Lithium-ion Battery Safety: A Comparison Study of a Combustion Inhibiting Electrolytes

P2SAC December 2024

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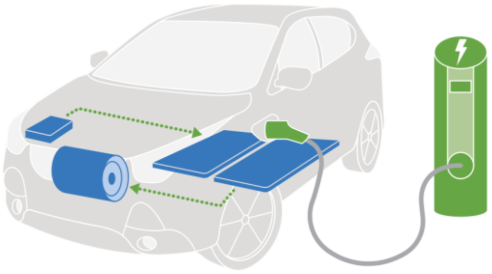
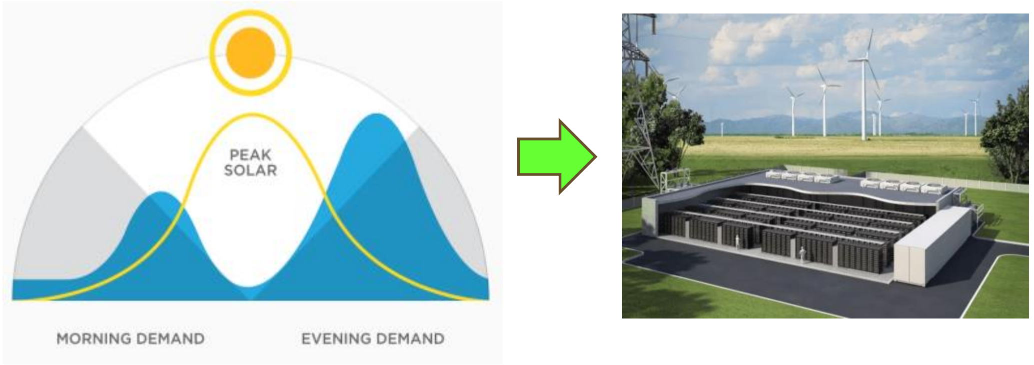
Big Picture Motivations

Plummeting Cost of Electrochemical Energy Storage
- **BNEF 2010: >** $1100/kWh
- **BNEF 2023: <** $139/kWh

Uneven Lithium-ion Battery Adoption:
- **Widespread** in **small-scale** LIB electronics
- **Rapidly developing** in **mid-scale** LIB electric vehicles (EV)
- **Developing** in **large-scale** grid, aviation, and shipping applications

As electrochemical energy storage via LIB increases in energy density and scale…





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BloombergNEF, Long-Term Energy Storage Outlook.

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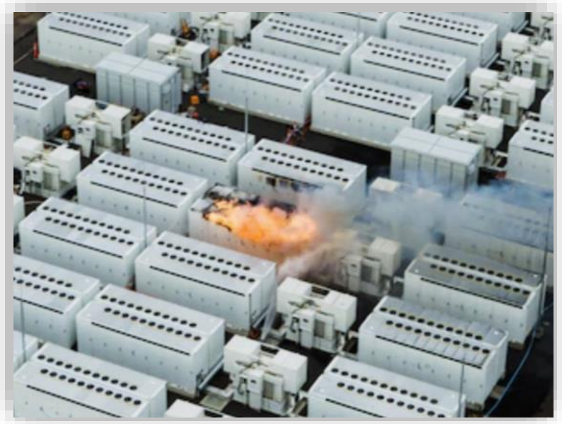
As electrochemical energy storage via LIB increases in energy density and scale…

Importance of long-term safety of energy storage systems also grows.

Tesla Model 3 Fire Nov 2021

Tesla Megapack Fire Sept. 2022



Courtesy of CNBC

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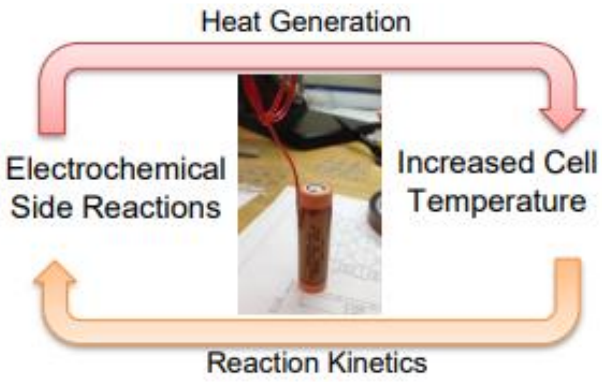
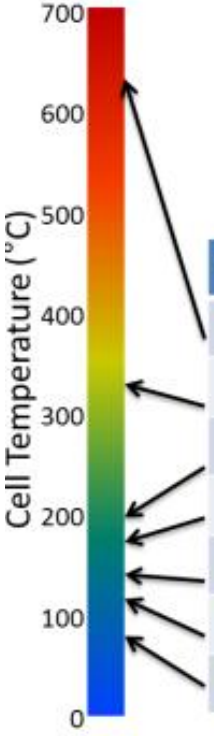
August 2024 - Tulsa, Oklahoma

News On 6/KOTV, https://www.youtube.com/watch?v=HrQ7VMMHY0w (skip to 0:45)

Thermal Runaway: Combustion Focus

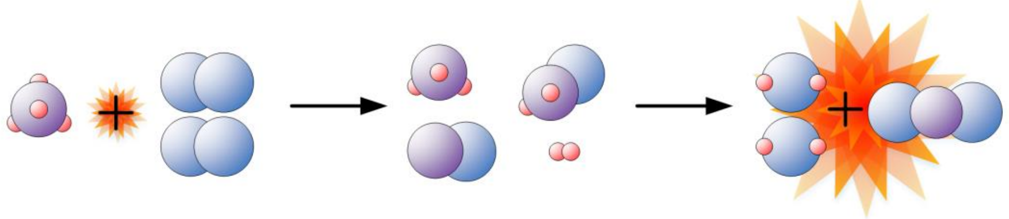




Onset T (°C)	Side Reaction
660	Aluminum melts
330	Anode collapse
160-225	Electrolyte vaporization and combustion
130-180	Separator melts, internal short
140	Cathode decomposition and electrolyte reaction
110-140	Secondary SEI formation and decomposition
85-105	Primary anode SEI decomposition

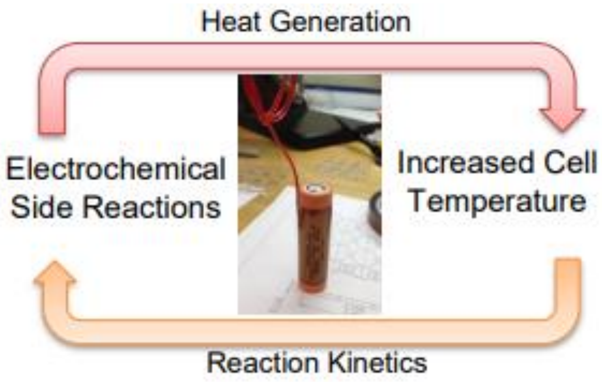
Lopez, J. Electrochemical Society, 162, A1905 (2015).

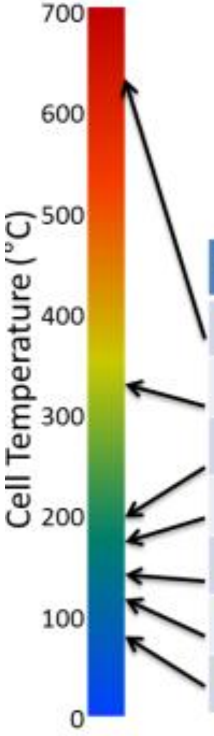
Fuel & Oxygen	Transient Free-Radicals	Final Combustion Products
$CH_4 + 2O_2$ →	(CH_3, CH_2O, CO, H_2) →	$2H_2O + CO_2$



Underwriters Laboratories

The Ideal of the Nonflammable Electrolyte





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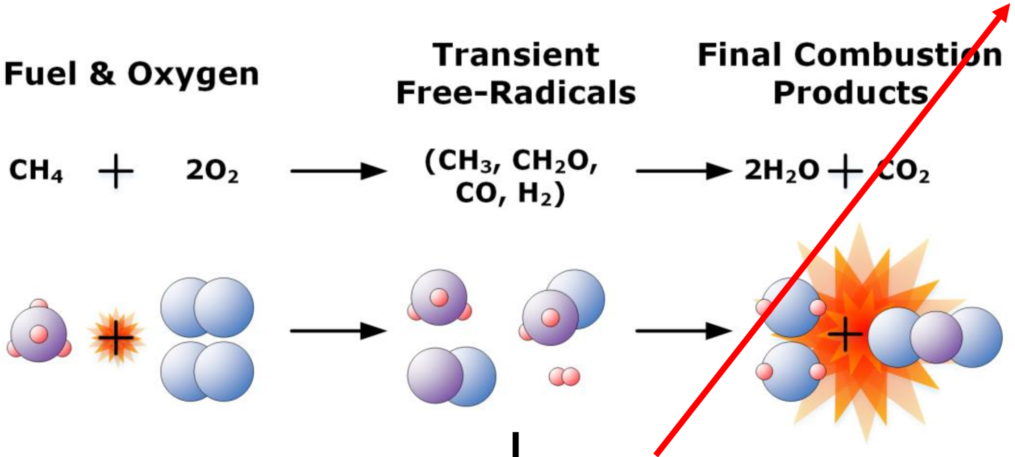

Combustion Inhibition

$PO\bullet + H\bullet \rightarrow HPO$

$PO\bullet + OH\bullet \rightarrow HPO_2$

$HPO + H\bullet \rightarrow H_2 + PO\bullet$

$OH\bullet + H_2 + PO\bullet\ r\rightarrow H_2O + HPO$

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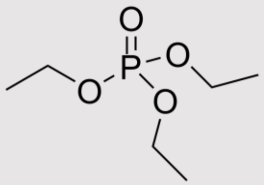
Schartel *et al. Materials* 3, 10 (2010): 4710–45.

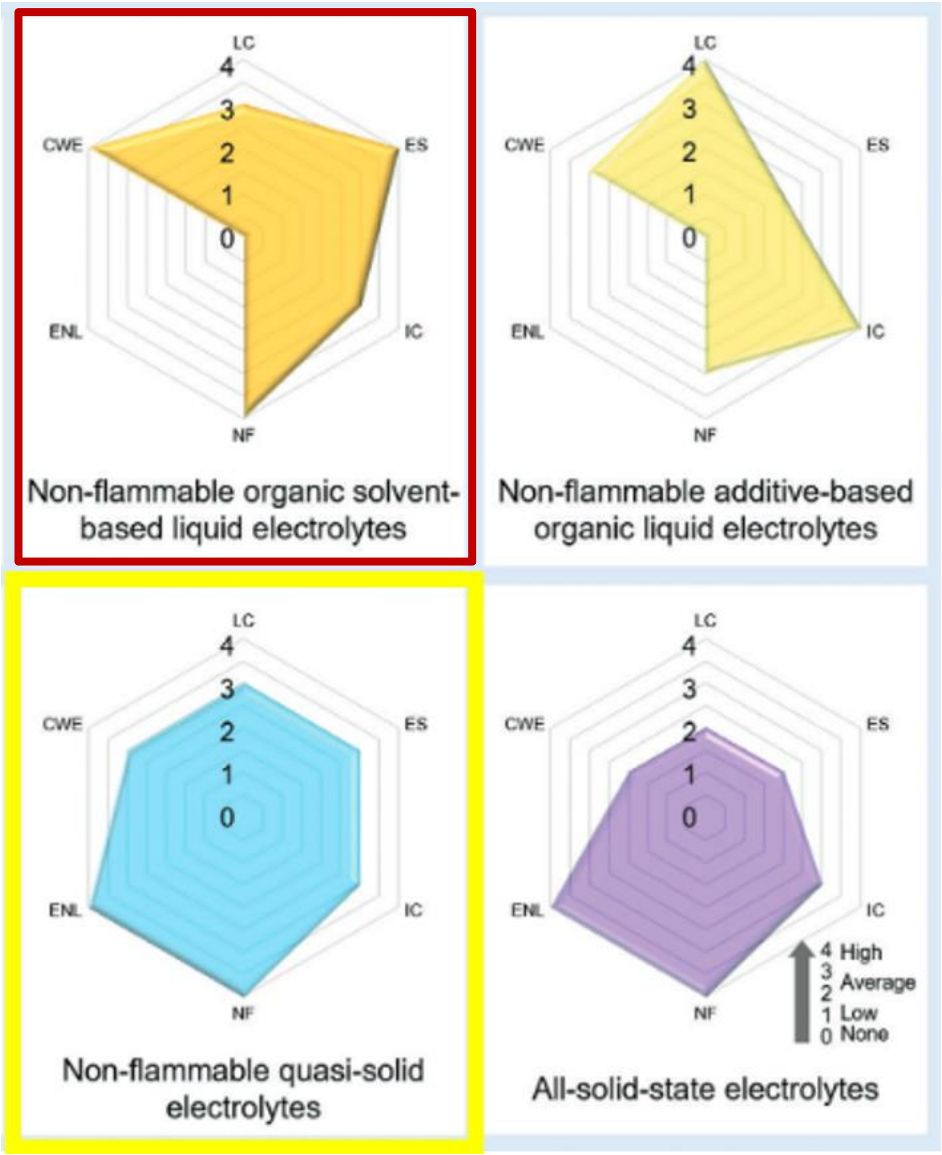
How can we compare nonflammable electrolyte design?

PLE – phosphate liquid electrolyte with additives

Triethyl Phosphate (TEP)



SSE – semisolid electrolyte with integrated phosphate fire retardant



LC: low cost
ES: electrochemical stability
IC: ionic conductivity
NF: non-flammability
ENL: electrolyte non-leakage
CWE: compatibility with electrodes

COMM – Representative commercially used carbonate electrolyte

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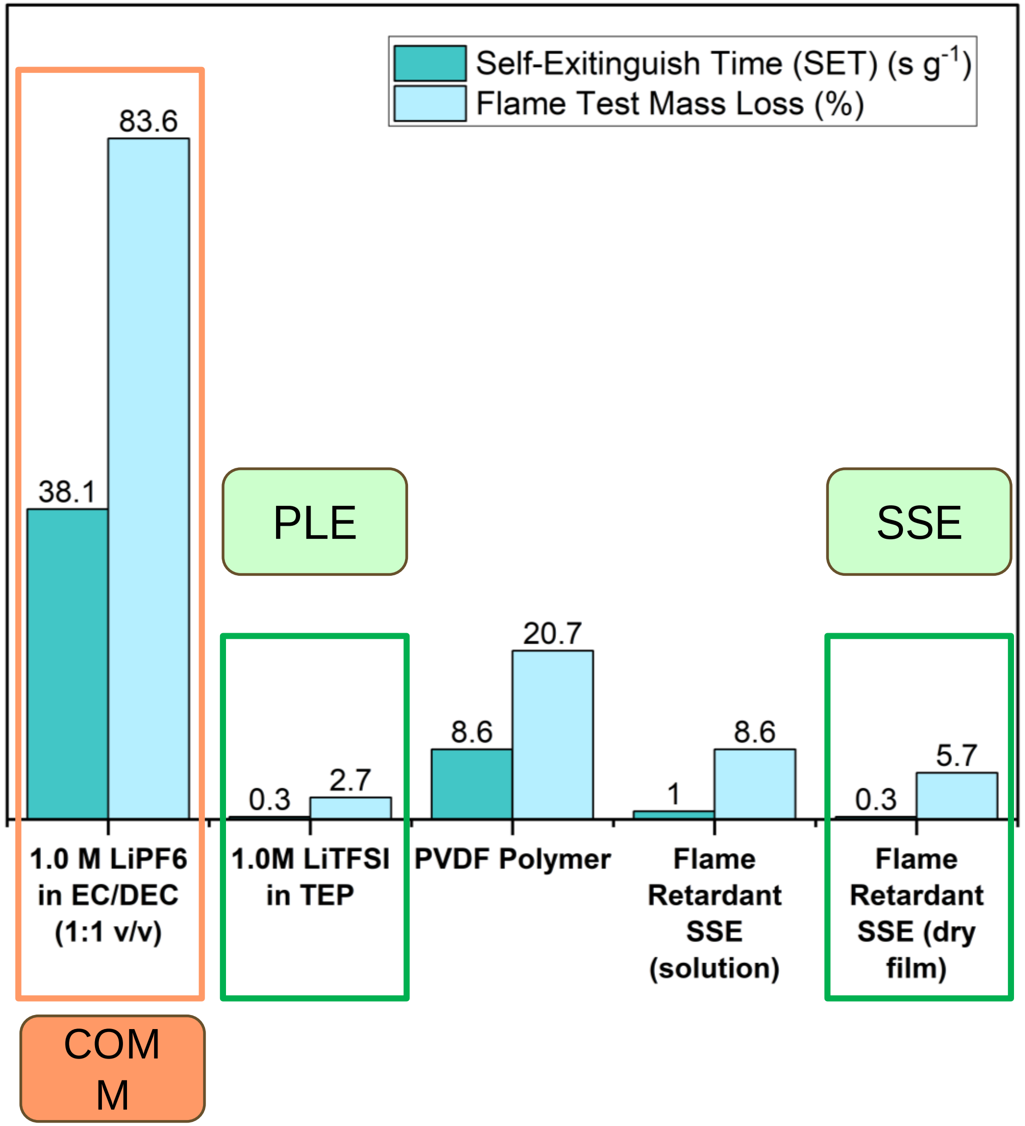
Jaumaux *et al. Advanced Functional Materials* **31**, 2008644 (2021).

Material-level Thermal Safety

COMM
Liquid electrolyte

SSE
Semisolid electrolyte

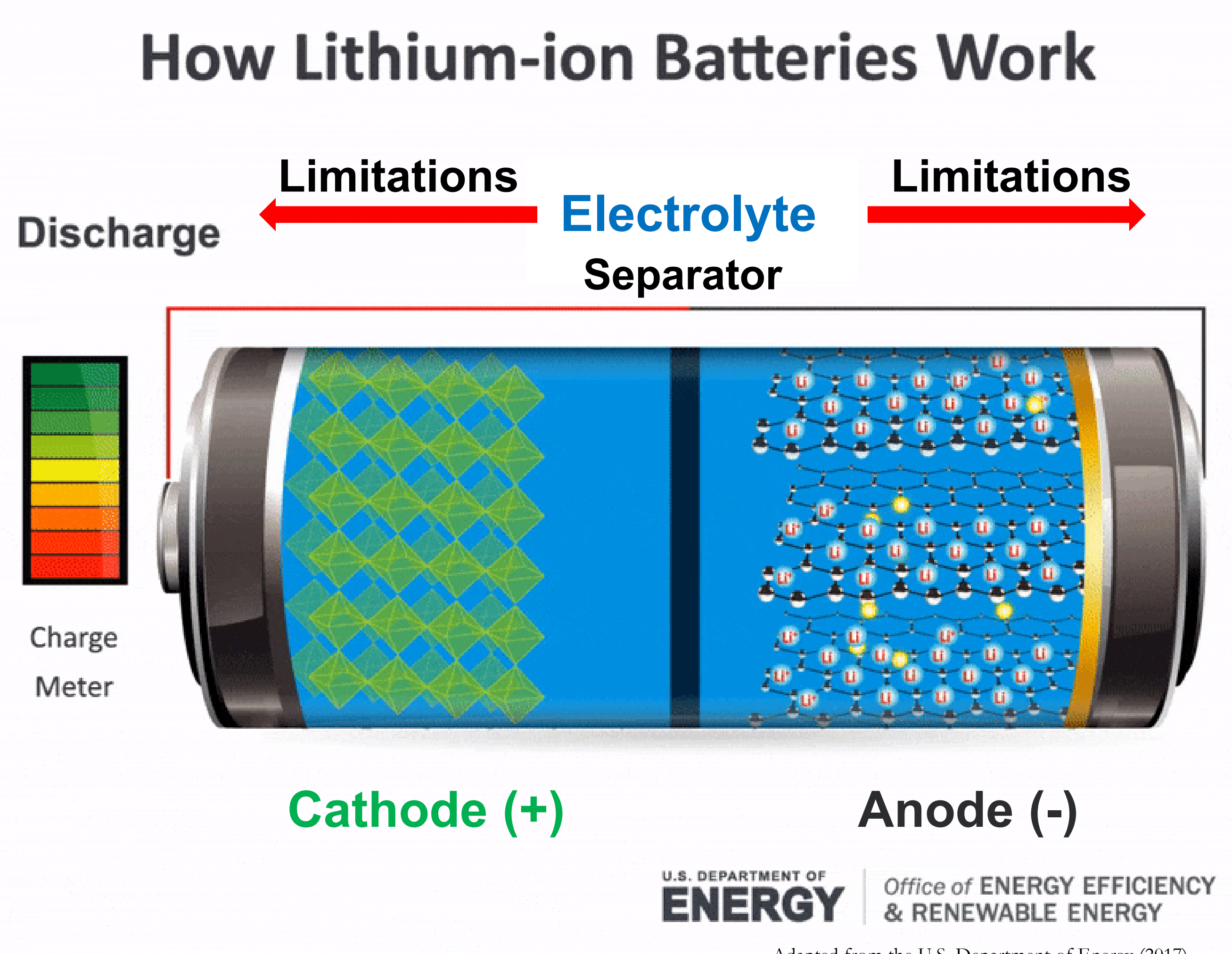


Of course, this is only a fragmentary view of lithium-ion battery safety...

Electrochemical Energy Storage via Lithium-ion Battery

Safety

- **Combustible** organic liquid electrolytes
- **Chemical cross-talk**
- **Separator failure**
- Internal **short-circuit**
- Thermal runaway



Adapted from the U.S. Department of Energy (2017)

Energy Density

- organic liquid electrolytes with **limited voltage window**
- **diminishing returns** in energy density from conventional chemistries

$$\text{Energy Density} = \frac{\text{Capacity} \times \text{Voltage}}{\text{Volume or Mass}}$$

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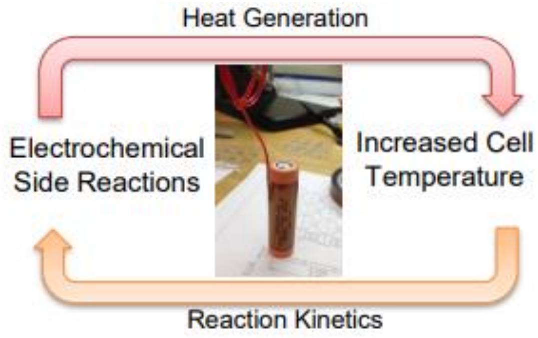

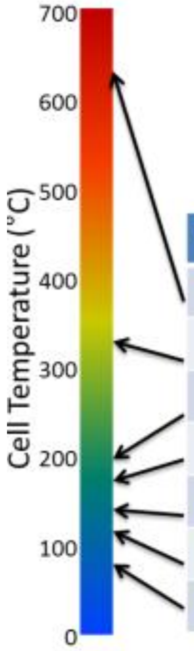

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Exothermic Inhibition

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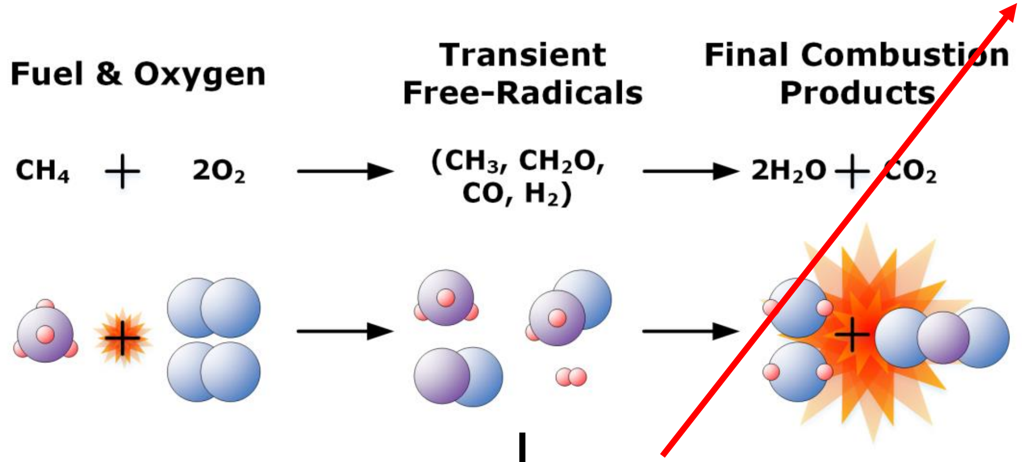

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Thermal factors beyond bulk nonflammability

Bulk electrolyte flammability

- Self-extinguish time (SET)
- Phase requirements
- Sufficient availability of retardant

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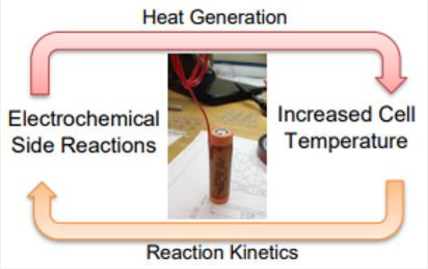
Interfacial thermal behavior

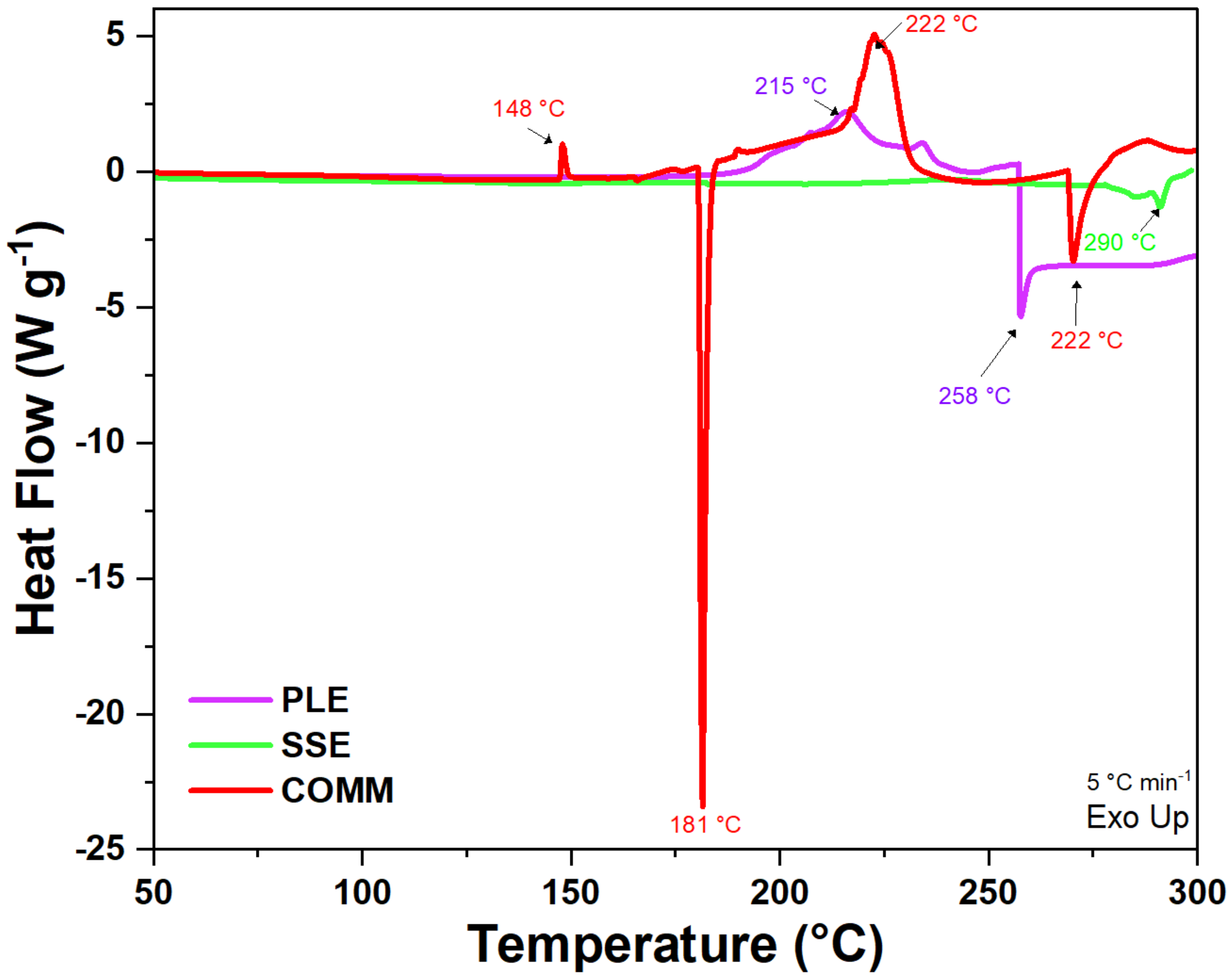
- Interfacial degradation
- Electrolyte reaction at interfaces before and during thermal runaway

Exothermic Inhibition



Mitigation of heat accumulation: combustion inhibition in another flavor

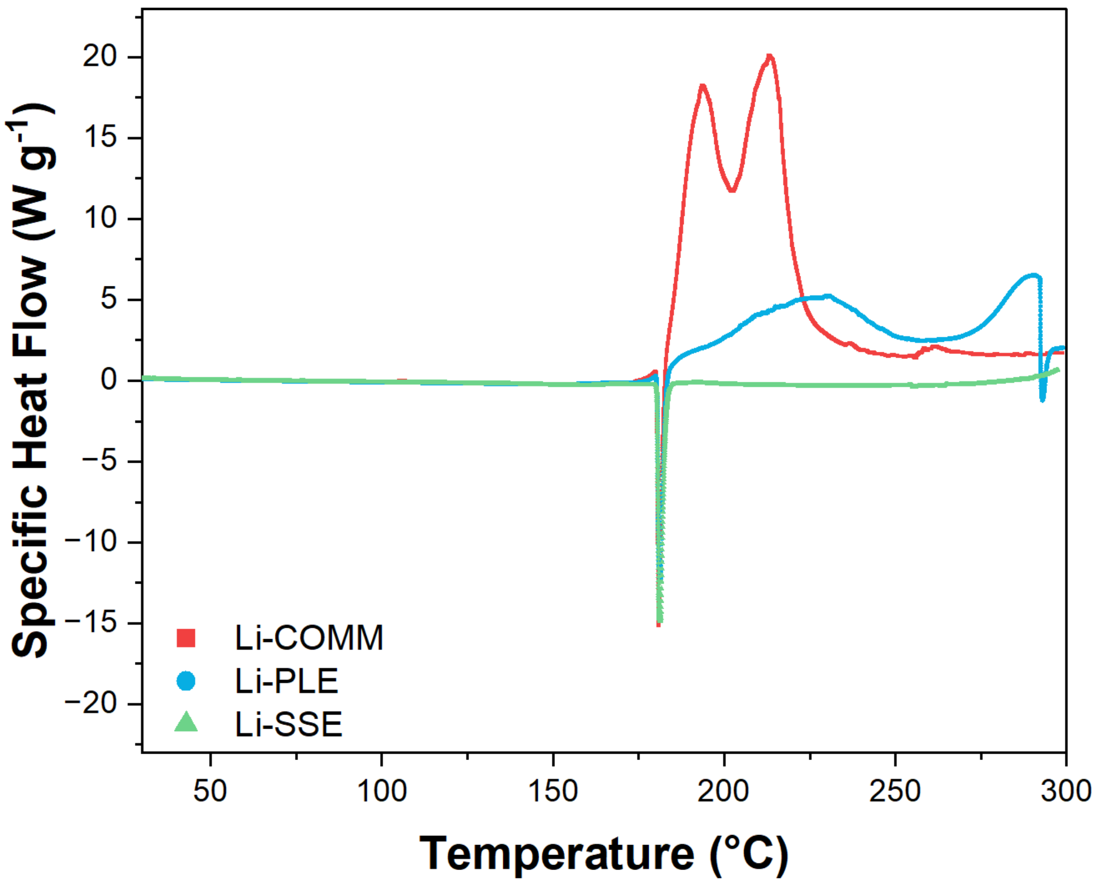
Differential Scanning Calorimetry for materials

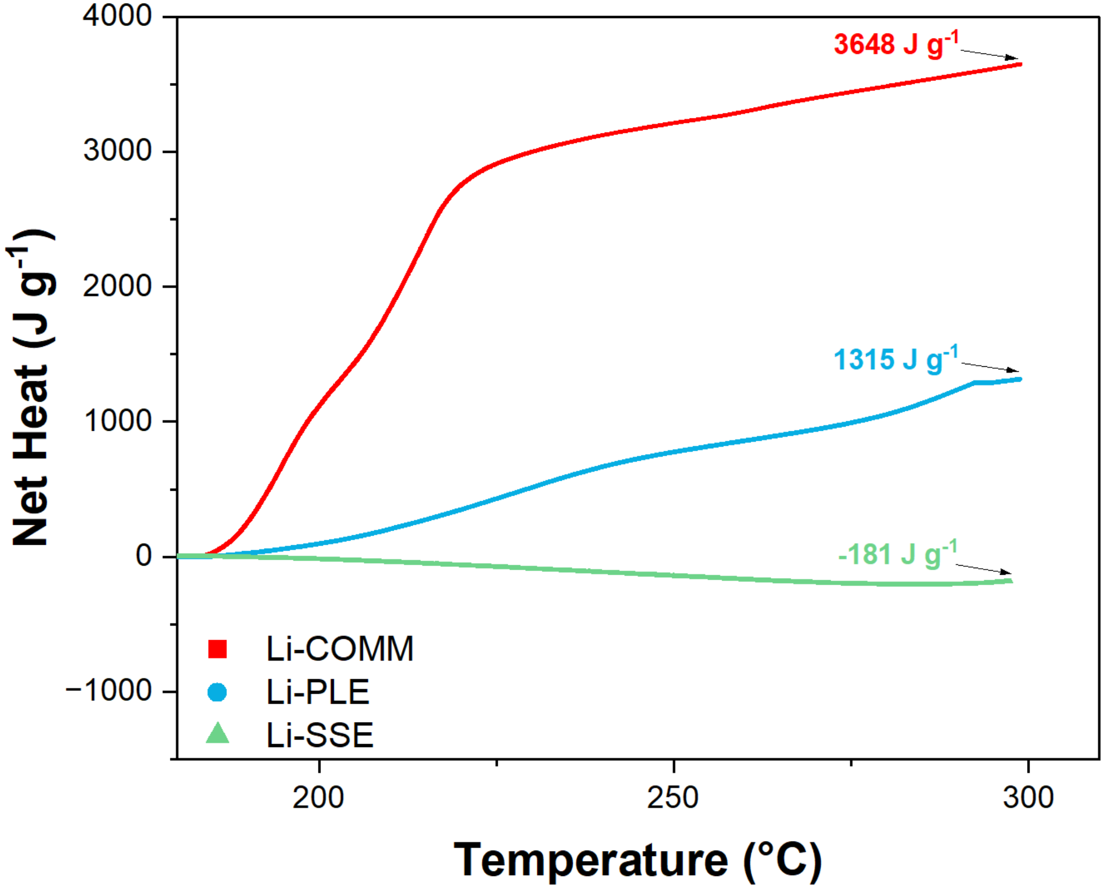


COMM shows significant exothermic behavior in isolation at DSC scale.

Milligram-scale thermal analysis.

Multiscale Thermal Analyses: DSC





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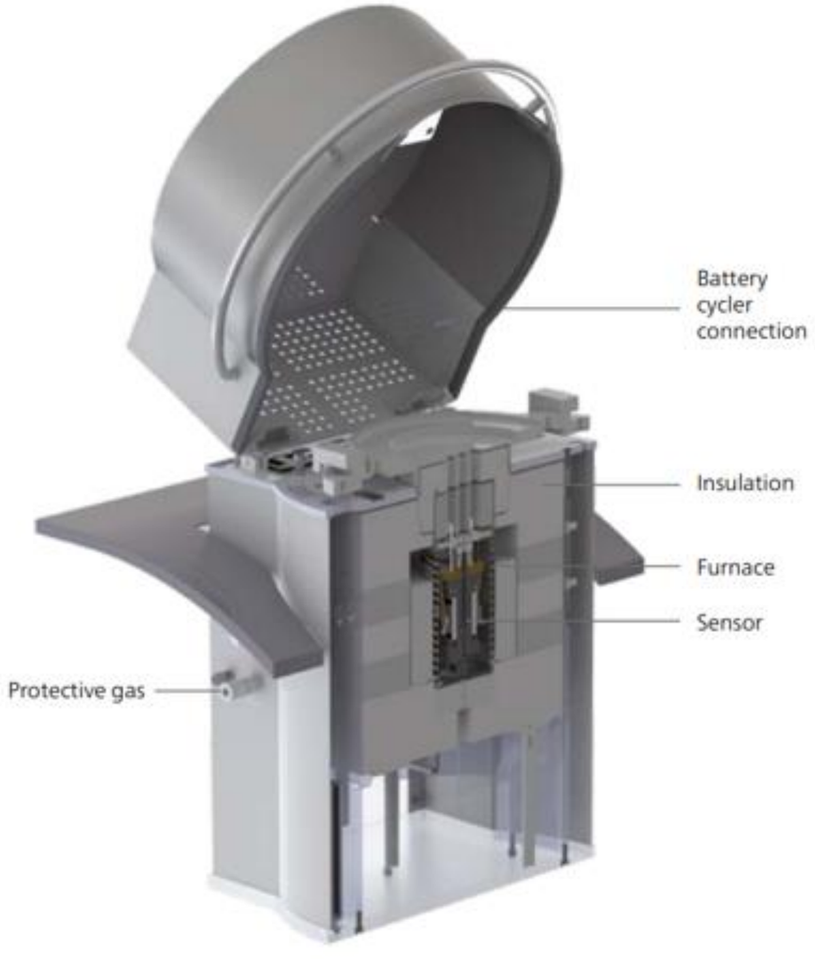
Carbonate electrolyte (COMM) shows notably more significant exothermic behavior in isolation and with fresh Li at DSC scale…

Multimodal Calorimetry (MMC)

- Monitoring of heat flux in coin cells in tandem with recording battery data

- Advantages:
  - Analysis of coin cell configurations with cathode, anode, electrolyte, separator interactions
  - Identify temperature and heat fluxes associated with **internal short-circuit** (ISC, OCV ~ 0)
  - Identify **phase changes and reactions** associated with exothermic and endothermic peaks



Cross section of the Coin Cell Module

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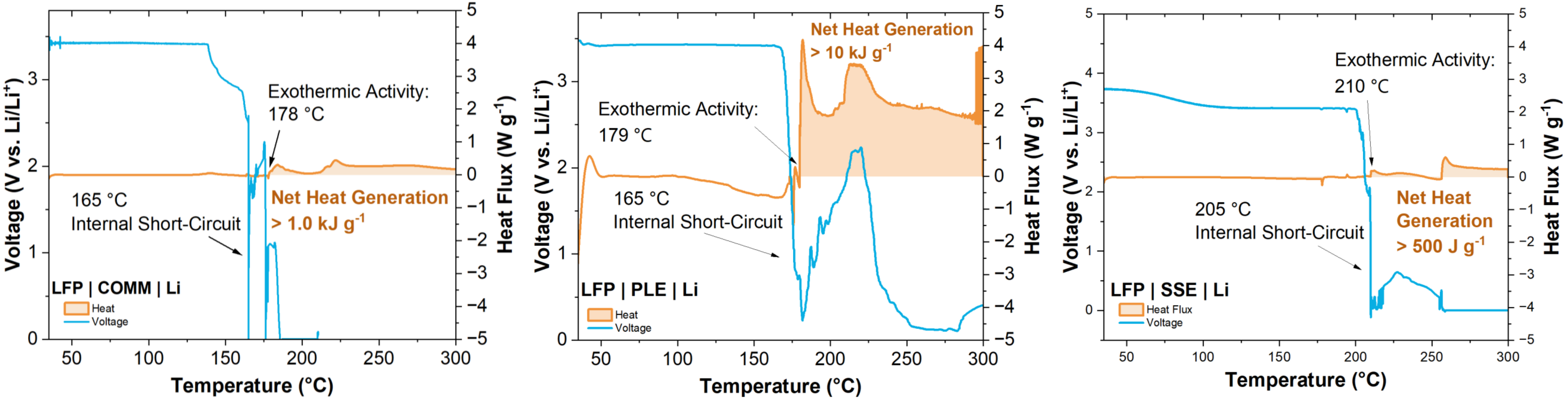
Coin cell scale yields a surprising result



Increase in cell scale highlights the **significance of interfacial reactions** in overall thermal behavior.

1) About **10 kJ g^{-1}** in exotherms from PLE nonflammable liquid electrolyte!

2) Some exothermic heat (**0.5 kJ g^{-1}**) from the SSE despite showing none in DSC.

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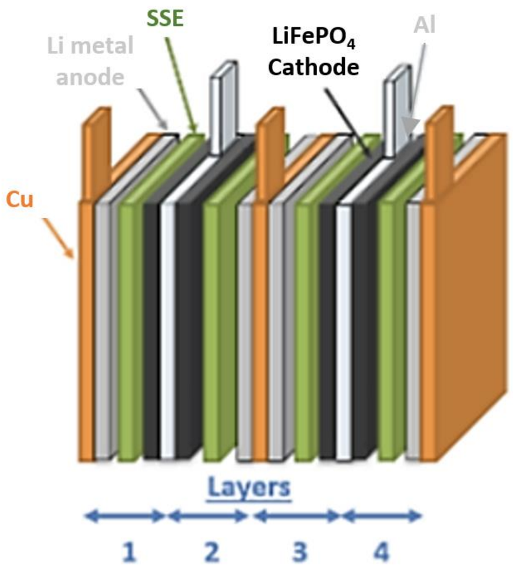
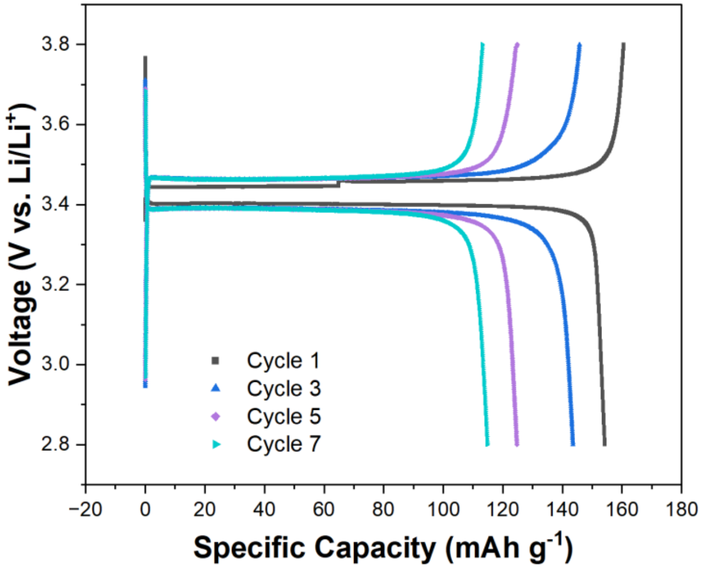
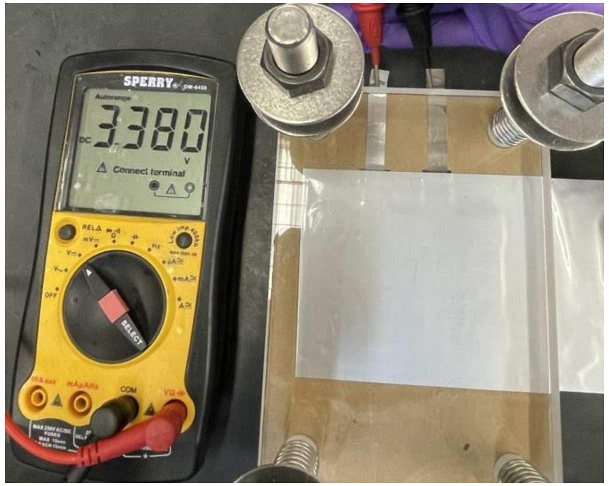
Multilayer Lithium Metal Pouch Cells

Cell Design: 4 layers - 120 mAh



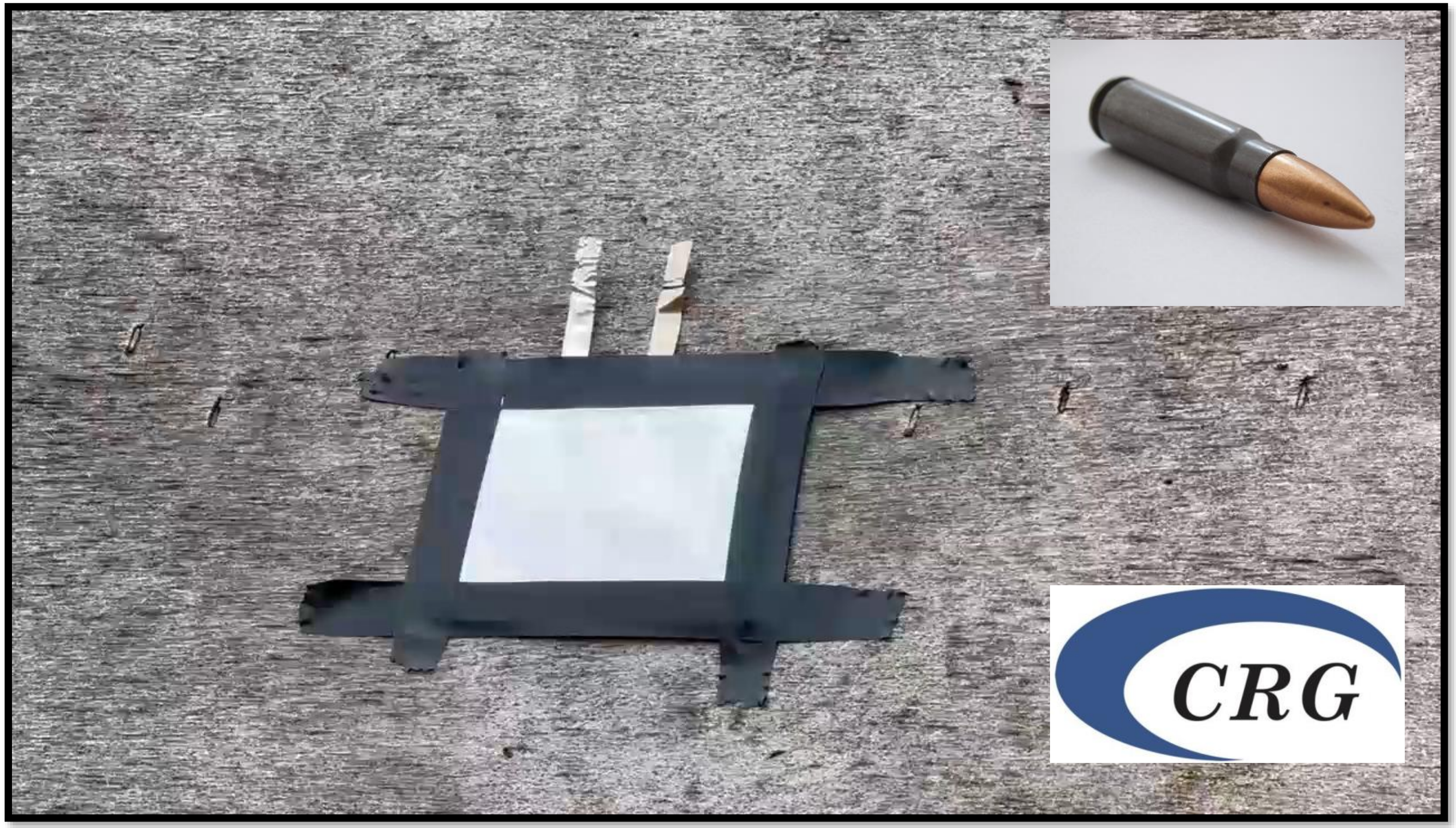




- **Design Parameters:**
  - 120 mAh cell with four internal layers separated by semisolid electrolyte (SSE)
  - 5.3 cm x 7.7 cm pouch cell
  - Two double-sided $LiFePO_4$ cathodes with areal capacity of 1.7 mAh cm^{-2}
  - N/P = 6.5 (20 micron thick Li/Cu anode)
  - Assembled in dry room at the Battery Innovation Center in Newberry, IN

- Cycled at 5.0 mA g^{-1}
- Initial Coulombic efficiency: 96.1%
- 110 mAh of charge delivered for target design of 120 mAh

Ballistic Testing of 100% SOC Multilayer Pouch Cell



- Collaborative ballistic testing courtesy of Cornerstone Research Group (CRG) in Ohio
- **Cell configuration**:
  - 120 mAh; 5-layer pouch
  - LFP Full Cell | fire retarding electrolyte | Li anode
- **Testing Protocol**
  - Precycled and fully charged
  - Shot with 7.62x39mm round (cartridge size of AK-47)
  - Visual/IR monitoring for smoke, flame, or temperature increase

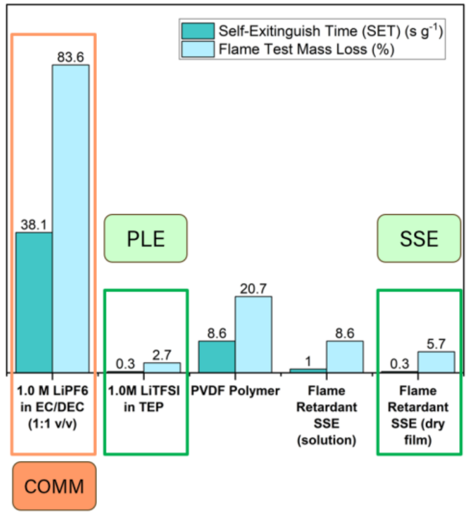
Bullet Type	Velocity (m/s)	Energy (J)	Time of Impact (s)	Temperature Increase from impact to 10s
8.0 g FMJ	738.0 m/s	2,179 J	2.20 s	None detected by IR

Time of Impact Frame by Frame

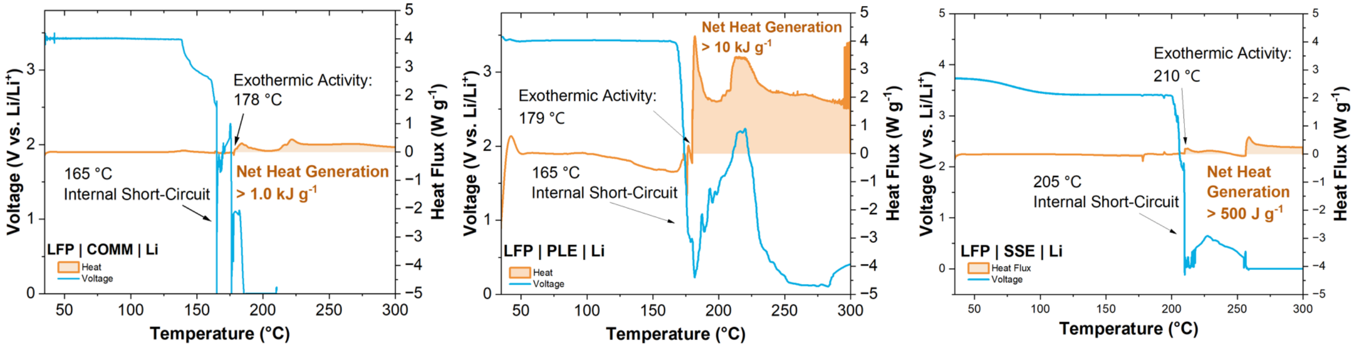
2.20 s **2.23 s** **2.27 s**

Conclusions and Outlook

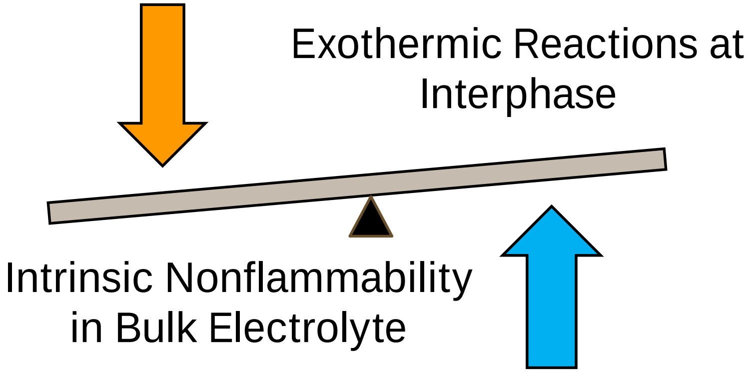
1. Fire retardancy may be conferred on liquid and semisolid electrolytes through integration of combustion inhibitors.



2. However, materials-level thermal analysis of cell safety overlooks exothermic activity at interfaces, especially under extreme conditions similar to thermal runaway.



3. More work remains to analyze interfacial reactions at multiple scales and assess the effectiveness of nonflammable electrolyte design strategy.



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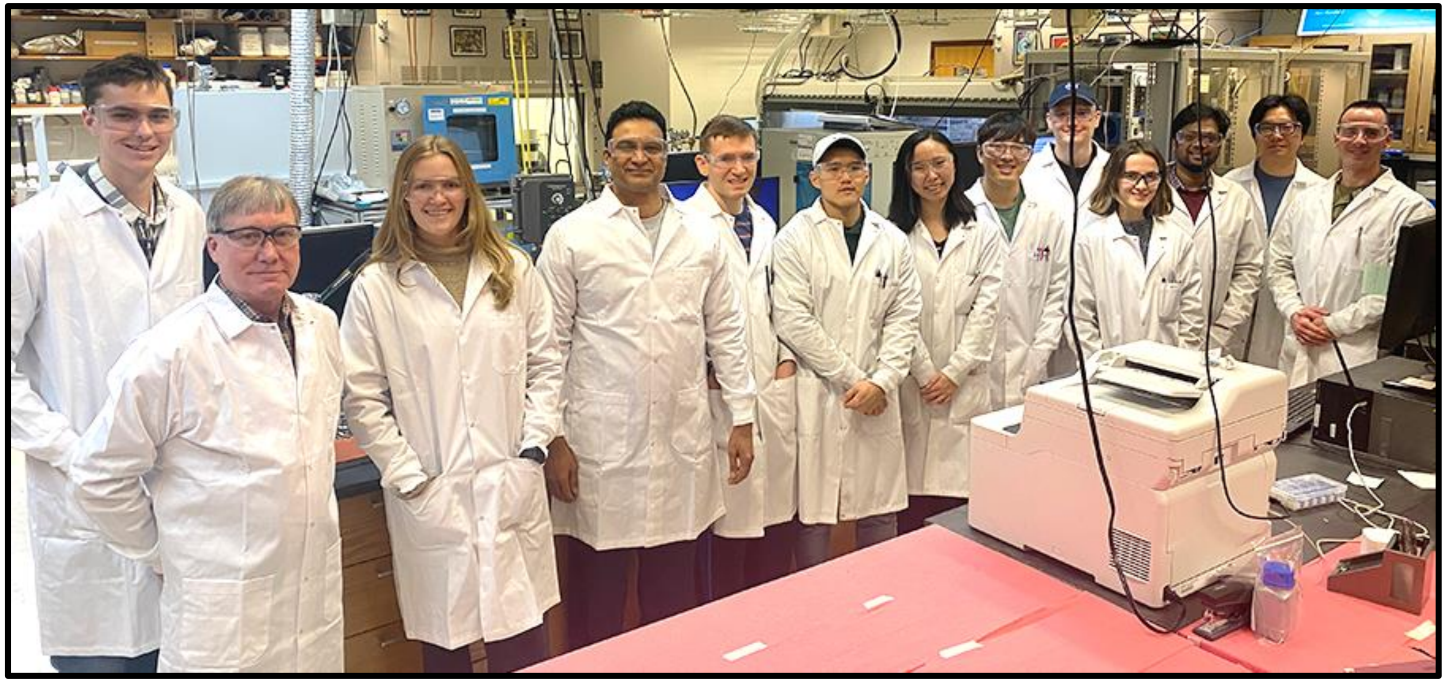
Acknowledgements



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