MODELING THERMAL RUNAWAY BEHAVIOR OF SILICON-GRAPHITE ANODES AND MICROCELLS

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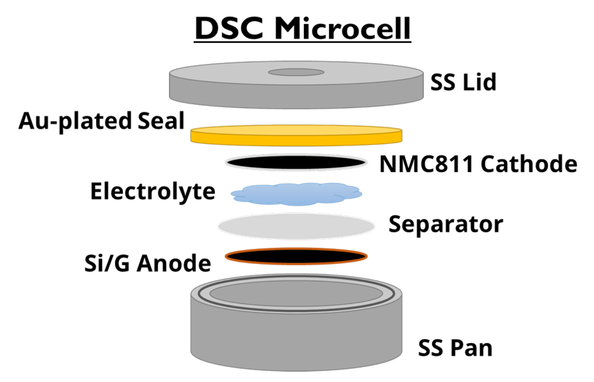
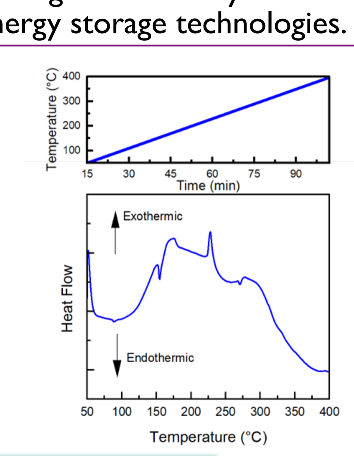
Background

Project Goal	Use **modeling of the degradation** of Si/graphite anodes and NMC811 cathodes in DSC microcells to better understand the **kinetics and mechanism** of cell failure.
Current Practice	Large scale safety testing allows for measurement of full batteries during failure, but the relative **complexity** of these systems means that it can be difficult to gain a deeper understanding of the underlying chemistry at play.
Why SNL?:	SNL has ***established expertise in many forms of battery testing*** and staff with experience in microcell safety testing and modeling of battery safety tests.
Innovation	This work ***bridges the gap*** between small-scale electrode-only safety testing and full-cell testing to ***improve 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 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 also reduce cost, allowing for development of more ***affordable*** energy storage technologies.

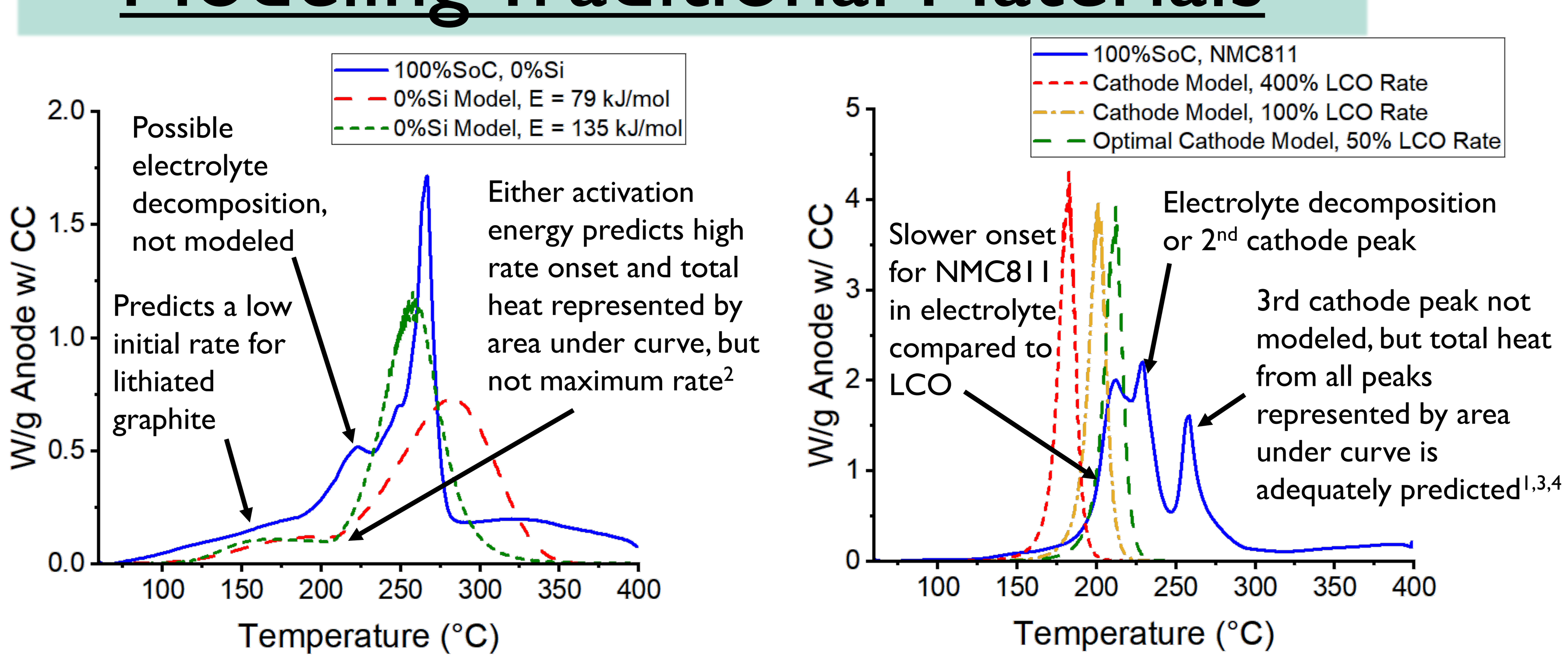


Sealed DSC pan can become a "microcell" battery, containing all essential components of a battery

Measure heat removed/supplied with a fixed temperature ramp to make sample temperature match an inert reference



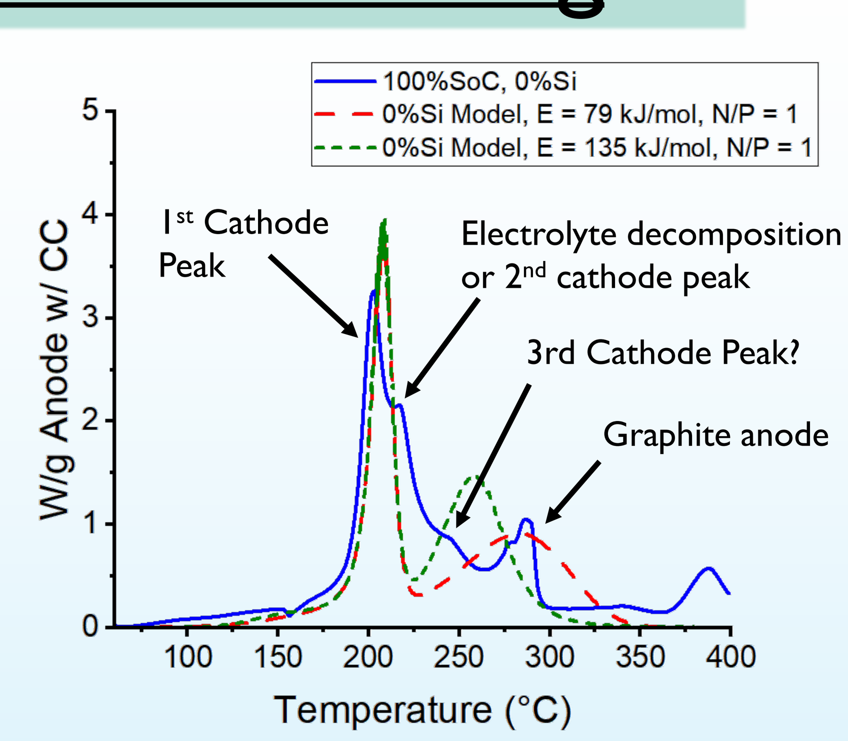
Modeling Traditional Materials



- Legacy models for graphite anode and $LiCoO_2$ (LCO) cathode were upgraded in recent years to enable prediction of cascading propagation rates[1]
- Anode model assumes reaction between lithium and electrolyte on graphite surface, adding material to the surface-electrolyte interphase (SEI)[2]
  - A slow, tunneling-limited initial rate is followed by a large exotherm
  - Previous work has considered 2 possible activation energies
  - Hypothesis is that similar processes occur on silicon anodes, suggesting existing models can be applied with only minor modifications
- Layered metal oxides like the various delithiated NMC and NCA materials have decomposition behavior similar to LCO due to shared crystal structure
  - Heats of reaction are similar and known for these materials[3]
  - 2-step or 3-step processes have been observed in calorimetry,[3,4] but 1-step global reaction is sufficient for most practical applications[1]
  - Assume fixed activation energies; only vary pre-exponential factor

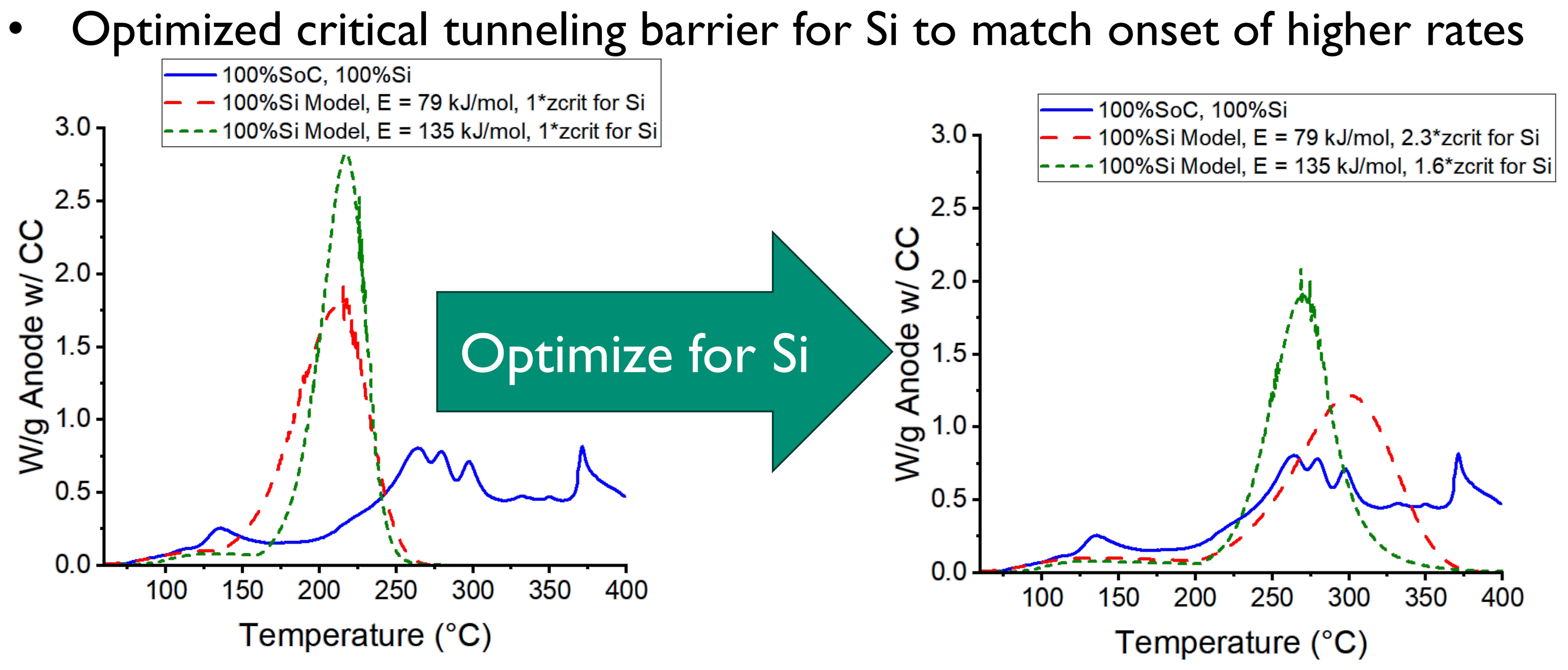
Gr-NMC Microcell Modeling

- Predicts initial slow rates at correct order of magnitude
- Predicts onset of first cathode peak
- Lower activation energy appears better for subsequent fast anode rate



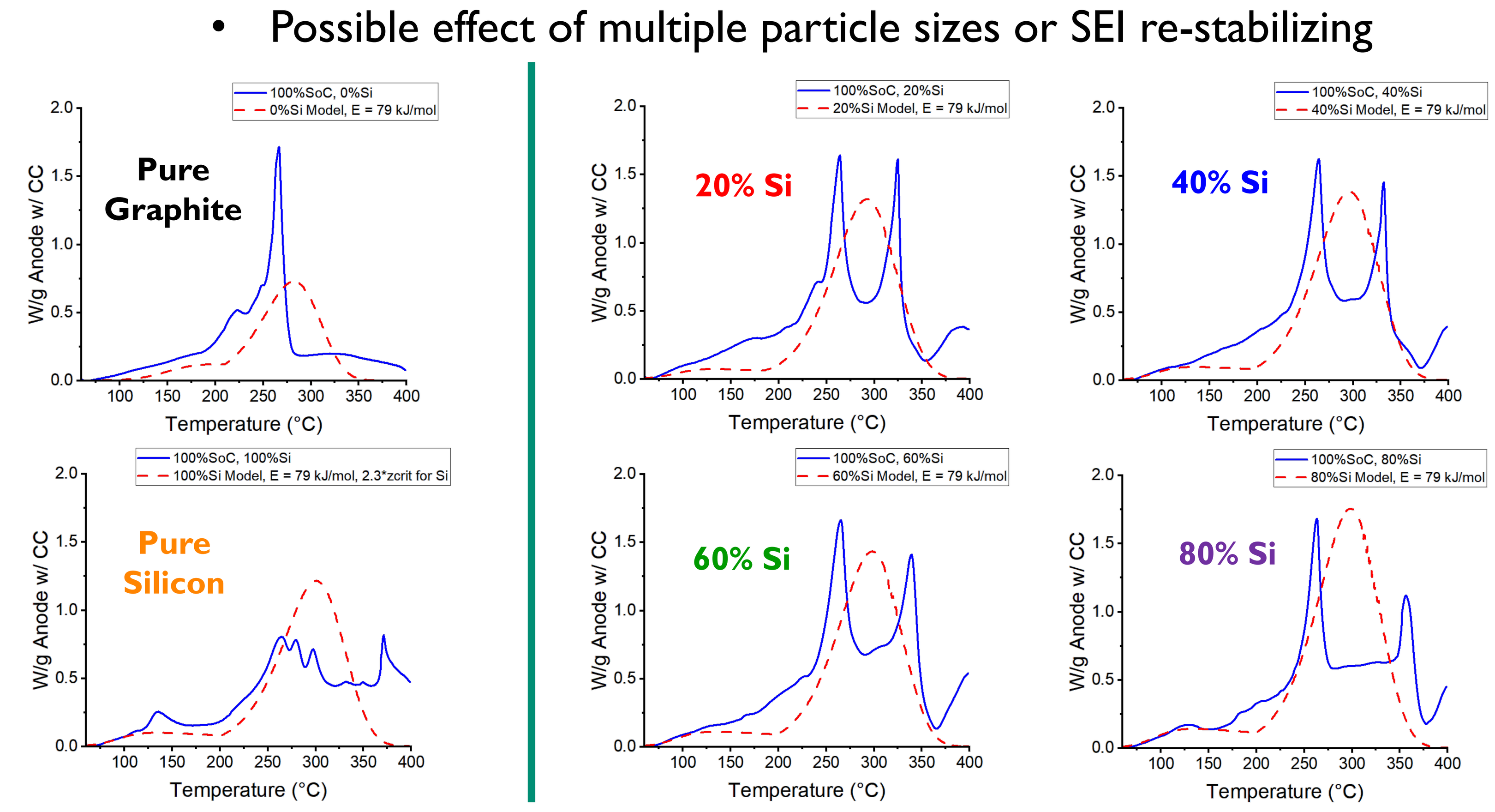
Modeling Si Anodes

- Reasonable prediction of slow initial rates with minimal change in model
  - Replaced graphite edge area with total surface area of Silicon
- Lower activation energy from lithiated graphite model appears suitable
- Optimized critical tunneling barrier for Si to match onset of higher rates



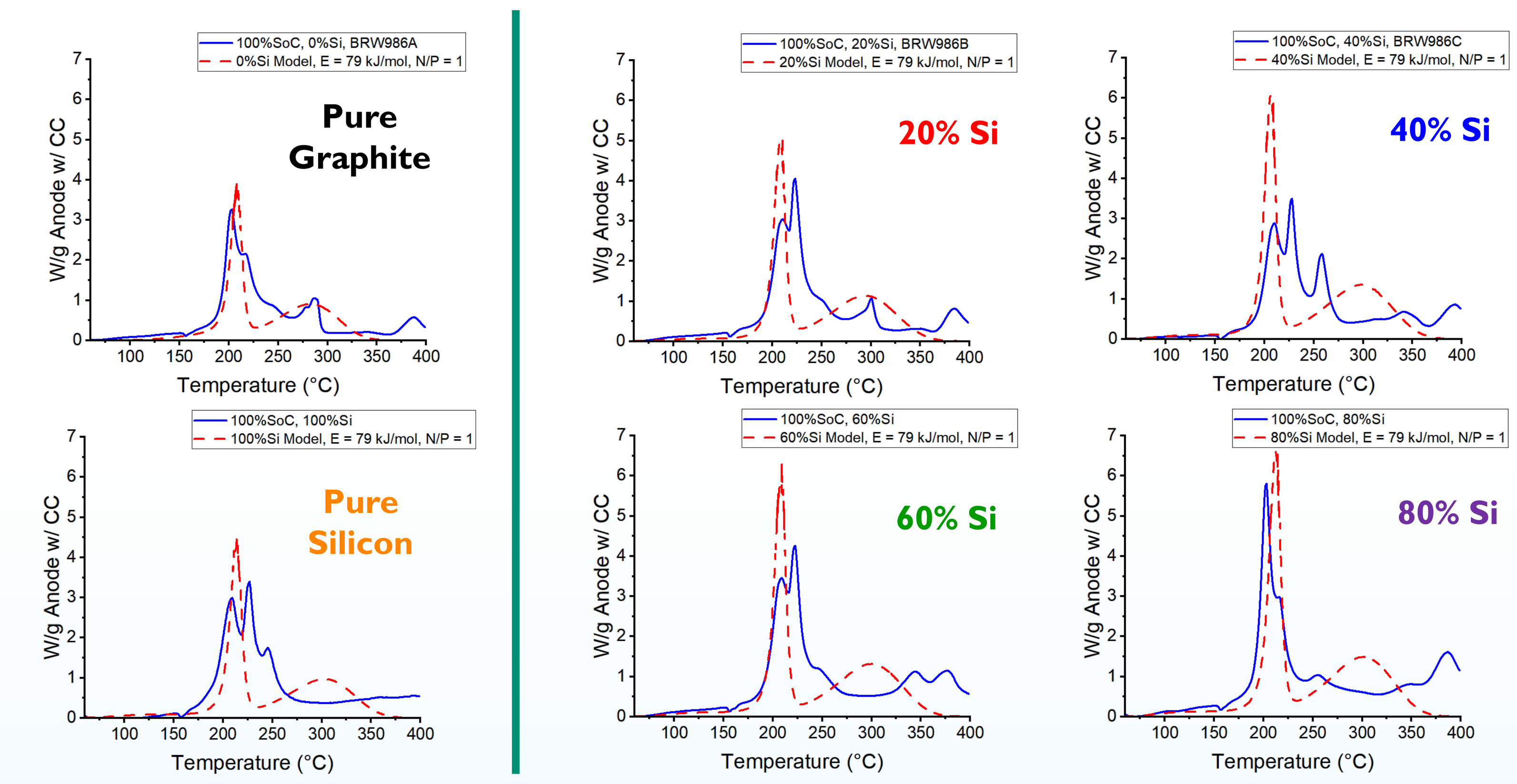
Modeling Si-C Anodes

- Predicts initial slow rates and onset of fast rates reasonably
  - Fast onset almost identical for lithiated Si and Gr; peaks overlap
- Dual peaks with intermediate plateau observed whenever Si is present
  - Possible effect of multiple particle sizes or SEI re-stabilizing



Si-C Microcell Modeling

- First peak cluster corresponds to cathode
  - Slight shifts could be experimental noise or anode preheat effects
  - Global 1-step cathode area adequate match for all cathode peaks
- Anode peak(s) appears flatter and shifted in microcell when Si is present



Conclusions + Future Directions

- Model for lithiated graphite decomposition adapted to lithiated silicon
- Consider upgrading model to predict multiple peaks for Si
- Investigate apparent changes to Si anode reaction with cathode present

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