SNL Energy Storage Technology and Systems – Energy Storage Safety
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# Multi-scale Thermal Stability Study of Lithium-ion Batteries as a Function of Chemistry and State of Charge

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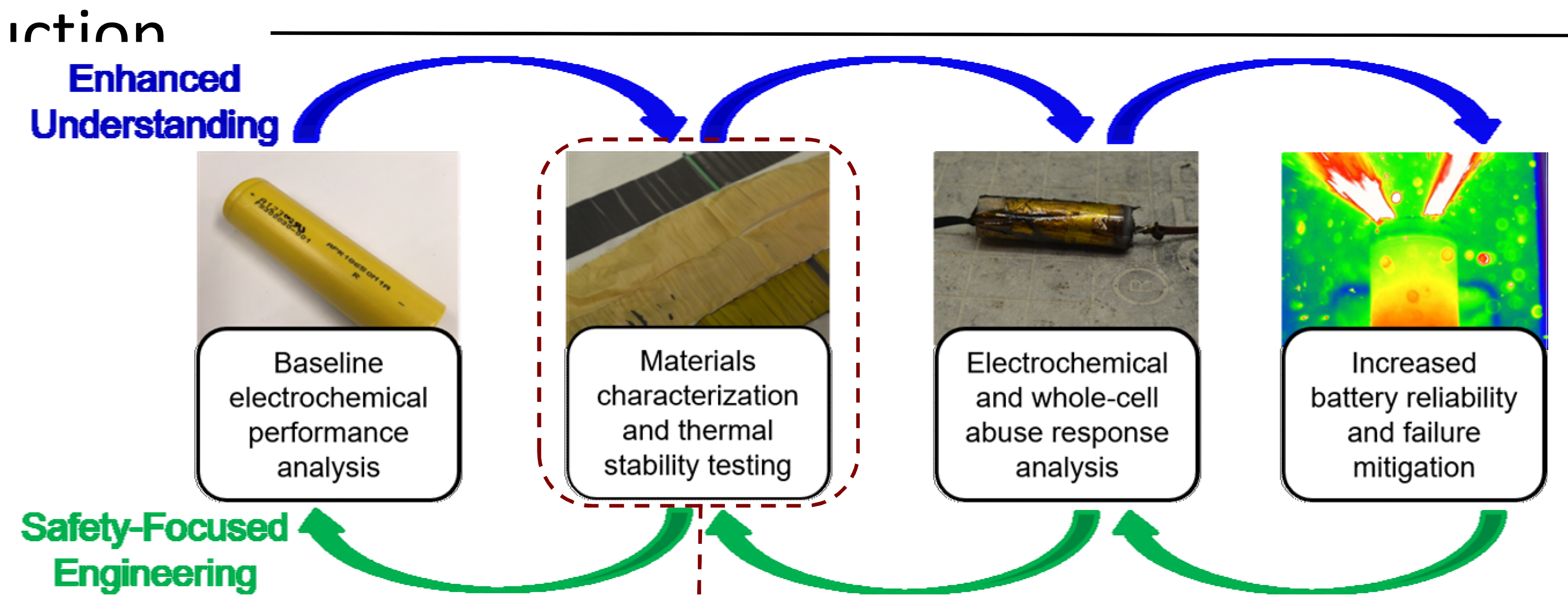
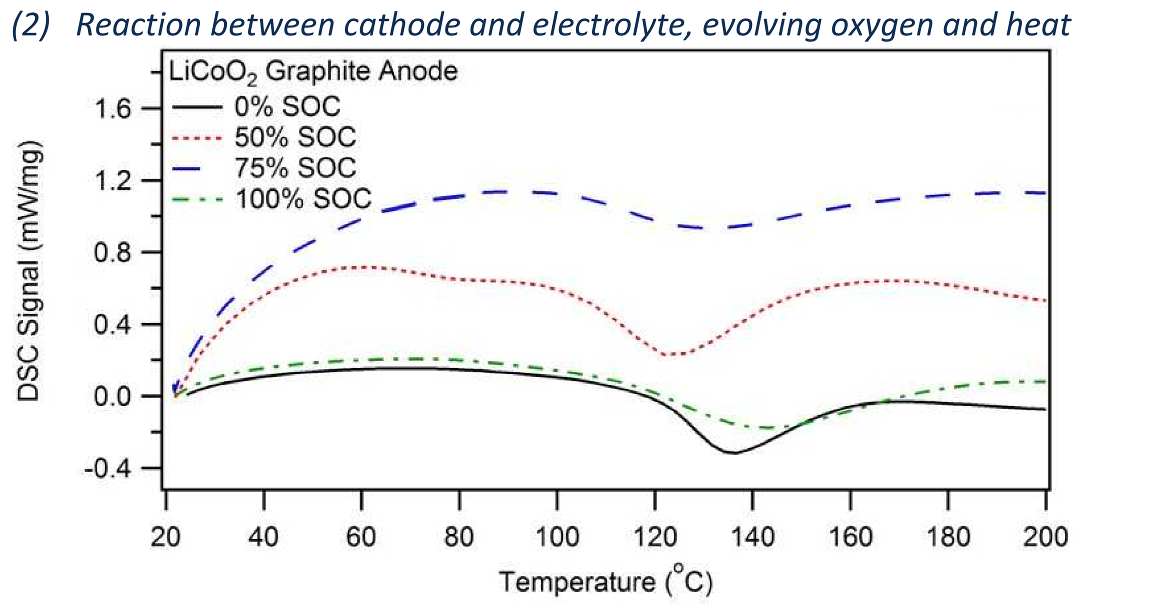
## Introduction

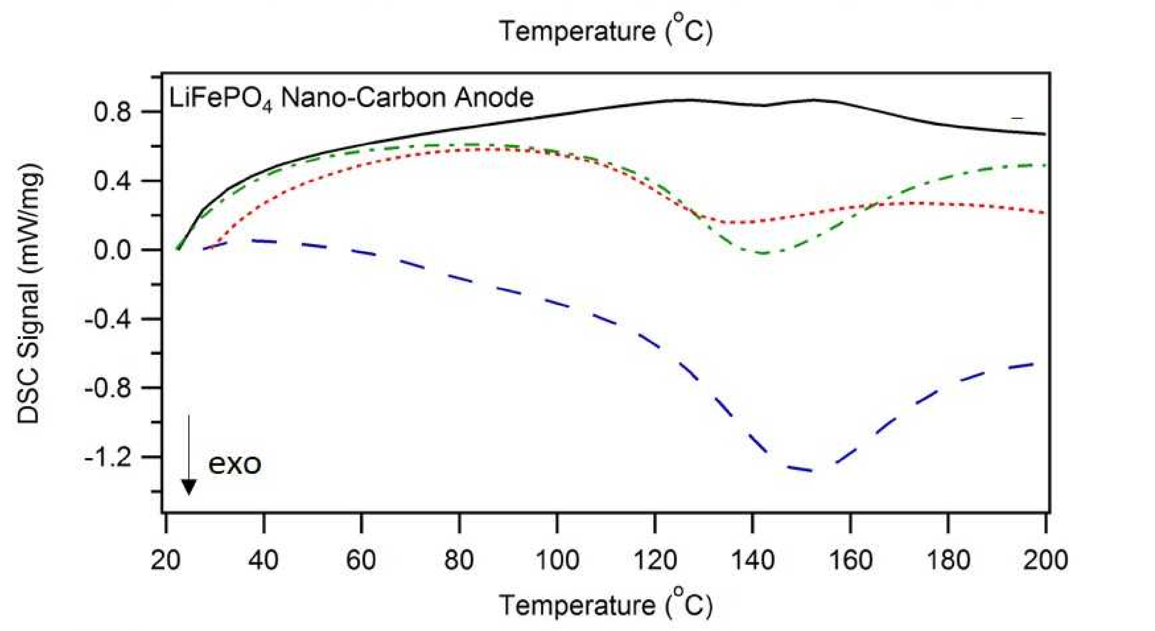
- Stationary energy storage systems (ESS) are increasingly deployed to maintain a robust and resilient grid
- Unknown safety and reliability in lithium-ion batteries (LiB) increases cost and slows adoption in ESS
- Holistic approach: materials and whole-cell abuse will fill knowledge gaps
- The few studies on commercial lithium-ion battery thermal stability focus on whole cell failure without component analysis
- A deeper understanding of commercial cell thermal runaway is required to develop failure mitigation strategies and/or inherently safe cells

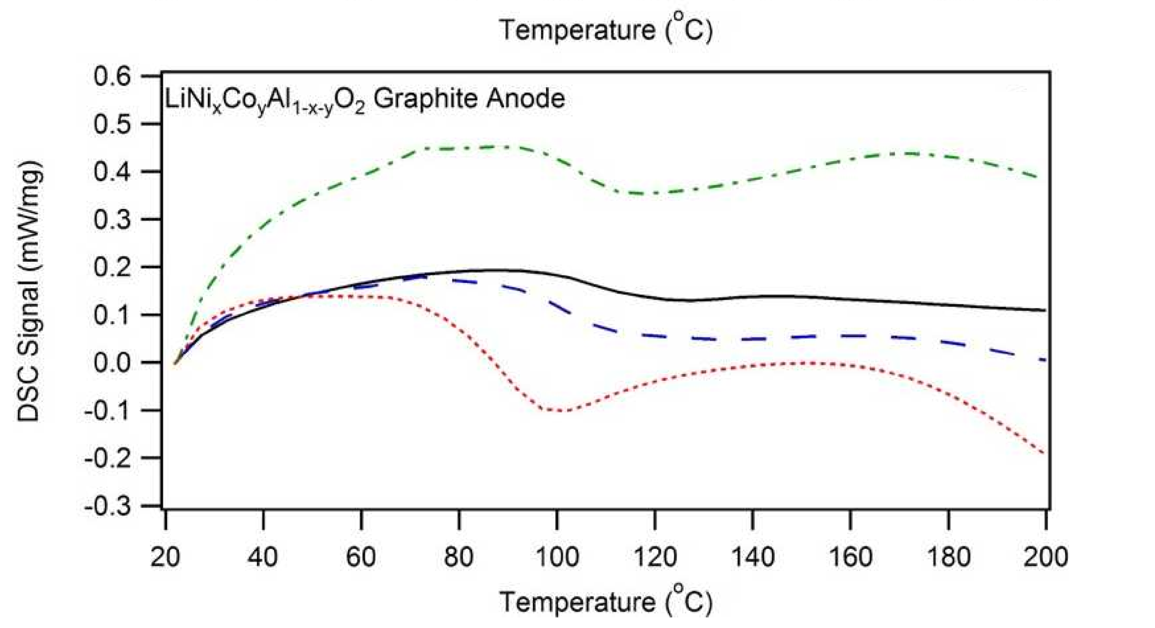



## Anode Failure

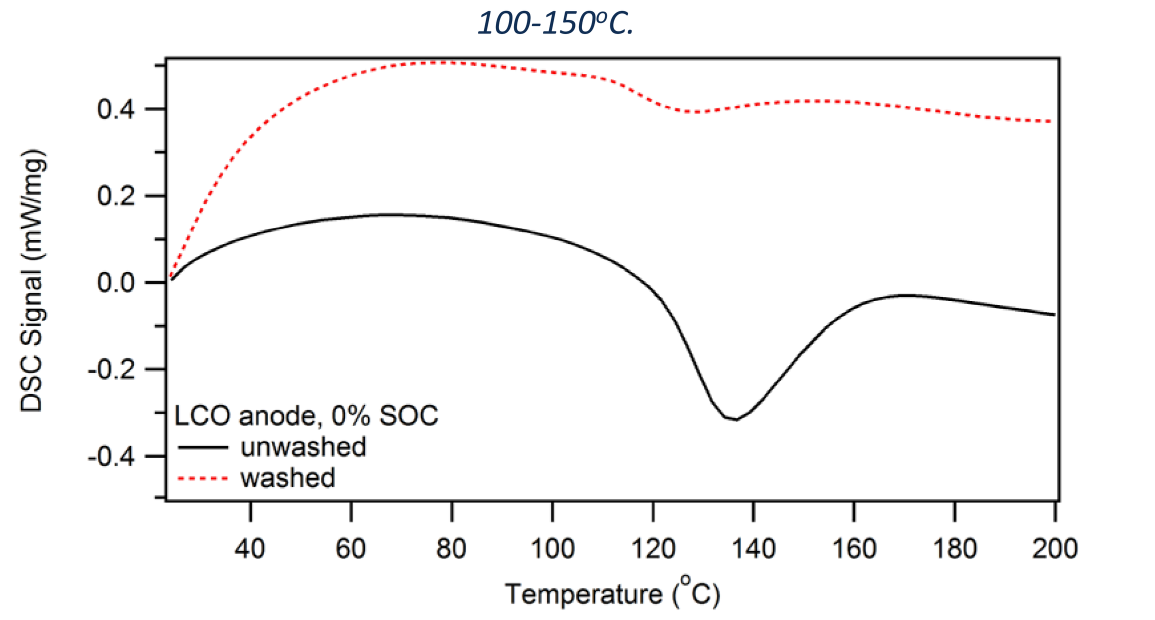
*The thermal runaway process can be generally broken into two main steps:*
*(1) Decomposition of solid-electrolyte interface and reaction between intercalated lithium ions and electrolyte*
*(2) Reaction between cathode and electrolyte, evolving oxygen and heat*



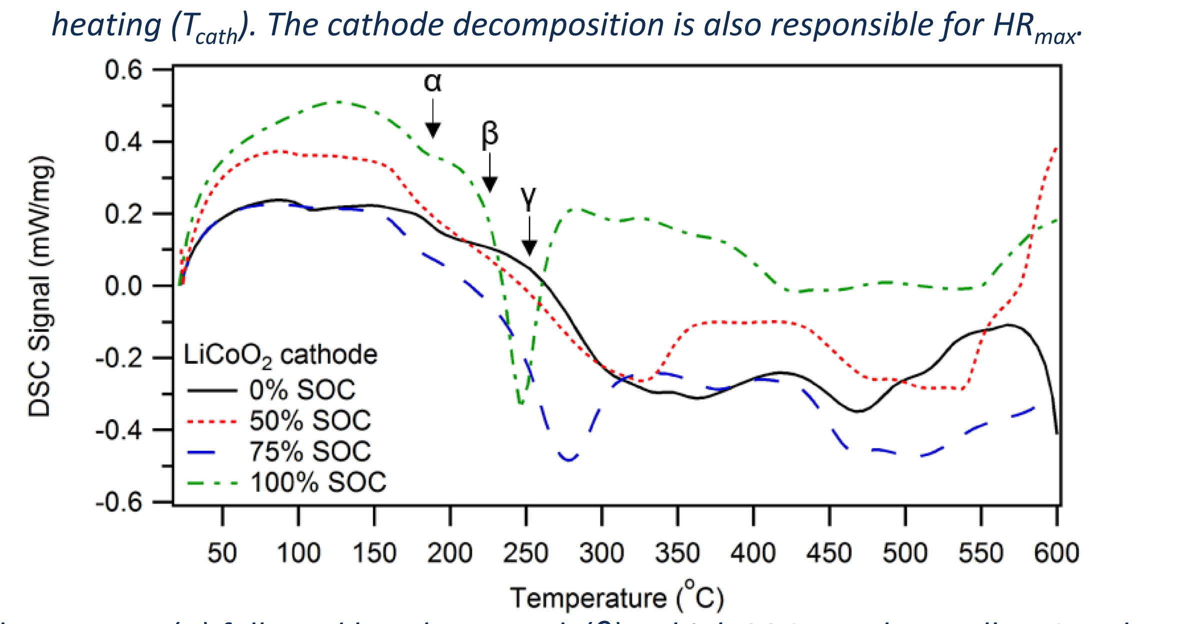

*DSC measurements on anode materials show an exothermic peak with onset between 100-150°C.*



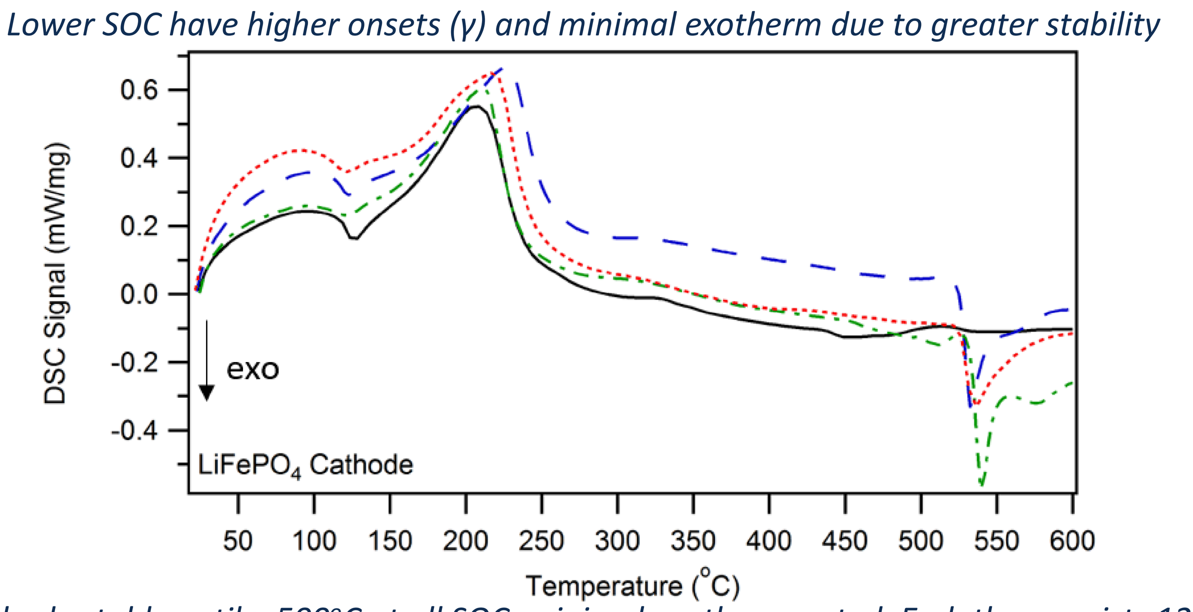

*Exothermic peak is from metastable SEI + electrolyte decomposition. Washing the anode in DMC removes metastable SEI/electrolyte and also eliminates the exotherm.*

## Cathode Failure

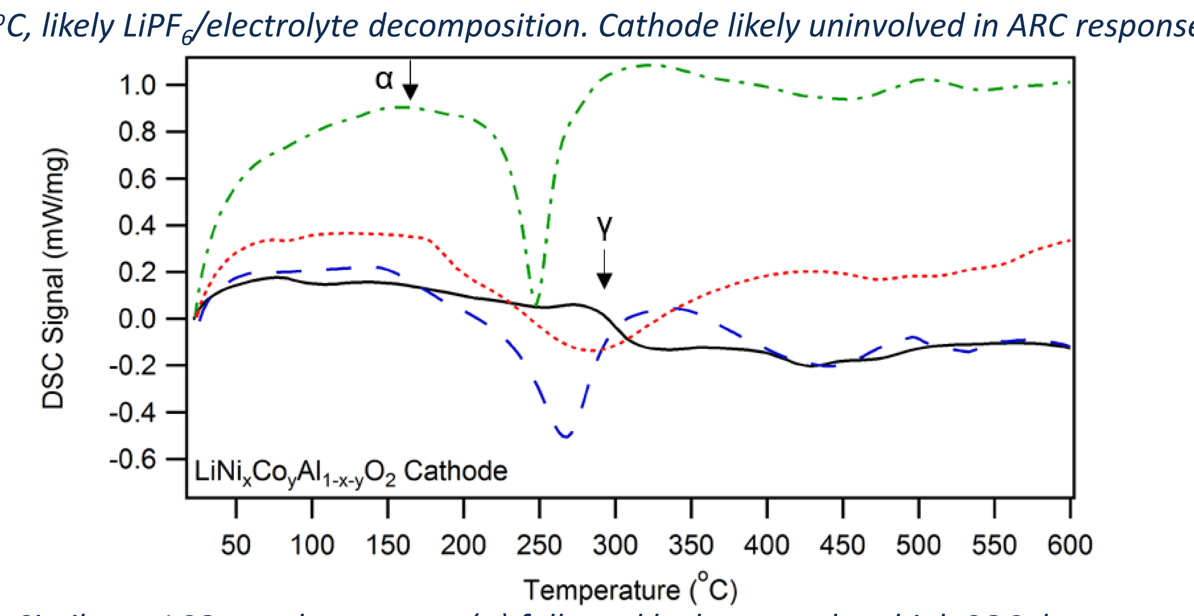
*Cathode decomposition reaction is detected in ARC by a sudden, large increase in self heating ($T_{cath}$). The cathode decomposition is also responsible for $HR_{max}$.*



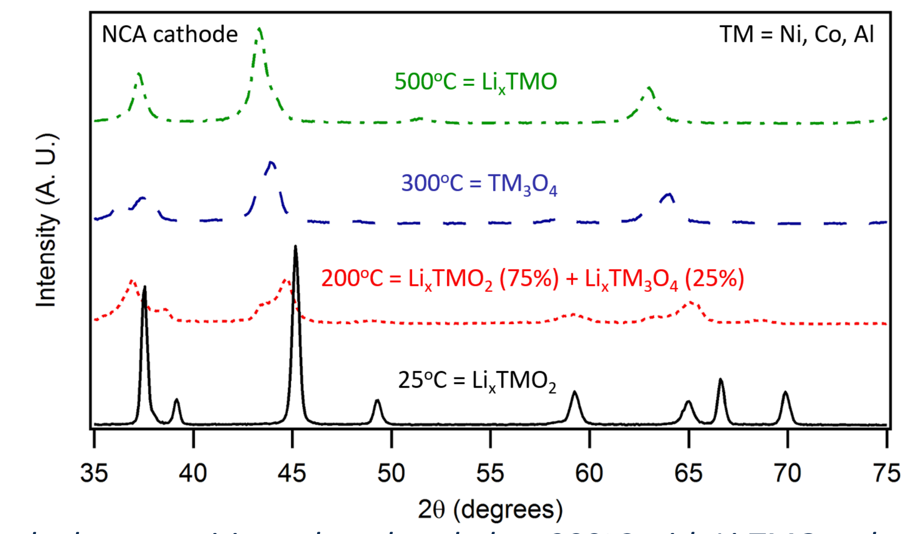

*Exotherm onset (α) followed by a large peak (β) at high SOC matches well ARC and XRD. Lower SOC have higher onsets (γ) and minimal exotherm due to greater stability*




*Cathode stable until > 500°C at all SOC, minimal exotherm noted. Endotherm exists 125-250°C, likely $LiPF_6$/electrolyte decomposition. Cathode likely uninvolved in ARC response.*

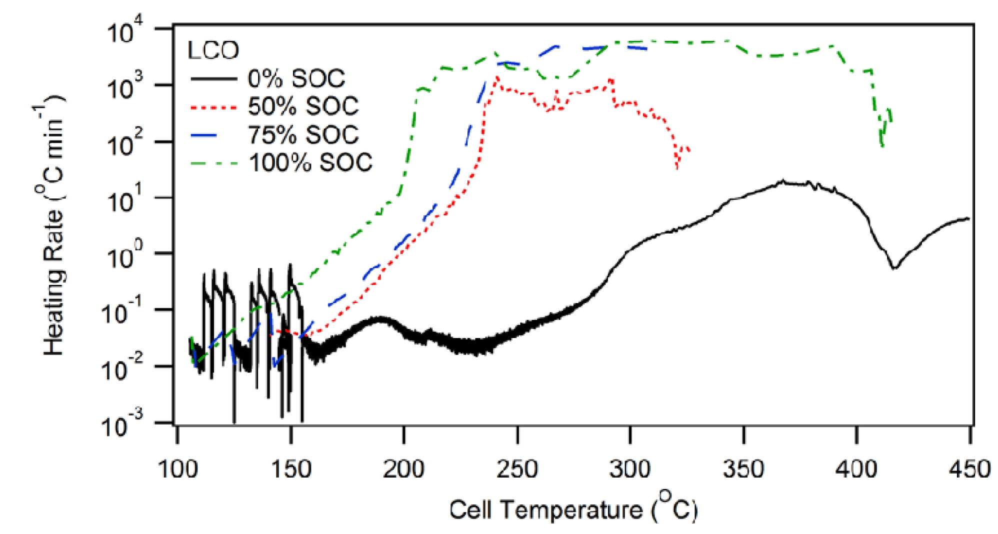


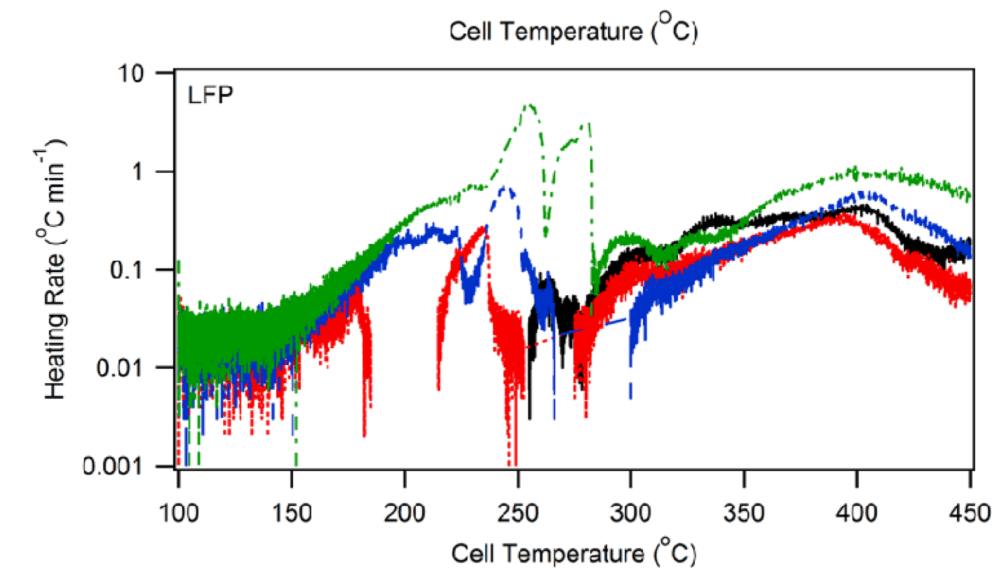

*Similar to LCO, exotherm onset (α) followed by large peak at high SOC due to metastability of delithiated layered metal oxides. Lower SOC cathodes are stable (γ).*

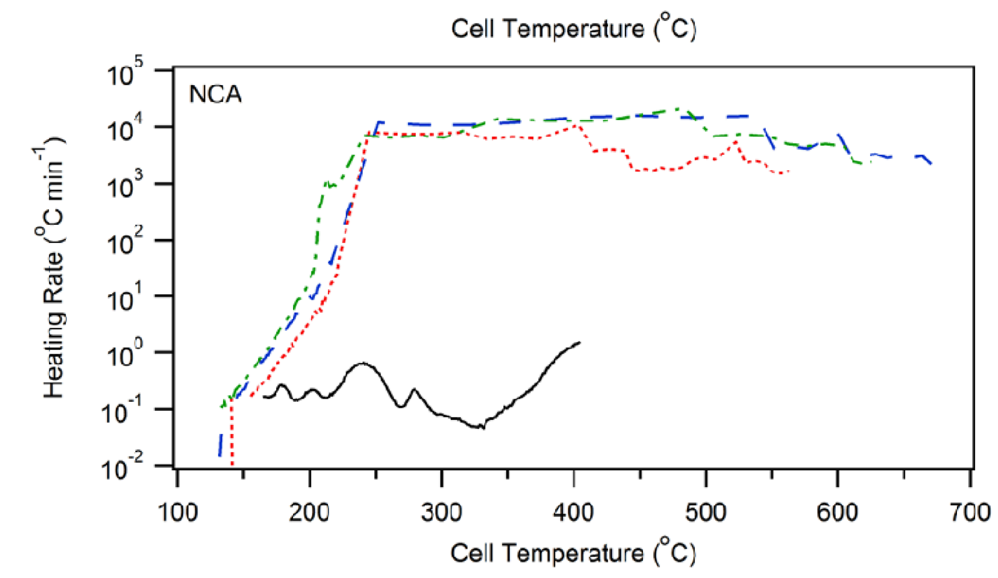



*NCA cathode decomposition takes place below 200°C with $Li_xTMO_2$ releasing $O_2$ and heat, turning into $Li_xTM_3O_4$. Cathode involvement is likely responsible for $HR_{max}$.*

## Whole Cell Failure




*Cathode chemistry and SOC have the most profound impact on thermal runaway behavior, as they dictate $HR_{max}$.*

| Cell | SOC (%) | $T_{onset}$ (°C) | $T_{exo}$ (°C) | $HR_{max}$ (°C $min^{-1}$) | $HR_{max,norm}$ (°C $min^{-1}$ $Ah^{-1}$) |
|---|---|---|---|---|---|
| [redacted] | | | | | |
| | 50 | 106.2 | 197.8 | 1361.1 | 544.4 |
| [redacted] | | | | | |
| | 100 | 106.4 | 168.4 | 6053.5 | 2421.4 |
| [redacted] | | | | | |
| | 50 | 100.8 | --- | 0.3 | 0.3 |
| [redacted] | | | | | |
| | 100 | 100.9 | 240.5 | 4.5 | 4.1 |
| [redacted] | | | | | |
| | 50 | 140.7 | 182.2 | 10810.3 | 3603.4 |
| [redacted] | | | | | |
| | 100 | 132.5 | 165.9 | 21480.4 | 7160.1 |

*$T_{onset}$ = HR > 0.033°C $min^{-1}$ $T_{exo}$ = HR > 1°C $min^{-1}$*

## Conclusions

- Variability in ARC ($T_{onset}$, $T_{cath}$, & $HR_{max}$) can be traced back to cell component chemistry and SOC
- SEI decomposition is the onset of thermal runaway
- Stable cathodes (LFP at all SOC, LCO and NCA at 0% SOC) do not contribute to ARC heating rates
- Metastable (delithiated) cathodes decompose energetically at lower temperatures
- NCA releases the most $O_2$ at low temperatures (< 200°C), resulting in large $HR_{max}$ values

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