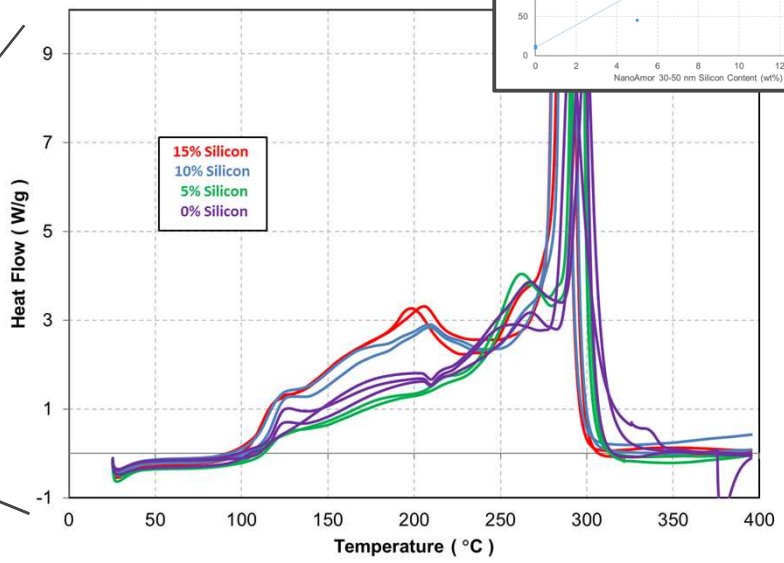
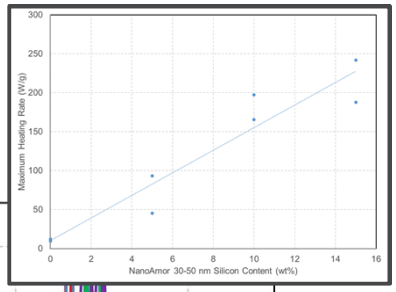
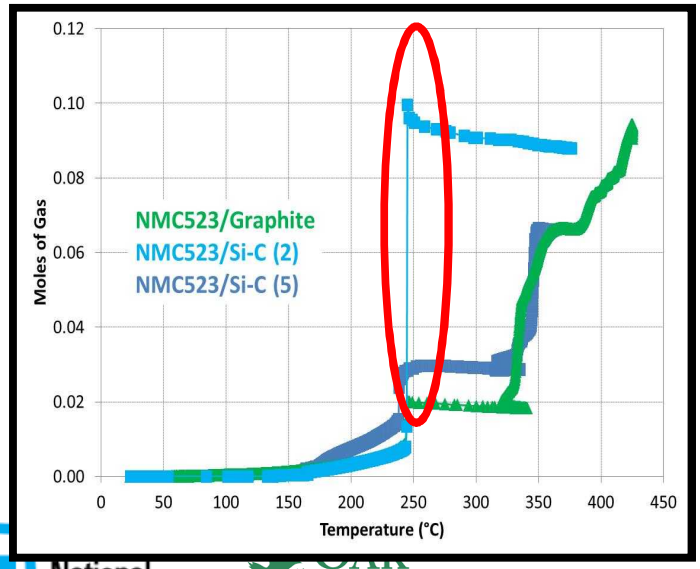
UNEXPECTED DSC PERFORMANCE





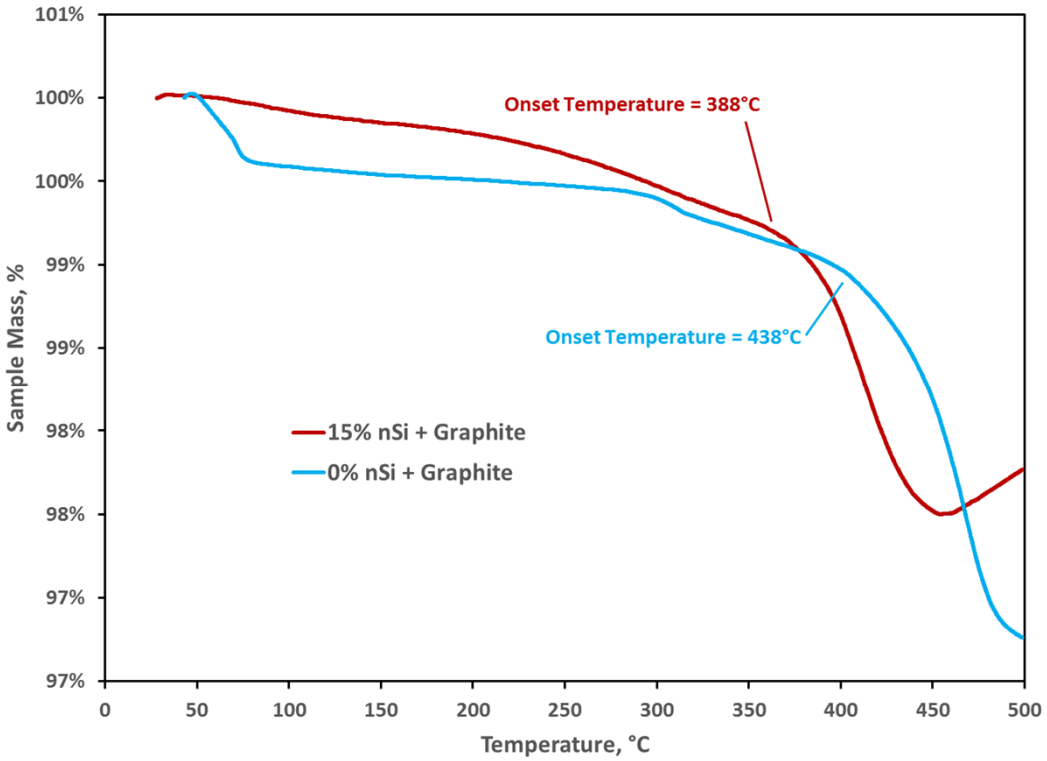




- Unclear behavior at full charge on the 50-70 nm materials
- No apparent sample leakage, no movement within instrument
- Resemblance to odd gas generation behavior previously seen in 18650 Si/graphene nanocomposites?

TGA EVALUATION

Dry ANL electrode films



- TGA carried out on samples of dry ANL electrodes (no electrolyte) under argon
- Small overall mass loss
  - Earlier onset of mass loss for nSi containing film

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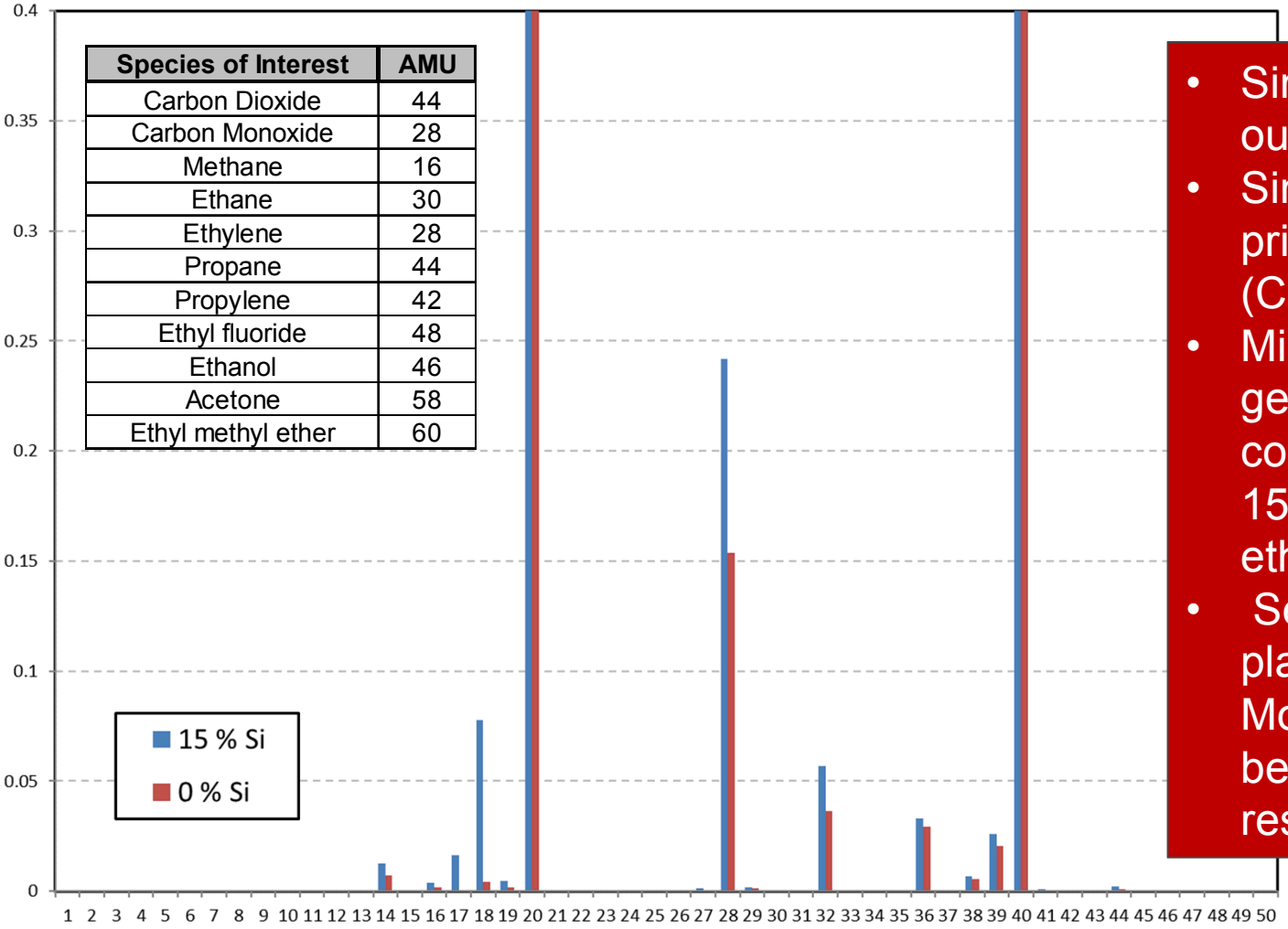
MS EVALUATION

Dry ANL electrode films



Species of Interest	AMU
Carbon Dioxide	44
Carbon Monoxide	28
Methane	16
Ethane	30
Ethylene	28
Propane	44
Propylene	42
Ethyl fluoride	48
Ethanol	46
Acetone	58
Ethyl methyl ether	60

- Similar overall gas output
- Similar output for primary components (CO, CO_2)
- Minimal increases in generation for some components with 15% Si (methane, ethylene)
- Sensitivity issues at play for analysis. Moving towards better mass spec resolution

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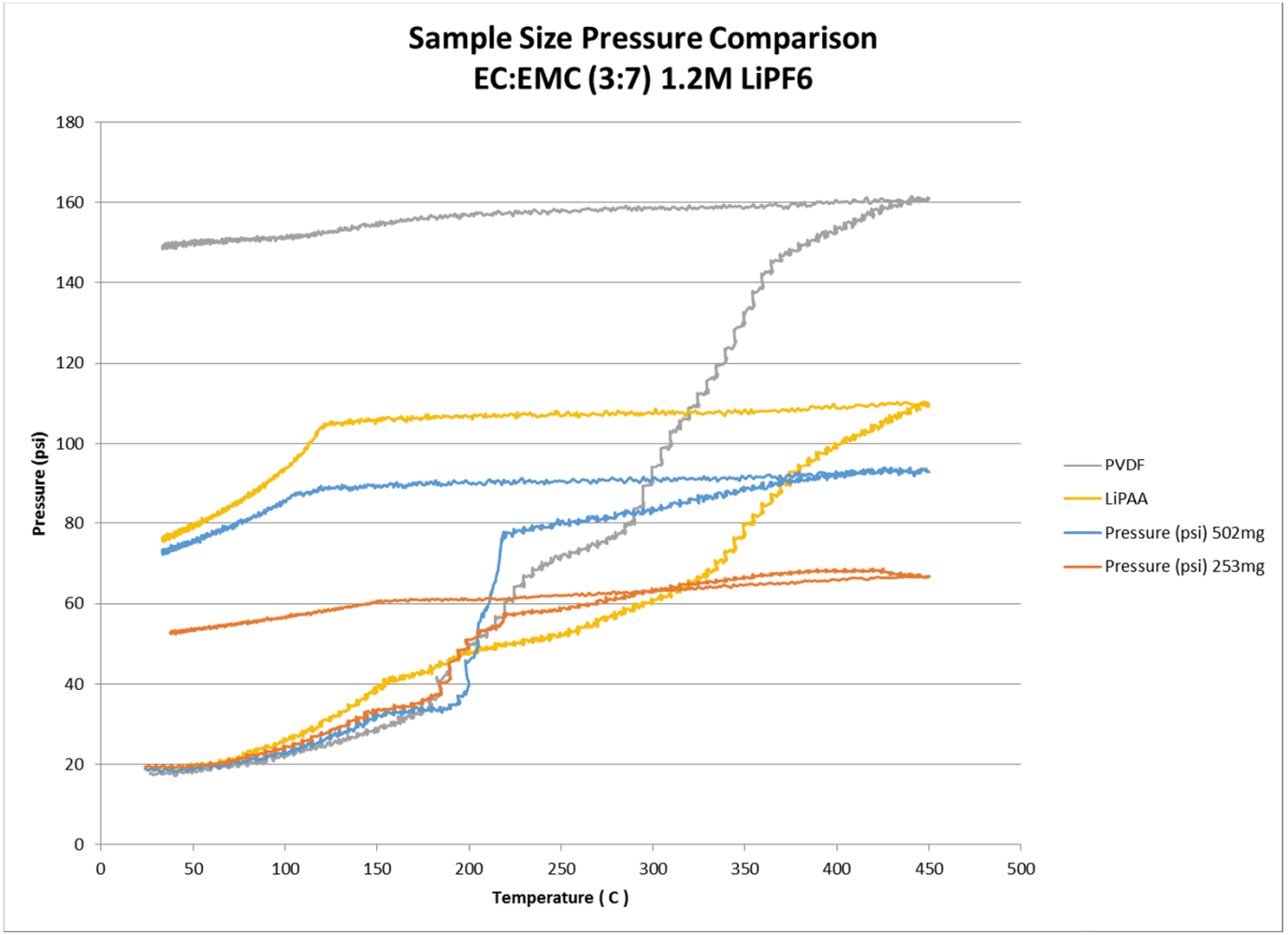
ARC MATERIALS EVALUATION

Materials Evaluation of Contribution to Runaway



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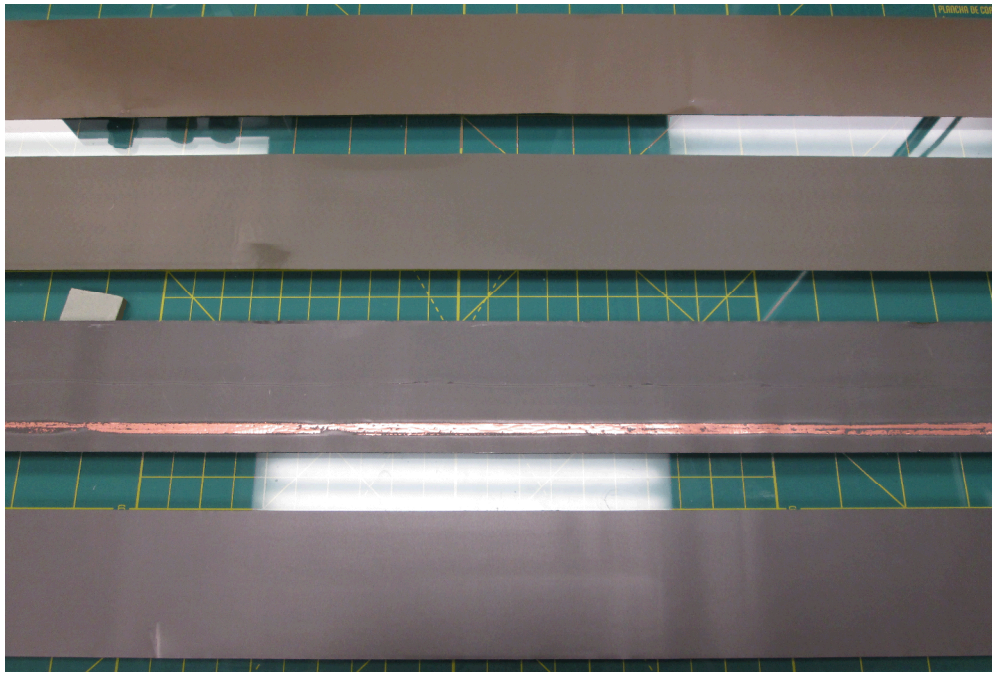
CYLINDRICAL CELL EVALUATIONS

18650 Evaluations for Abuse Response

- **CAMP 18650 Electrode Coating**
  - Coatings with lower Si loading were difficult to coat uniformly for winding
  - Coating difficulties may have implications for cell impedance
  - Distinct color variation with Si loading – may not show in pictures



15% Si

10% Si

5% Si

0% Si

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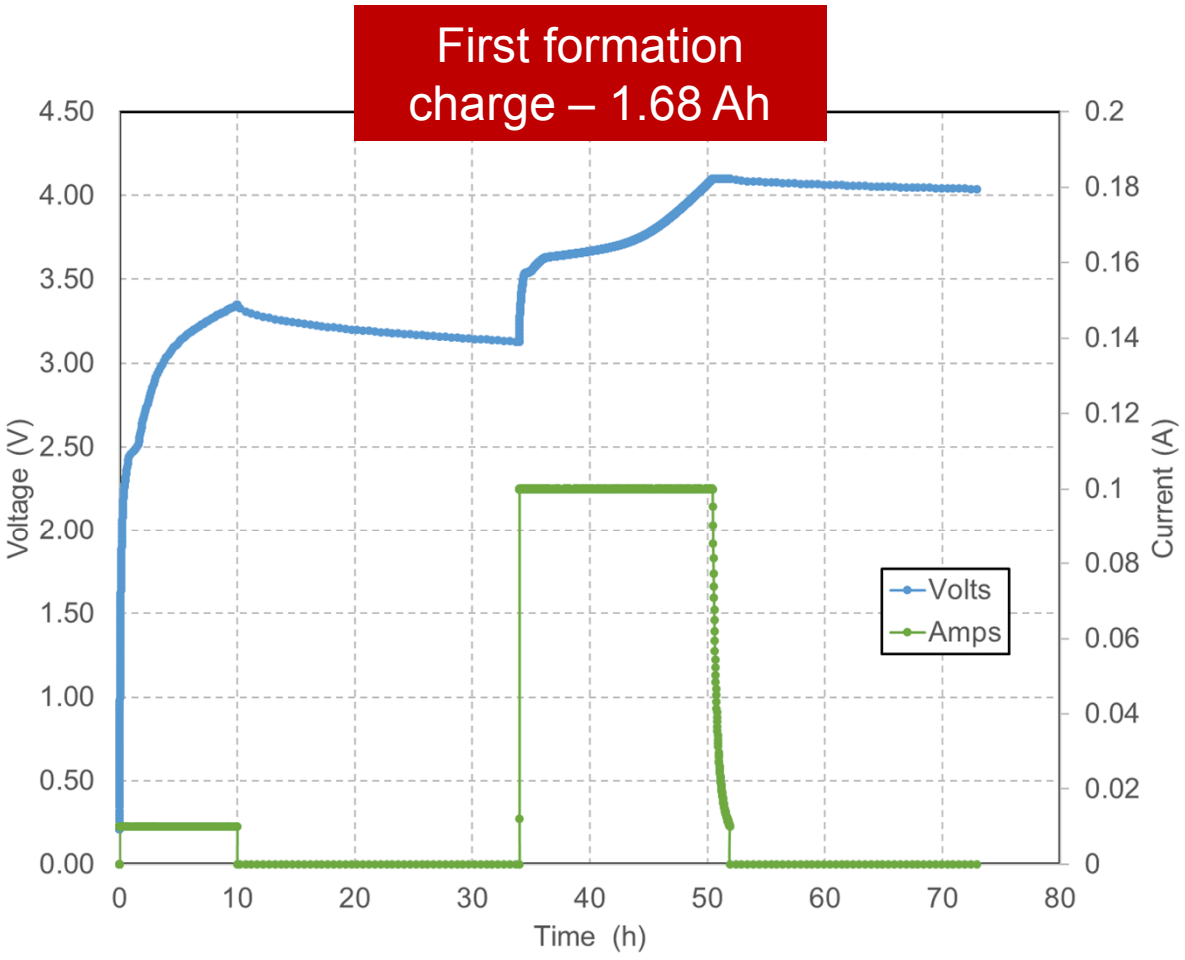
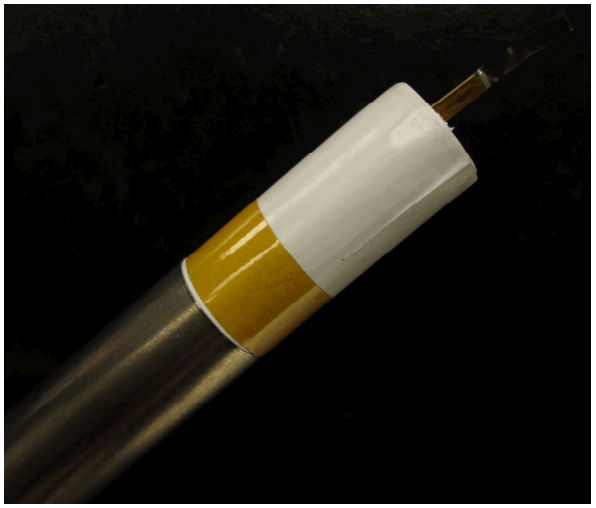
CYLINDRICAL CELL EVALUATIONS

18650 Evaluations for Abuse Response





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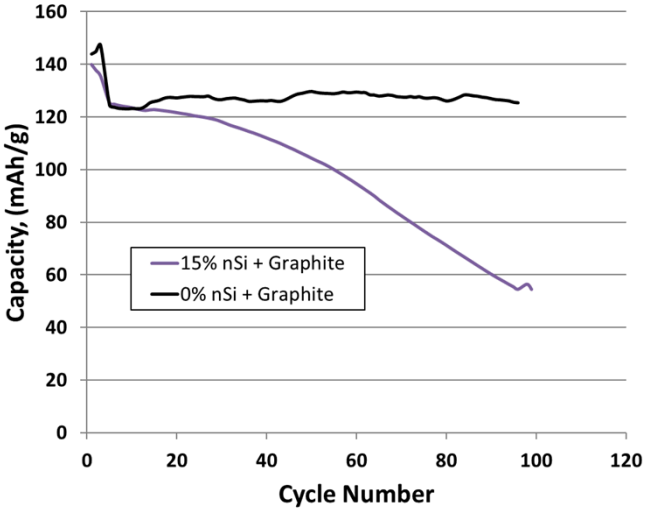
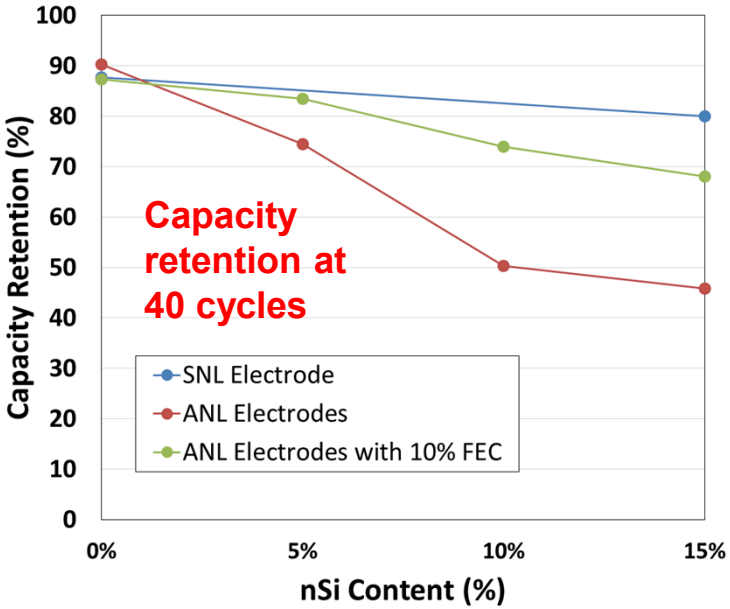
EXTRA SLIDES

FULL CELL CYCLE LIFE

SNL electrodes cycled without FEC

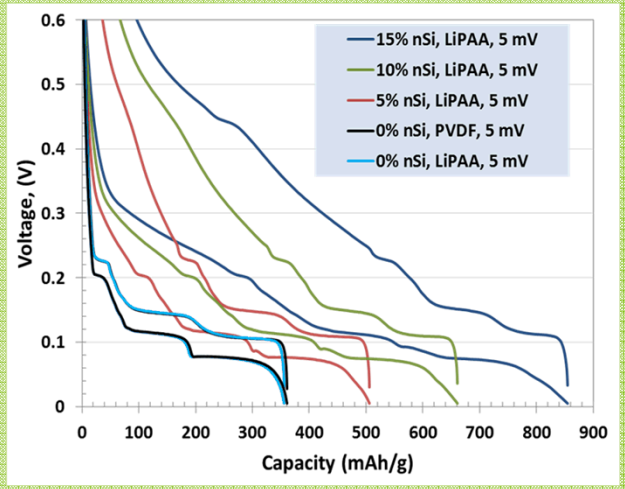


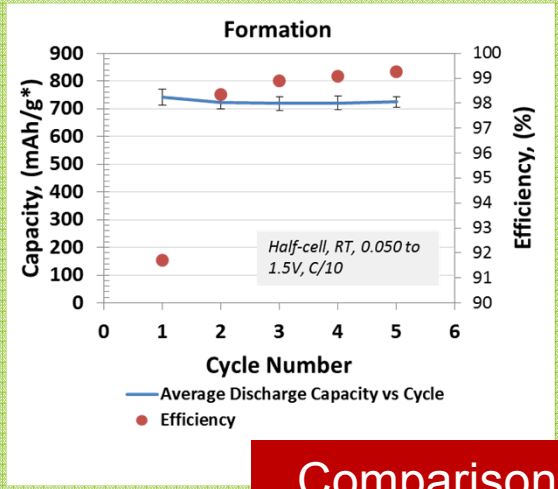


- Capacity retention of ANL electrodes improves significantly with 10% FEC addition
- SNL electrodes show high capacity retention but also have lower areal loading and higher porosity

NANOAMOR MATERIAL EVALUATION

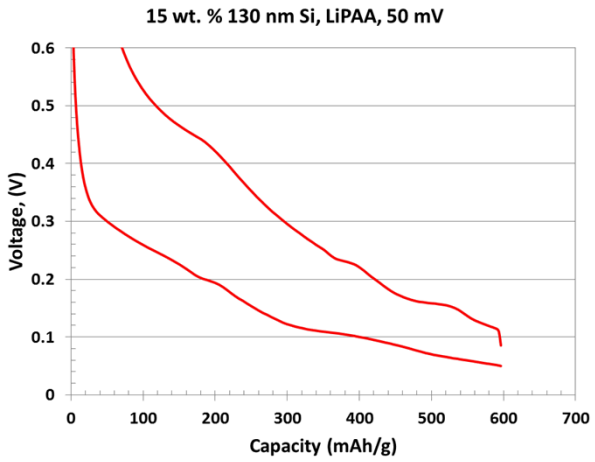
Electrode comparison and baseline

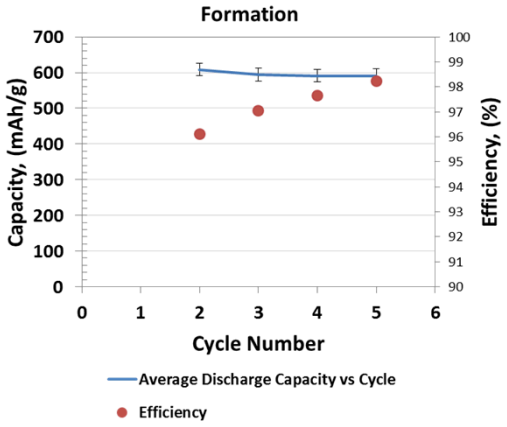




- Data from ANL using 50-70 nm NanoAmor silicon with 10 % FEC in electrolyte
- Charge / discharge profiles to 5mV
- Observed specific capacity upon discharge to 50 mV

Comparison with baseline CAMP cells comparable performance for SNL

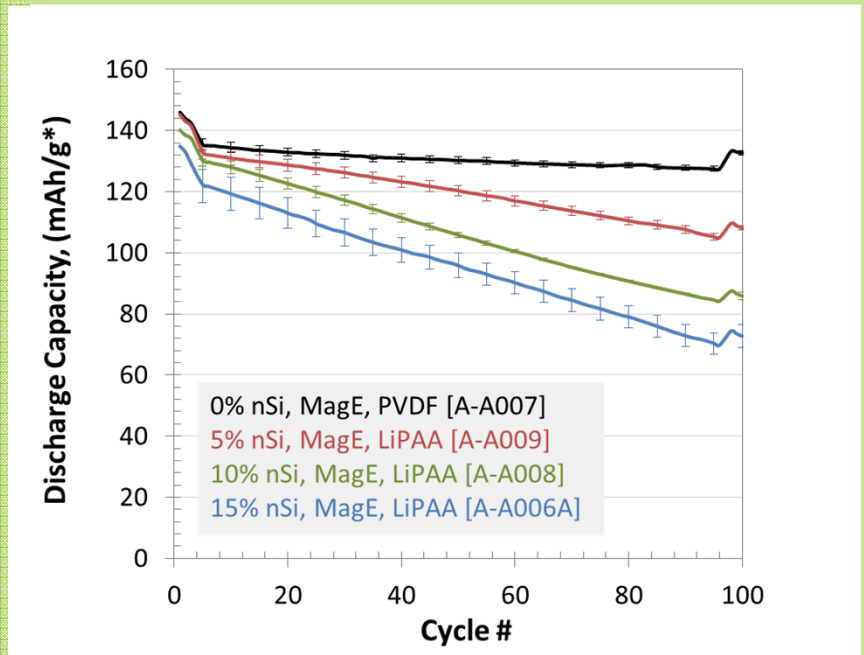




- Electrodes prepared at SNL using 130 nm NanoAmor silicon, all other aspects prepared in accordance with ANL processes, **no FEC**
- Only 15 wt. % nSi tested thus far
  - Areal Loading ~ 4.75 mg/cm^2 active material (Gr + Si)
  - Areal capacity ~ 1.6 mAh/cm^2
- Lower specific capacity and CE

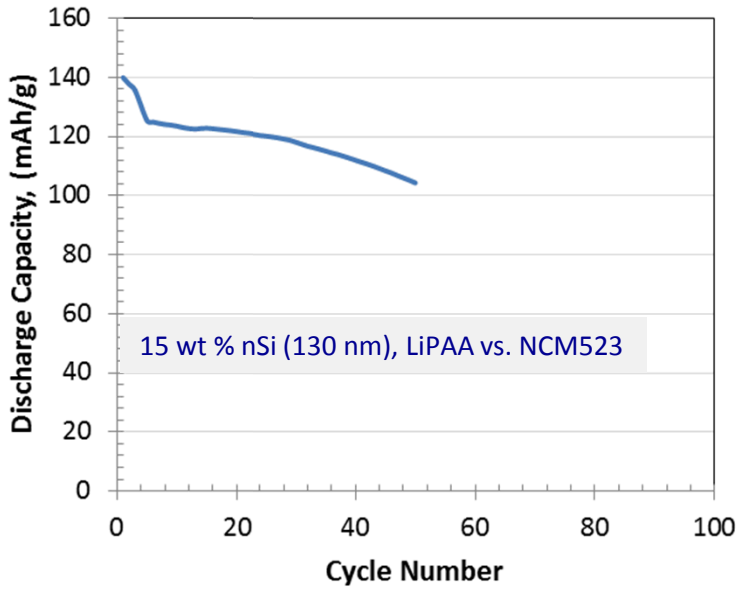
NANOAMOR MATERIAL EVALUATION

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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