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MICROCELL DSC ANALYSIS OF SI-GRAPHITE ANODES PAIRED WITH HIGH ENERGY DENSITY CATHODES

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DOE Office of Electricity Energy Storage Program Annual Meeting and Peer Review 2025

McLean, VA

August 6, 2025

U.S. DEPARTMENT of ENERGY NNSA National Nuclear Security Administration

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SAND2026-16056C

PROJECT OVERVIEW

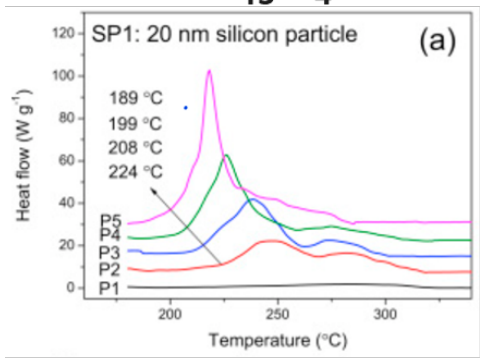
Project Goal	Use ***microcell safety testing*** to understand how Si content impacts the ***safety of Si/graphite anodes*** when paired with an energy dense cathode and balance safety and performance.
Current Practice	Large format batteries subjected to destructive tests require larger quantities of materials and infrastructure to safely conduct, ***slowing the rate at which testing proceeds.***
Why SNL?:	SNL has ***established expertise in many forms of battery testing*** and staff with experience in microcell safety testing.
Innovation	This work ***bridges the gap*** between small-scale electrode-only safety testing and full-cell testing, ***improving the speed and efficiency of safety testing***. Earlier work from SNL has demonstrated the value of this approach.
Impact	These results will be interesting to: battery scientists, safety researchers, and battery manufacturers. This provides ***foundational knowledge to improve the safety of two emerging battery chemistries.***
Alignment	This ***innovative*** microcell approach improves our ability to study the safety of emerging battery chemistries, improving the ***security*** and ***reliability*** of future energy technologies. Inherently safer batteries reduce cost, allowing for the development of more ***affordable*** energy storage technologies.

SAFETY CONCERNS FOR SI/G + NMC811

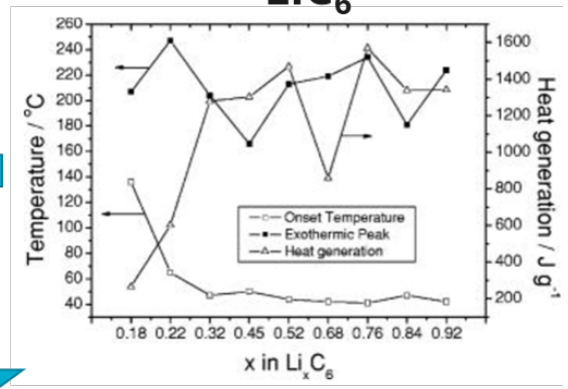
- Advanced materials like **silicon anodes** and Ni-rich $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (**NMC811**) **cathodes** are promising high-energy density chemistries for next-generation batteries

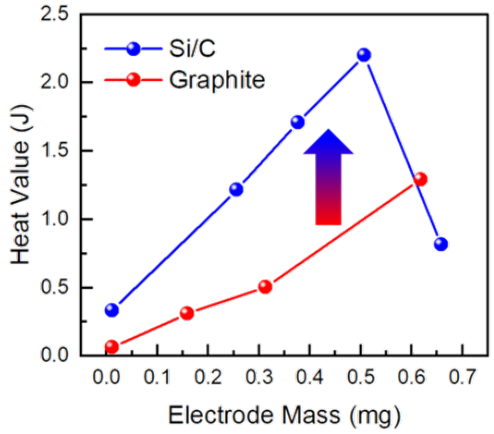
The relative safety of these materials <u>together</u> remains unknown!

$Li_{15}Si_4$



LiC_6

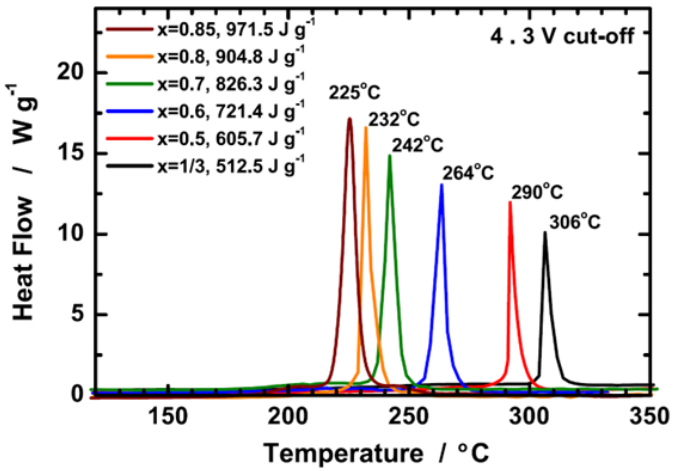




Mixing Si with graphite results in greater heat release than graphite alone

NMC

Increasing [Ni]



Increasing Ni content increases heat flow and decreases onset temperature

Li *et al., J. Power Sources*. **2016**, *335*, 38-44, J. Choi *et al., Adv. Energy Mater*. **2020**, *10*, 2002027, Zhao *et al., J. Power Sources*. **2012**, *203*, 78-83, Noh *et al., J. Power Sources*. **2013**, *223*, 2121-130, Wang *et al., J. Electrochem. Soc.*, **2006**, *153*, A329-A333

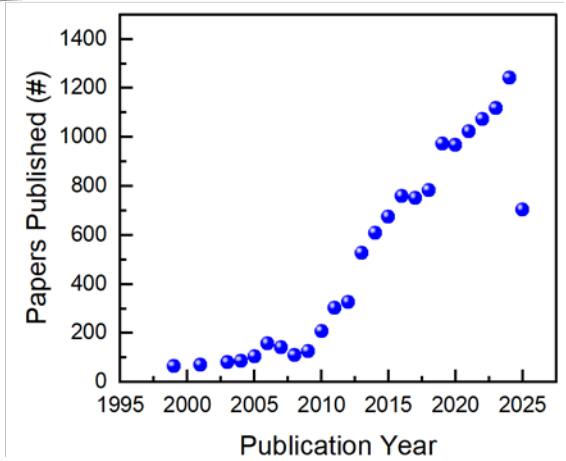
SI ANODES- A PROMISING GRAPHITE REPLACEMENT

Silicon anodes are an increasingly popular target for next-gen Li-based batteries for many applications

The Age of Silicon Is Here...for Batteries › The mainstay material of electronics is now yielding better energy storage

BY PRACHI PATEL | 04 MAY 2023 | 6 MIN READ

https://spectrum.ieee.org/silicon-anode-battery



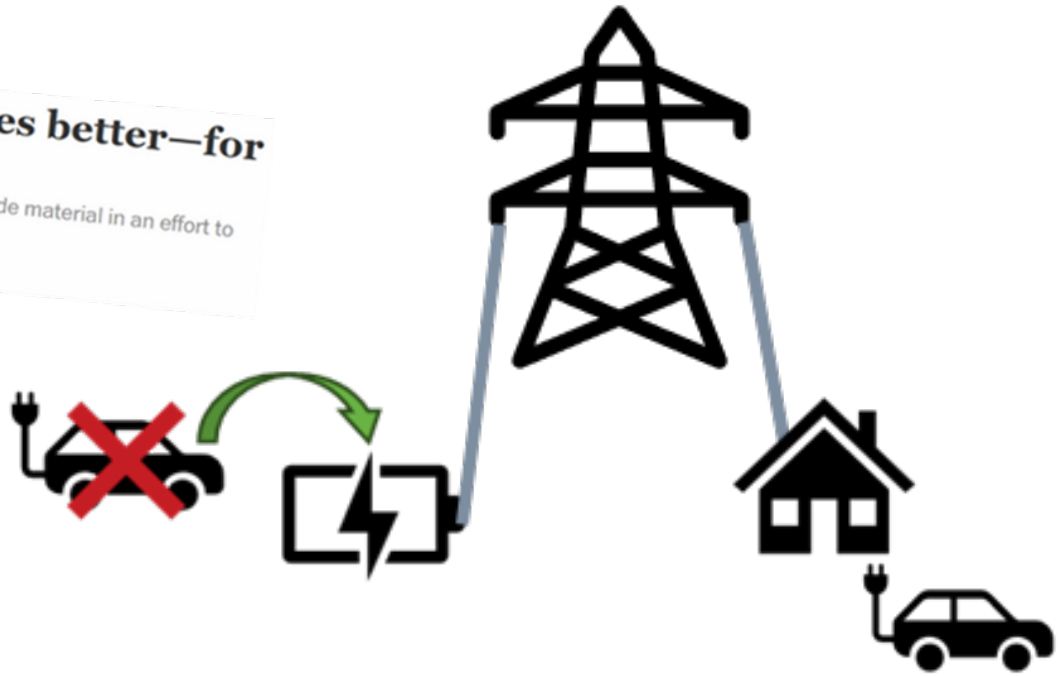
Silicon could make car batteries better—for a price

Several companies aim to lower the cost of the high-capacity anode material in an effort to dethrone graphite

By Matt Blois

February 4, 2024 | A version of this story appeared in Volume 102, Issue 4

https://cen.acs.org/energy/energy-storage-/Silicon-make-car-batteries-better/102/i4



Batteries from multiple sources, and thus likely some with Si anodes, are likely to find their way to grid applications

NEWS | ENERGY

EVs Are Essential Grid-Scale Storage › Before long, there will be more EV battery capacity than the grid can use

BY CHARLES Q. CHOI | 20 JAN 2023 | 2 MIN READ

Charles Q. Choi is a contributing editor for IEEE Spectrum.

https://spectrum.ieee.org/electric-vehicle-grid-storage

Article | Open access | Published: 16 May 2024

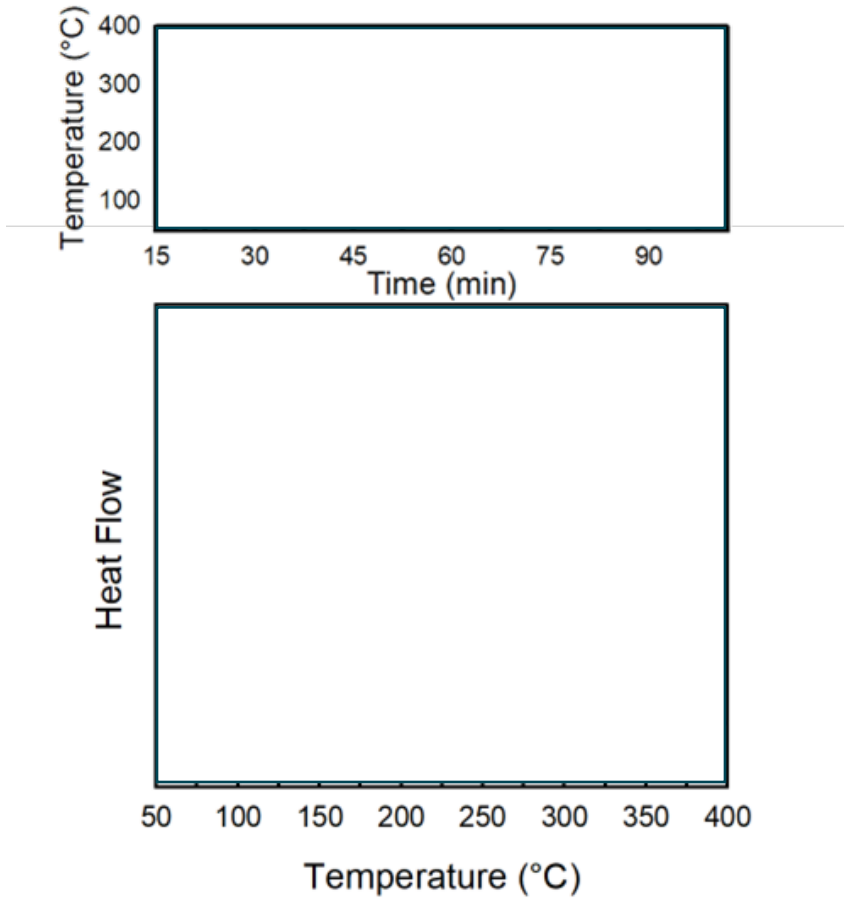
On the potential of vehicle-to-grid and second-life batteries to provide energy and material security

Fernando Aguilar Lopez, Dirk Lauinger, François Vuille & Daniel B. Müller

Nature Communications **15**, Article number: 4179 (2024) | Cite this article

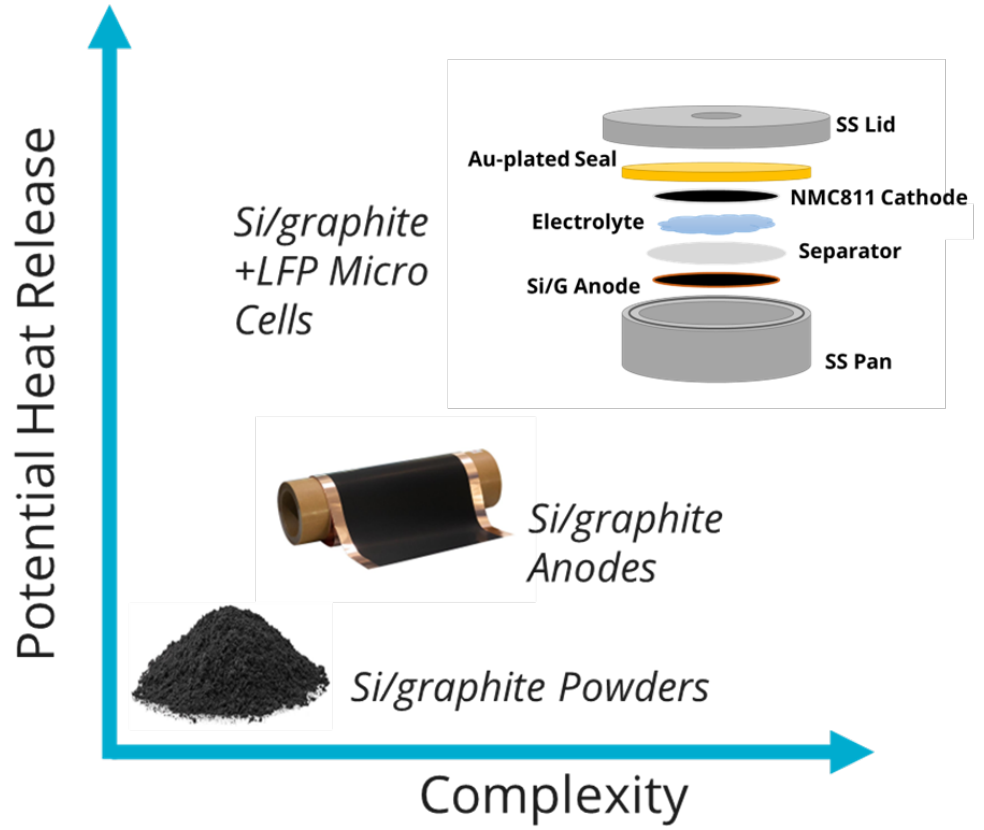
Aguilar F. *et al. Nat Commun.* **2024**, *15*, 4179

MATERIALS CHARACTERIZATION OF THE SAFETY OF SIG ANODES



Differential Scanning Calorimetry (DSC)

Gradually ramp the sample temperature while measuring heat flow from the sample



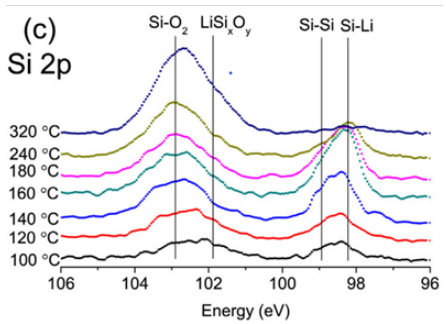
Increase sample complexity in order to better understand fundamental reactions

Li *et al., J. Power Sources*. **2016**, *335*, 38-44, Inoue *et al., ACS Appl. Mater. Interfaces*. **2017**, *9*, 1507-1515

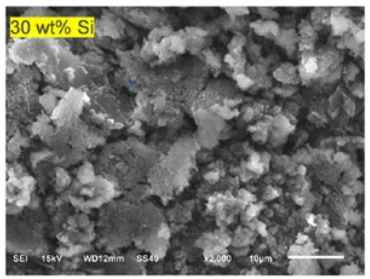
BOTTOM-UP MATERIALS CHARACTERIZATION OF THE SAFETY OF SILICON/GRAPHITE (SIG) ANODES

- Use pre- and post-DSC characterization as well as modeling to analyze *how* and *why* Si/G and NMC811 materials change

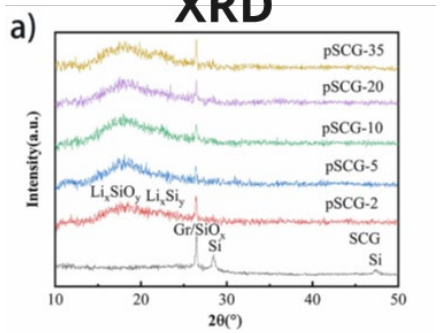
XPS



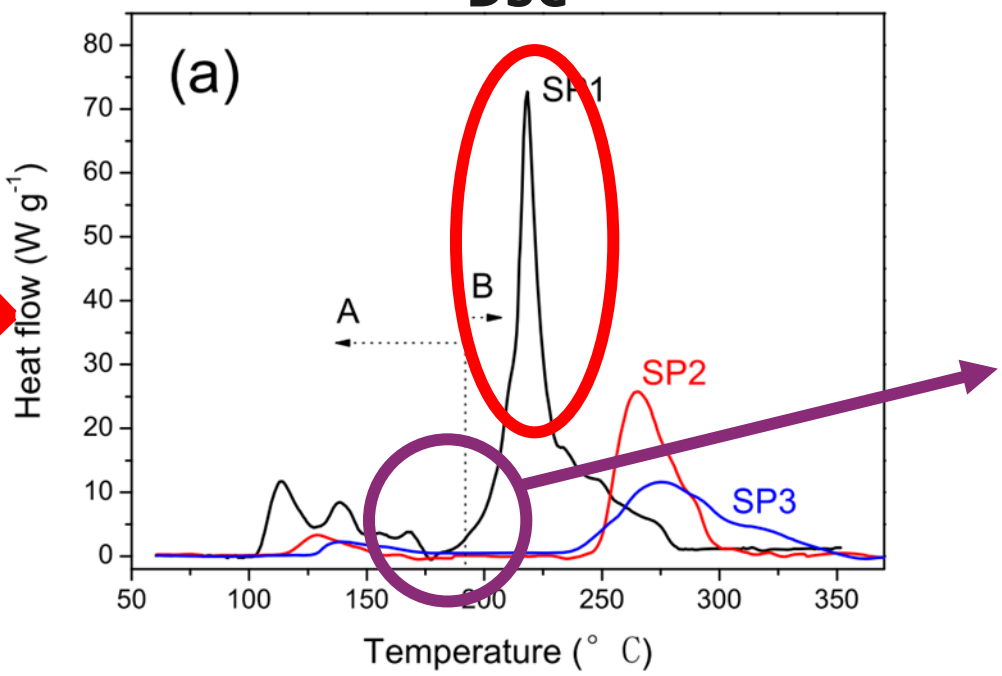
SEM



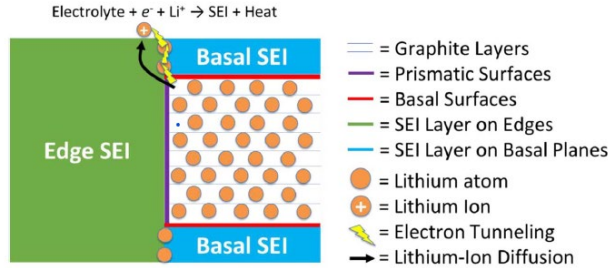
XRD

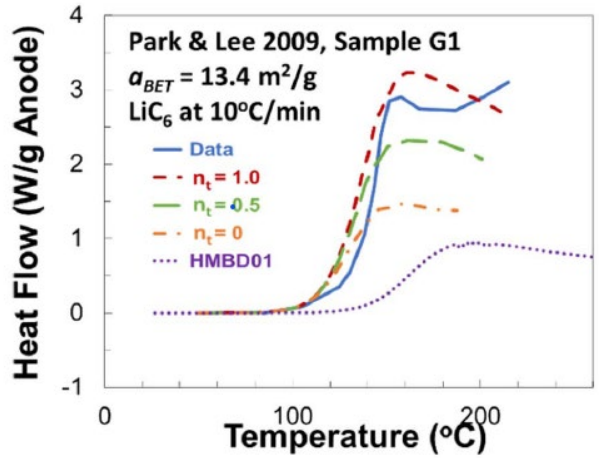


DSC



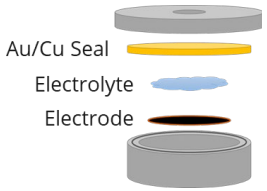
Modeling

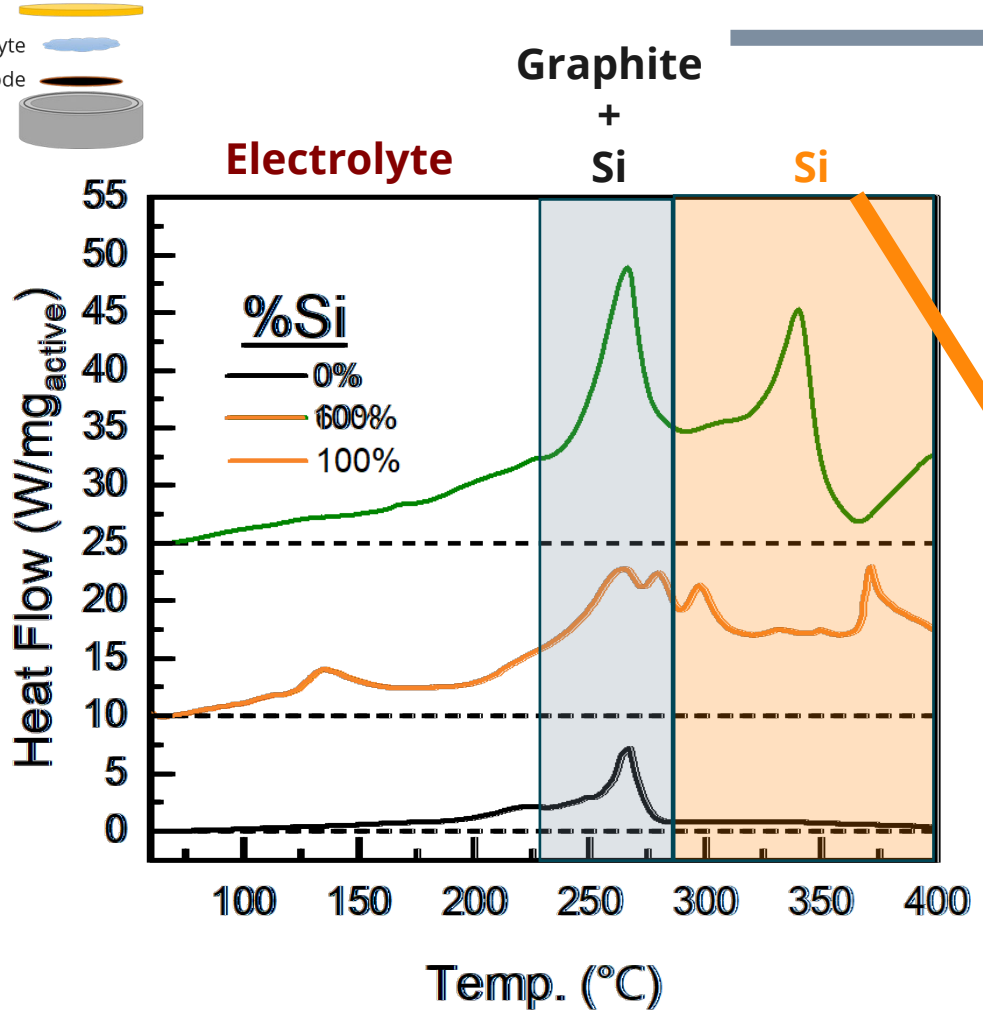


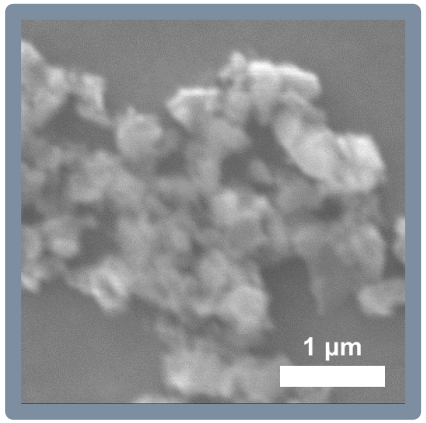


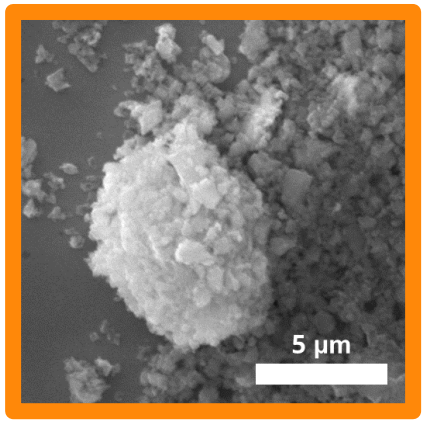
Noh *et al., J. Power Sources*. **2013**, *223*, 2121-130, Yang *et al., ACS Appl. Mater. Interfaces*. **2021**, *13*, 56073-56084, Inoue *et al., ACS Appl. Mater. Interfaces*. **2017**, *9*, 1507-1515, Lai *et al., Solid State Ionics*. **2023**, *403*, 116415, Zhao *et al., J. Power Sources*. **2012**, *203*, 78-83, Li *et al., J. Power Sources*. **2016**, *335*, 38-44, Park *et al., Electrochim. Acta*. **2009**, *54*, 3339-3343, Shurtz *et al., J. Electrochem. Soc.* **2018**, *165* (16), A3891-A3902

THERMAL RELEASE FROM ANODE-ONLY DSC





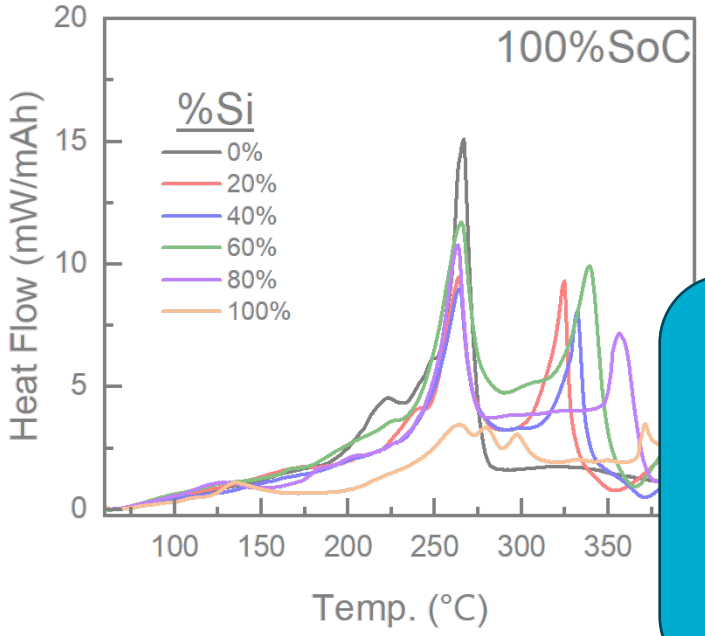




- 100%SoC anodes show similar thermal features largely related to the decomposition of **Li-Si** and **Li-C**
  - 230-290°C → **Li-C** + **Li-Si**
  - >290°C → **Li-Si**
- Prior studies suggest that at 100%SoC, larger Si particles yield higher degradation temperatures
- **Mixed Si/graphite** DSC shows intermediate peaks between the temperature for pure Li-C or Li-Si decomposition

Li *et al.*. *J. Power Sources* **2016**, *335*, 38-44.

THERMAL RELEASE FROM ANODE-ONLY DSC

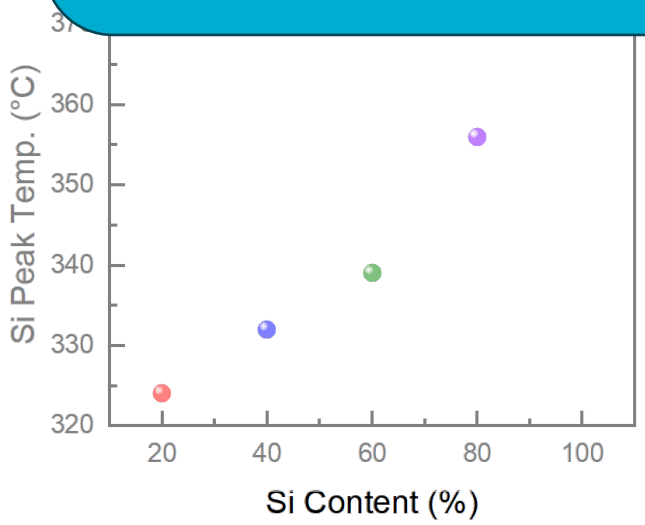


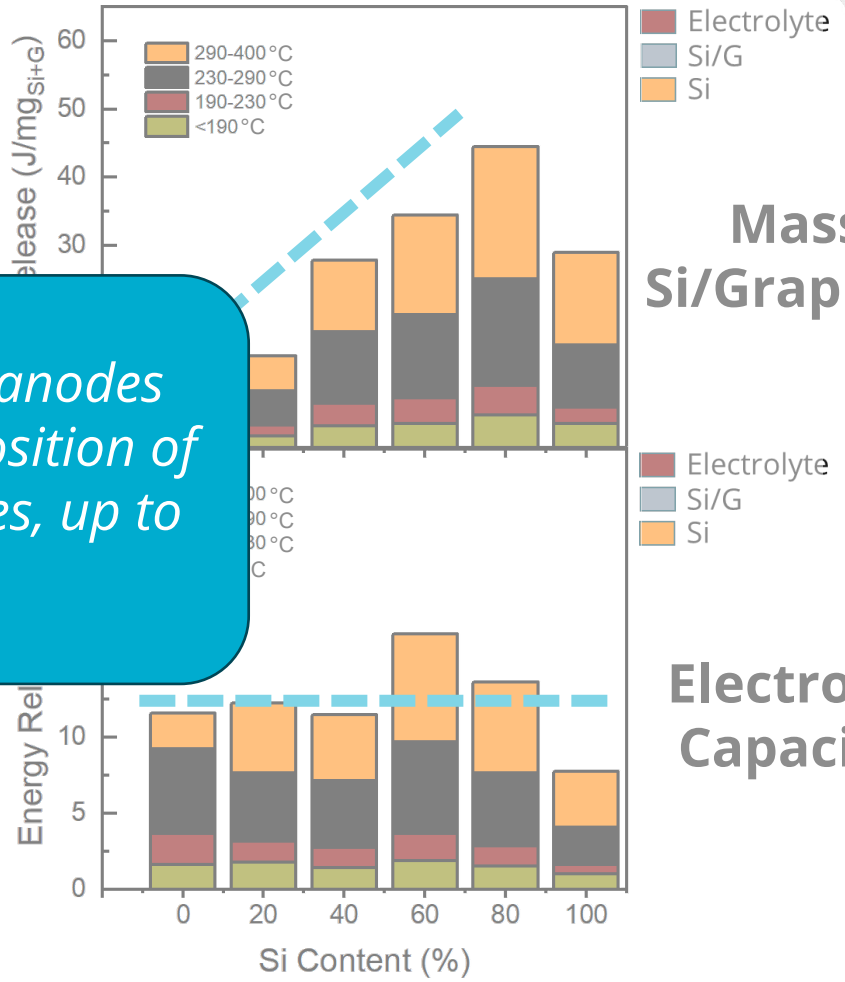
- Mixed Si/graphite anodes **all** exhibit a sharp exotherm from Li-Si and Li-C decomposition at ~265 °C

In absence of a cathode, charged anodes release more energy from decomposition of Li-Si and Li-C as Si content increases, up to 80 wt.% Si

- Increasing Si content drives decomposition peak to higher temperatures

- Si agglomerates my be diluted by graphite, resulting in less "bulk" behavior at low Si content

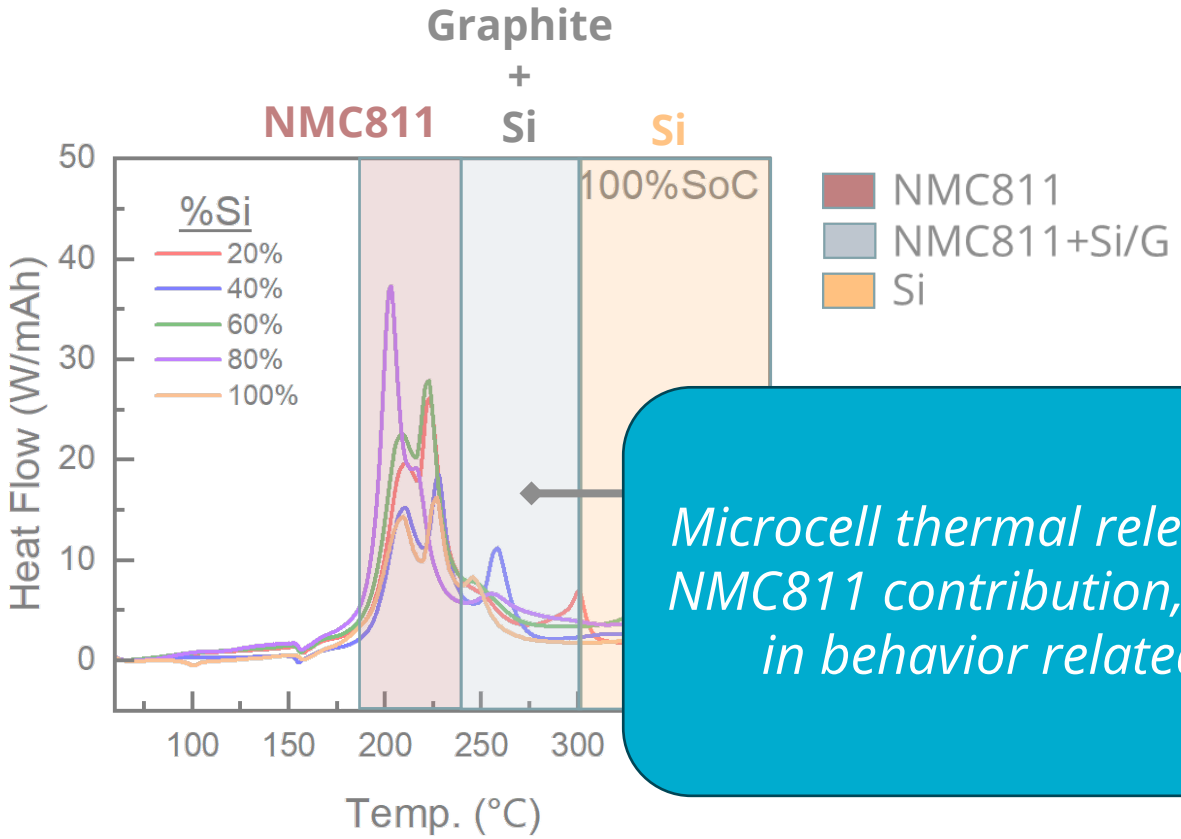




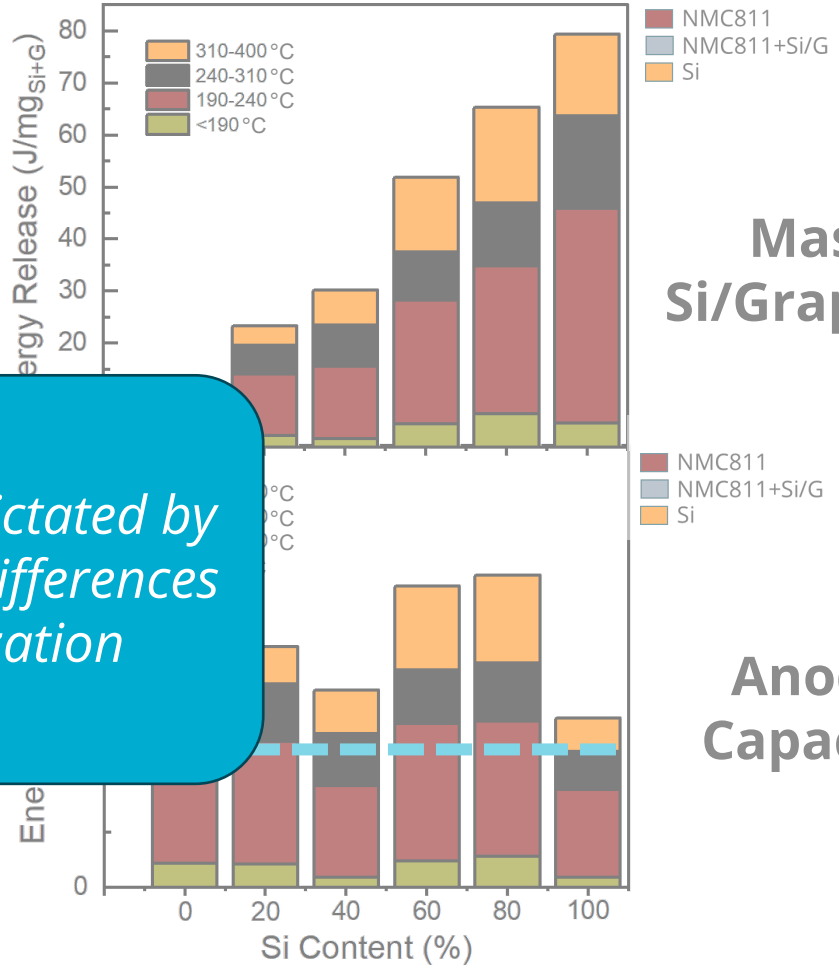
- How you normalize and interpret your energy release matters.
- Trends differ between J/mg and J/mAh

Li *et al.*. *J. Power Sources* **2016**, *335*, 38-44.

THERMAL RELEASE FROM MICROCELLS



Microcell thermal release largely dictated by NMC811 contribution, with some differences in behavior related to normalization

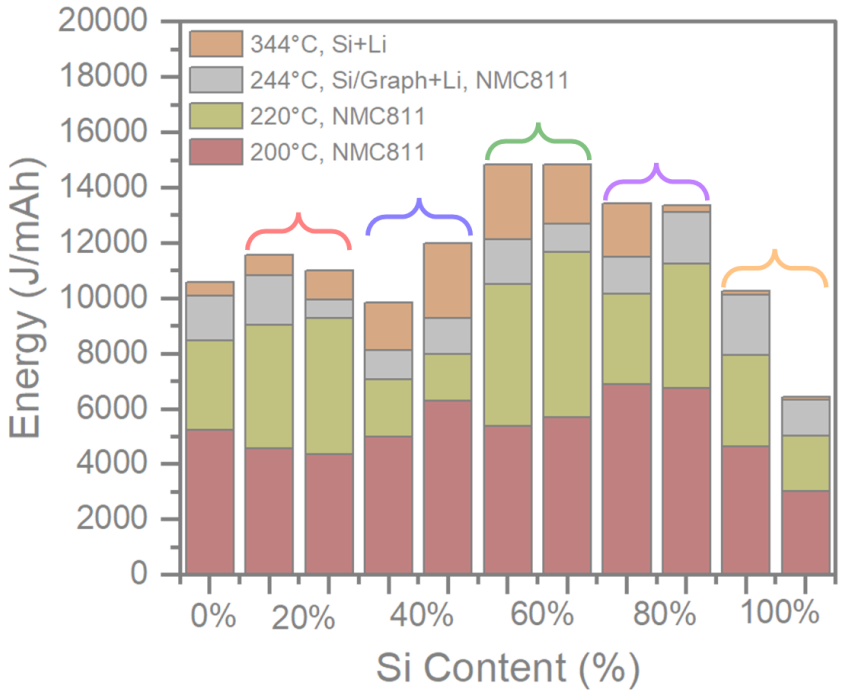


- 100%SoC microcell behavior dominated by **NMC811** decomposition below 240 °C
- Smaller peaks >240 °C appear to correspond to the **Si**-induced doublets from the anode, but are more uniform

- Total energy released still trends upwards with the quantity of Si
- Energy release from microcells appears to be more dependent on capacity than anode-only

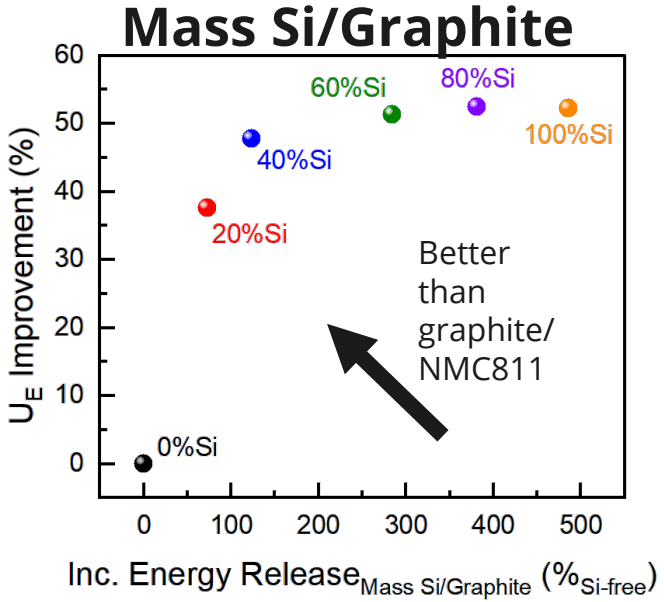
Li *et al.*. *J. Power Sources* **2016**, *335*, 38-44.

REPRODUCIBILITY OF RESULTS AND SAFETY IMPLICATIONS



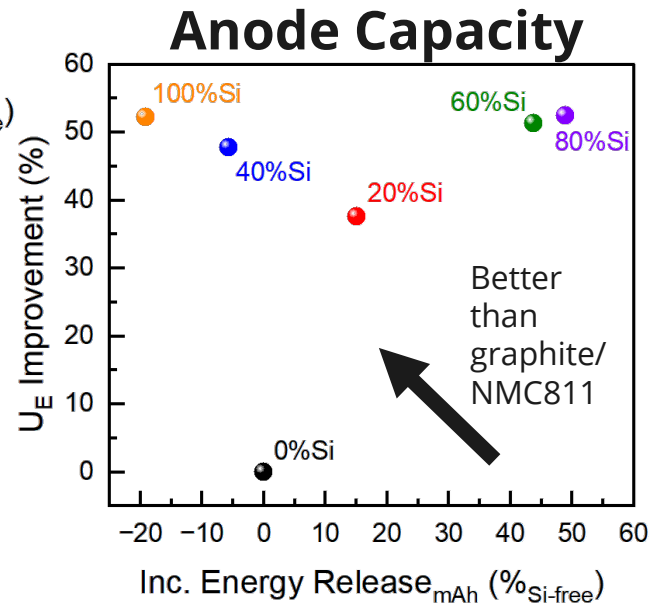
- Replicate microcells with Si/graphite mixtures tend to have relatively good reproducibility
- Relative ratios tend to be conserved for various peaks

Microcells tend to have fairly reproducible DSC results



- Total energy released can be used as yardstick for overall safety, allowing comparison based on potential improvement to energy density (U_E)

Normalization matters, but ~20-40%Si shows best compromise

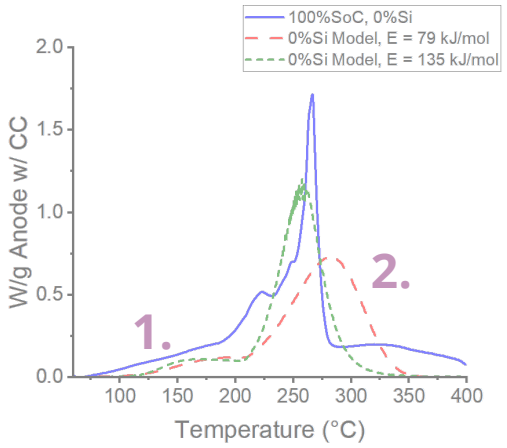


Yim *et al.*,. *J. Electrochem. Soc.* **2016**, *164* (1), A6294-A6302

MODELING OF SI/GRAPHITE ANODES AND NMC811 CATHODES

Graphite Anode

(Confirmation of Existing Model)

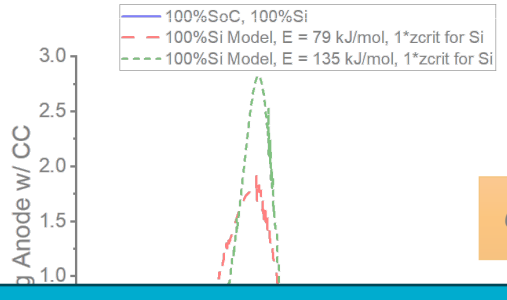


1.
Prediction of low initial rate

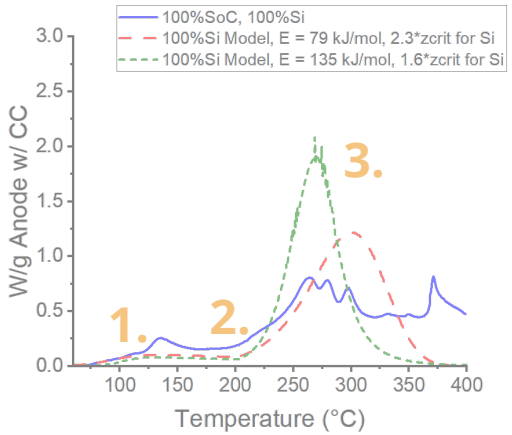
2.
Predicts high rate onset and total heat repr
und
t
act

Si Anode

(1 parameter changed from graphite model)



Optimize



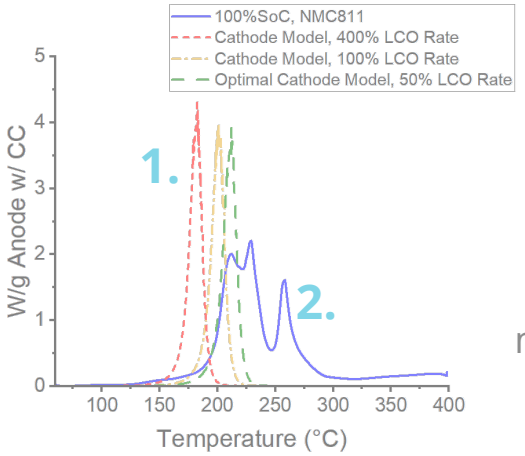
2.
tunneling
increased
tch higher
te onset

3.
Lower activation energy provides better match for Si

Graphite, Si, and NMC811 DSC behavior can be adequately captured by existing models

NMC811 Cathode

(1 parameter changed from LCO model)

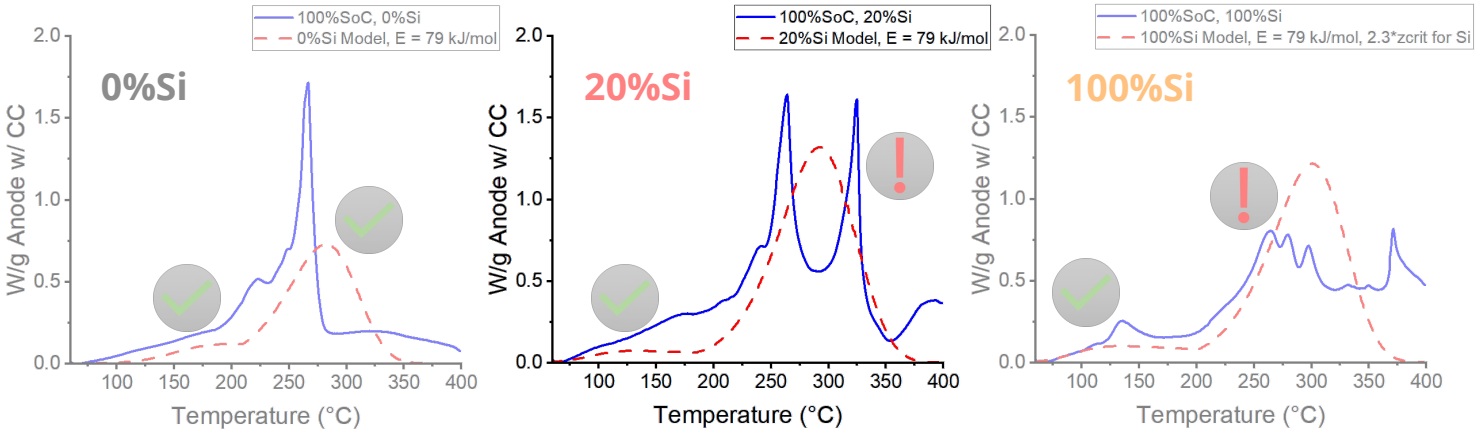


NM
electrolyte slower than LCO

2.
Secondary/tertiary cathode peaks not modeled, but total heat from all peaks adequately predicted

MODELING OF SI/GRAPHITE ANODES AND MICROCELLS

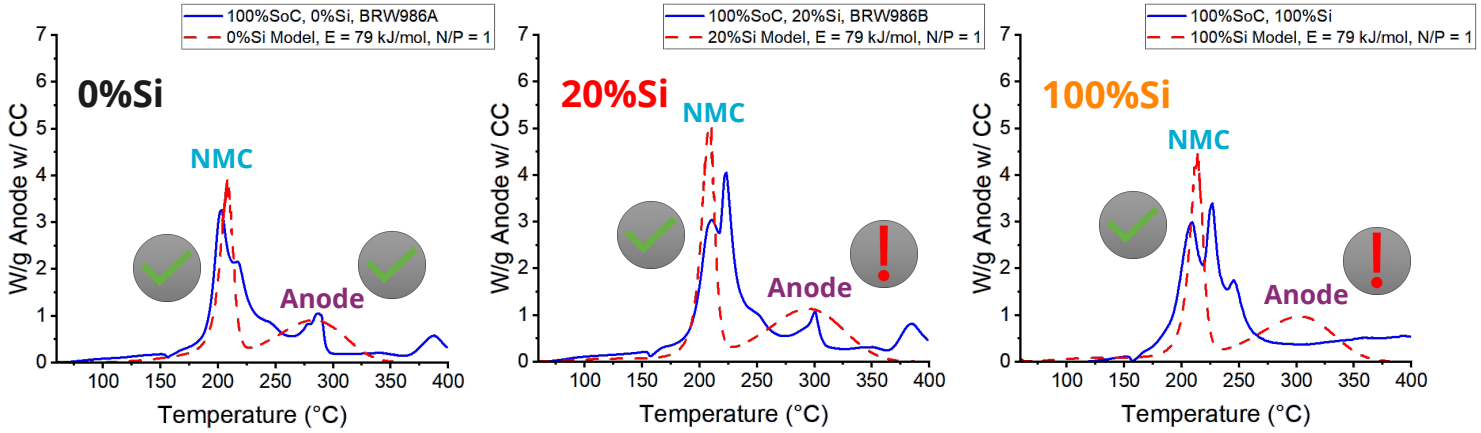
Anodes Only



- Prediction of slow initial rate consistent for both graphite and Si anodes
- Onset of higher rates well predicted, **but** multiple peaks appear to be more common with Si present
  - Model only designed for single peak.

Microcells

- Behavior of cathode appears well predicted for all microcells
- Continue to see two anode peaks in experimental data; model with one peak overpredicts max anode rate
- Predicts total heat release of anode peak



Mixture of Si and Graphite results in unexpected deviations from modeled behavior in anode that can be explored by changing the model

CONCLUSIONS AND FUTURE DIRECTIONS (FY26+)

Conclusions

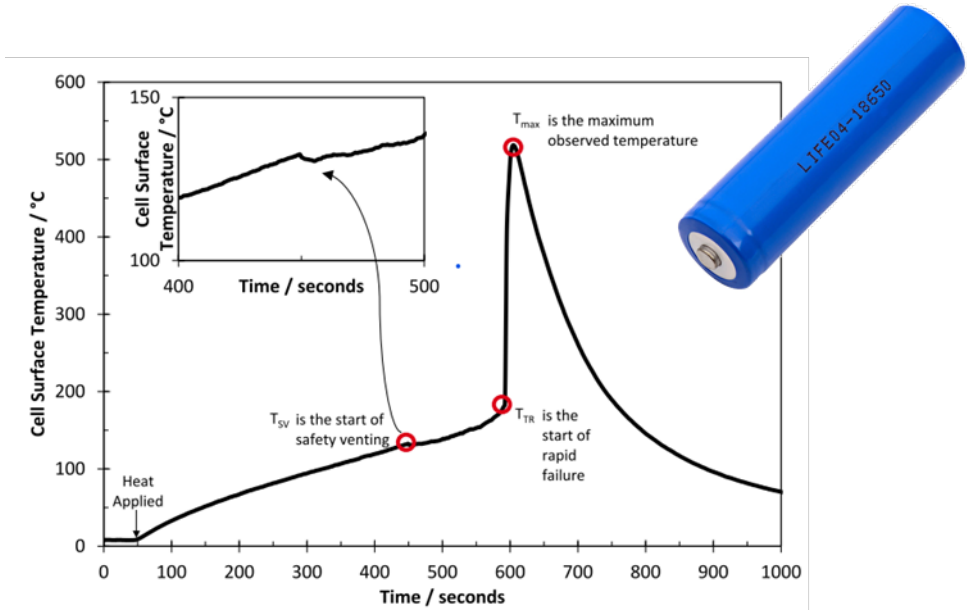
1. Mixture of Si and graphite *does* impact heat release, likely through Si agglomerate size

2. Most microcell energy released during NMC811 degradation, but *is* influenced by Si content

3. 20-40% Si best balances battery safety and performance for Si/graphite anodes paired with NMC811 cathodes

Future Directions

- Larger scale (18650) safety tests using selected Si/graphite mixtures



Abbot *et al.*,. *J. Energy Storage* **2023**, *65*, 107293

ACKNOWLEDGEMENTS

- *Project Team*
  - Dr. Loraine Castro-Torres
  - Dr. Randy Shurtz
- *Experimental Data Collection*
  - Melissa Meyerson (XPS)
  - Dr. Nathan Johnson (DSC)
- *Funding*
  - DOE Office of Electricity, Energy Storage Program

U.S. DEPARTMENT of ENERGY | Office of Electricity

Energy Storage

This work was supported by the U.S. Department of Energy, Office of Electricity. Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

THANK YOU