PURDUE UNIVERSITY

Energy and Transport Sciences Laboratory

Mechanistic Understanding of Battery Safety

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P2SAC Fall 2024 Conference

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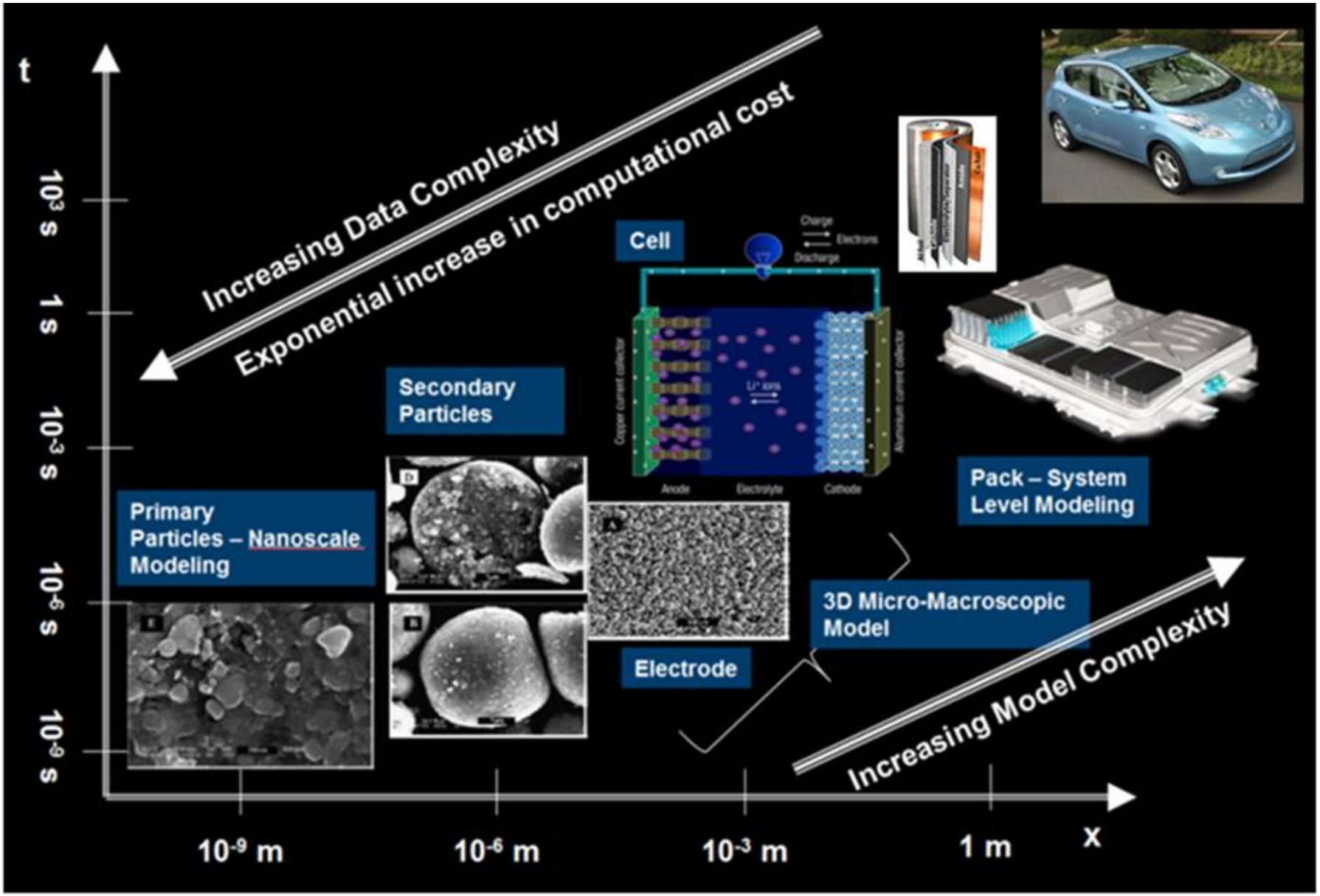
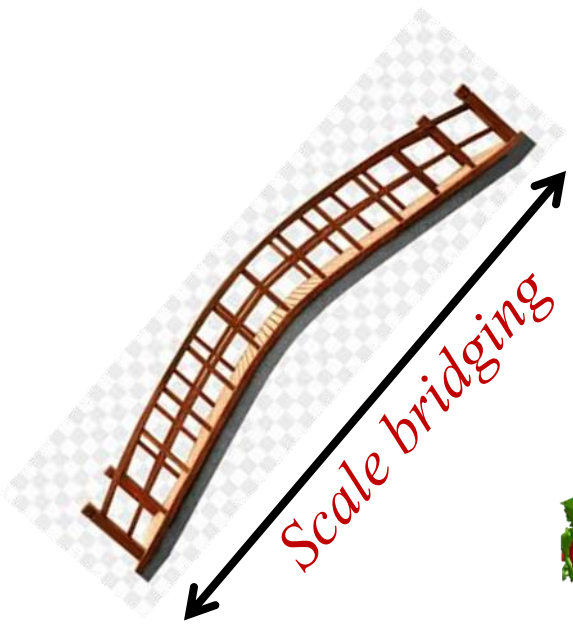
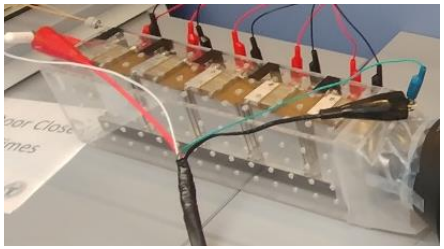
Lithium-ion battery – multi-scale problem

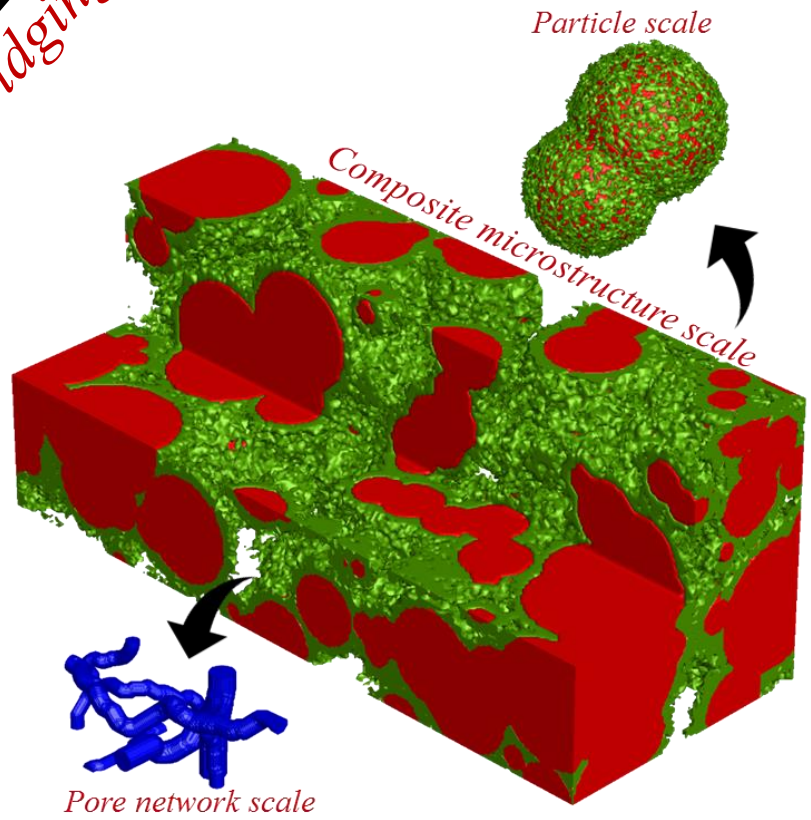


*Mukherjee, Pannala, Turner, *Handbook of Battery Materials* (2011); *Lithium Power Conference* (2011).

Heterogeneity and stochasticity at scales





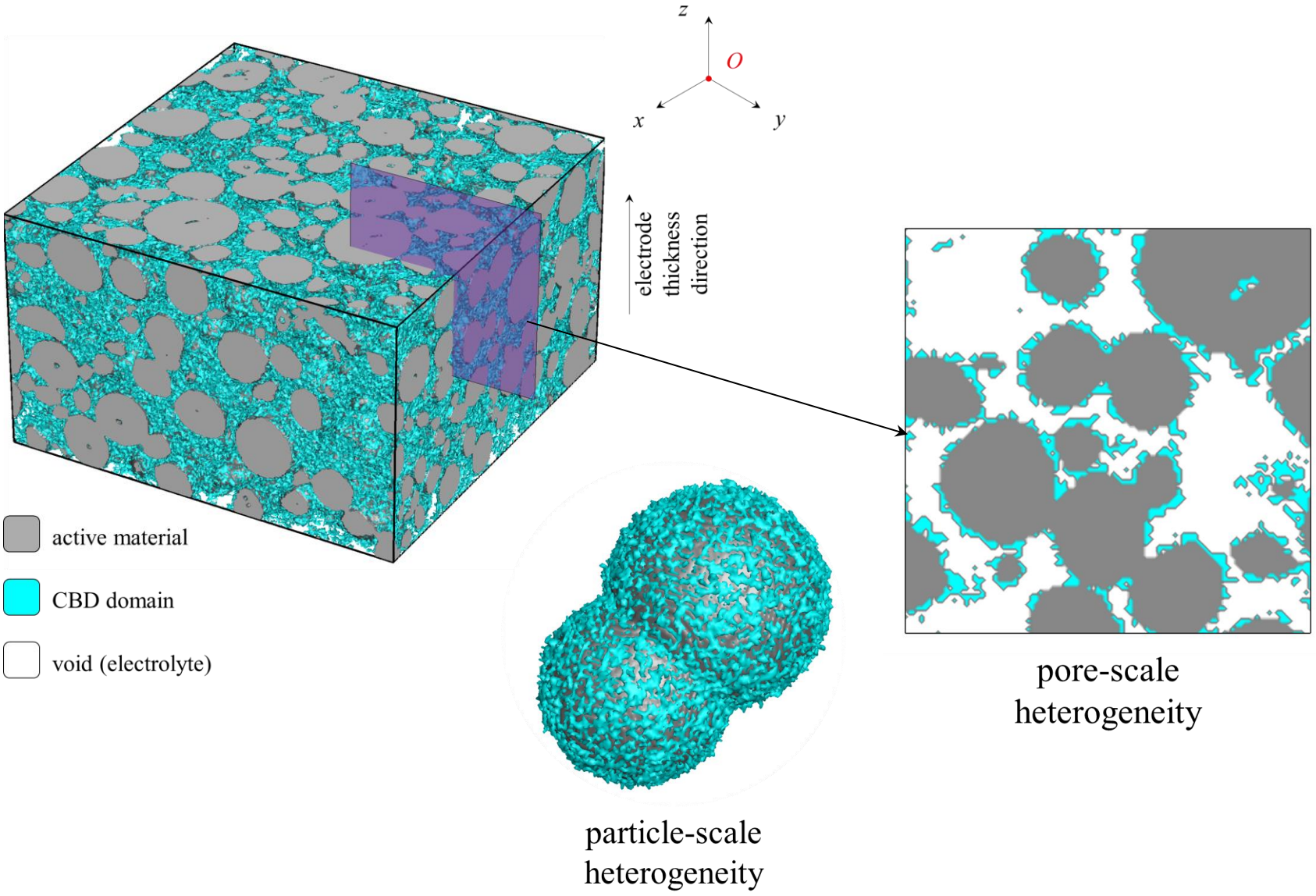


Safety & degradation

Physics-based analytics (modeling & experiments) at scales

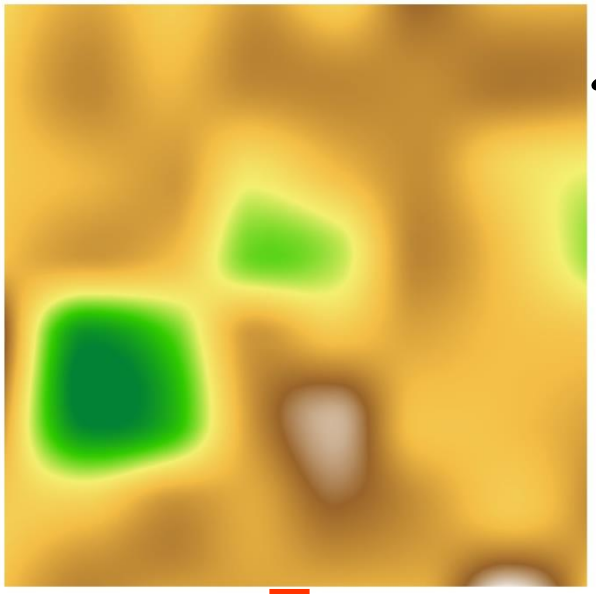
*Mistry, Smith and Mukherjee, *ACS Applied Materials and Interfaces* **10**, 28644 (2018)

Electrode heterogeneity at scales



*Mistry, Smith and Mukherjee, *ACS Applied Materials and Interfaces* 10, 28644 (2018)
*Tomography data from Ebner *et al.*, *Advanced Energy Materials* 3, 845 (2013)

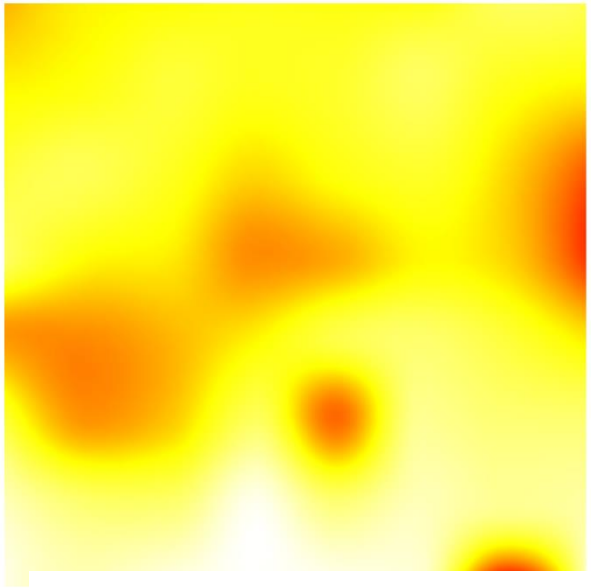
Electrode stochasticity map→ nonuniform fields



ε_a (%vol.)

70
65
60
55
50
45
40
35
30

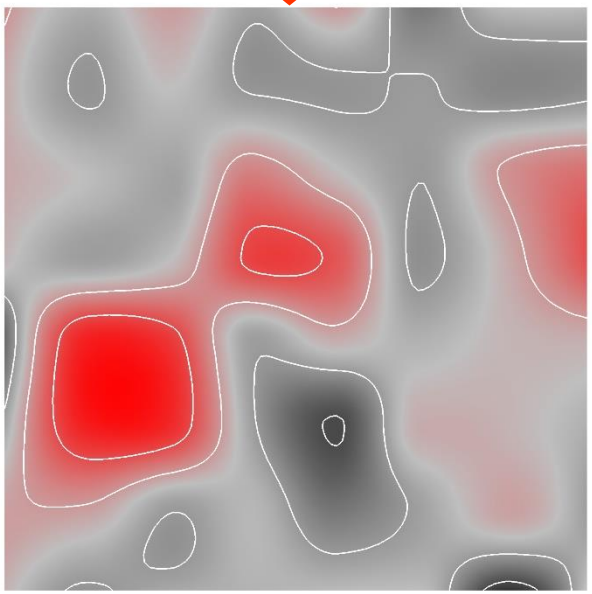
Intrinsic stochasticity



$\pi^* / \pi^*_{\max}$

1
0.8
0.6
0.4
0.2
0

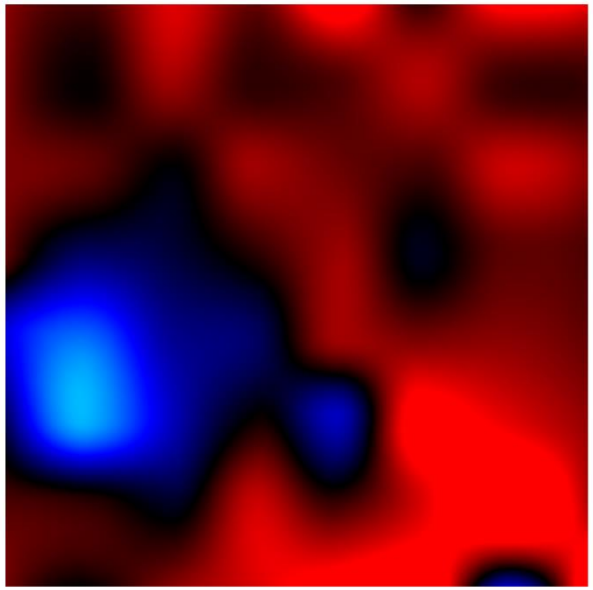
Lithium plating signature



x in Li_xC_6

1
0.9
0.8
0.7
0.6
0.5

Electrochemical signature



Q(J/cc)

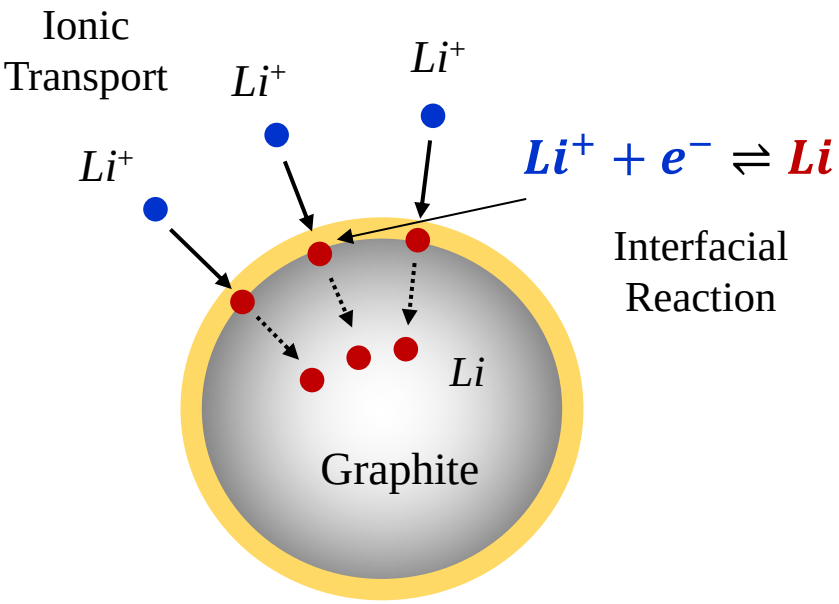
135
130
125
120
115
110
105
100

Thermal signature

*Mistry, Mukherjee *et al.*, *Journal of The Electrochemical Society*, **167**, 090542 (2020)

Interfacial reactive transport interactions

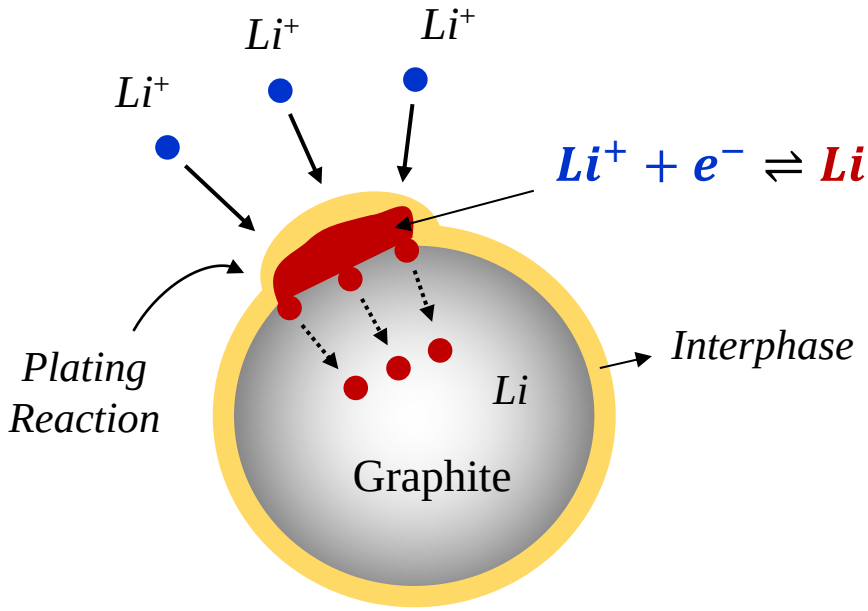
Reactive transport: nominal operating condition



Mass balance at particle surface:

Ionic flux (electrolyte) ~ Diffusive flux (particle)

Reactive transport: operational extremes



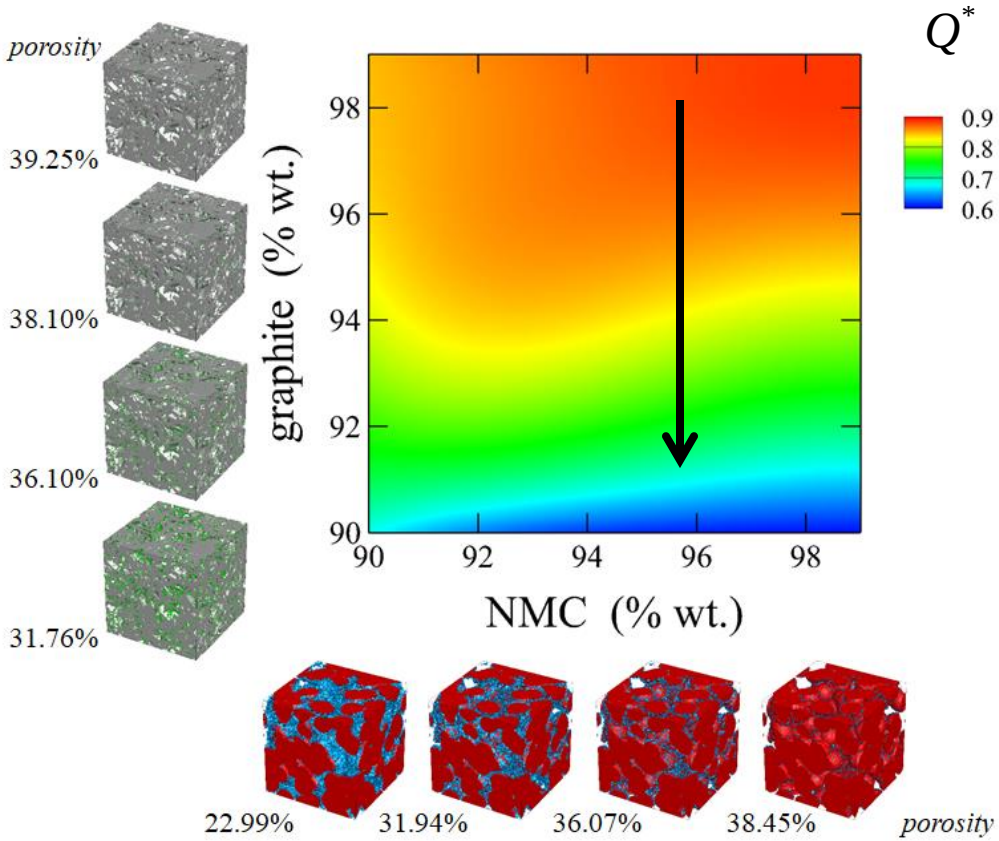
Mass balance at particle surface:

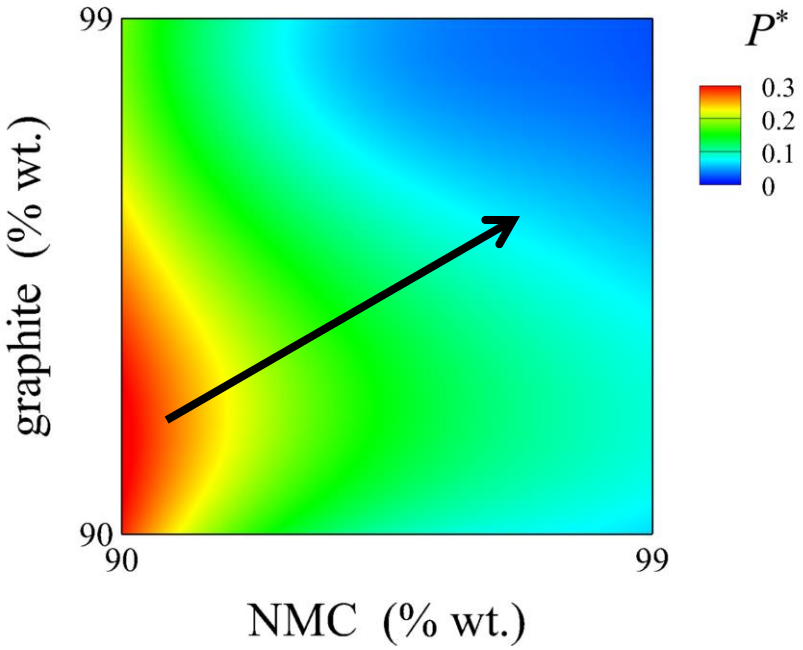
Ionic flux (electrolyte) > Diffusive flux (particle)

Implications:

- Fast Charging of lithium-ion batteries
- Low-temperature operation

Electrochemical – thermal – chemical interactions





propensity for plating

*Mistry, Smith and Mukherjee, *ACS Applied Materials and Interfaces* 10, 28644 (2018)

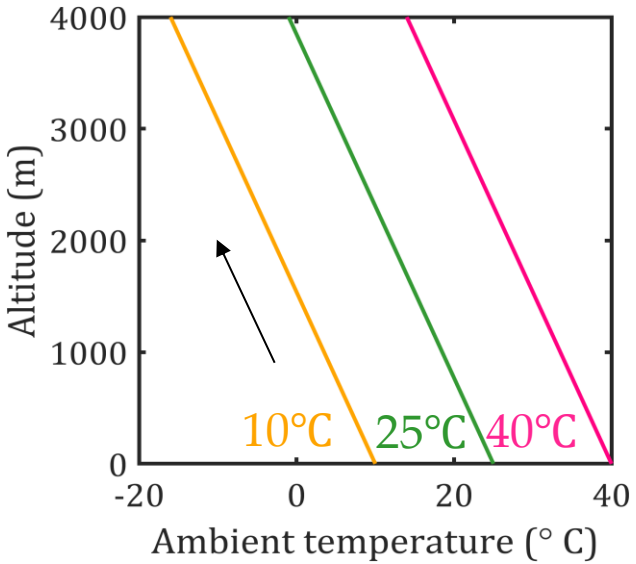
Sustainable mobility solutions: rise of eVTOLs

Electric vertical take-off and landing (eVTOL) aircrafts

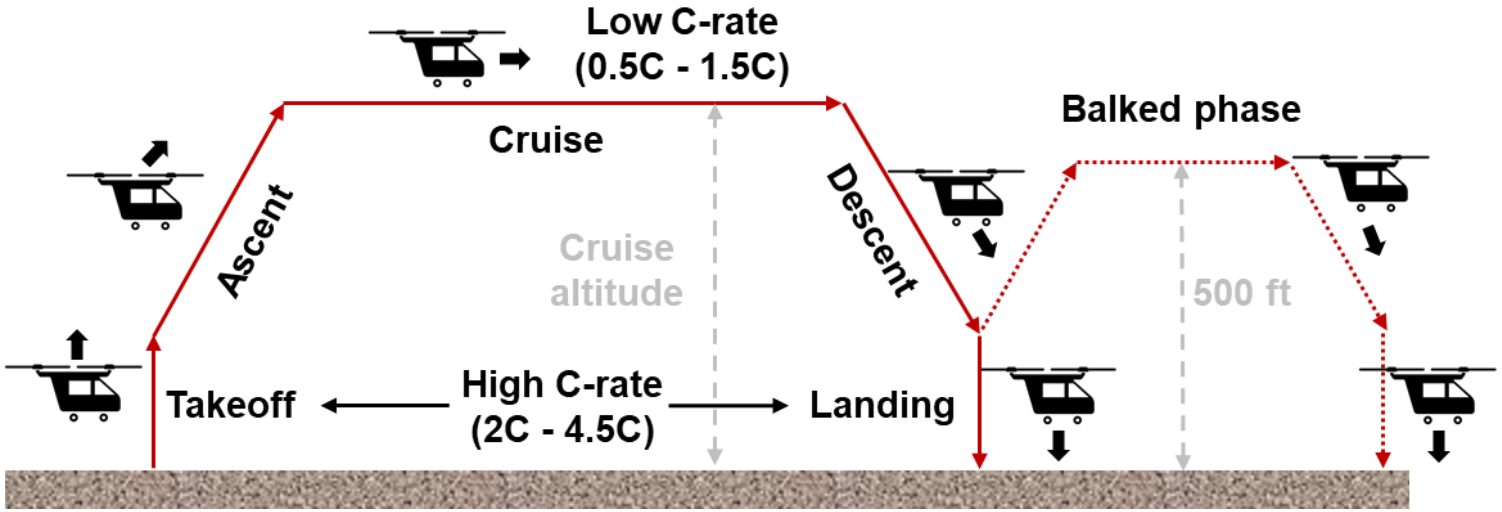
*https://www.volocopter.com/solutions/

*https://www.jobyaviation.com/

Variation in ambient environment



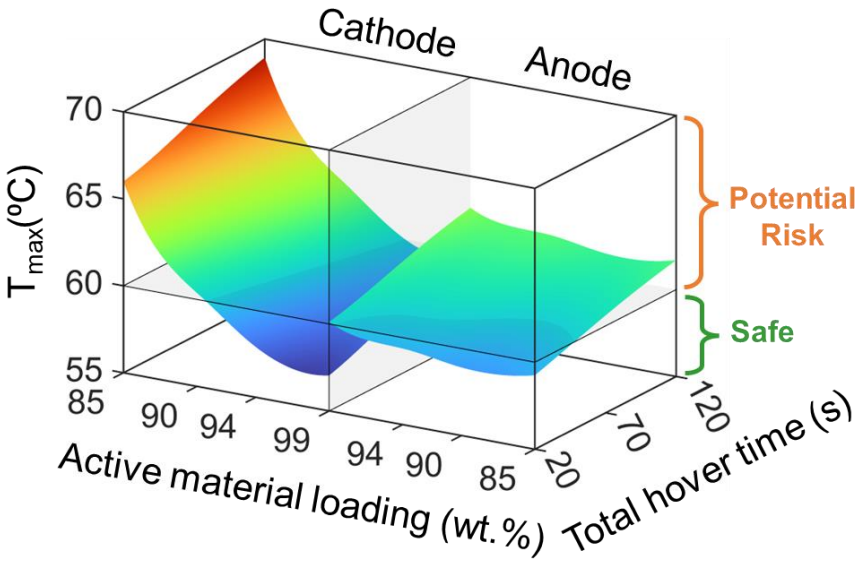
Typical eVTOL mission scenario



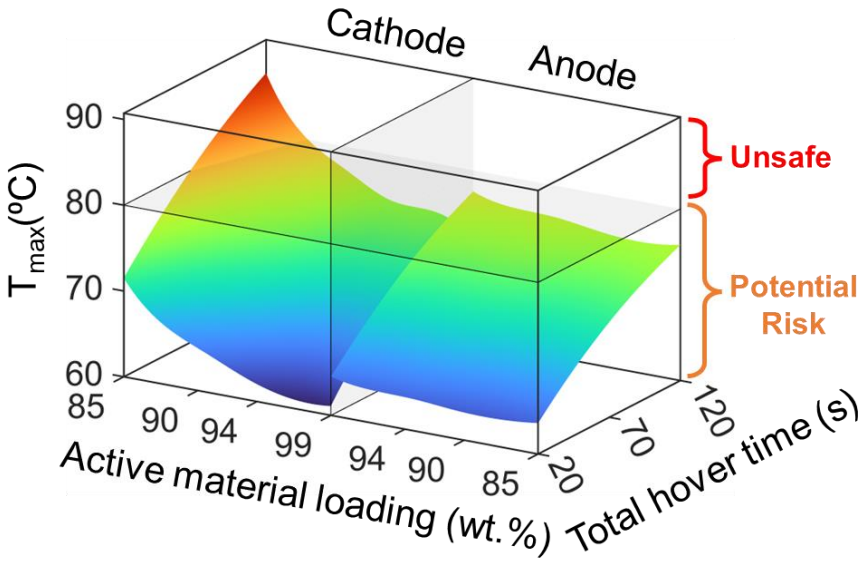
*Ayyaswamy, Vishnugopi and Mukherjee, *Joule,* **7(9),** 2016 (2023).

Thermal safety considerations in eVTOLs

After mission phases

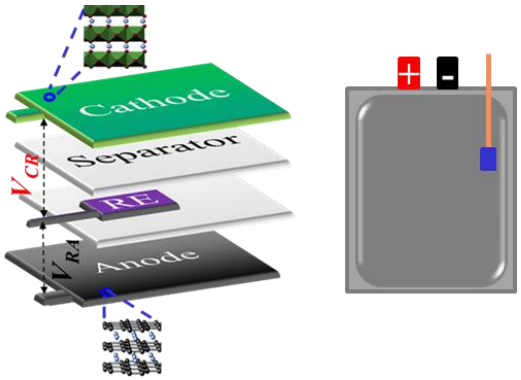


After balked phases

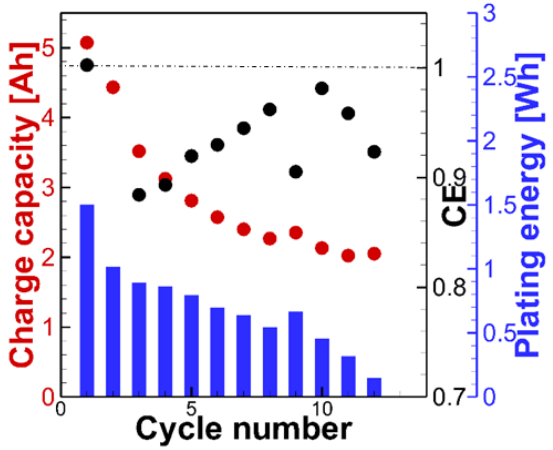


- Morphological differences in electrodes can deliver asymmetrical temperature response under eVTOL operation.
- Safety analysis of eVTOL batteries must always exercise inclusion of emergency balked phases, since they exhibit highest cell temperatures during any mission.

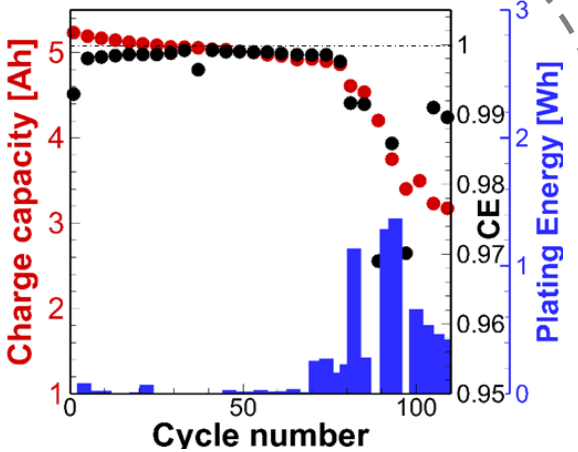
Degradation under operational extremes



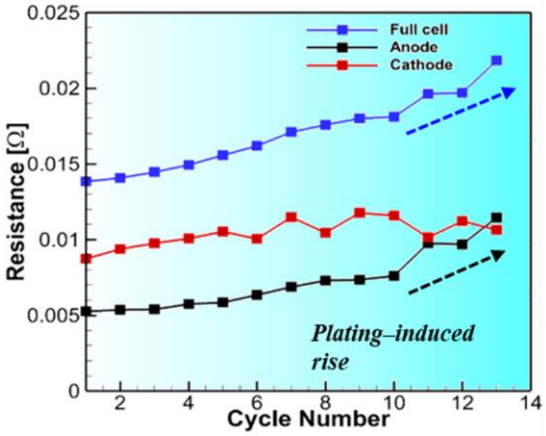
3-electrode analytics

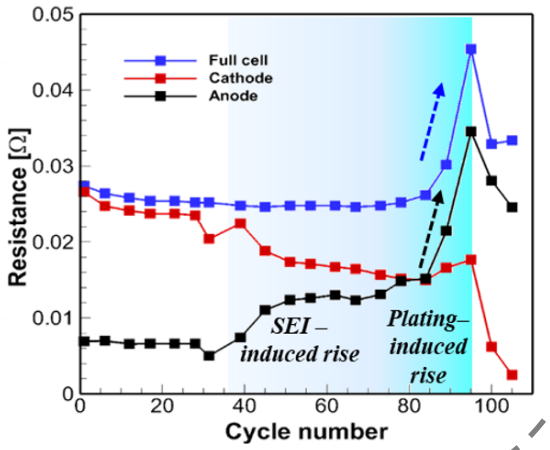


-5°C



40°C

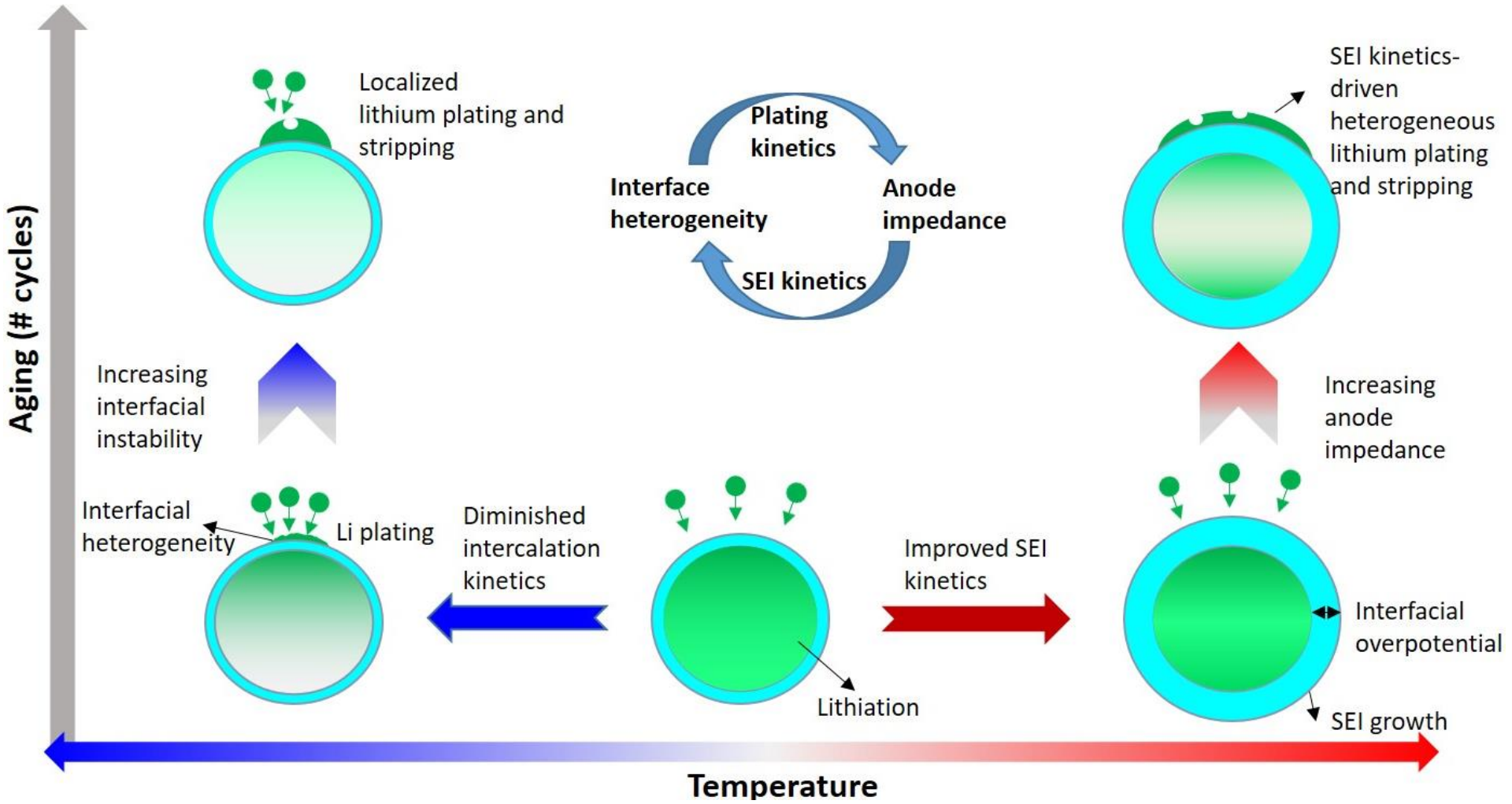




*Rangarajan, Mukherjee *et al., Cell Reports Physical Science*, 3, 100720 (2022).

*Rangarajan, Mukherjee *et al.*, *ACS Omega, 6*, 33284 (2021)

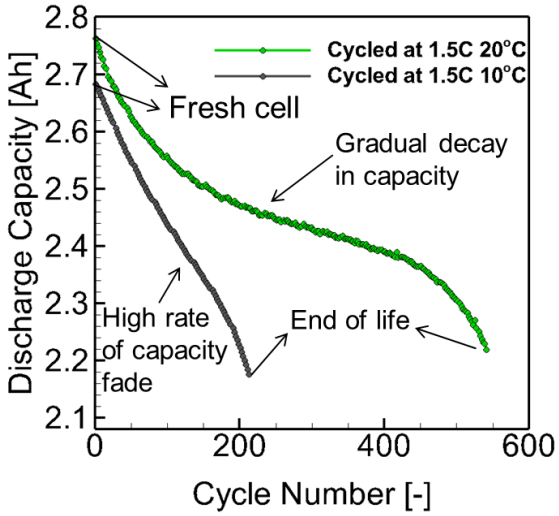
Mechanistic interactions: temperature-degradation-safety



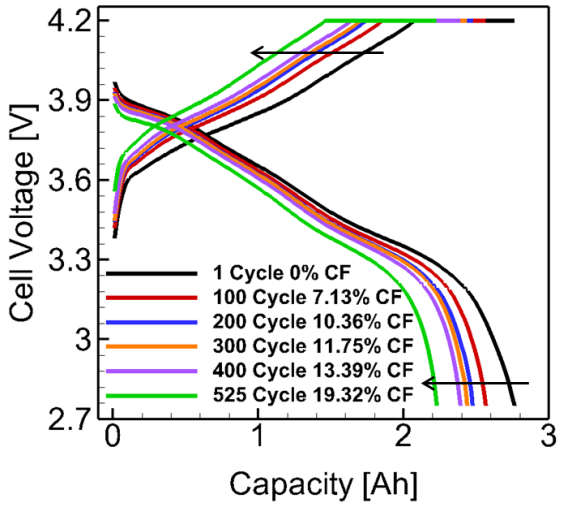
*Rangarajan, Mukherjee *et al.*, *Cell Reports Physical Science*, 3, 100720 (2022)

Cell Aging Characteristics: Temperature dependence

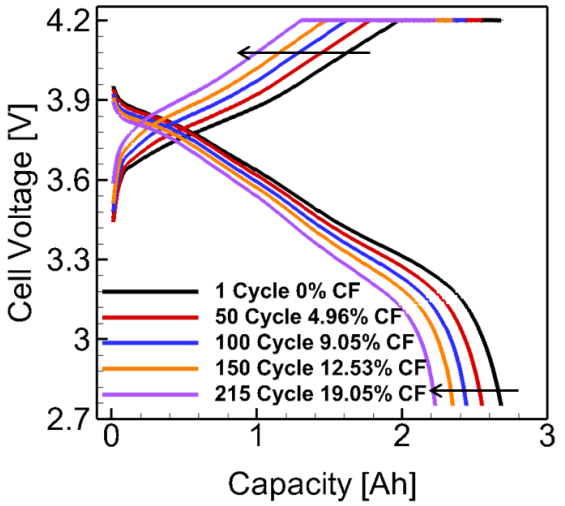
Cell capacity loss



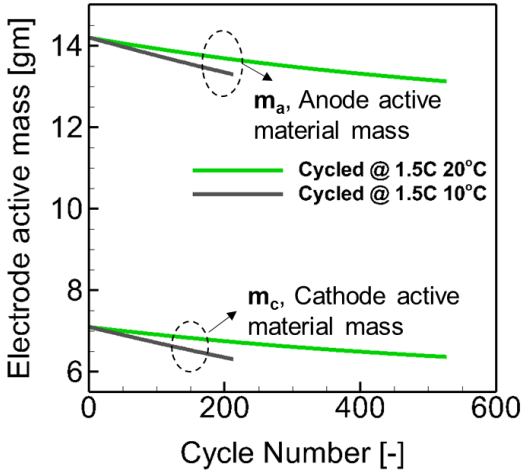
Cell cycled at 1.5C, 20°C

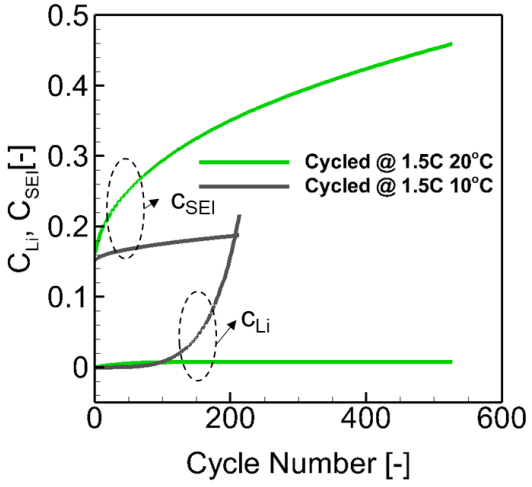


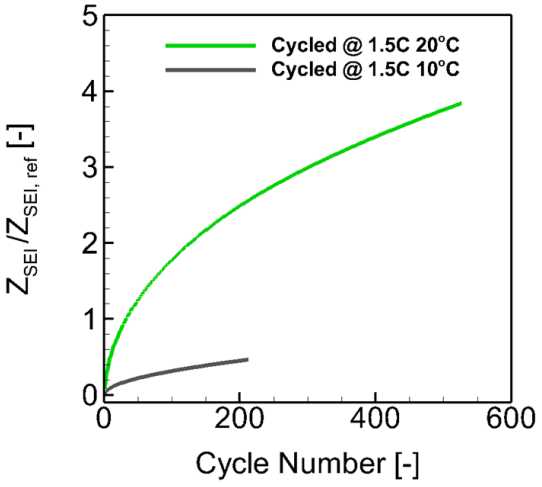
Cell cycled at 1.5C, 10°C



Quantification of aging parameters: Electrochemical aging framework







*Kabra, Karmakar, Vishnugopi, Mukherjee, *Energy Storage Materials* (accepted), 2024.

Exothermic Reactions Mechanisms of Fresh/Aged Cells

Progression of Thermal Runaway in an aged Li-ion Cell

Temperature

$$Q_{ISC} = \frac{\eta_{ISC} CV}{\tau_{ISC}} \qquad if\ T \geq T_c,\ t_c \leq t \leq \tau_{ISC} + t_c$$

Internal Short Circuit (ISC)

$$Q_e = H_e A_e c_e exp\left(\frac{-E_{a,a-e}}{RT}\right)$$

Electrolyte Decomposition

$$Q_c = H_c A_c \alpha(1-\alpha) exp\left(\frac{-E_c}{RT}\right)$$

Cathode Decomposition

$$Q_{a-e} = H_{a-e} A_{a-e} c_{a-e} exp\left(\frac{-Z_{SEI}}{Z_{SEI,ref}}\right) exp\left(\frac{-E_{a-e}}{RT}\right)$$

Anode-Electrolyte Reaction

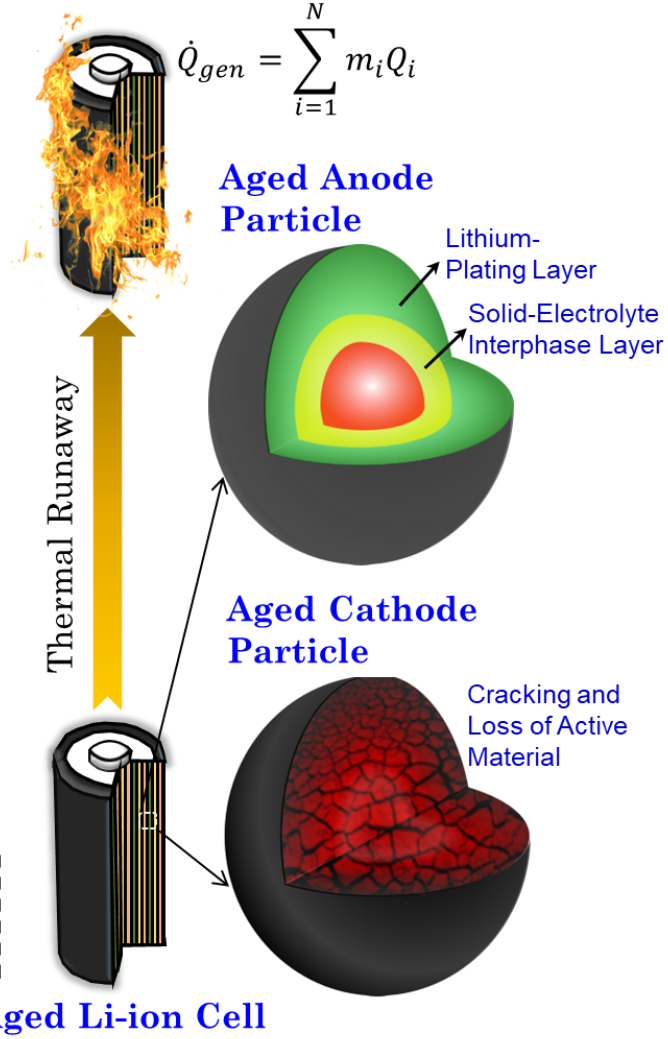
$$Q_{Li-e} = H_{Li-e} A_{Li-e} \frac{k_{Li} c_{Li}}{1 + k_{Li} c_{Li}} c_e exp\left(\frac{-E_{a,Li-e}}{RT}\right)$$

Plated Lithium-Electrolyte Reaction

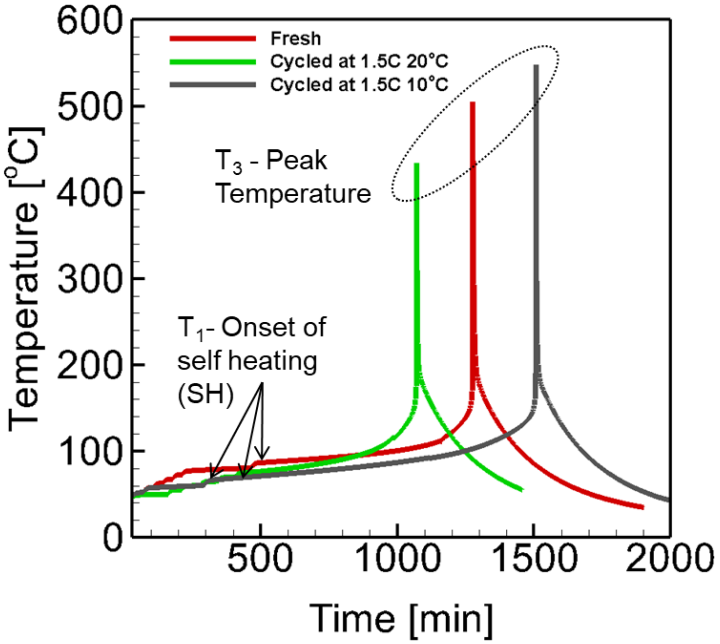
$$Q_{SEI} = H_{SEI} A_{SEI} c_{SEI} exp\left(\frac{-E_{a,SEI}}{RT}\right)$$

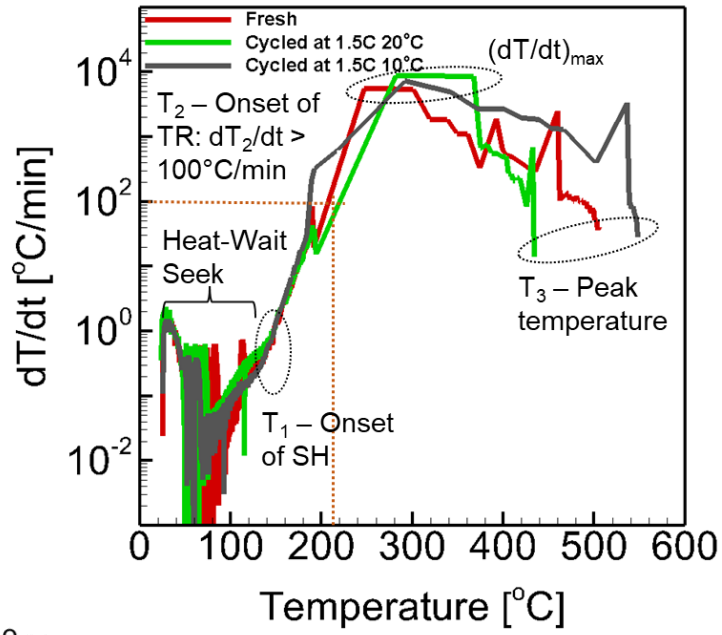
Metastable SEI Decomposition

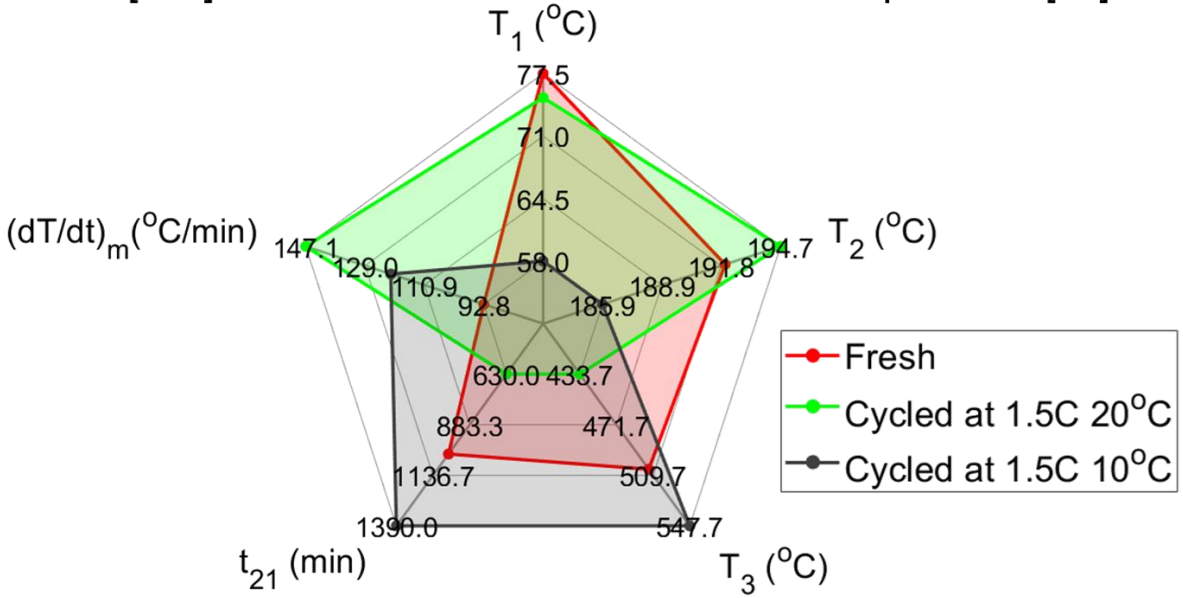
$$\dot{Q}_{gen} = \sum_{i=1}^{N} m_i Q_i$$



ARC Thermal Signatures of Fresh/Aged Cells





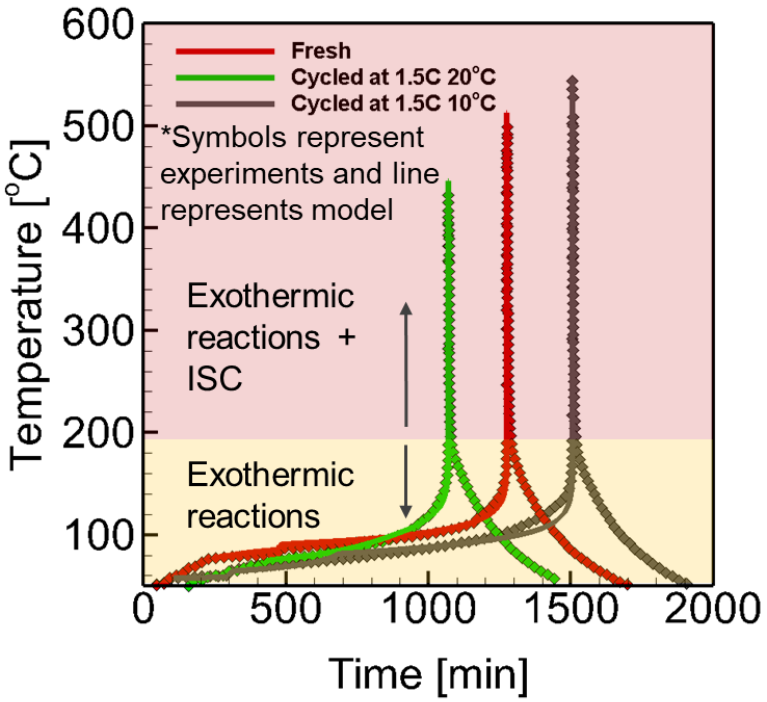


Thermal Runaway: Model Validation

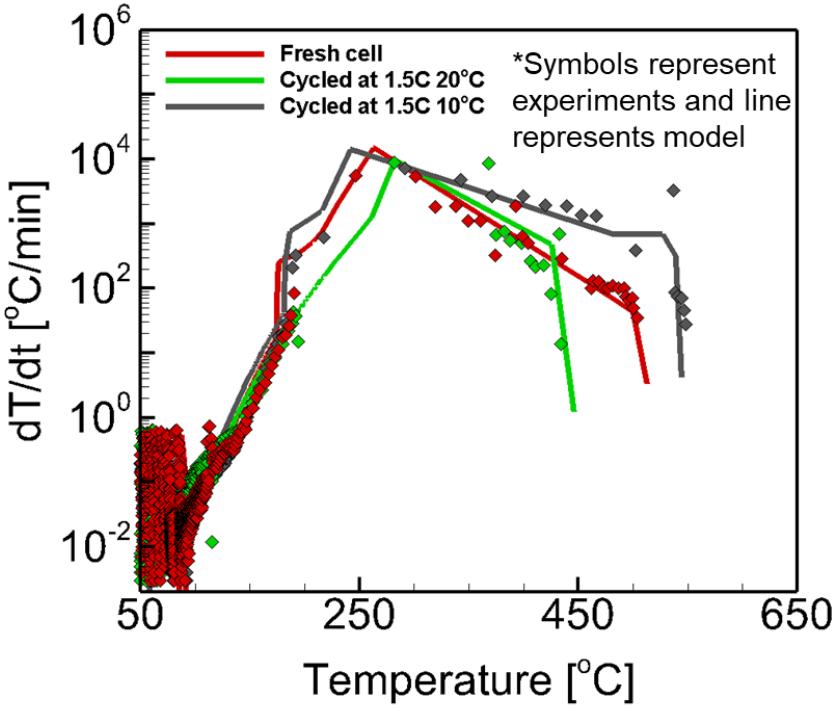
Virtual ARC simulations of Fresh/Aged Cells

Energy Equation: $M_{cell}C_{p,cell}\frac{dT_{cell}}{dt} = \dot{Q}_{gen} - h_{ARC}S_{cell}[T_{cell} - T_{ARC}]$

Temperature Verification



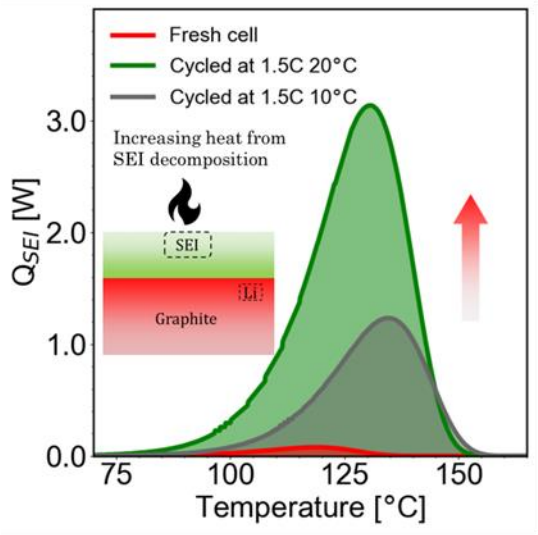
Temperature Rate Verification

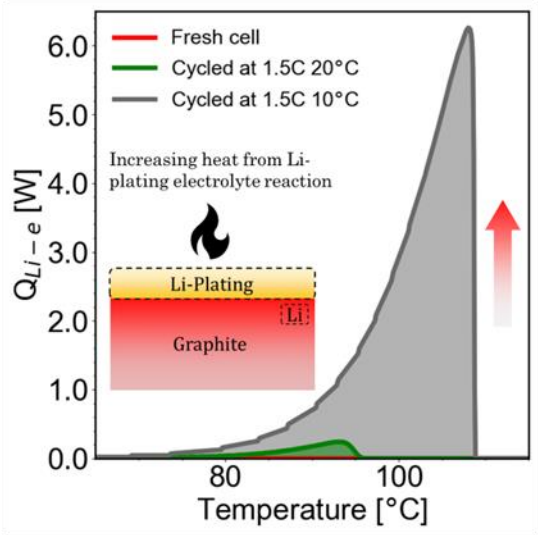


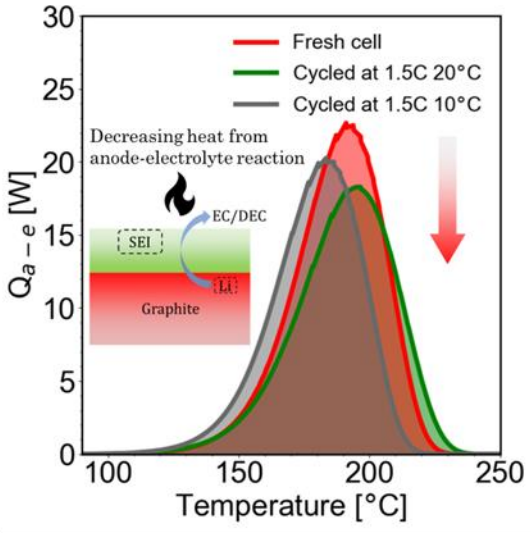
*Kabra, Karmakar, Vishnugopi, Mukherjee, *Energy Storage Materials* (accepted), 2024.

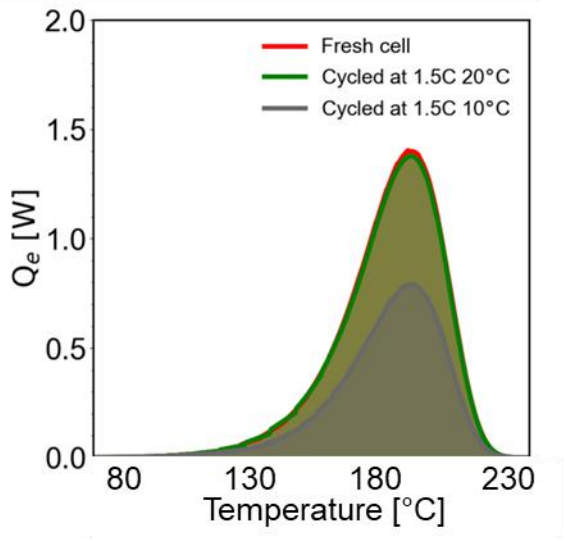
Insights from ARC Thermal Runaway Model

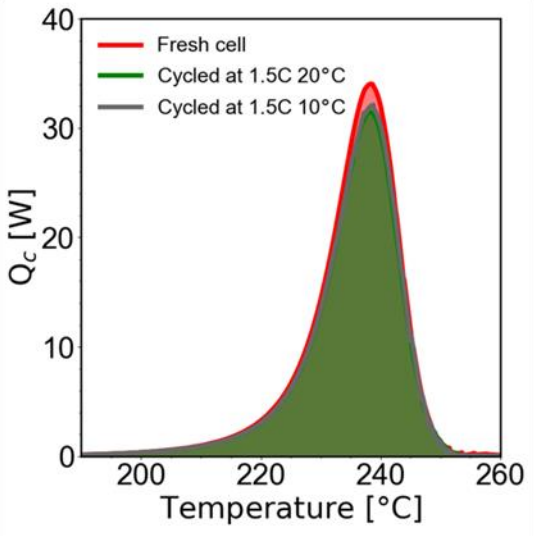
Heat Generation Characteristics from Exothermic Reactions

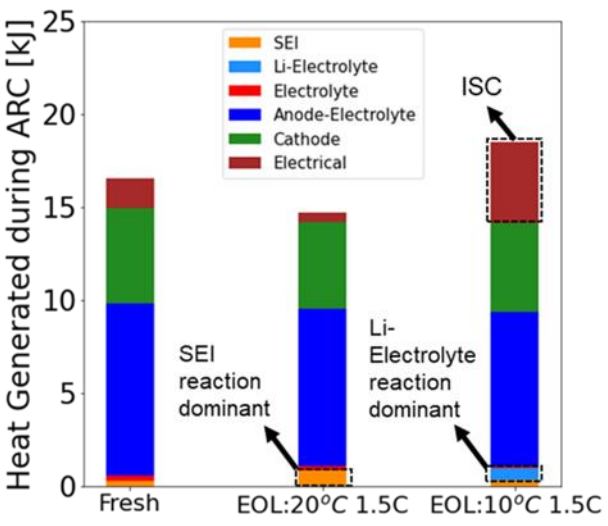






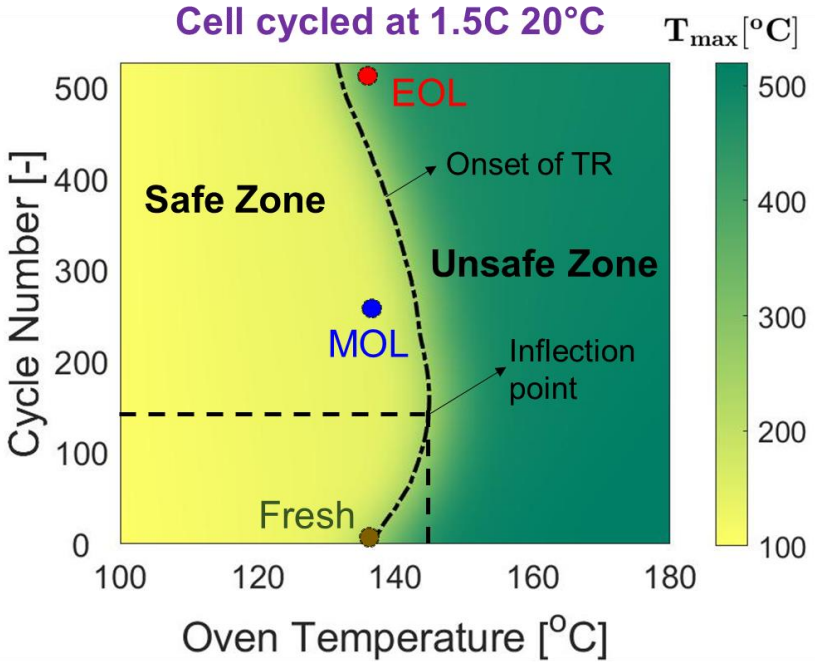


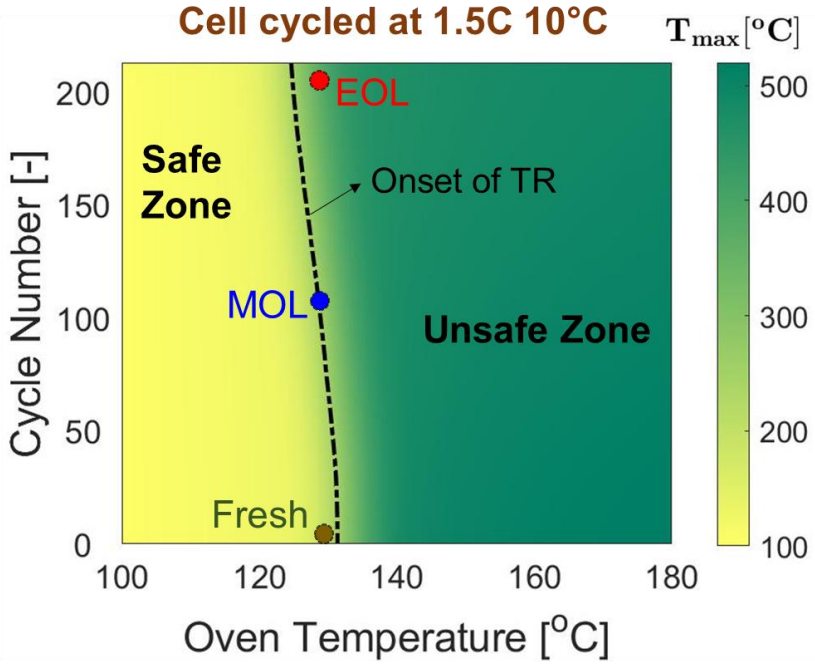




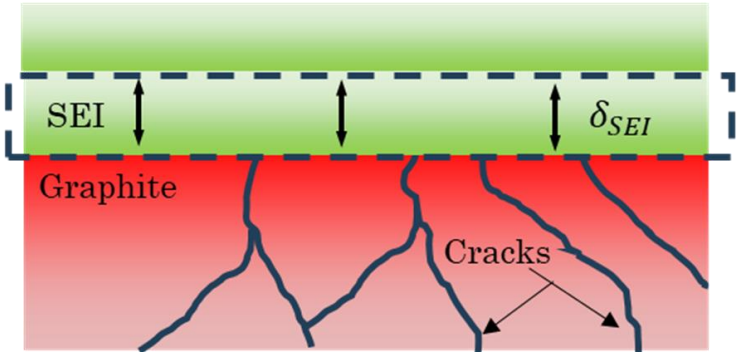
*Kabra, Karmakar, Vishnugopi, Mukherjee, *Energy Storage Materials* (accepted), 2024.

Thermal stability: fresh & aged Cells

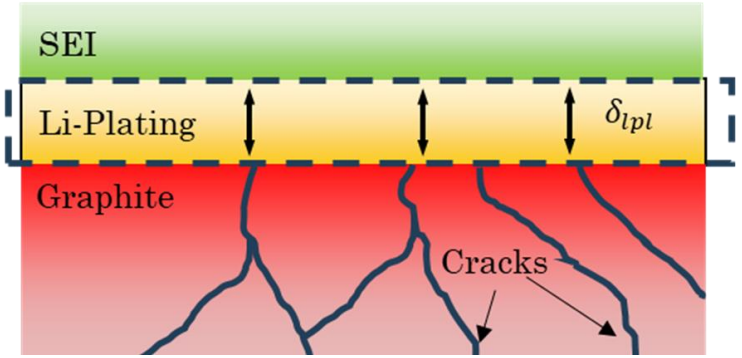




High-Temperature Cycling

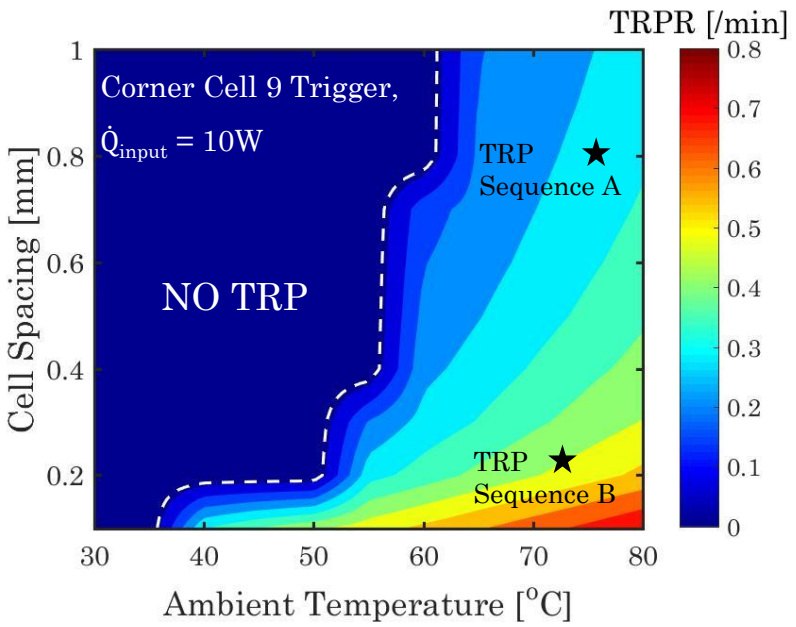


Low-Temperature Cycling

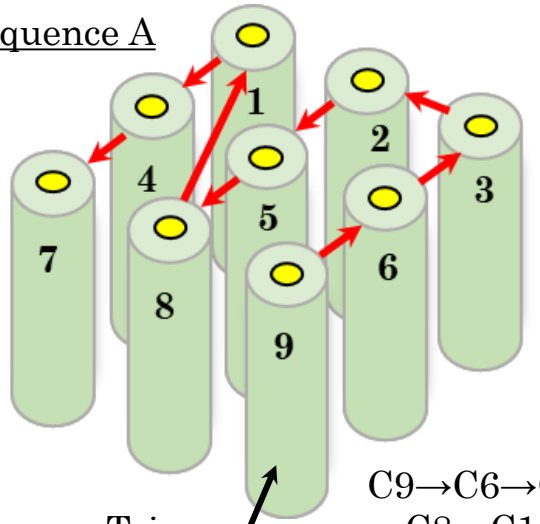


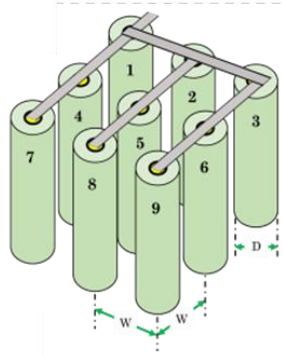
*Kabra, Karmakar, Vishnugopi, Mukherjee, *Energy Storage Materials* (accepted), 2024.

Thermal runaway propagation (TRP) characteristics



TRP Sequence A

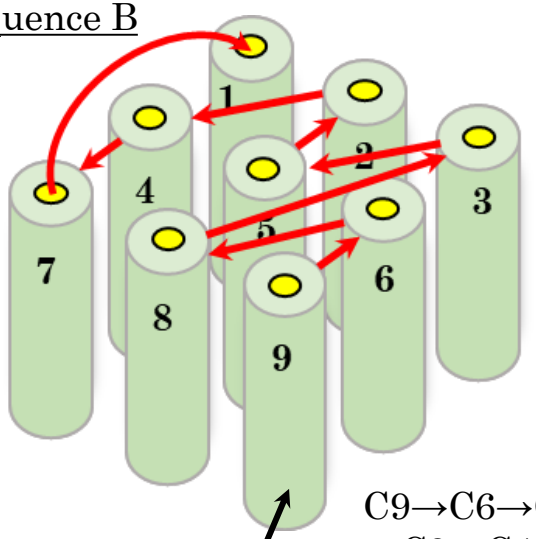




Trigger Cell

C9→C6→C3→C2→C5 →C8→C1→C4→C7

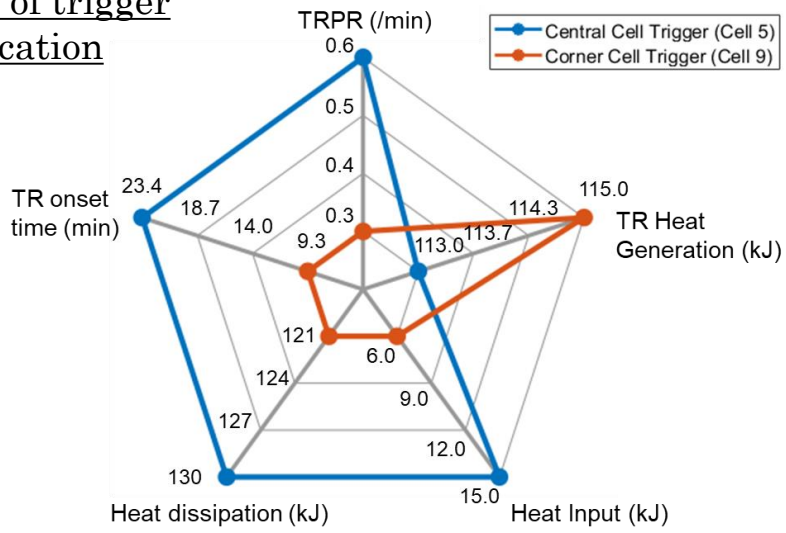
TRP Sequence B



Trigger Cell

C9→C6→C8→C3→C5 →C2→C4→C7→C1

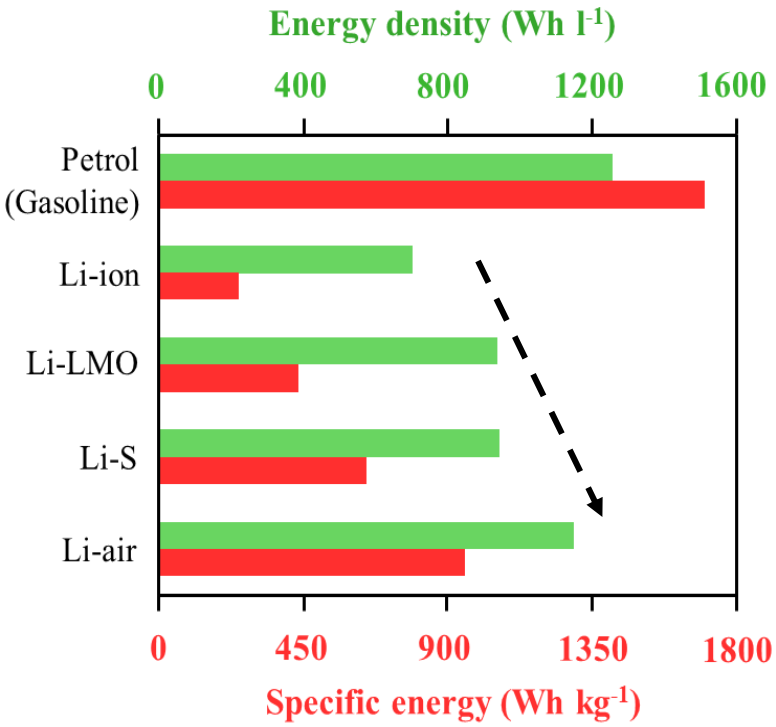
Effect of trigger cell location

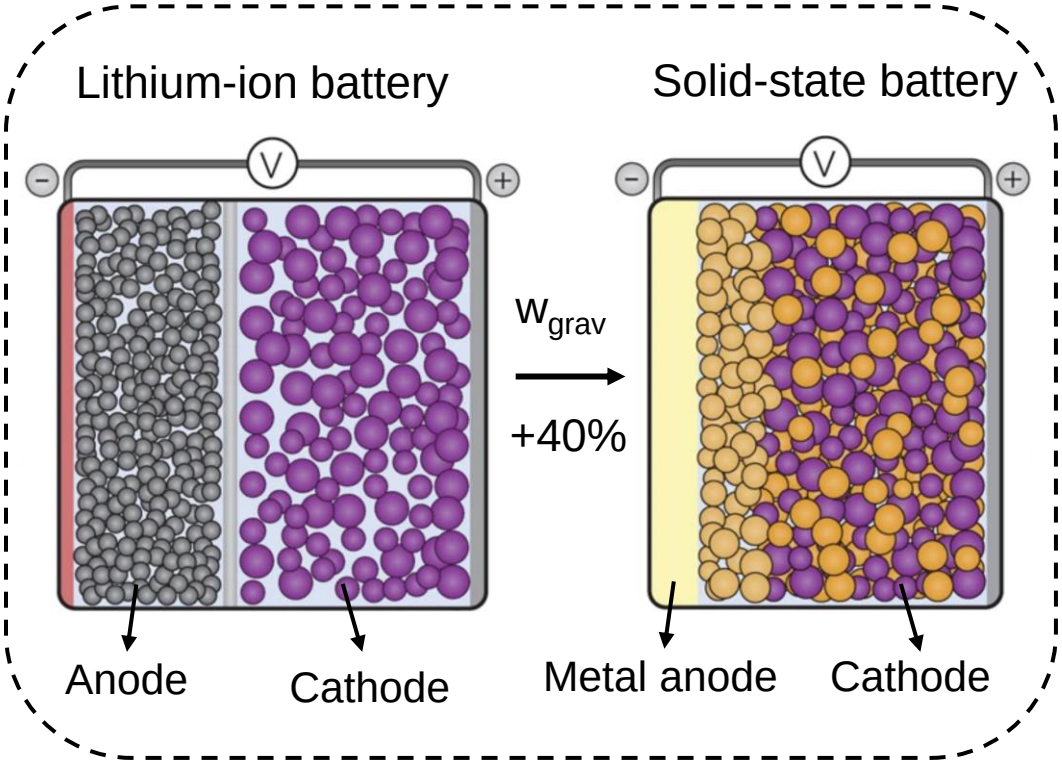


*Karmakar, Mukherjee *et al.*, *Energy Technology*, 12 (2), 2300707 (2022).

*Karmakar, Mukherjee *et al.*, *Journal of The Electrochemical Society*, 171, 010529 (2024).

Opportunities for Li metal chemistry

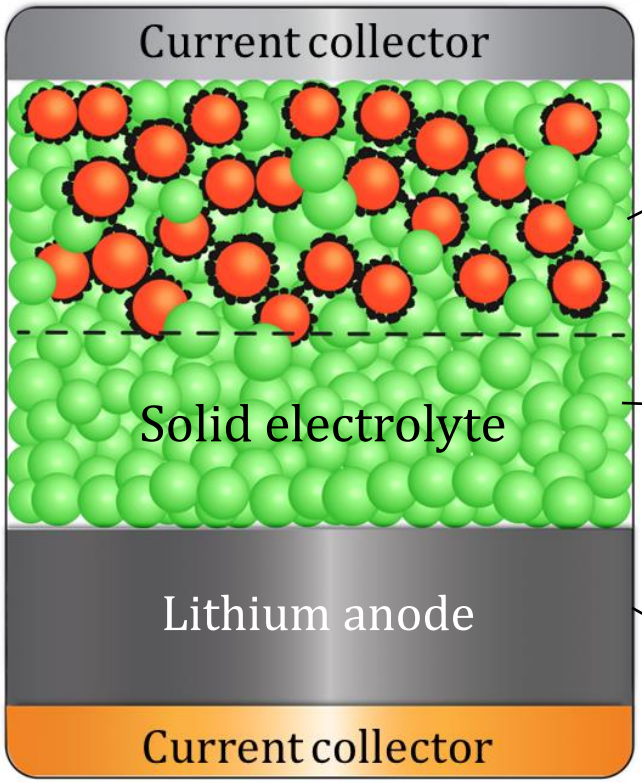




*Lin *et al.*, *Nature nanotechnology*, 12, 194 (2017).

*Janek and Zeier, *Nature Energy,* 2016, 1, 1 (2016).

Why do we need to evaluate solid-state battery safety?



Cathode active material

Solid electrolyte

Solid-state cathode with **fast charge** capability

Challenge: large heat generation, oxygen liberation from cathode

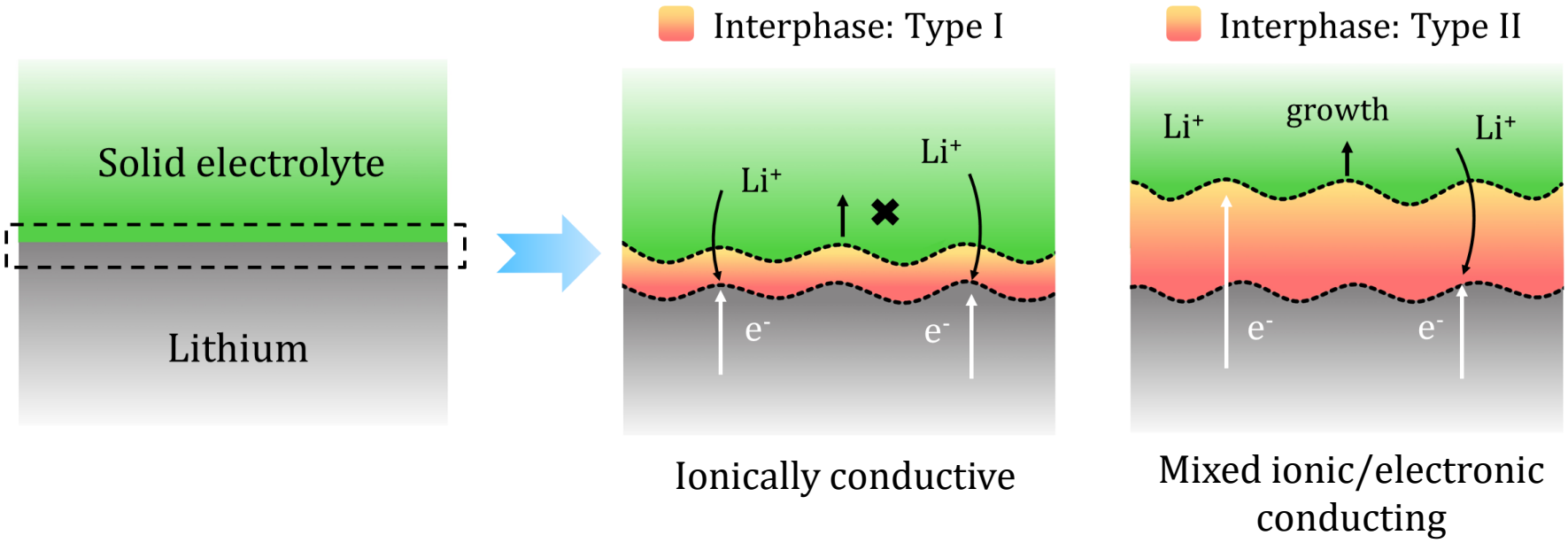
Thin separator for **high energy** density

Challenge: short-circuit (e.g., filaments)

Li anode for high energy/power density

Challenge: high reactivity, low melting point

Solid electrolyte/lithium interface



Hypothesis: fundamental correlation between electrochemical interactions and thermal stability

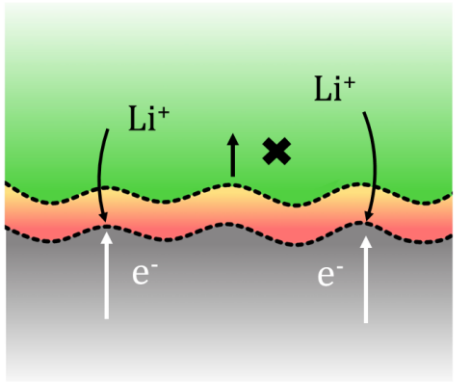
(1) In the pristine state, does the solid electrolyte/Li-metal interface undergo thermal runaway?

(2) Do degradation mechanisms at the solid-solid interface (e.g., interphase growth) alter the thermal stability?

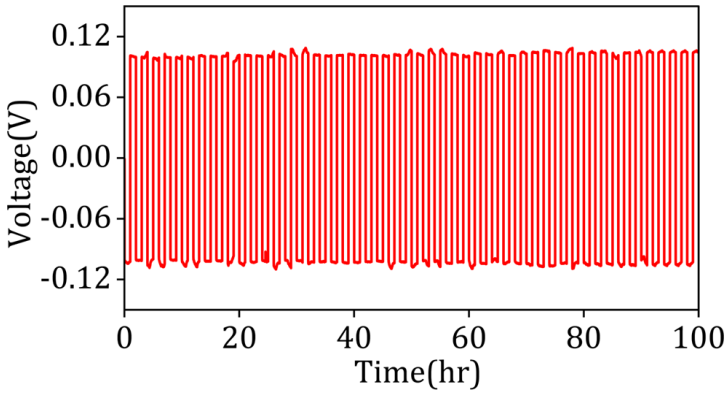
*Vishnugopi, Hasan, Zhou and Mukherjee, *ACS Energy Lett.*, 8, 398 (2023).

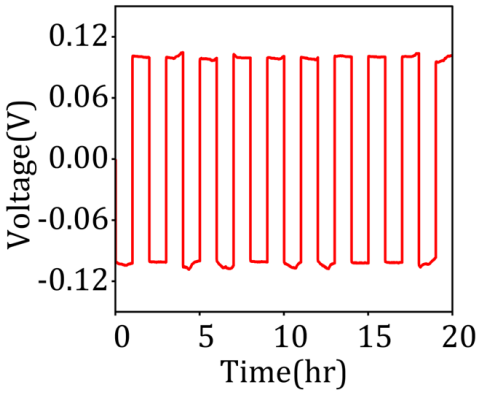
Electrochemical signature: interphase

Interphase: Type I

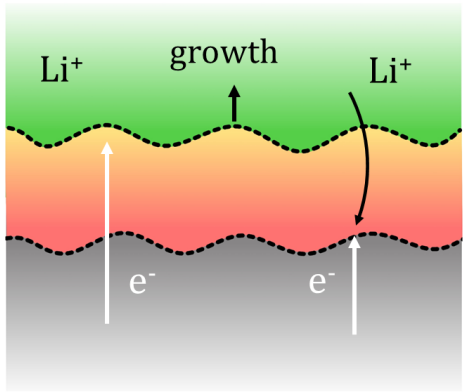


Li/**LPS** (Li_3PS_4)/Li

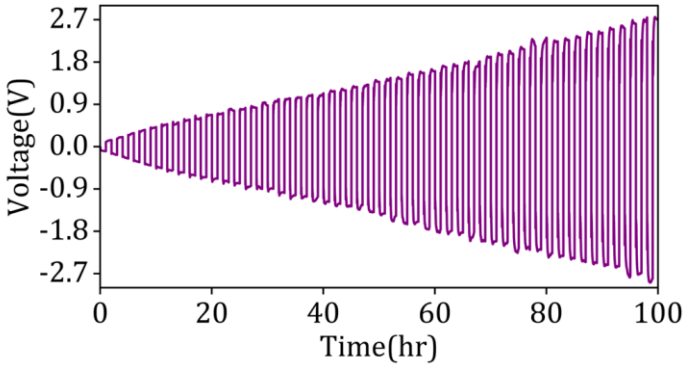


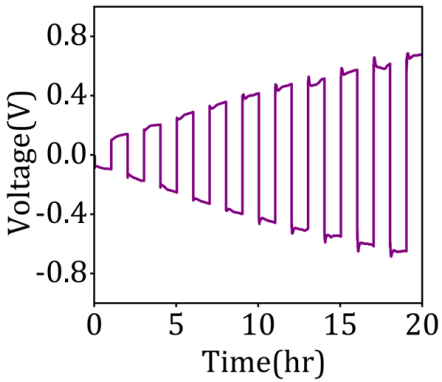


Interphase: Type II



Li/**LSPS** ($Li_{10}SnP_2S_{12}$)/Li

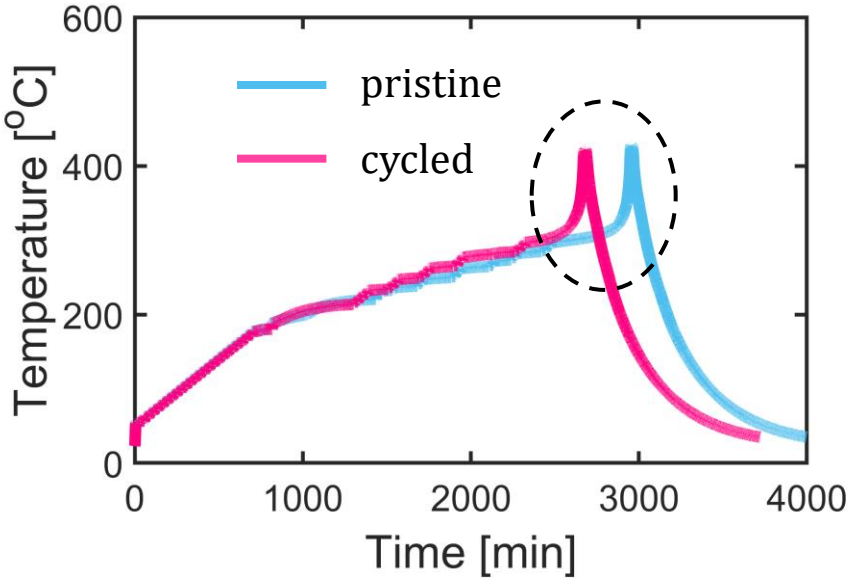




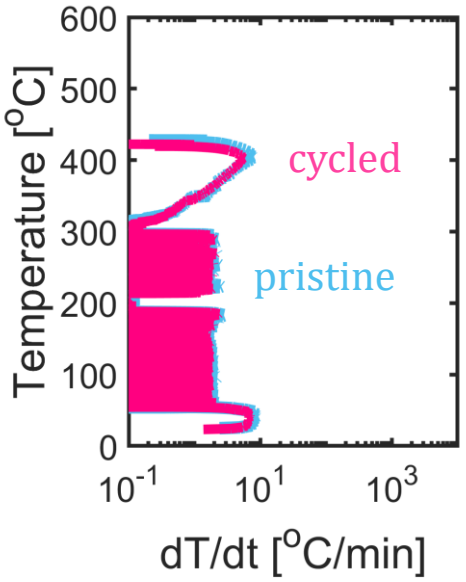
Current density: 0.1 mA/cm^2 ; total capacity: 10 mAh/cm^2

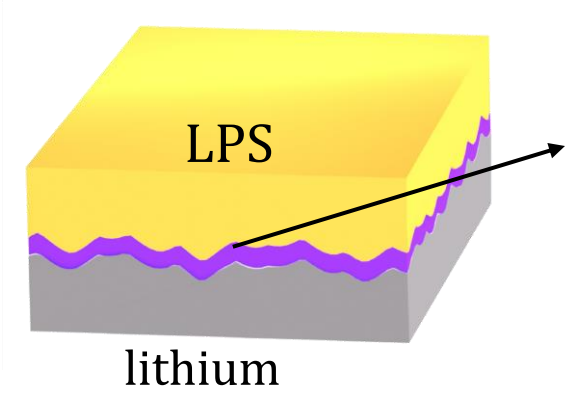
Thermal stability: *solid electrolyte-anode interface*

Thermal signature: Li-Li_3PS_4 (LPS)-Li



Self-heating rate



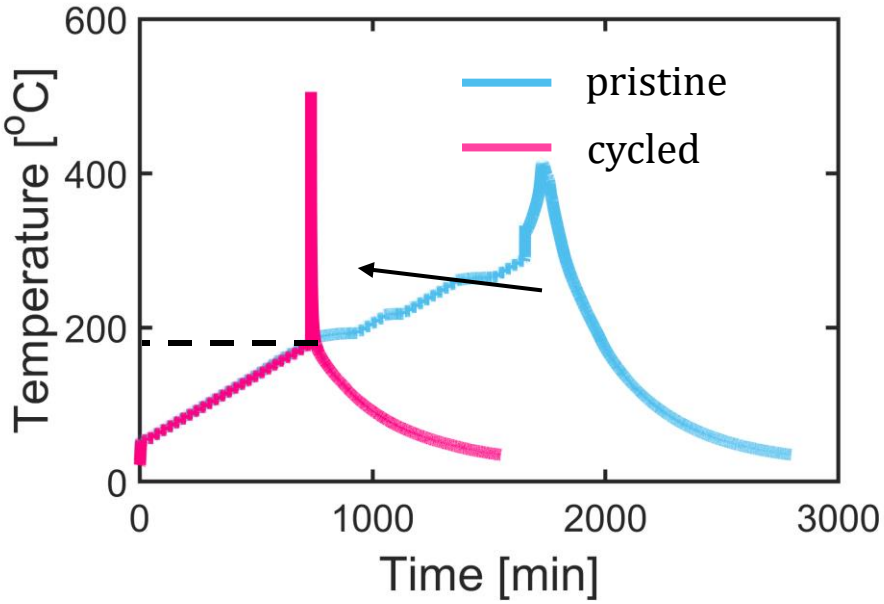


Non-progressive interphase

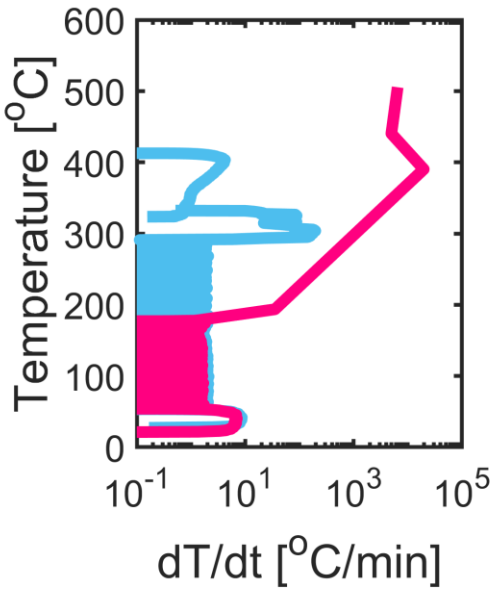
(at the LPS/Li interface)

Thermal stability: *interphase* effect

Thermal signature: Li-$Li_{10}SnP_2S_{12}$ (LSPS)-Li



Self-heating rate

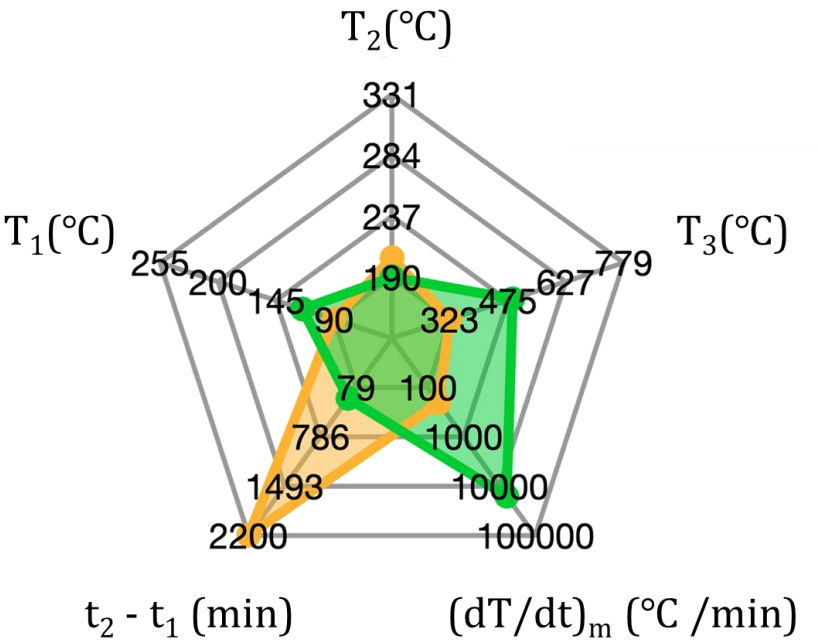


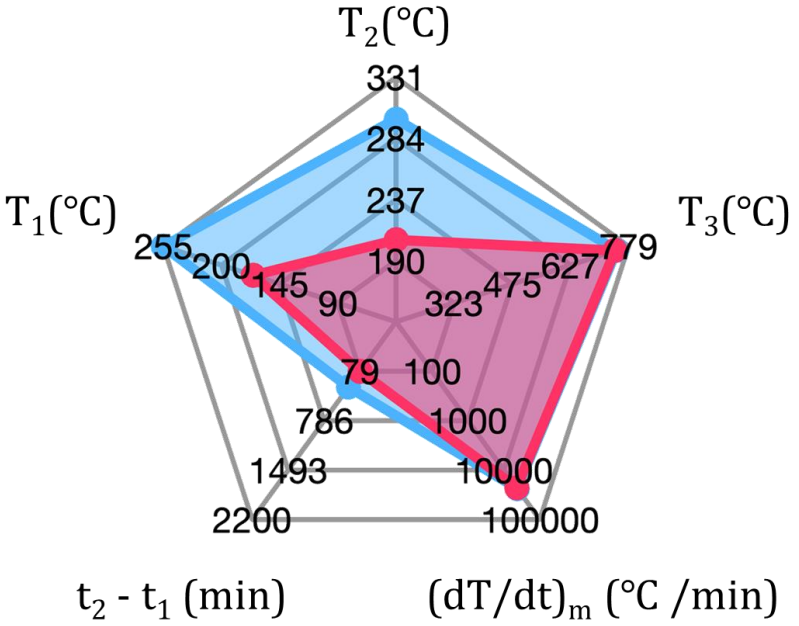
- ***Progressive interphase growth*** - mixed ionic/electronic conducting

- Fundamental correlation between the solid-solid interphase/interface dynamics and ***thermal stability***?

*Vishnugopi, Hasan, Zhou and Mukherjee, *ACS Energy Lett.*, 8, 398 (2023).

Li-ion & solid-state battery cell: safety comparison





Graphite | $LiPF_6$ | LCO

Li |$LiPF_6$ | LCO

Uncycled Li | LSPS | LCO

Cycled Li | LSPS | LCO

T_1 – onset for self-heating

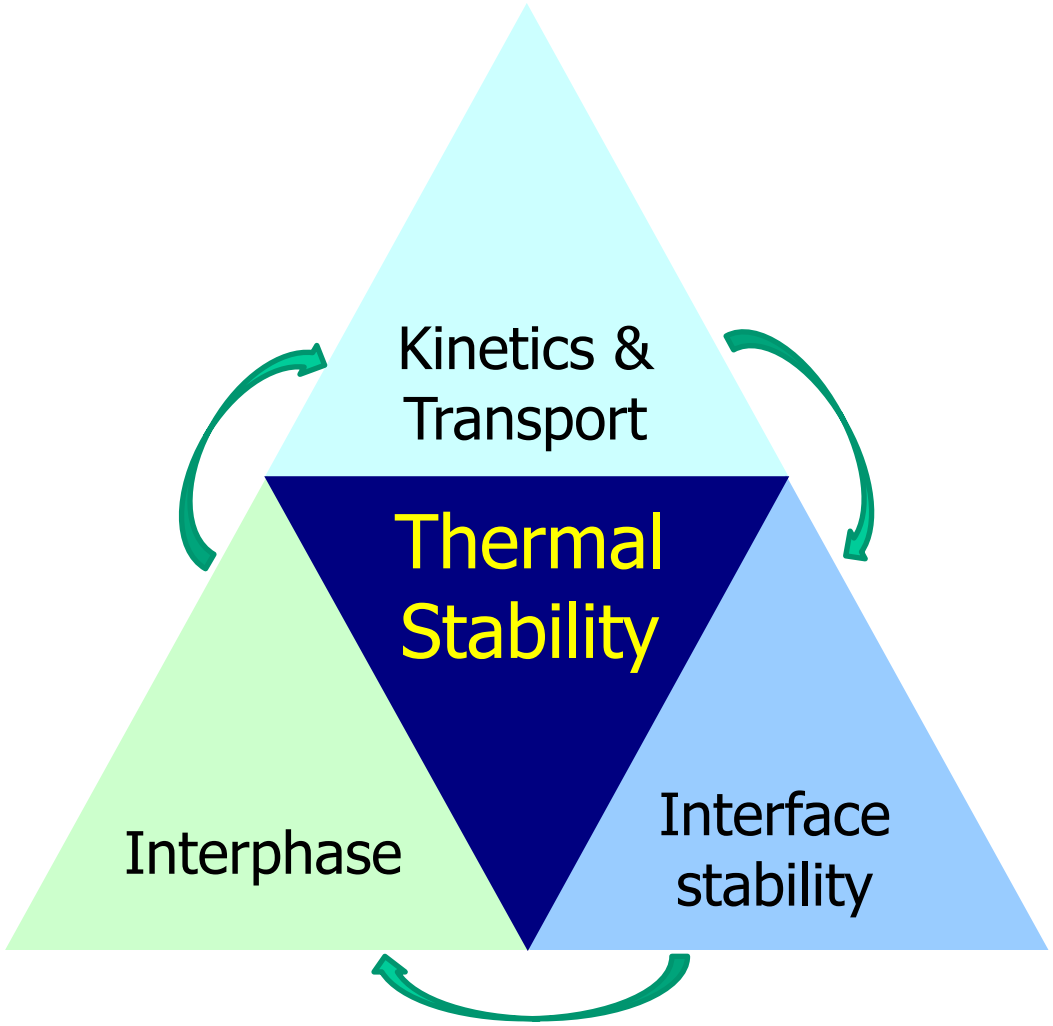
T_2 – thermal runaway onset

T_3 – maximum temperature

t_2- t_1 – time interval between T_1 and T_2

$(dT/dt)_m$ – maximum rate of temperature rise

Summary & Outlook



Non-flammability of the solid electrolyte does not imply thermal stability.

Acknowledgement

BES, EERE
DOE EFRC

THE END

for now...

THANK YOU!