Thermal Runaway analysis of Lithium Metal Anode Cells: a review of current testing protocols and findings

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Lithium metal and its various possible electrolytes

Liquid electrolytes

Ceramic electrolytes (LIPON, Oxide, Sulfide…)

Solid polymer electrolytes (PEO…)

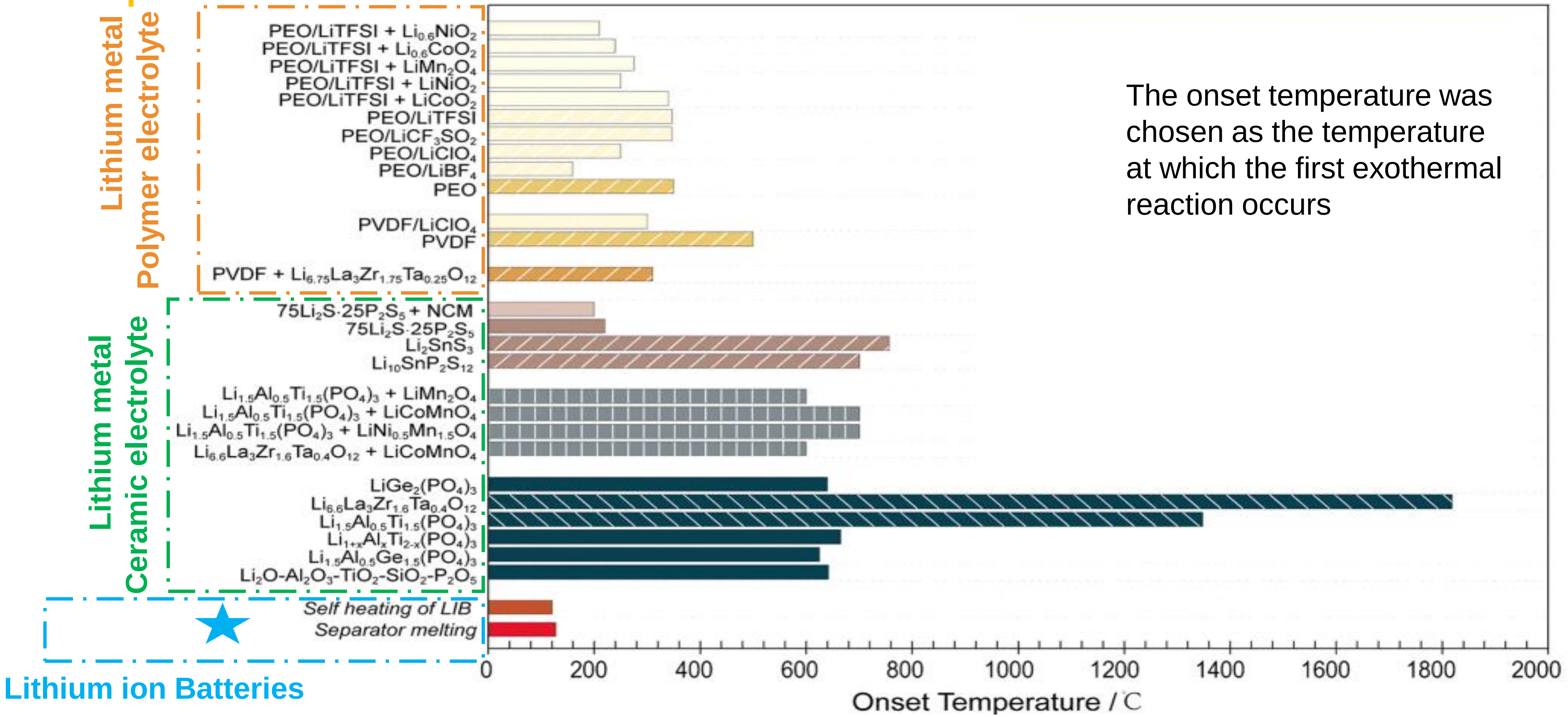
Hybrid electrolytes (gel polymer…)

Different characteristics

- Chemical-electrochemical stability
- Thermal stability
- Interfacial compatibility
- Mechanical strength

→ Thermal Runaway happens and have been reported with different Solid State Electrolyte-based Lithium metal anode batteries

Thermal behaviors of various Lithium metal batteries



The onset temperature was chosen as the temperature at which the first exothermal reaction occurs

Cells with different chemistries have varying onset TR temperatures, some close to those of contemporary Li-ion technology

Chen, R.; Li, Q.; Yu, X.; Chen, L.; Li, H. Approaching Practically Accessible Solid-State Batteries: Stability Issues Related to Solid Electrolytes and Interfaces. Chem. Rev. ***2020****, 120 (14), 6820–6877.* *https://doi.org/10.1021/acs.chemrev.9b00268.*

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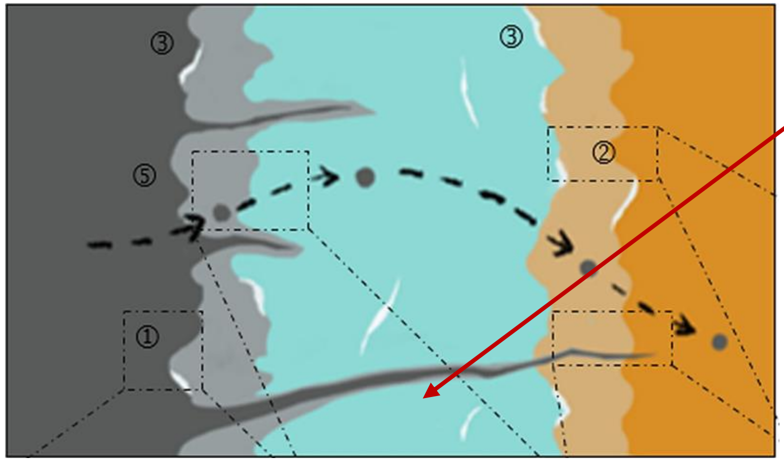
Thermal-related reaction and degradation in the Solid State Lithium Batteries



Lithium dendrite growth

Internal short-circuit

Li metal Solid electrolyte Cathode

LIB (Lithium-Ion Batteries) < **Li Metal**

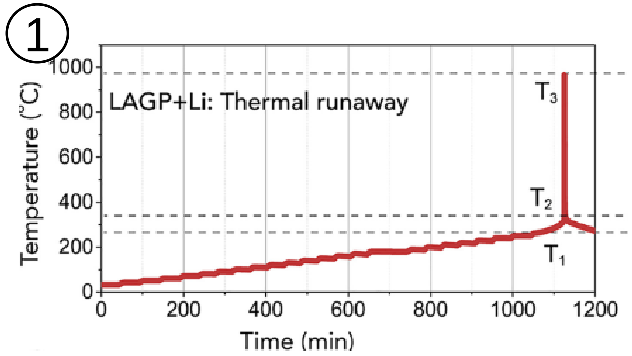
up to 300 Wh kg^{-1} Energy density up to 500 Wh kg^{-1}

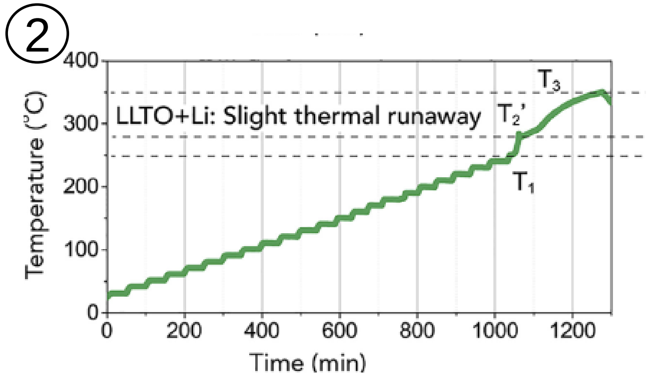
(1) *Wang, J.; Yang, K.; Sun, S.; Ma, Q.; Yi, G.; Chen, X.; Wang, Z.; Yan, W.; Liu, X.; Cai, Q.; Zhao, Y. Advances in Thermal-related Analysis Techniques for Solid-state Lithium Batteries. InfoMat* ***2023****, 5 (4), e12401. https://doi.org/10.1002/inf2.12401.*

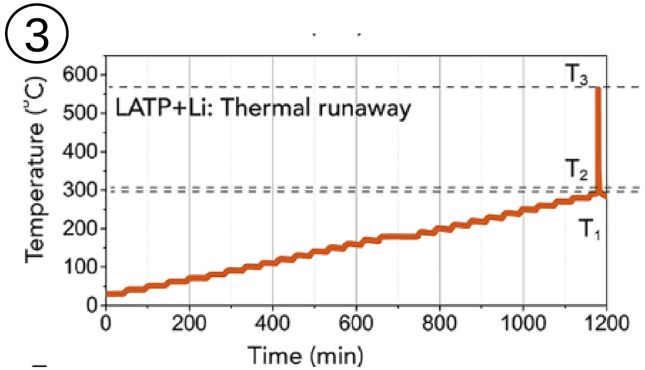
(2) *Jie, Y.; Tang, C.; Xu, Y.; Guo, Y.; Li, W.; Chen, Y.; Jia, H.; Zhang, J.; Yang, M.; Cao, R.; Lu, Y.; Cho, J.; Jiao, S. Progress and Perspectives on the Development of Pouch-Type Lithium Metal Batteries. Angewandte Chemie* ***2024****, 136 (7), e202307802. https://doi.org/10.1002/ange.202307802.*

Thermal Runaway response of four different oxide Solid State Electrolytes with a metallic lithium anode

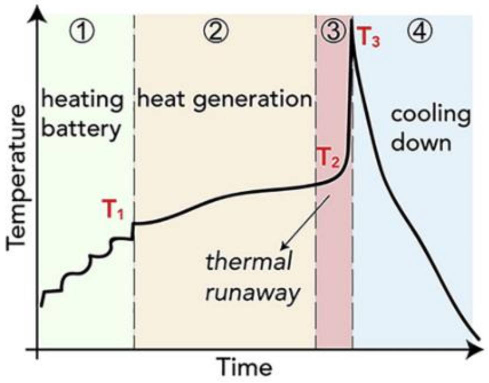
Different Lithium metal and oxide-based Solid Electrolyte underwent TR







Similar process to LIB during thermal runaway



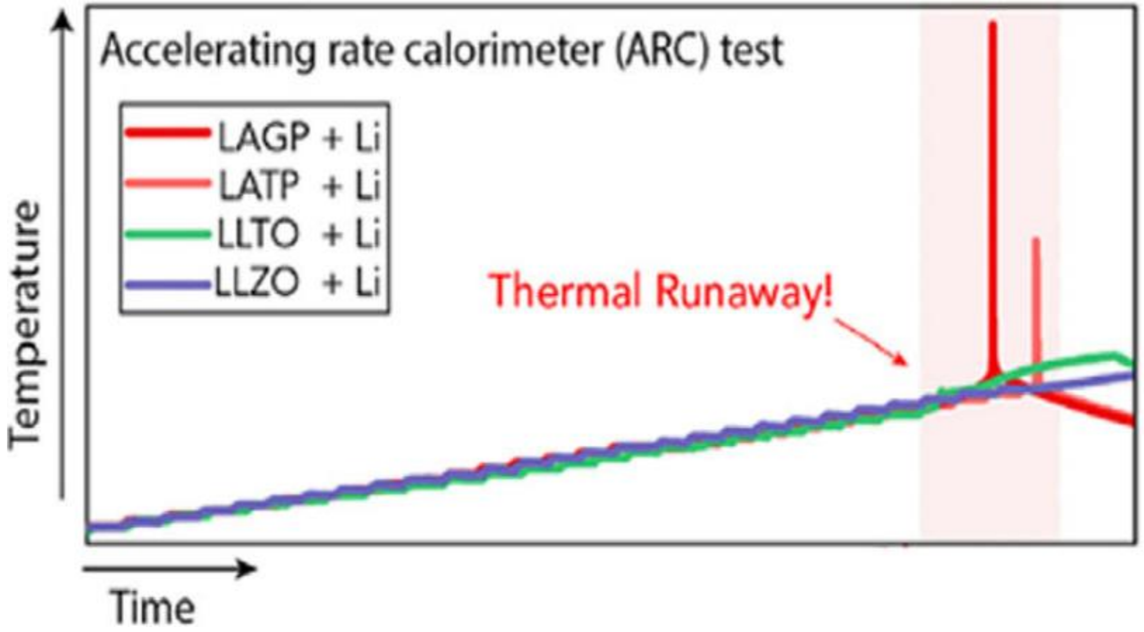
Triggering TR by heating the cell in the arc chamber

This example demonstrates that **SSBs are not absolutely safe when compared with conventional LIBs**.

(1) *Chen, R.; Nolan, A. M.; Lu, J.; Wang, J.; Yu, X.; Mo, Y.; Chen, L.; Huang, X.; Li, H. The Thermal Stability of Lithium Solid Electrolytes with Metallic Lithium. Joule* ***2020****, 4 (4), 812–821. https://doi.org/10.1016/j.joule.2020.03.012.*

(2) *Zhao, Z.; Hu, H.; He, Z.; Zhu, H.; Davari, P.; Blaabjerg, F. Advanced Solid-State Lithium Battery and Its Safety. CPSS Transactions on Power Electronics and Applications (CPSS TPEA)* ***2023****, 8 (4), 348–362. https://doi.org/10.24295/CPSSTPEA.2023.00027.*

Thermal Runaway response of four different oxide Solid State Electrolytes with a lithium metal anode



Thermal response of pouch cells with different SSEs **oxide/Li systems** :

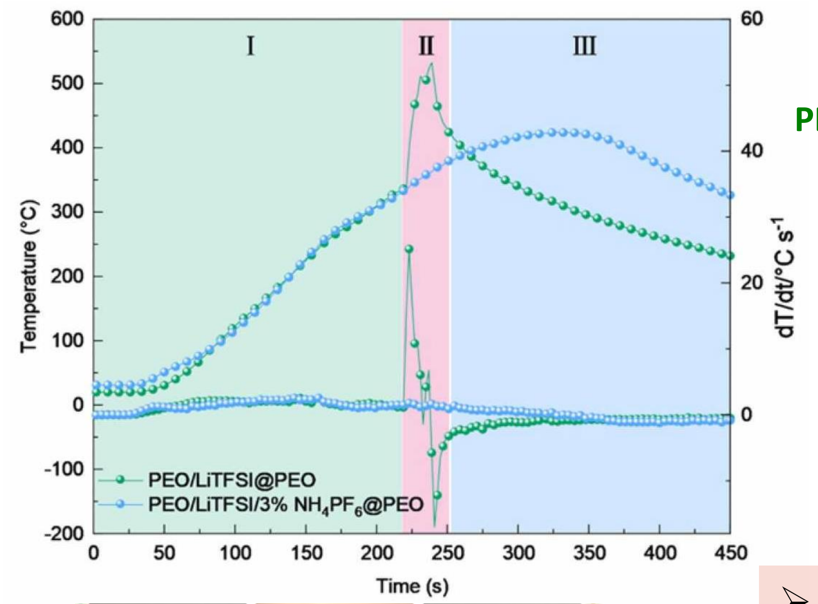
Displayed significantly **different thermal responses**

Triggering TR by heating the cell in the arc chamber

Chen, R.; Nolan, A. M.; Lu, J.; Wang, J.; Yu, X.; Mo, Y.; Chen, L.; Huang, X.; Li, H. The Thermal Stability of Lithium Solid Electrolytes with Metallic Lithium. Joule ***2020****, 4 (4), 812–821. https://doi.org/10.1016/j.joule.2020.03.012.*

Thermal Runaway response of a Polymer electrolyte with a lithium metal anode

Using a heating plate to induce thermal runaway in the pouch cell

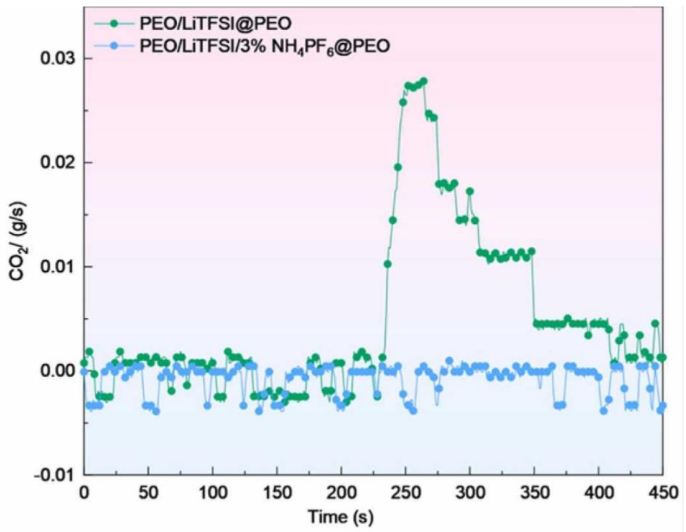


PEO polymer electrolyte Lithium metal

PEO polymer electrolyte Lithium metal with a flame retardant

- The pouch cell PEO polymer electrolyte Lithium metal went into TR
- The temperature of the pouch battery rises rapidly to about 500 °C at **burns at 210 s**
- And the **battery flame goes out at 236 s**.

CO_2 production starts around 210 seconds



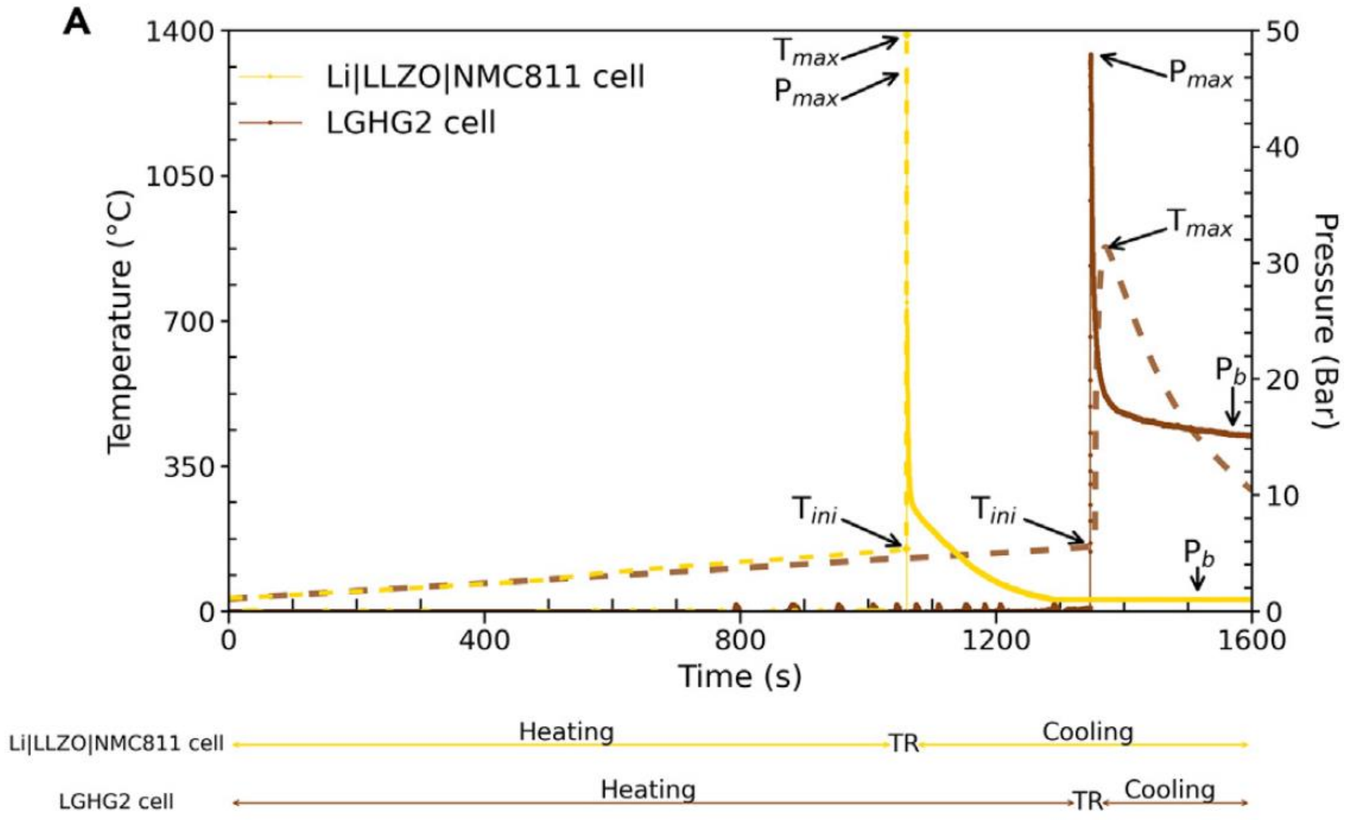
European Commission

Han, L.; Liu, Y.; Liao, C.; Zhao, Y.; Cao, Y.; Kan, Y.; Zhu, J.; Hu, Y. Noncombustible 7 Mm-Thick Solid Polymer Electrolyte for Highly Energy Density Solid State Lithium Batteries. Nano Energy ***2023****, 112, 108448.* https://doi.org/10.1016/j.nanoen.2023.108448.

Thermal Runaway response of a Polymer electrolyte with a lithium metal anode

Li|LLZO|NMC811 cell-Lithium as anode material, PEO-LLZO ((poly(ethylene oxide)-lithium lanthanum zirconium oxide) as electrolyte and a commercial 18650-type cell NMC (LGHG2, 3Ah)

Triggered by an external heater



The cell is wrapped with a heating wire (9A power supply, 300V) to trigger TR

In this study, the thermal runaway of a reassembled ASSB with a lithium negative electrode is much faster than that of a Lithium ion battery

European Commission

Charbonnel, J.; Dubourg, S.; Testard, E.; Broche, L.; Magnier, C.; Rochard, T.; Marteau, D.; Thivel, P.-X.; Vincent, R. Preliminary Study of All-Solid-State Batteries: Evaluation of Blast Formation during the Thermal Runaway. iScience ***2023***, *26 (11), 108078. https://doi.org/10.1016/j.isci.2023.108078.*

Conclusion

- Lithium metal anode cells with ceramic and polymer electrolytes are shown to be able to go into thermal runaway (TR)
- Lithium metal anode cells have varying onset TR temperatures, some close to those of contemporary Li-ion technology; TR in lithium metal anode cells can be more violent
- The stages of TR are similar to those in lithium-ion batteries with liquid electrolytes
- Initiation methods used for triggering TR in Li-ion cells with liquid electrolyte, e.g. external heating, heating in an ARC, have successfully been used to initiate TR in lithium metal anode cells.