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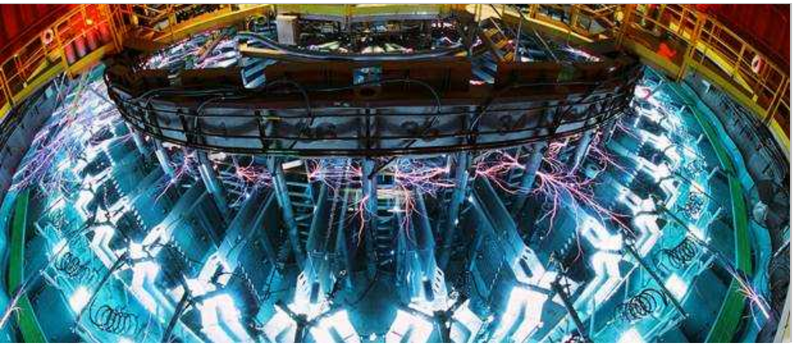

Impact of Next Generation Electrode Materials on Abuse Response

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Sandia National Laboratories

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Relevance and Objectives

Developing inherently safe lithium-ion cell chemistries and systems

1. **Evaluate Abuse Tolerance Improvements**
   - Improve abuse tolerance in lithium-ion cells
   - Develop strategies to reduce the negative effects of an energetic thermal runaway
   - Identify and develop advanced materials or combination of materials that will minimize the sources of cell degradation during abuse events, leading to enhanced safety
   - Build and test full size cells to demonstrate improved abuse tolerance
2. **Abuse Resilient Components**
   - Design and develop strategies to mitigate the severity of thermal runaway in lithium-ion cells
3. **Cell Fabrication**
   - Build and test full cells to demonstrate improved abuse tolerance
   - Work with other Labs to standardize electrode formulations
   - Deliver cells and electrodes to ABR Partners to support materials development programs

Approach

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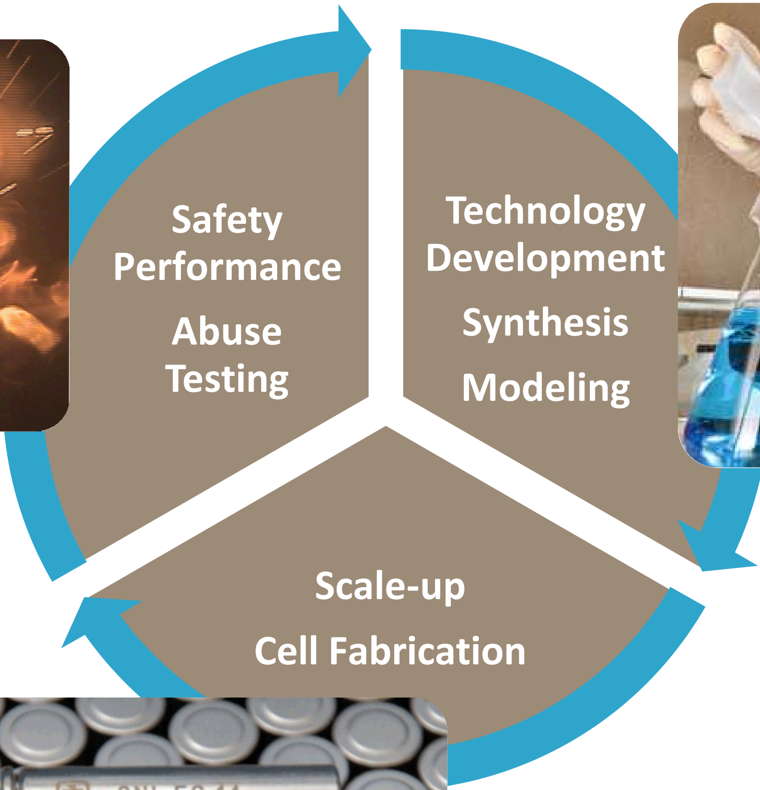

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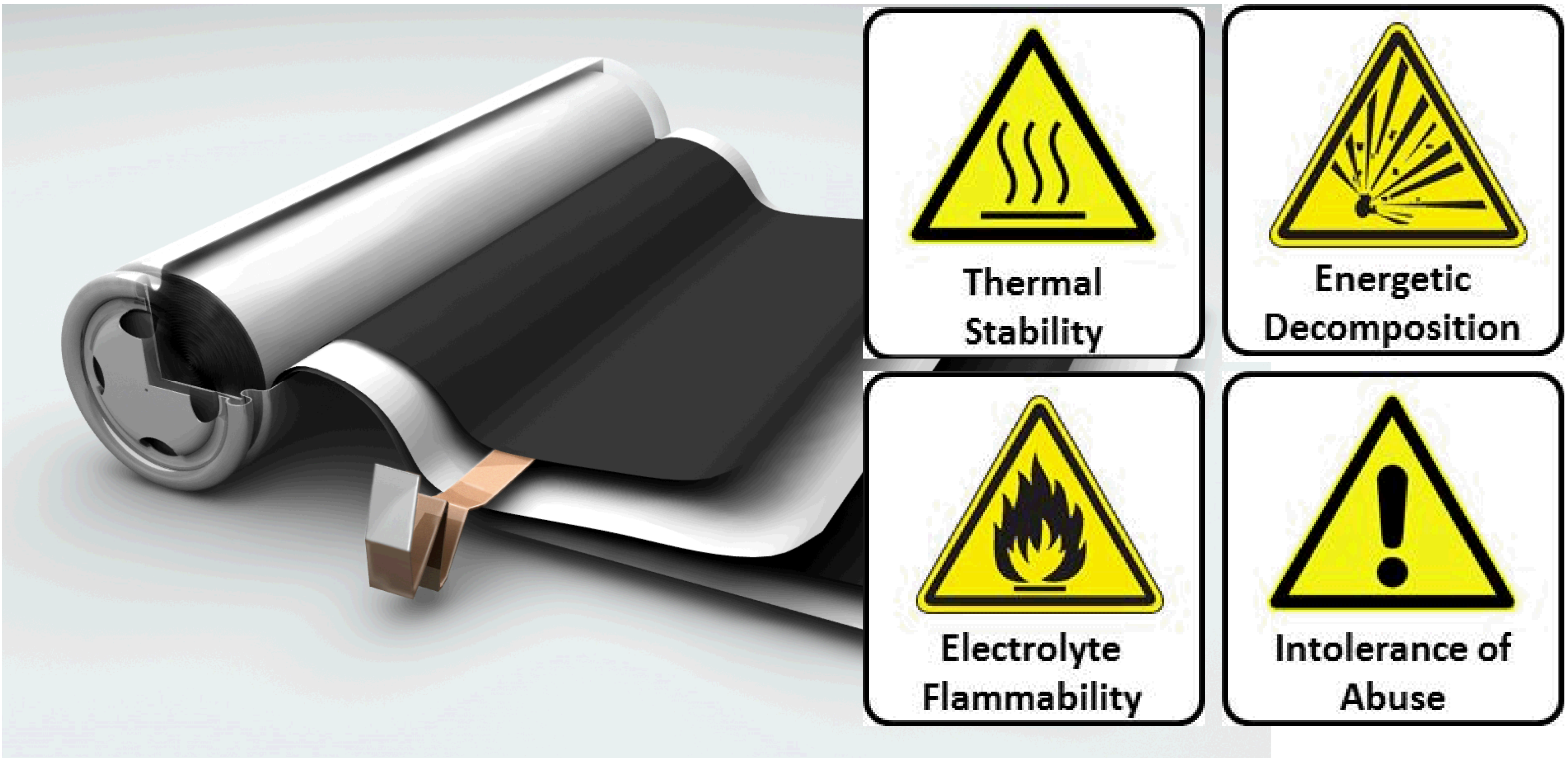
Challenges with Inherent Cell Safety

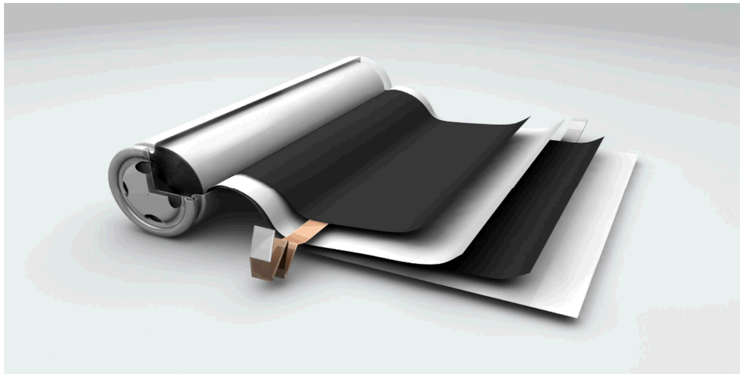


Need to address these issues at the cell materials level in order to field the most inherently safe energy storage products

Contribution to Runaway

As energy and power densities increase for PHEVs and EVs, materials level safety issues remain a concern

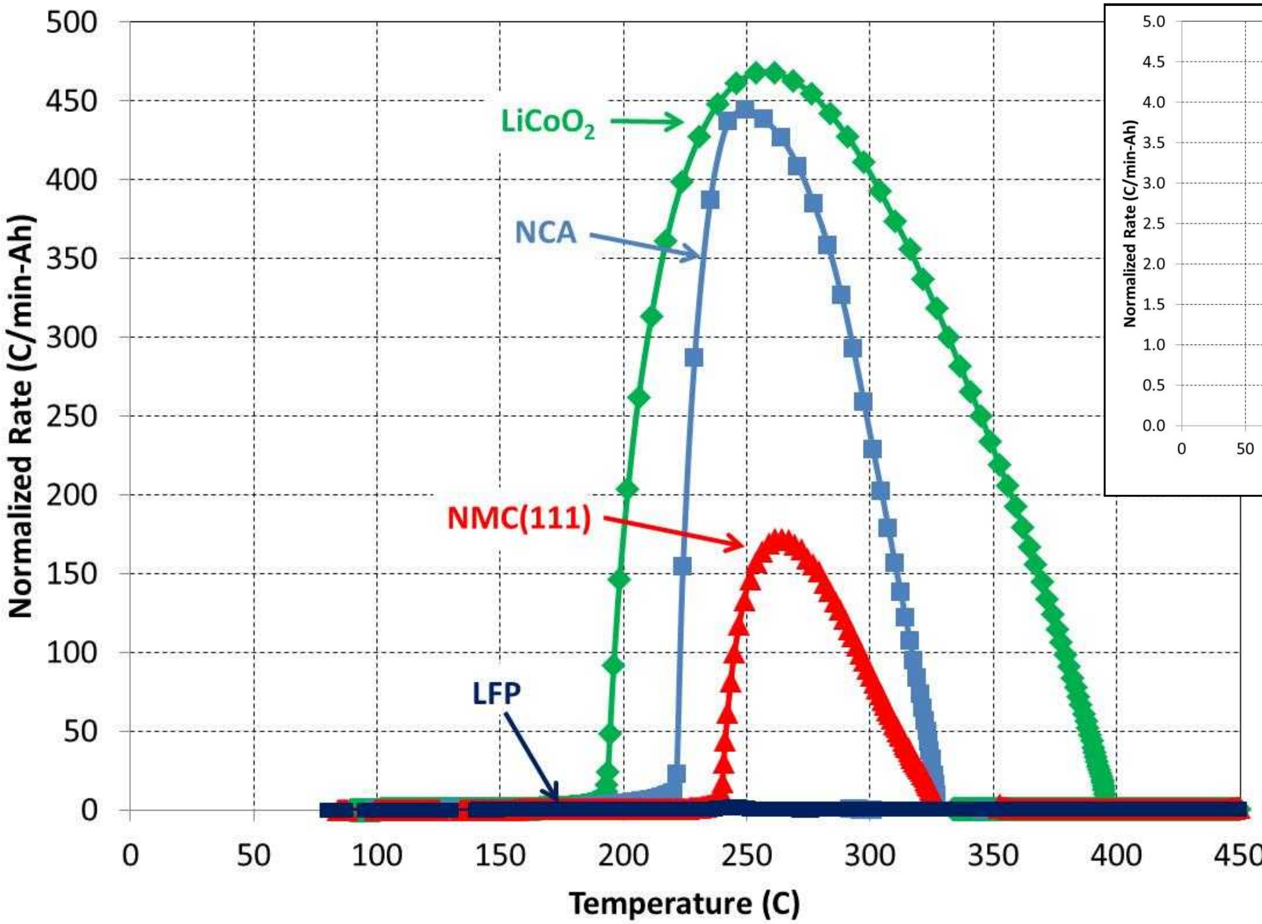
- Electrolytes
  - Gas generation/flammability of electrolytes remain significant safety issues
  - Using combinations of non-PF_6 salts and hydro-fluoro ether solvents as electrolytes to limit gas generation and reduce flammability
- Cathodes
  - Reactivity and flammability of vented solvent cathodes (LiM_xO_2)
  - Energetic thermal runaway
  - Gas generation upon decomposition & catalysis
  - Mitigated largely through new materials:
    - $LiFePO_4$, $LiMn_2O_4$ spinel etc.

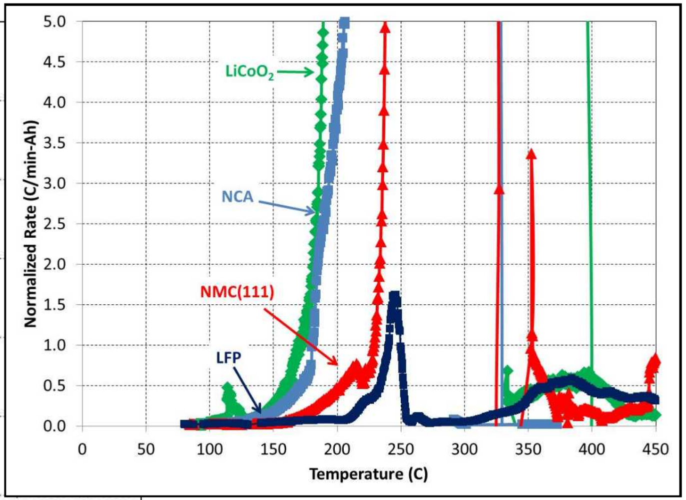


- Anodes
  - Breakdown of SEI layer leads to reaction/runaway at elevated temperatures
  - Mitigated through new materials and additives: $LiTi_5O_{12}$ (but sacrifice energy density) and vinylidene carbonate analogues
- Separators
  - Thermal/mechanical stability under abusive conditions
  - Susceptibility to internal short field failure
  - Mitigated through new materials – ceramic coatings, shutdown layers, etc.

Calorimetry of Lithium-ion Cells

Understanding the Thermal Runaway Response of Materials in Cells





Cathode Runaway	
Cathode	**$\Delta H_{runaway}$ (kJ/Ah)**
$LiCoO_2$	**15.9**
NCA	**9.8**
NMC111	**8.3**
LFP	**2.4**

Can high energy cathodes behave like LFP during thermal runaway?
Where do high capacity Si/C anodes fit on this plot?

Si/C Anode Abuse Tolerance

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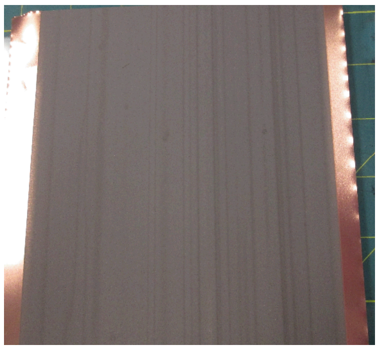
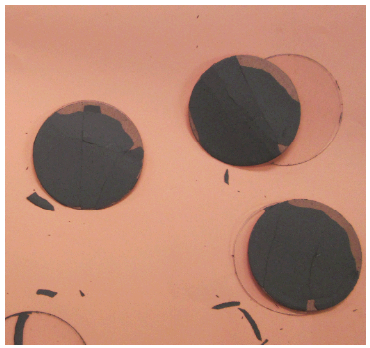
Understanding Safety Issues with Si Materials in Lithium-ion Cells

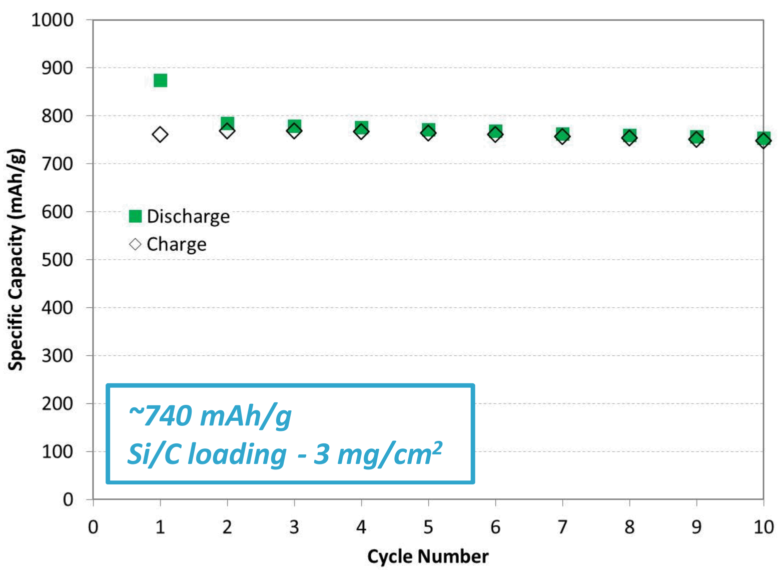
Electrode Processing Issues



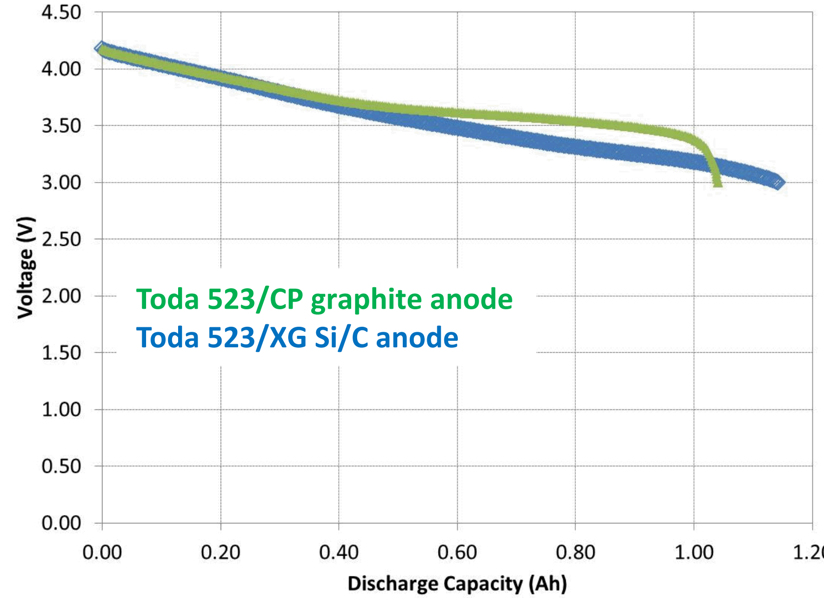
Slurry heterogeneity



Cracking > 4 mg/cm²



18650 Cell

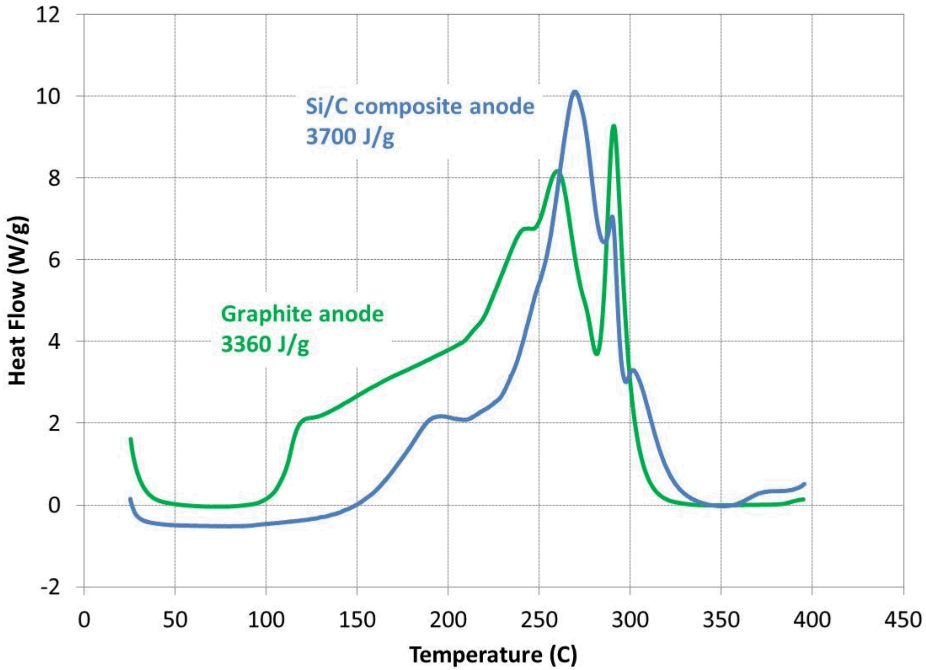


- **Cell parameters:**
  - **1.2 M $LiPF_6$ in EC:EMC (3:7)**
  - **No additives**
  - **N:P = 1.3**
- **~10% more capacity in the Si/C cell compared to the graphite anode cell**

Note: initial experiments done with EC. Subsequent experiments will be done to evaluate Si/C electrodes with FEC

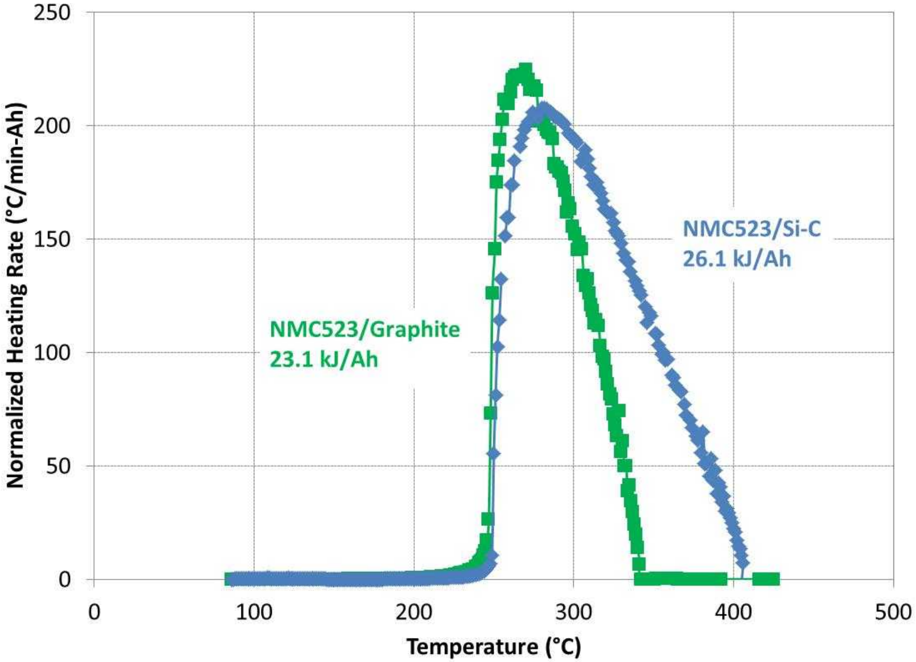
Si/C Anode Abuse Tolerance

Calorimetry on Si/C Materials



~10% increase in heat generation over graphite

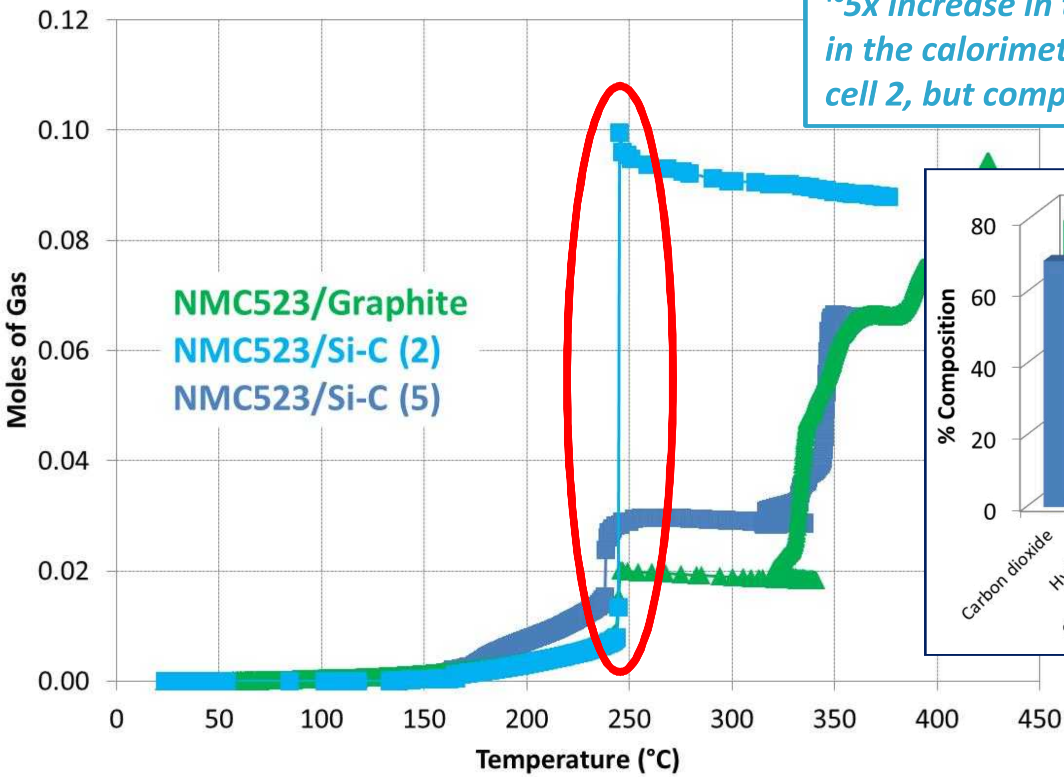
Calorimetry on Si/C in 18650 Cells



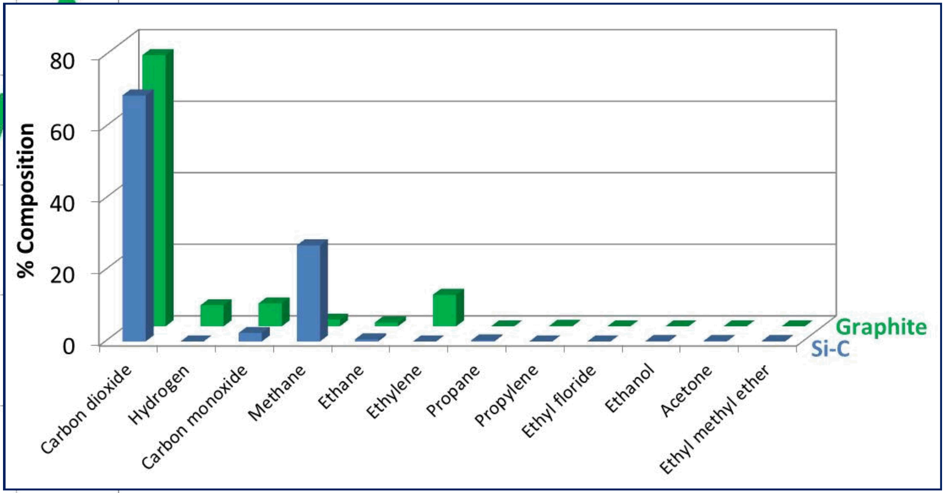
~10% increase in heat generation in cells

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

Si/C Anode Abuse Tolerance



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

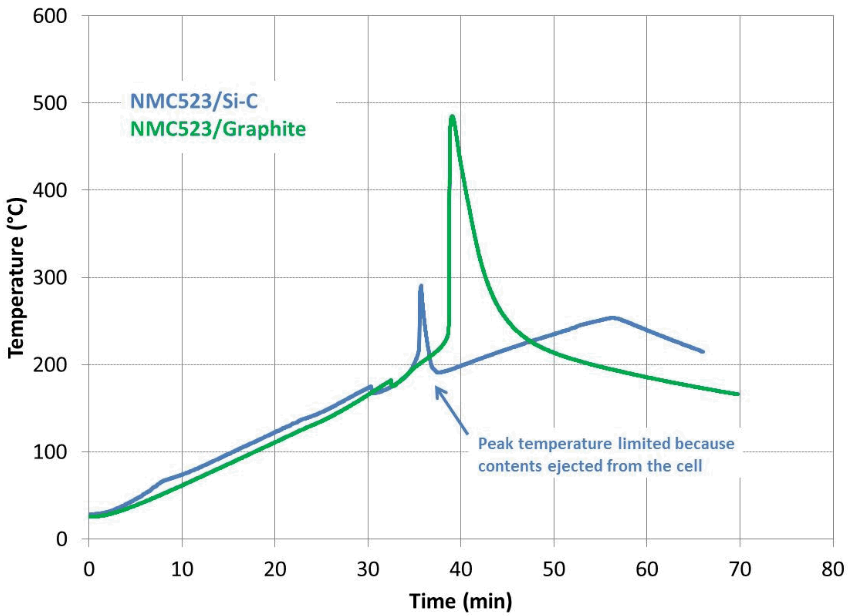


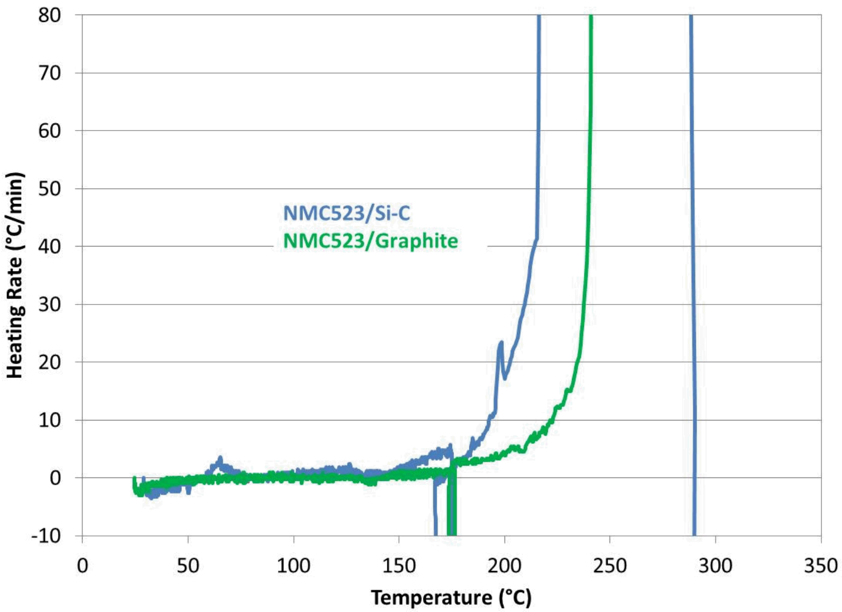
Significantly more methane and less hydrogen, carbon monoxide and ethylene produces in the Si-C cell compared to the graphite cell

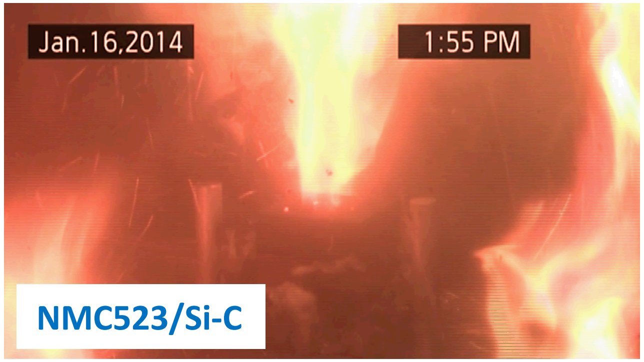
Difference in gas generation attributed to the differences in surface reactivity and surface products generated at the anode/electrolyte interface

Si/C Anode Abuse Tolerance

Thermal Abuse Testing





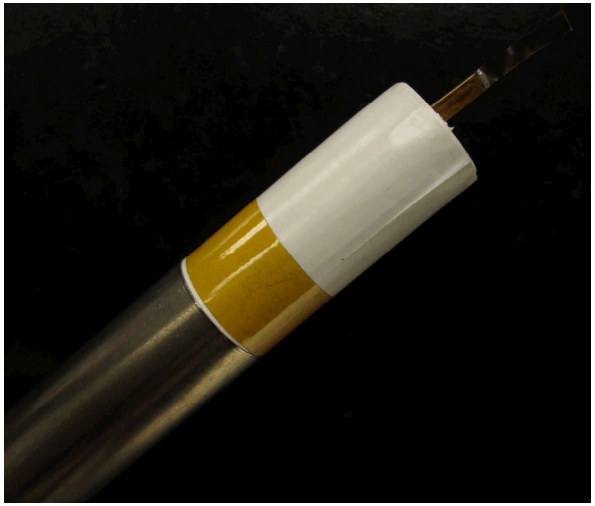


Comparable performance between the Si-C and Graphite cells, but self-ignition observed with the Si-C cell

NanoSi/Graphite Cell Design

Cathode

- 90 wt% Toda NCM 523
- 5 wt% Timcal C45
- 5 wt% Solvay 5130 PVDF
- 20 µm aluminum foil
- 63 µm total thickness (40 µm coating)
- 33.6 % porosity



0% Silicon Anode

- 91.83 wt% Hitachi MagE graphite
- 2 wt% Timcal C45
- 6 wt% Kureha 9300 PVDF
- 0.17 wt% oxalic acid
- 10 µm copper foil
- 51 µm total thickness (41 µm coating)
- 29.9 % porosity

5% Silicon Anode

- 83 wt% Hitachi MagE graphite
- 5 wt% Nano&Amor Silicon (50-70 nm)
- 2 wt% Timcal C45
- 10 wt% LiPAA (LiOH Titrate)
- 10 µm copper foil
- 59 µm total thickness (49 µm coating)
- 46.1 % porosity

10% Silicon Anode

- 78 wt% Hitachi MagE graphite
- 10 wt% Nano&Amor Silicon (50-70 nm)
- 2 wt% Timcal C45
- 10 wt% LiPAA (LiOH Titrate)
- 10 µm copper foil
- 43 µm total thickness (33 µm coating)
- 46.0 % porosity

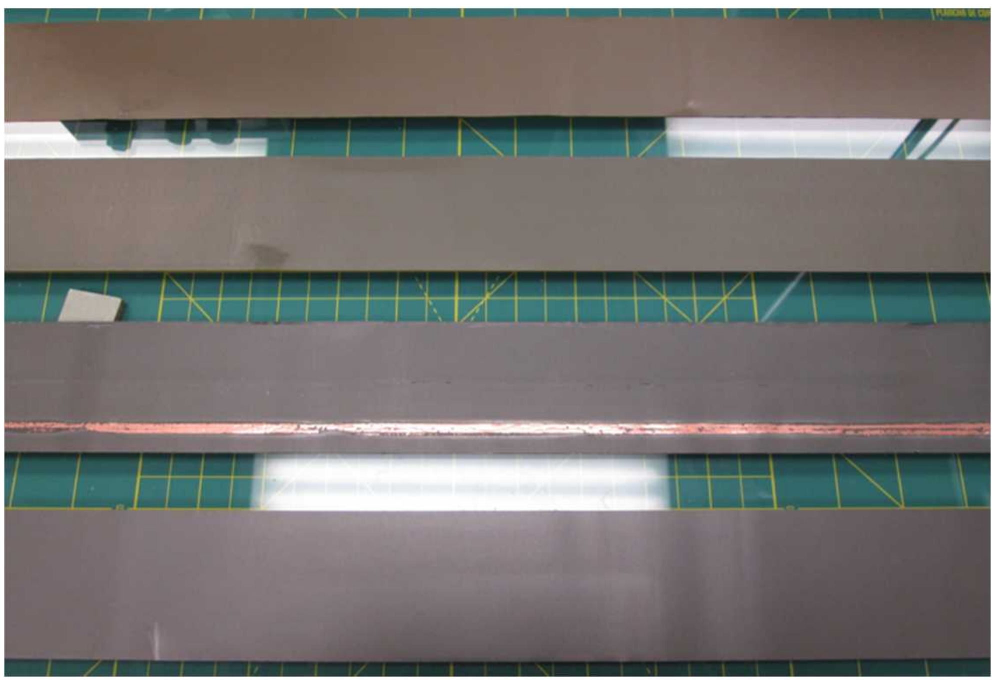
15% Silicon Anode

- 73 wt% Hitachi MagE graphite
- 15 wt% Nano&Amor Silicon (50-70 nm)
- 2 wt% Timcal C45
- 10 wt% LiPAA (LiOH Titrate)
- 10 µm copper foil
- 40 µm total thickness (30 µm coating)
- 46.4 % porosity

Cylindrical Cell Evaluations

18650 Evaluations for Abuse Response

- 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



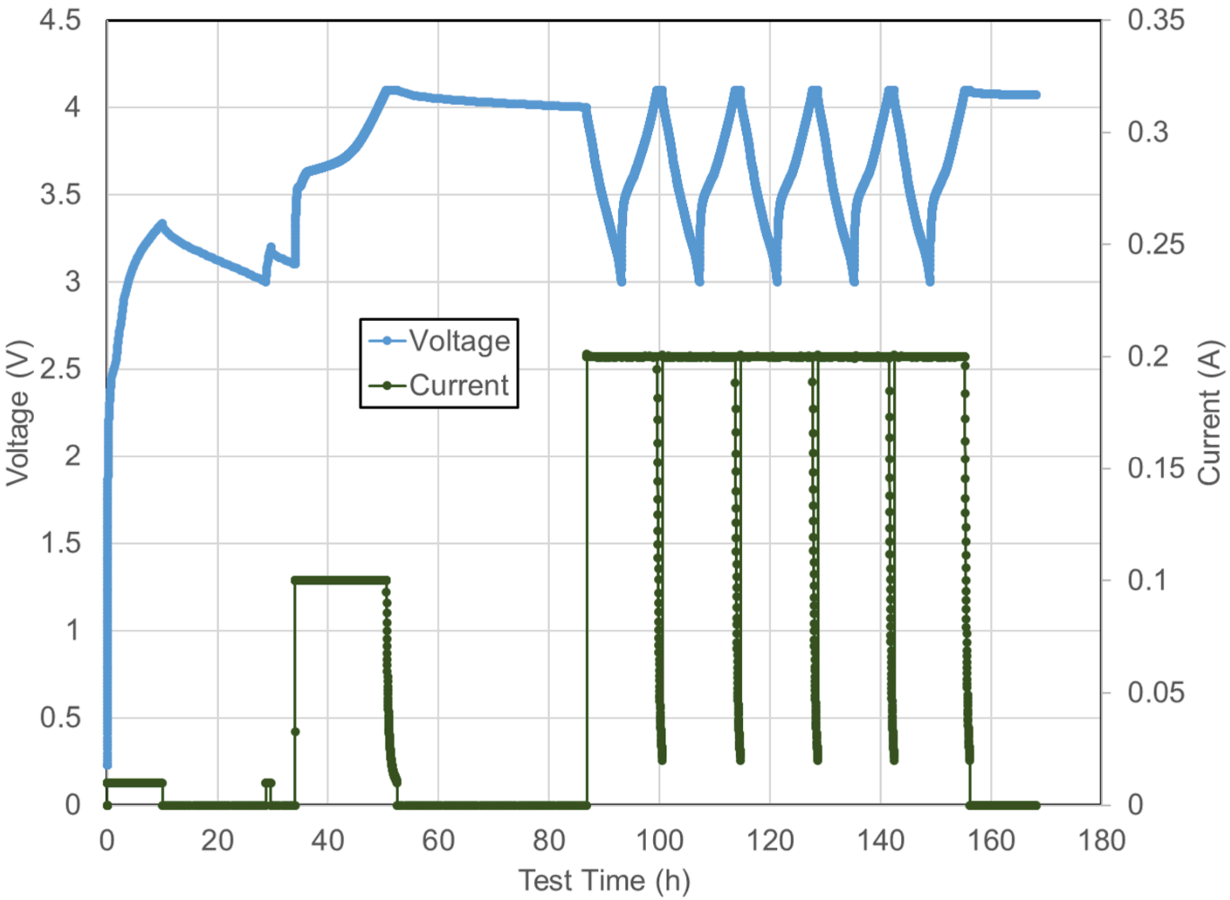
15% Si

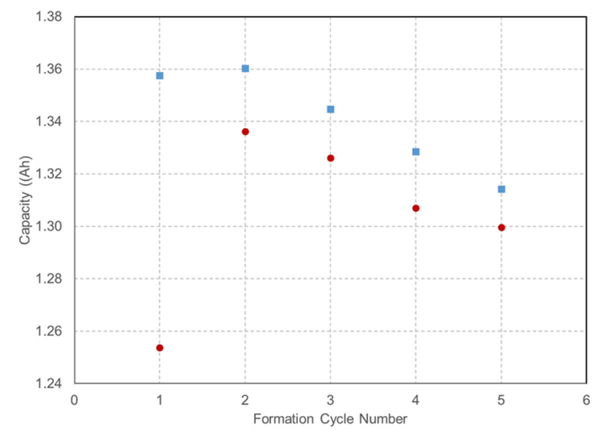
10% Si

5% Si

0% Si

Cylindrical Cell Evaluations

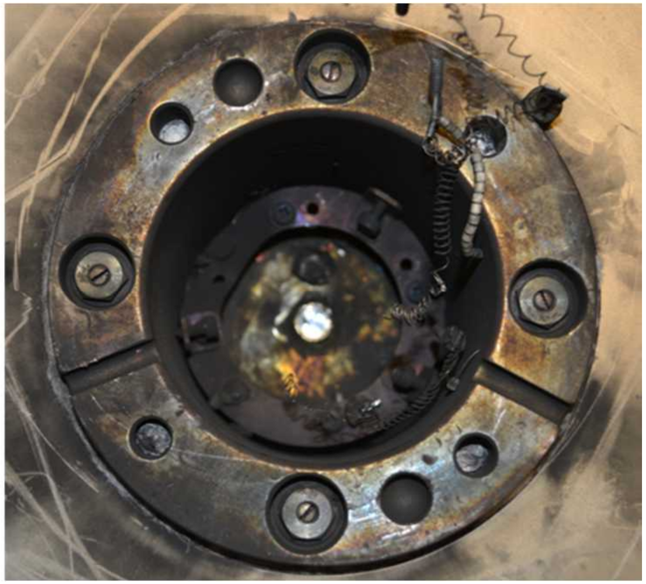




Capacity – 1.3 Ah

ARC Evaluation

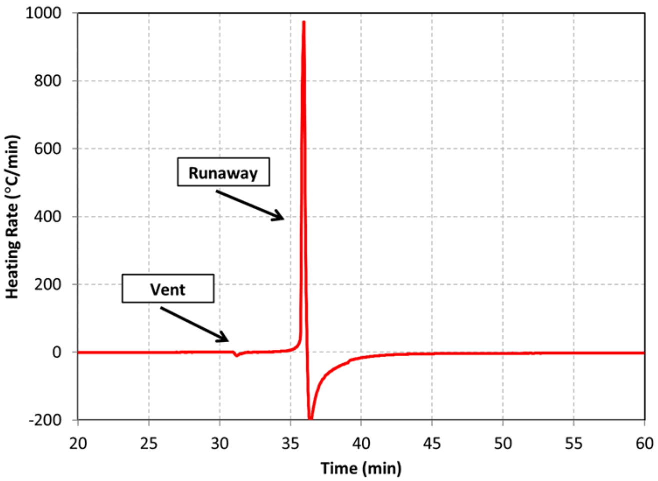
- ARC attempted for these materials – very high kinetic rates and output enthalpies seen from nano silicon materials:



Complete rupture for entire ARC system seen with nano silicon electrodes (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

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

Future Work

- Continued understanding of contributions to increased runaway for silicon based materials
- Evaluation of new silicon formulations and loadings
- Understanding fundamental contributions to runaway (particle size, morphology, surface energy, phase, etc.)

Acknowledgements

- Peter Faguy
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Questions?