PENNSTATE

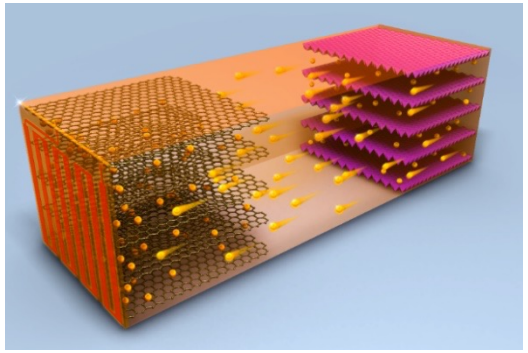
Electrochemical Engine Center

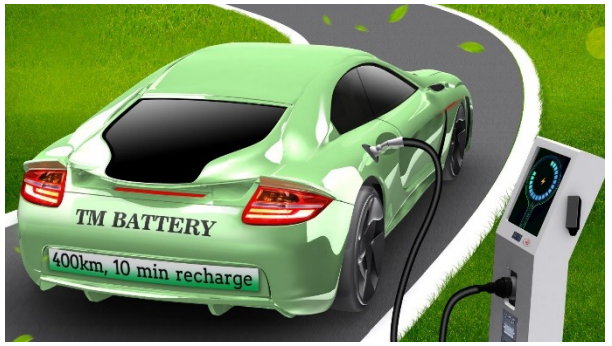
Battery Resilience under Extreme Conditions

Chao-Yang Wang

Pennsylvania State University

University Park, Pennsylvania, USA





Case 1: Extreme Cold

The New York Times

Electric Car Owners Confront a Harsh Foe: Cold Weather

In freezing temperatures, the batteries of electric vehicles can be less efficient and have shorter range, a lesson many Tesla drivers in Chicago learned this week.

Share full article 215



A driver charging his car in Denver on Tuesday. Tesla drivers across the United States have struggled with severely cold weather this week. David Zalubowski/Associated Press





January 17 2024 in Chicago, “electric vehicle charging stations became scenes of desperation: depleted batteries, confrontational drivers, and lines stretching out onto the street” – New York Times





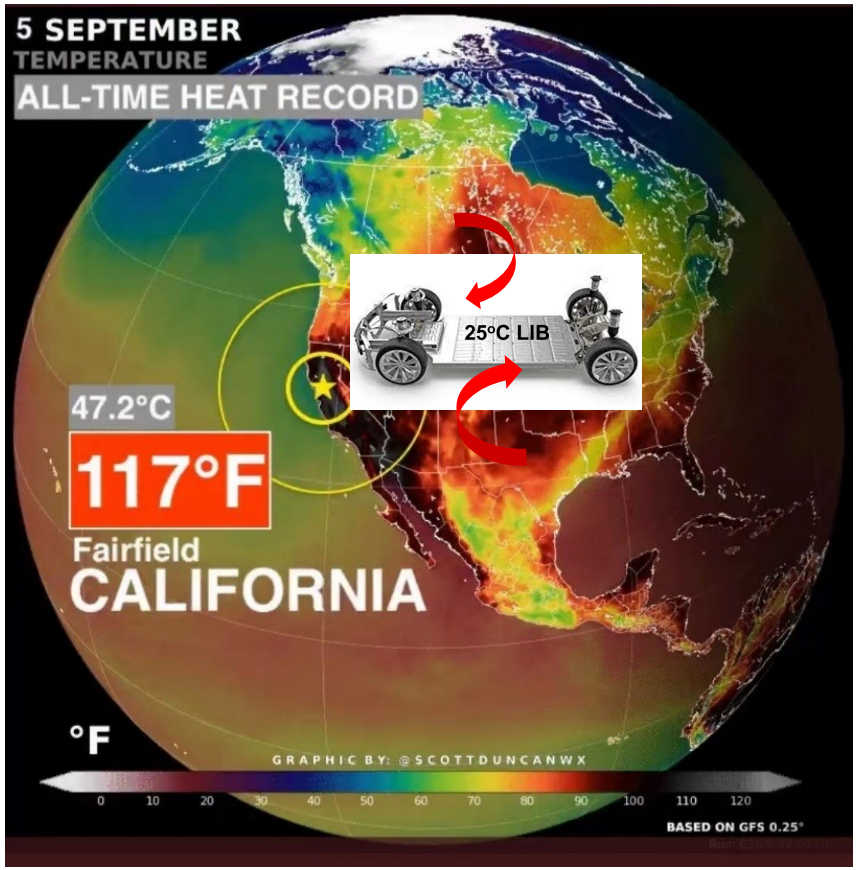


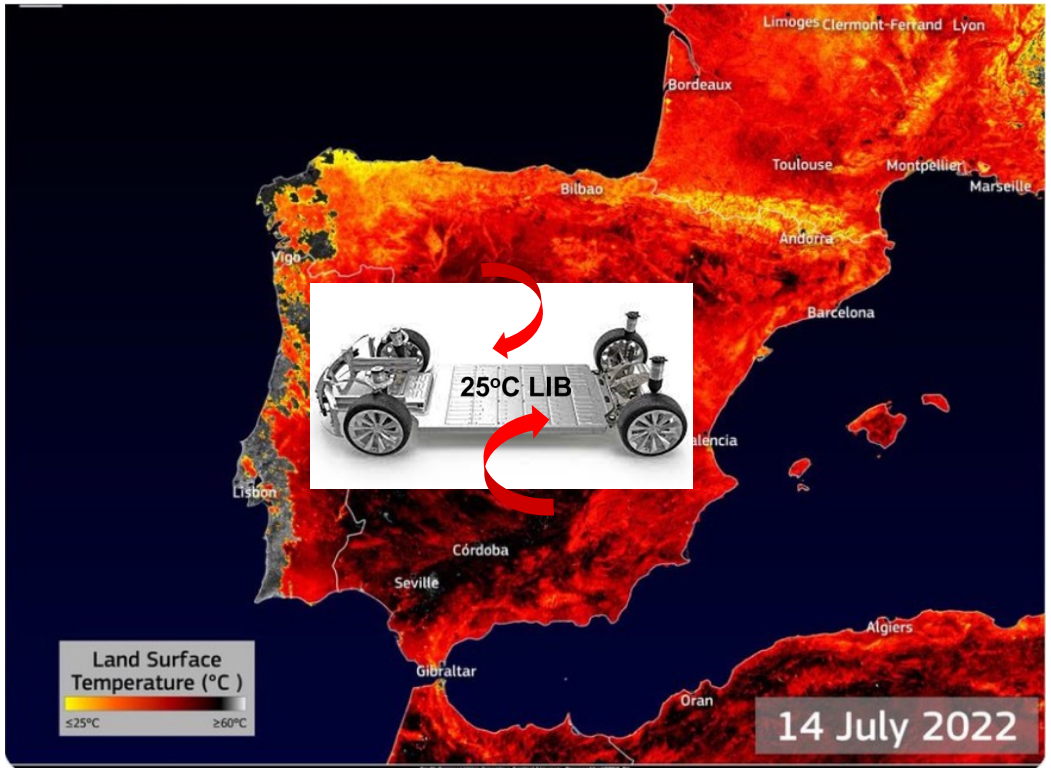
Tesla owners line up, hoping to get a charge

"I've been here for over five hours at this point and I still have not gotten to charge my car," Tesla driver Brandon Welbourne told CBS News Chicago, as car horns blared nearby. "A charge that should take 45 minutes is taking two hours."

Case 2: Extreme Heat

We live in surging air temperatures – hot summers are just beginning…

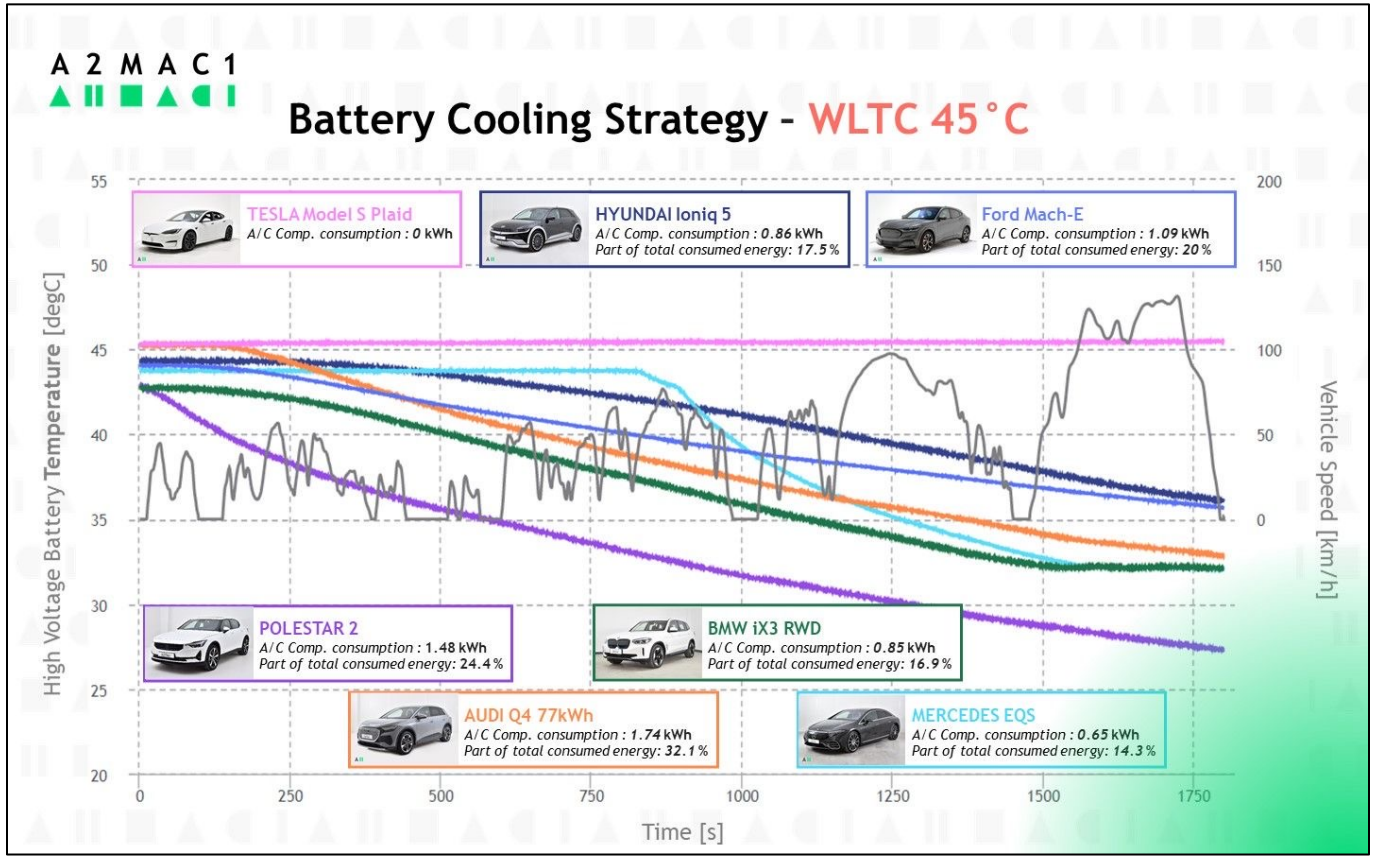




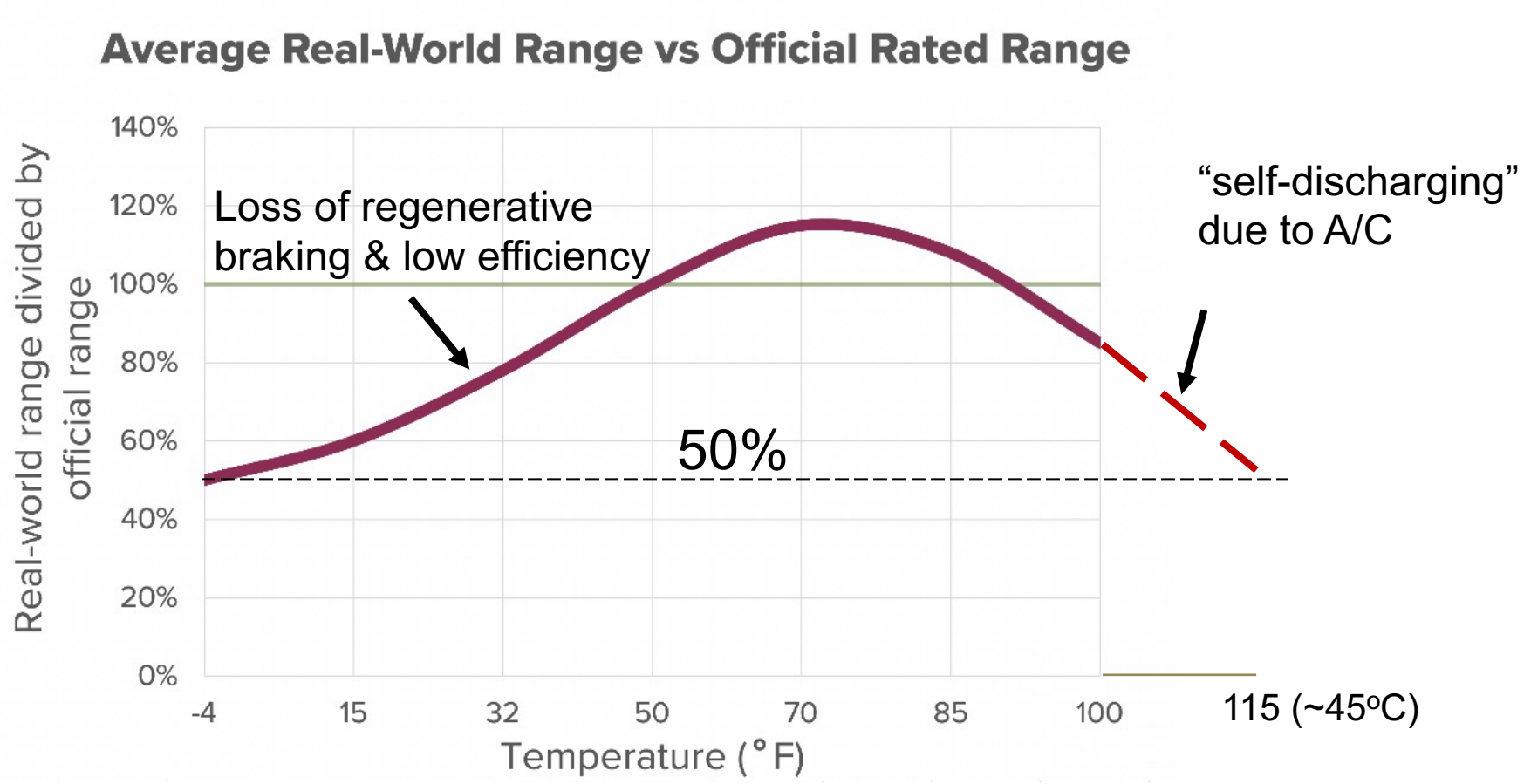
- Current LiBs are designed for 25°C and degrade rapidly at >35°C.
- How can LiBs survive and be fast-charged in hot weather?

Battery “Self-Discharging” in Hot Weather

- Long soaking in 45ºC. All electrical energy consumption is for battery cooling with no climate control request for cabin
- A/C compressor consumption ranges from 14.3-32.1% of total battery energy consumption. On average, there is 25% “self-discharge”.

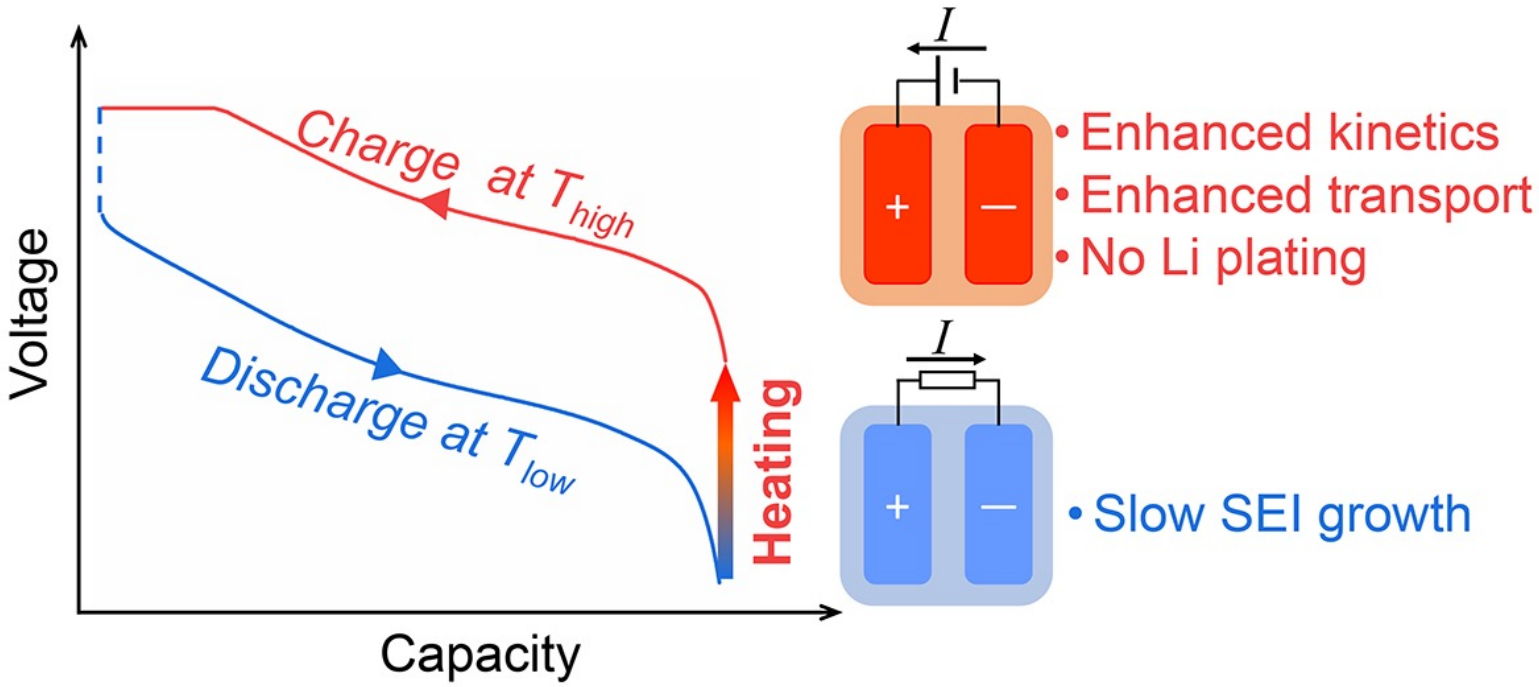


Cruise Range Halving 续航减半



Our Approach to Fast Charging in Extreme Cold

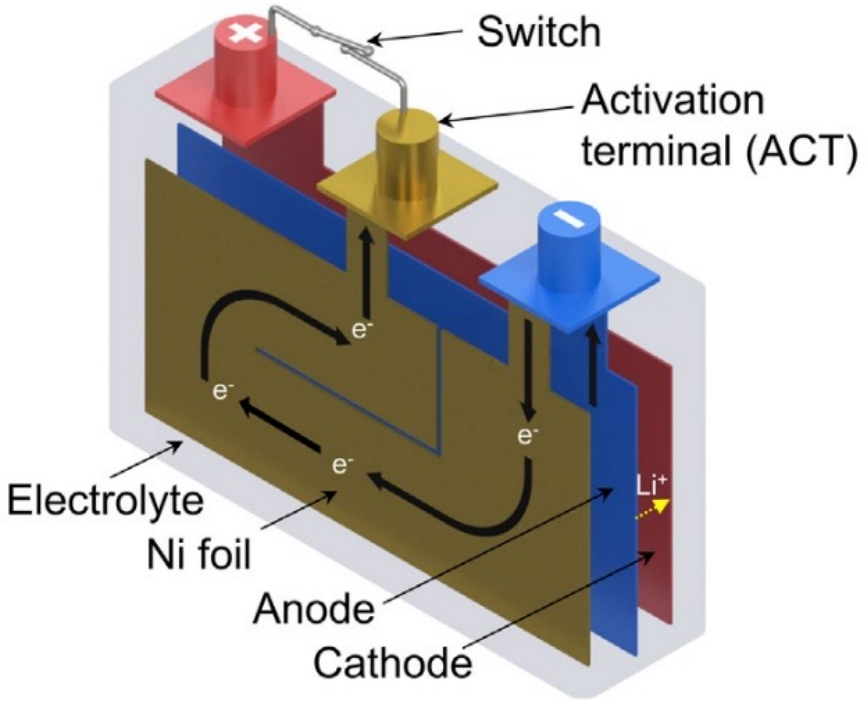
- **Asymmetric Temperature Modulation (ATM)** method: charge at a high temperature (60-75°C) to prevent Li plating, and discharge at ambient temperatures
- The cell stays at high temperature only during fast charge (~10-min per cycle) to avoid severe degradation due to high T.
- Rapid preheating prior to charging made possible by a self-heating structure; heating time is 1-2 min (heating speed >1°C/sec)



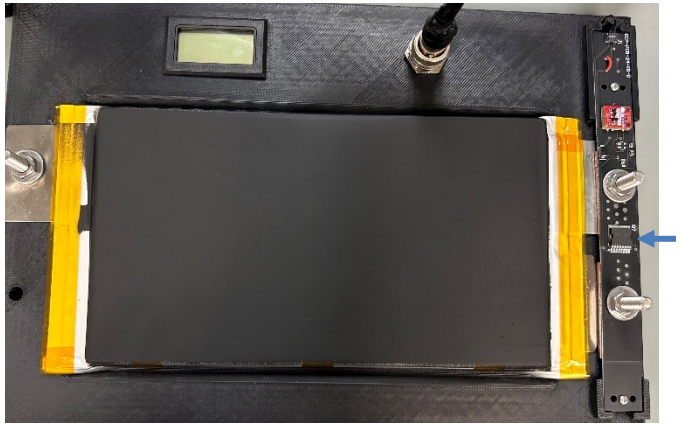
Rapid Intracell Heating is Key to ATM

Conventional external battery heating: ~0.5°C/min, Preheating >60 min

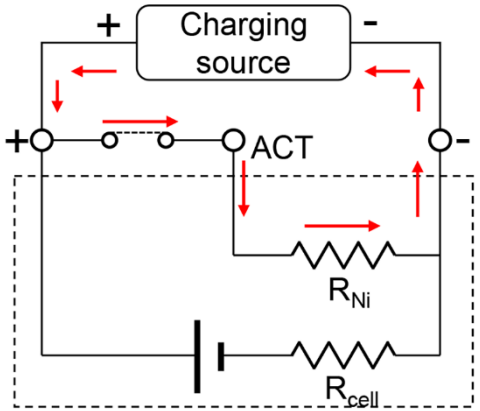
Self-Heating Structure: 60-100°C/min, 30-60 sec preheat



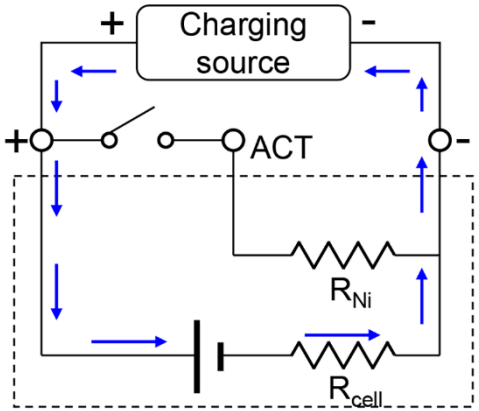
Wang et al. (2016) Nature 529 (7587), 515.



28-Ah LFP pouch cell

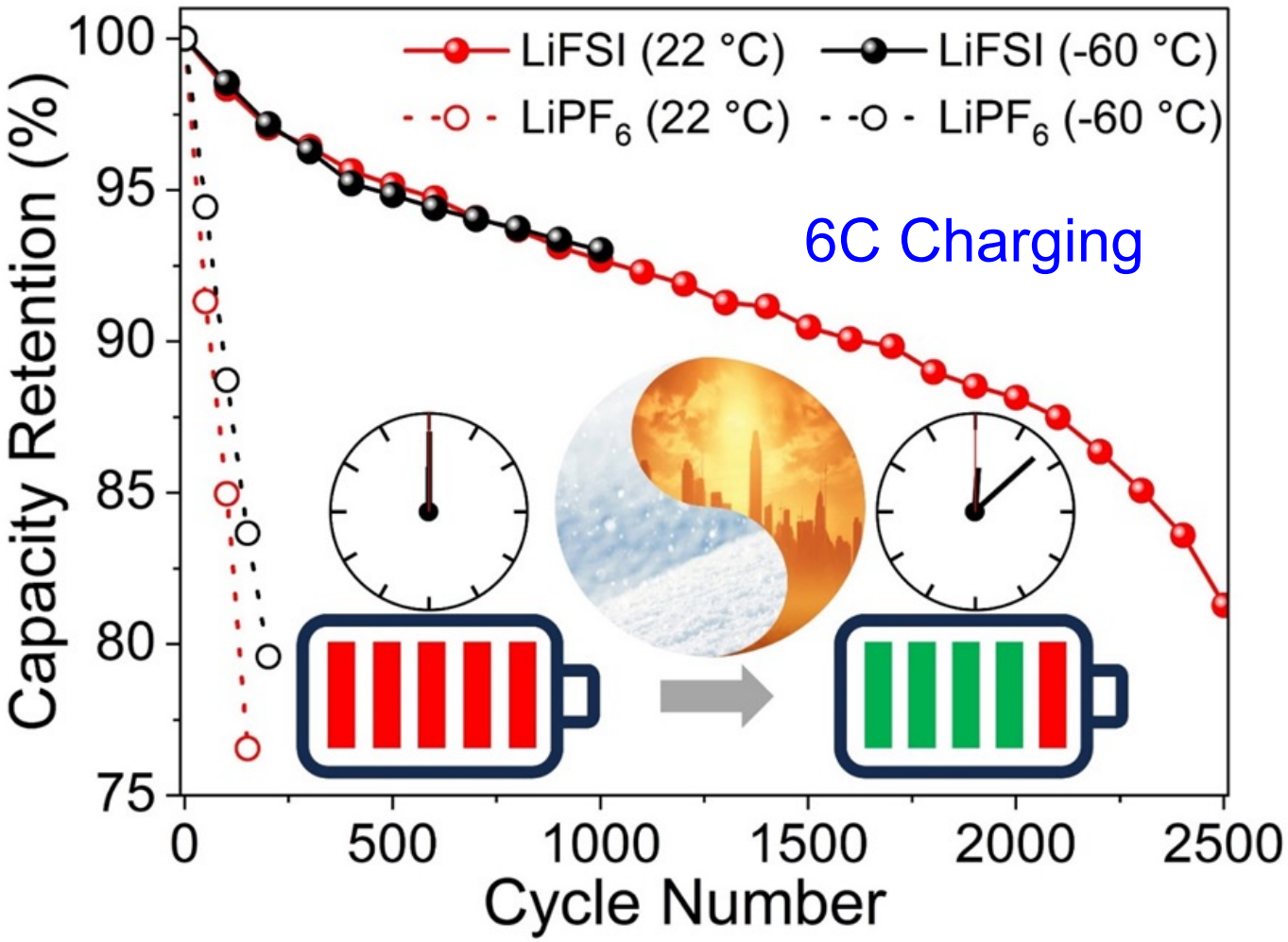


Switch ON: heating



Switch OFF: charging

210 Wh/kg LFP Battery & 6C Fast Charging



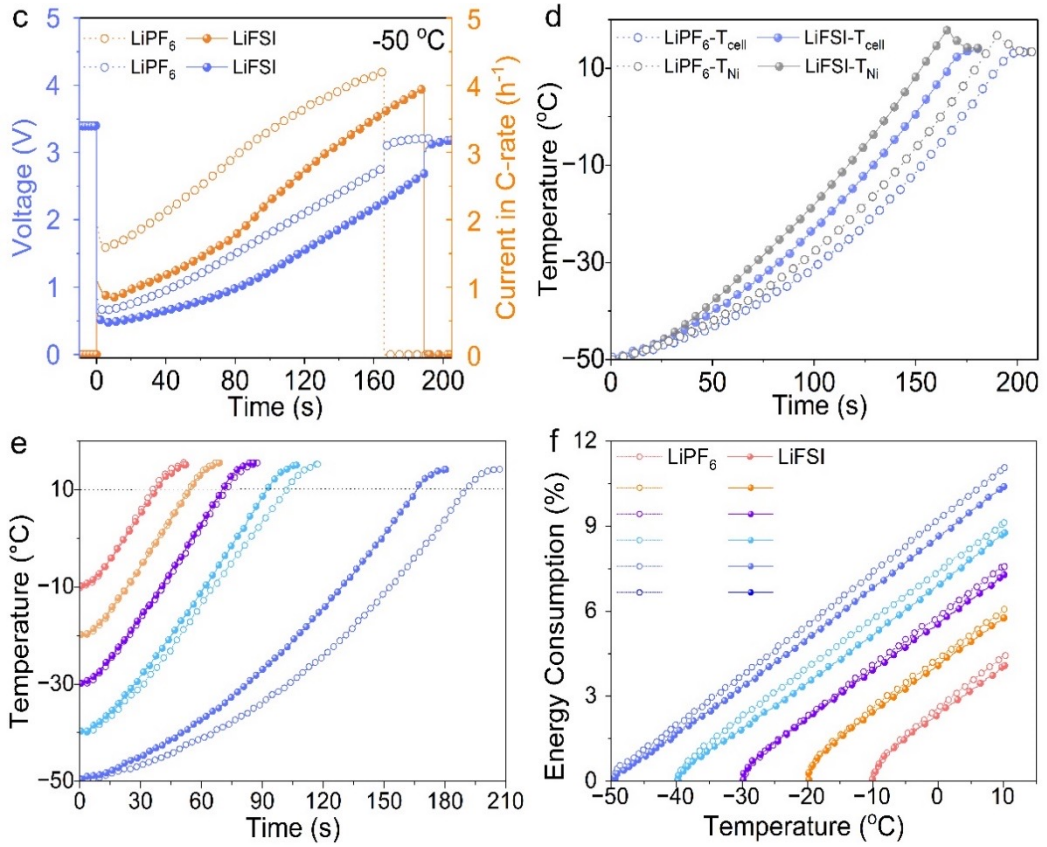


Battery charging in extreme cold is no longer anti-science

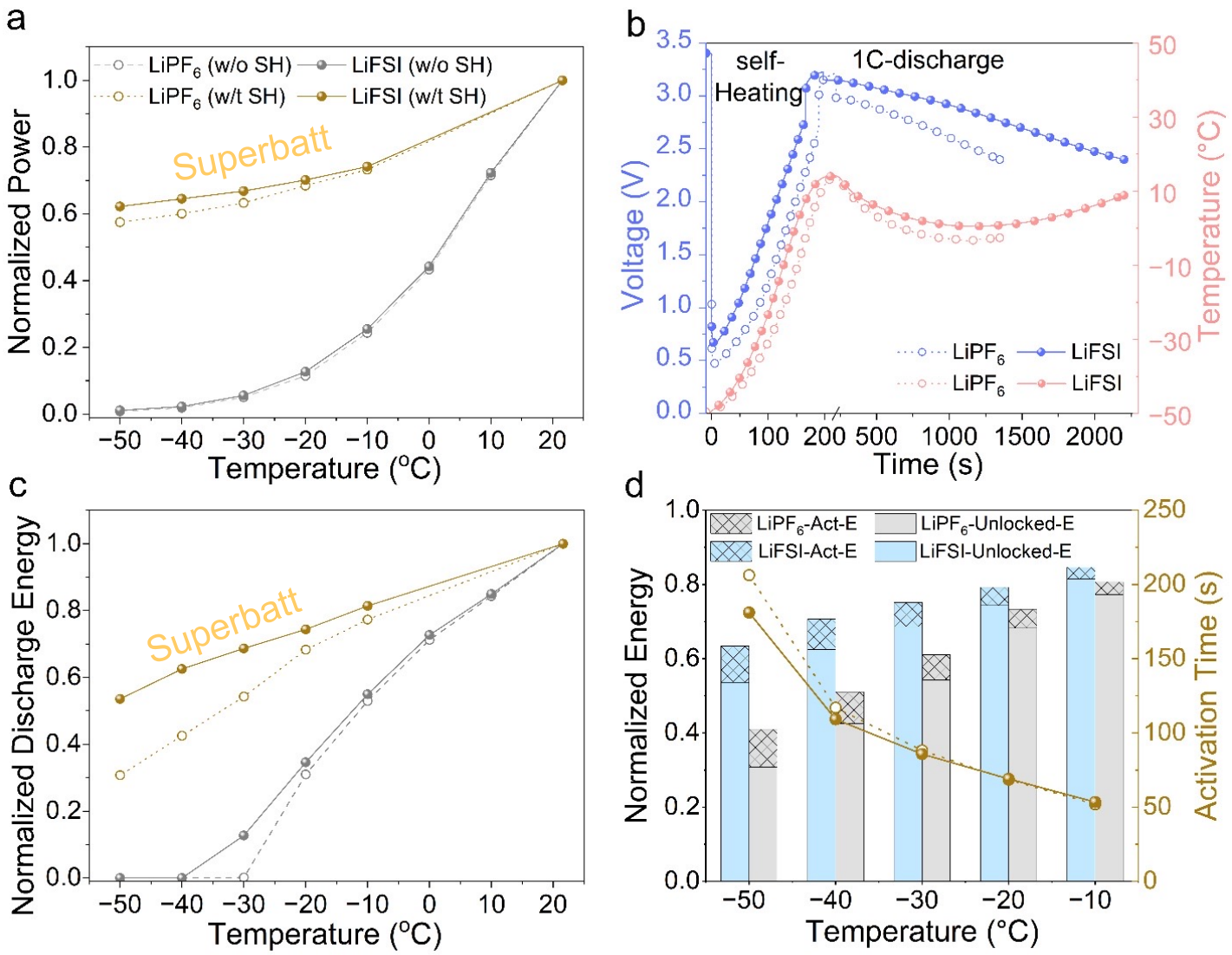
LFP Cell 6C Charging at all temp (-60°C to 45°C): 9-12 min + 170 Wh/kg + 2000+ cycles + passive cooling

Low-Temperature Resilience thru Self-Heating

Self-Heating from -10 to -50°C



Power & Energy after Self-Heating



Technology Demo at 2022 Winter Olympics



应用全气候电池技术的冬奥用车整装待发





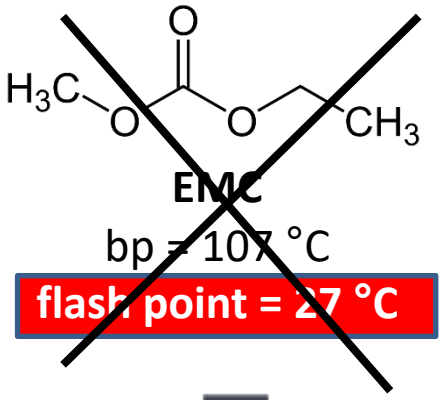
全气候电池模组





应用全气候电池技术的氢燃料客车完成交付

High-Temperature Resilience via Heat-Tolerant Materials

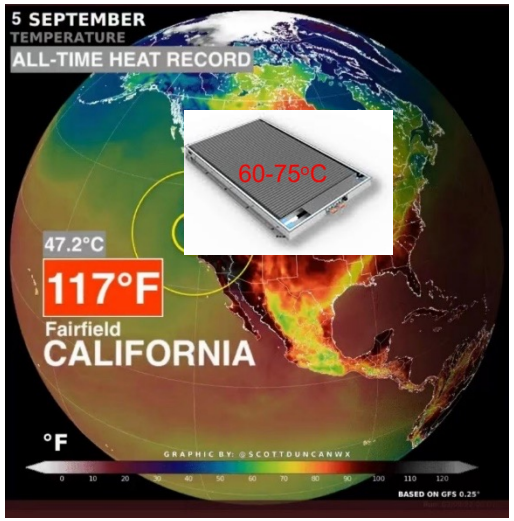




Please, never ever do this

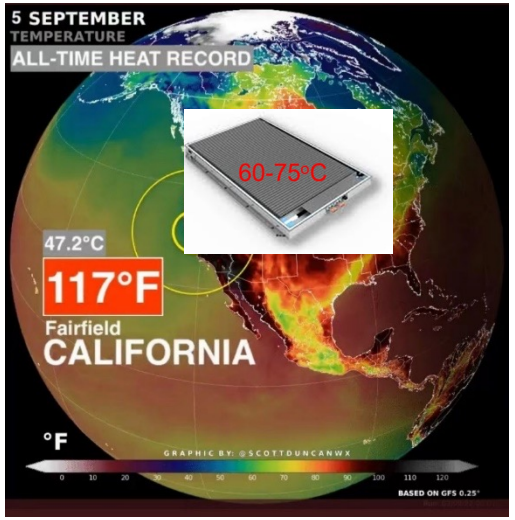
Heat-tolerant materials work stably at >60°C:

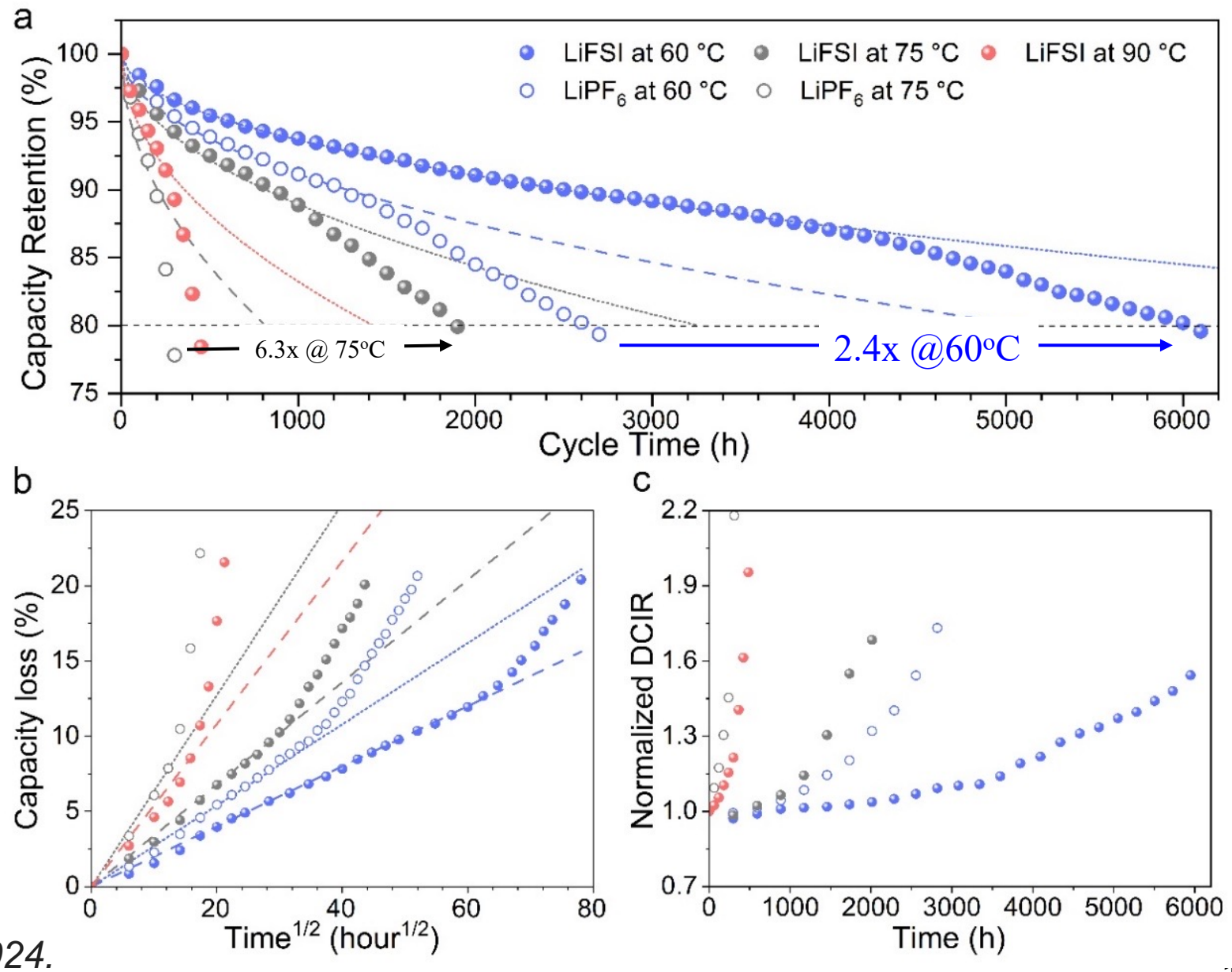
- No gas generation
- Little impedance growth
- Made of stable materials & interfaces



Heat-Tolerant Electrolytes

- Introduced LiFSI in EC:DEC (3:7)
- Stability improved by 2.4x at 60°C
- Stability improved by 6.3x at 75°C
- Can work up to 90°C
- Dump cell heat to 40-45°C ambient
- Can fast-charge in hot weather

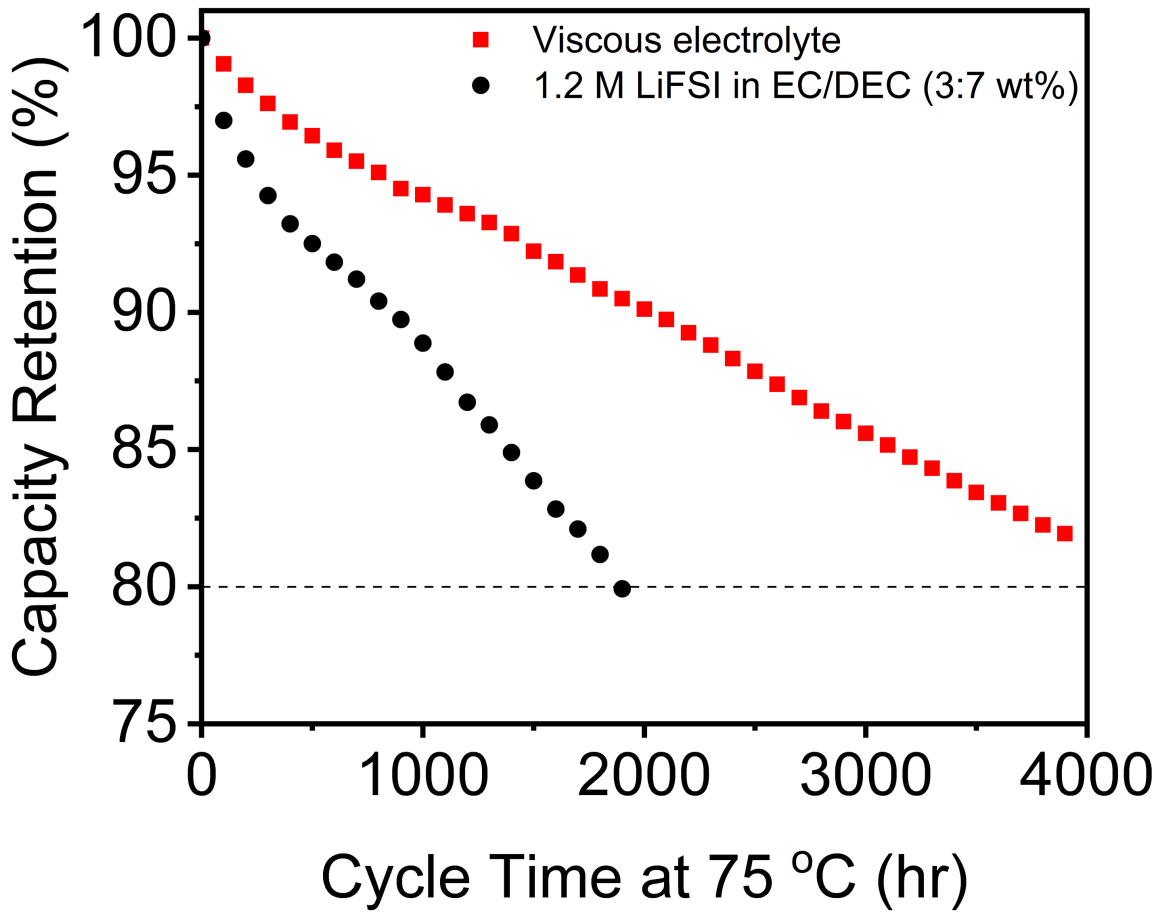




Liao et al., ACS Energy Lett., Jan. 2024.

Heat-Tolerant Electrolytes – High-BP & High Viscosity

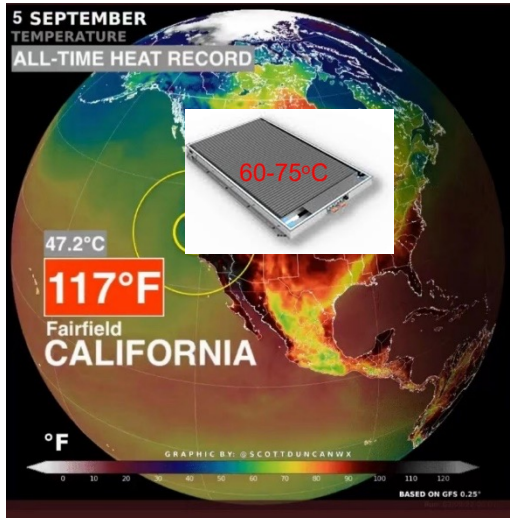
- High-BP and high-viscosity electrolytes are tolerant to extreme heat: e.g. EC/PC, dicarbonates, HCEs, ionic liquids, “condensed matters”, molten salts, solid electrolytes…

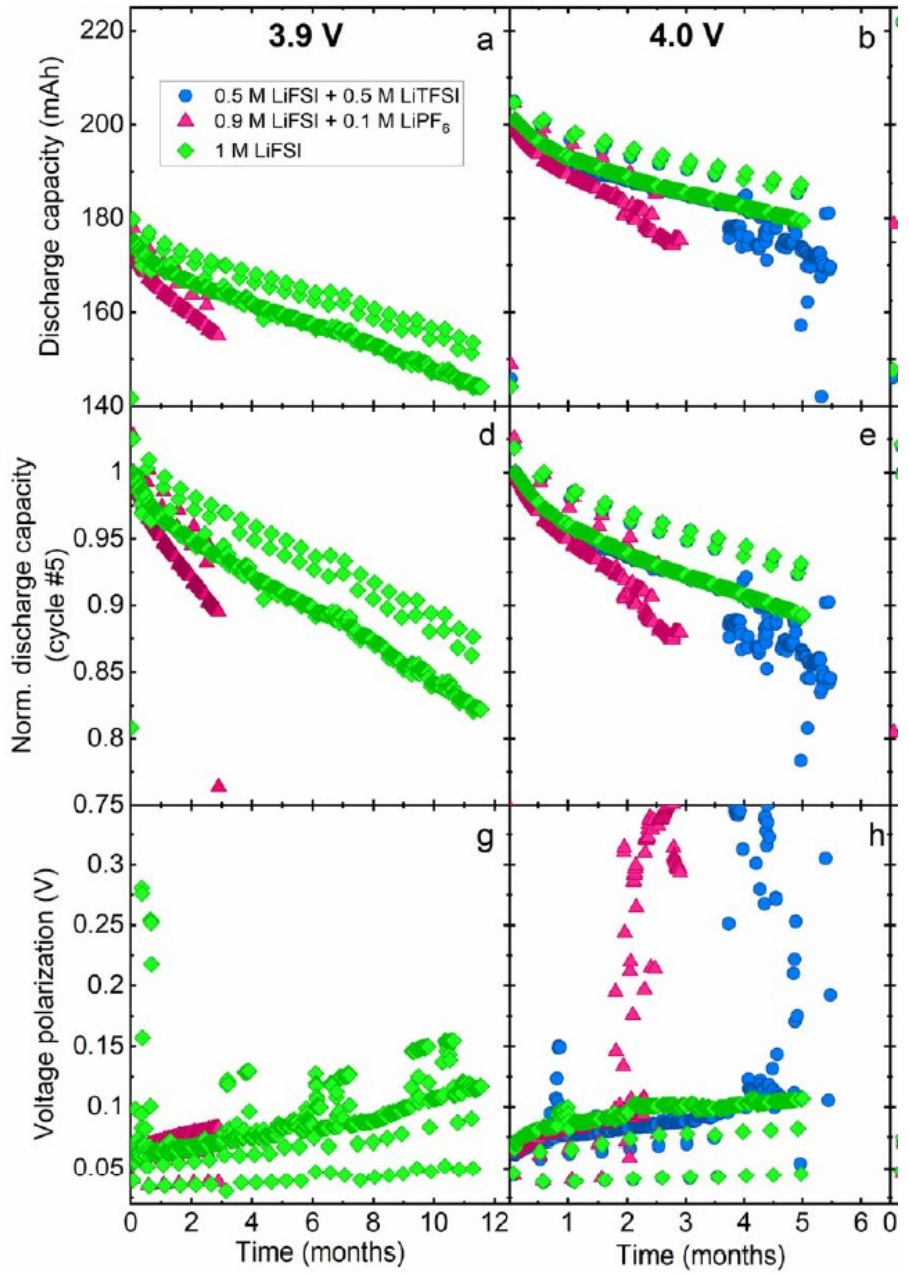


K.Q. Qin and C.Y. Wang, unpublished, 2022

Heat-Tolerant Electrolytes – Dahn Group

- Followed same strategy of LiFSI in EC/DEC & further changed EC:DEC to 5:5
- Achieved 8700 hrs cycling at 3.9V and ~4000 hrs at 4.0V at 85°C
- Can work up to 100°C
- Dissipate cell heat to 40-45°C ambient w/o A/C
- Eliminate A/C cooling all together

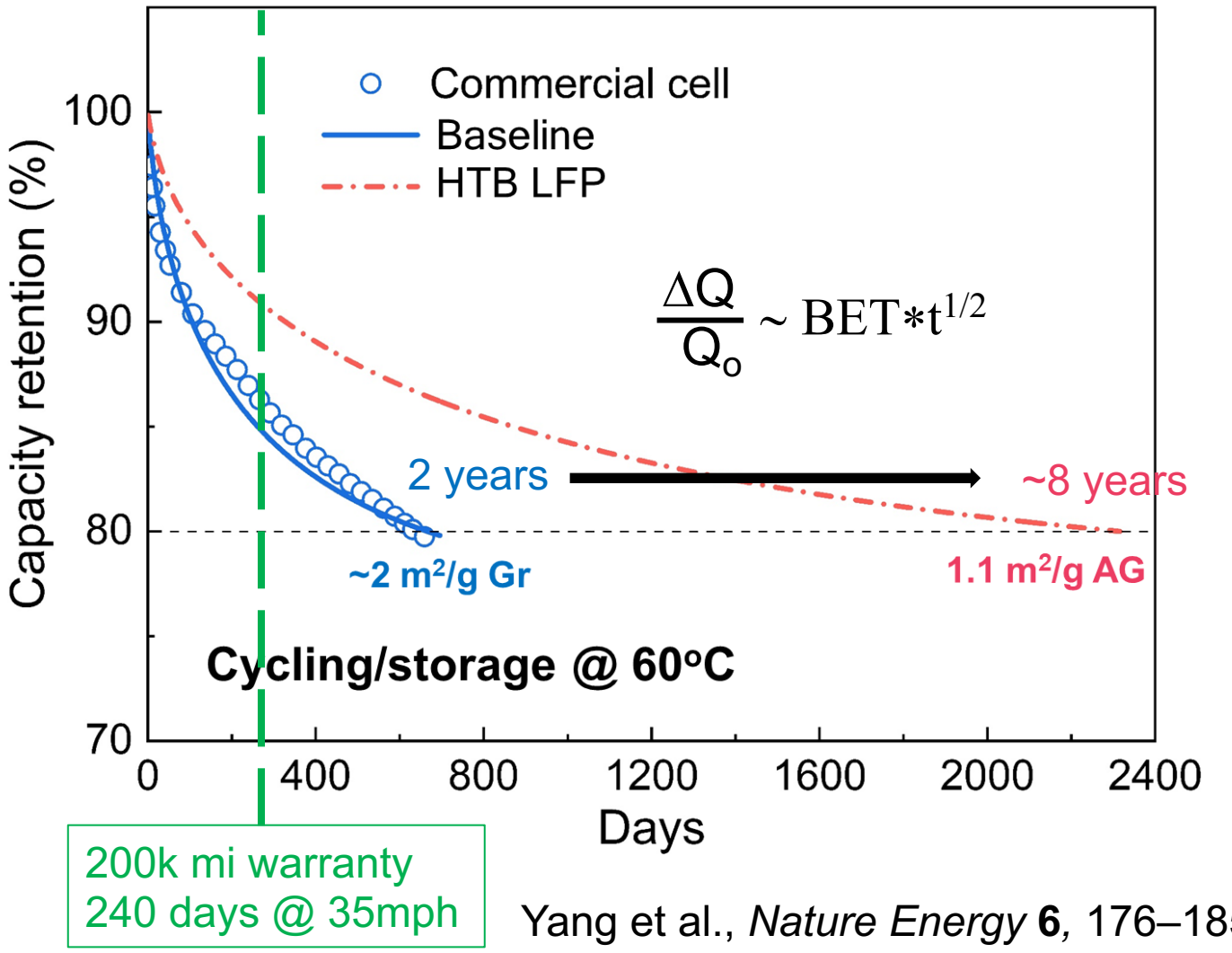




Tuul et al 2024 J. Electrochem. Soc. 171 040510

Heat-Tolerant Electrode Materials

>2M mile LFP battery working @ 60°C

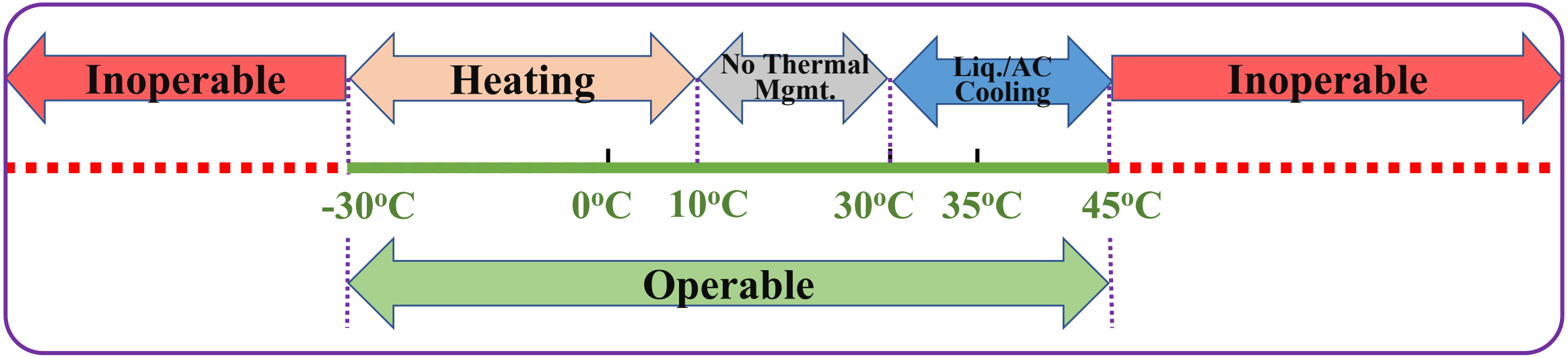


- Single-crystal oxide cathode materials work too!

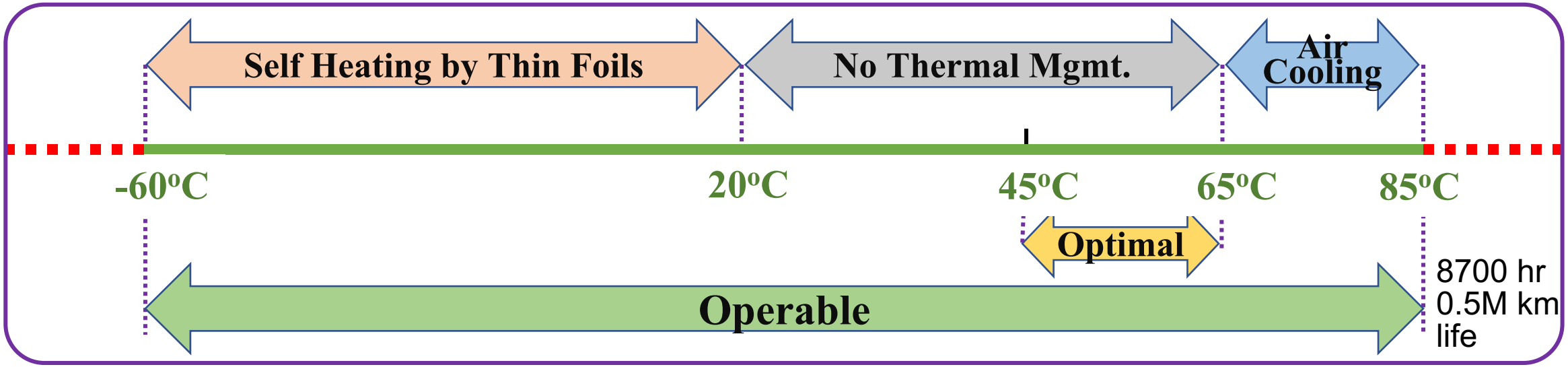
Yang et al., *Nature Energy* **6**, 176–185 (2021)

Paradigm Shift in Battery Thermal Management

- LiB Thermal Management



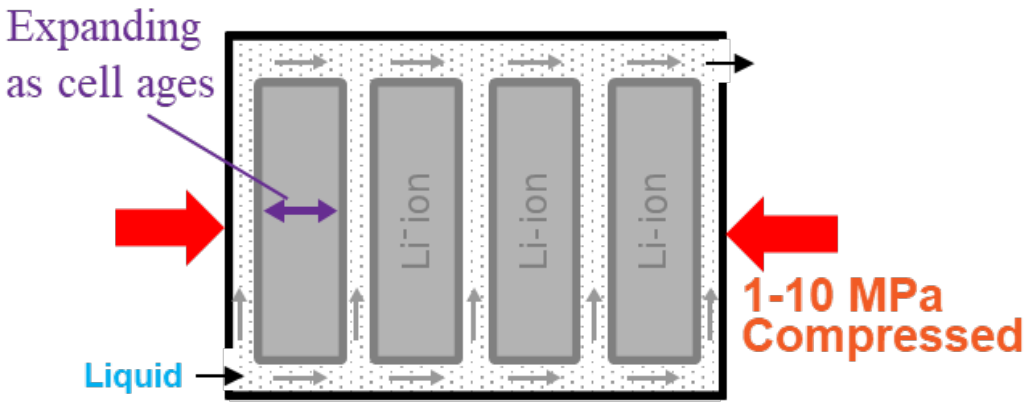
- HTB Thermal Management: simplified/robust, liquid-less, no power consumption



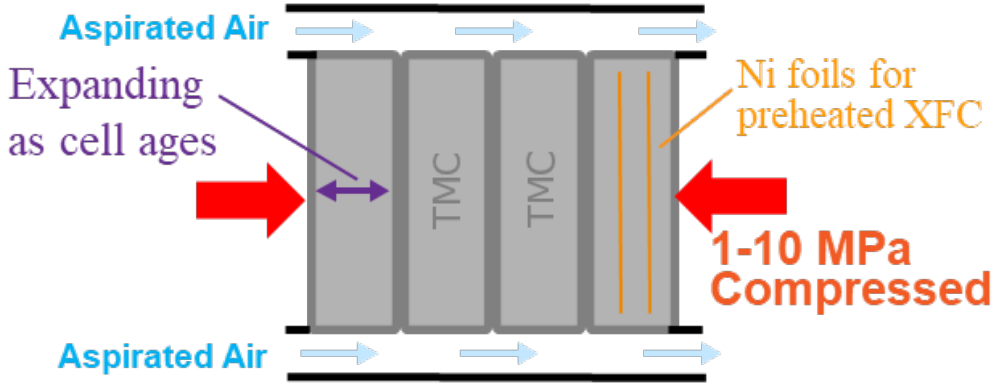
Liquid-Less Thermal Management

- Stably operating at 60-85^{o}C permits liquid-less thermal management system.
- BTM based on aspirated air convection becomes feasible. Here we exploit ΔT in $Q=hA\Delta T$.
- Liquid-less, zero-power BTM reduces pack cost and enhances reliability/safety

Liquid-cooled, Liq-everywhere Cell-to-Pack



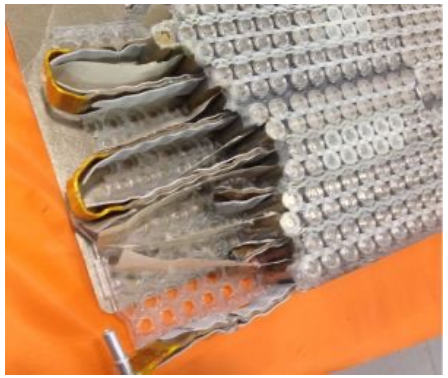
Air-cooled, Solid-state Cell-to-Pack

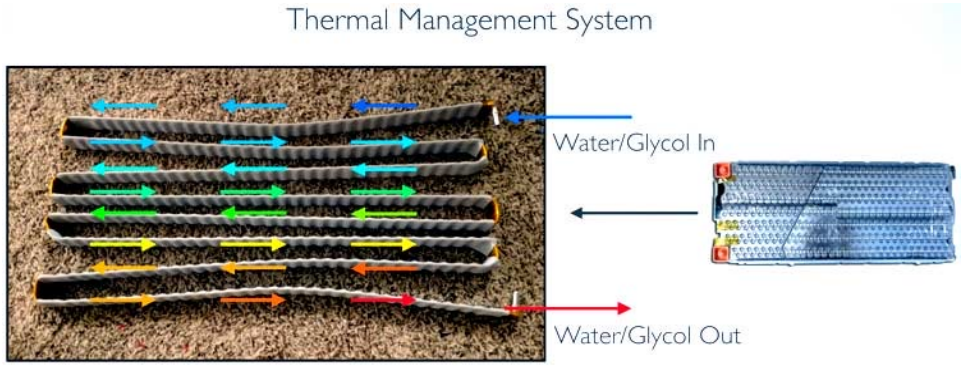


Wang et al. (2022) Nature 611 (7936), 485.

Power of Liquid-less Thermal Management

Today: Liquid-based

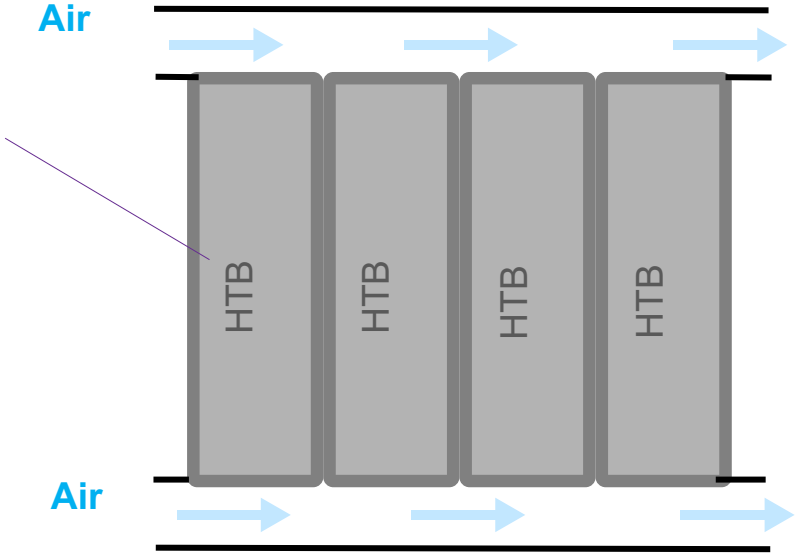




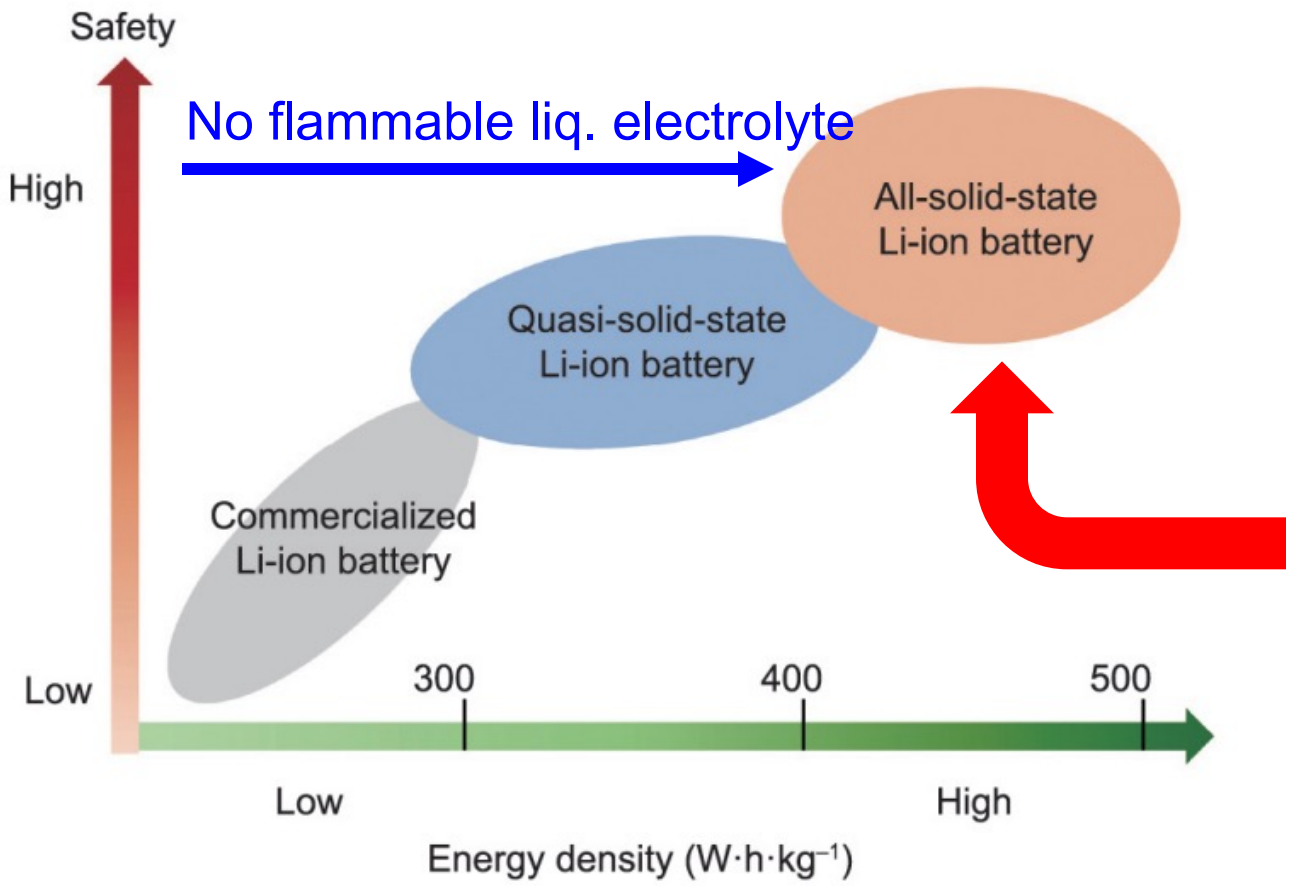
Tomorrow: Liquid-less

Next-Gen Battery

Utterly safe & simple pack



Case 3: Battery Safety & All Solid State Batteries



Wang and Sun, Engineering 21, 32-35 (2023)

Lithium Metal Anode

$4Li + O_2 \rightarrow 2Li_2O$
(Δh=4.3x10^7 J/kg; OF = 1/4)
Actual OF in NMC811 ~
0.5>1/4 (theoretical O_2)

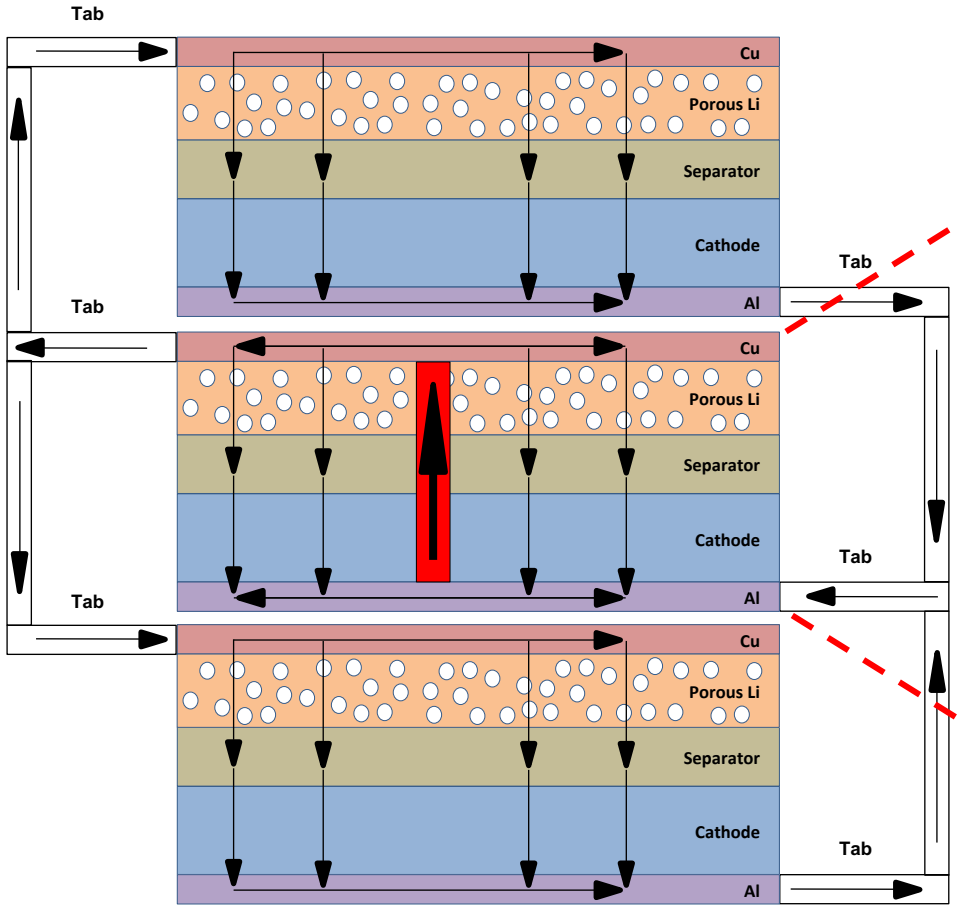
Unsafe All Solid State Batteries

Heat of combustion in various batteries

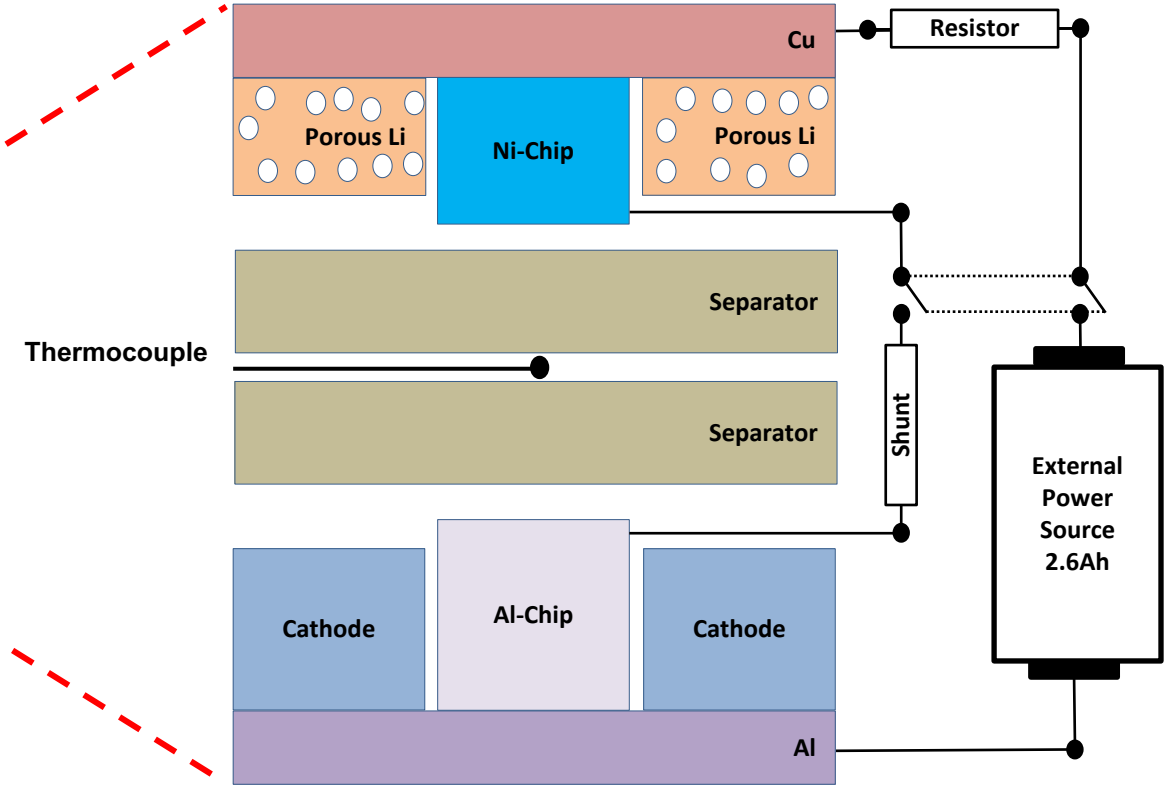
Fuel Sources	Thickness m	Heat of combust. J/kg	Mass kg/cm^2	Heat J/cm^2
in **LiBs**				
Ethylene carbonate (30wt%)		1.226E+07	1.697E-06	20.81
Ethyl methyl carbonate (70wt%)		1.841E+07	3.959E-06	72.89
Total				**93.69**
in **AFBs**				
20um Li metal deposited at 100%SOC	2.000E-05	4.300E+07	1.068E-06	45.92
DME in electrolyte		3.169E+07	1.116E-06	35.37
TTE in electrolyte		1.051E+07	7.186E-06	75.52
Total for AFB with LHCE				**156.81**
Total for solvent-free AFB				**45.92**
in **ASSBs** w/ 20um Li foil				
20um Li foil + 20um deposited at 100%SOC	4.000E-05	4.300E+07	2.136E-06	91.85
Total				**91.85**

Single-Layer Internal Shorting of LMBs

Physical Problem



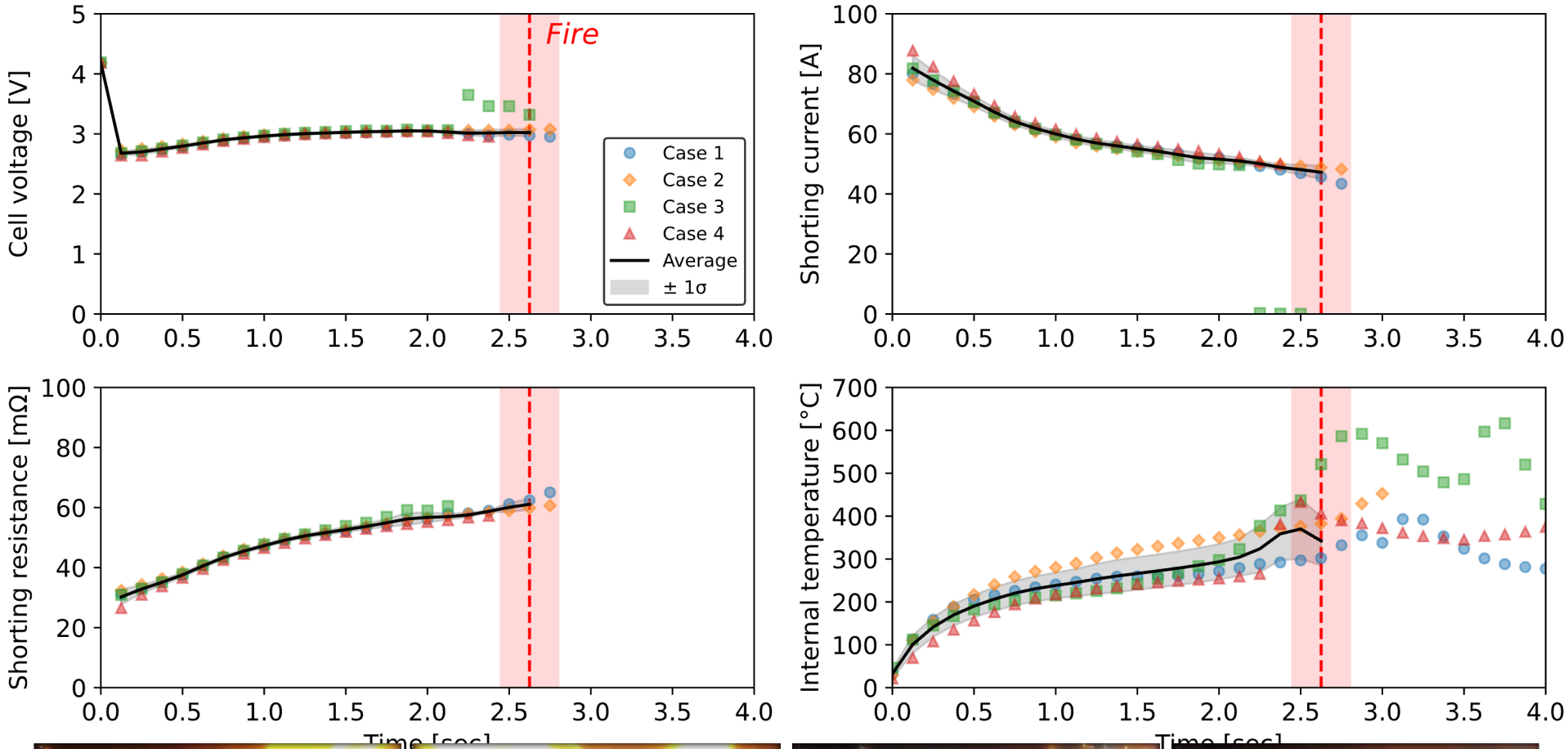
Experimental Setup



Violent Fires of Anode-Free Batteries with Liquid Electrolyte

NMC811/LHCE/Anode-free undergoes internal shorting:

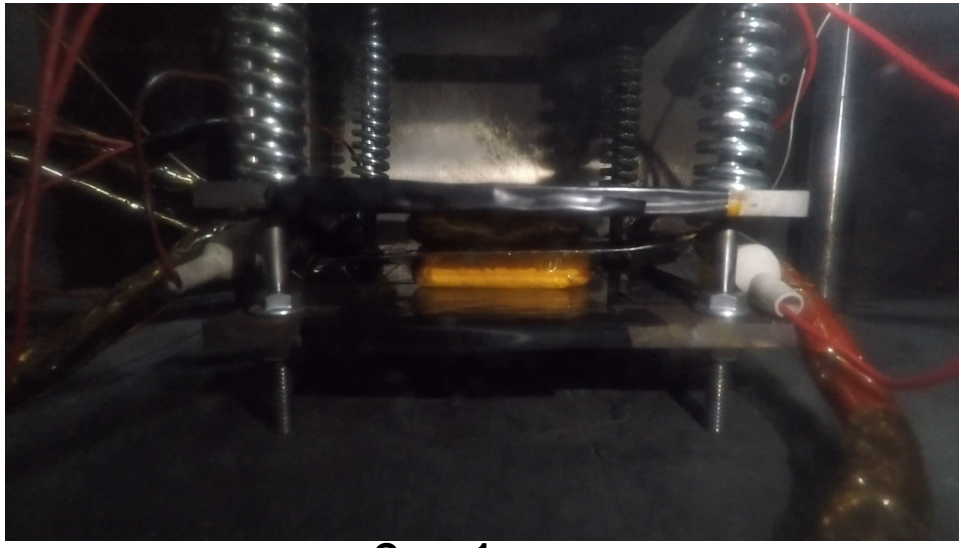
- There is fire in all 4 cases with the average ignition time of 2.6 sec (σ=0.18)



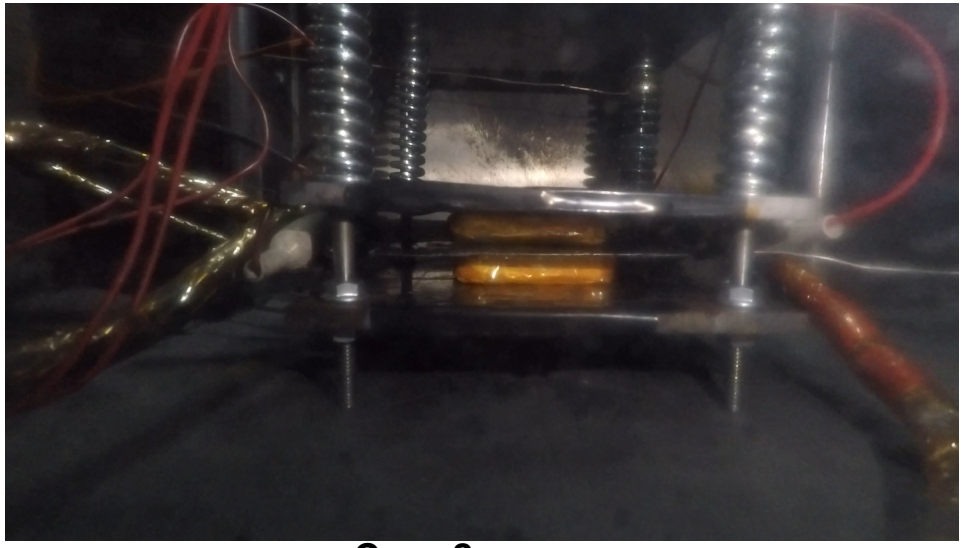
At t=3.6 sec



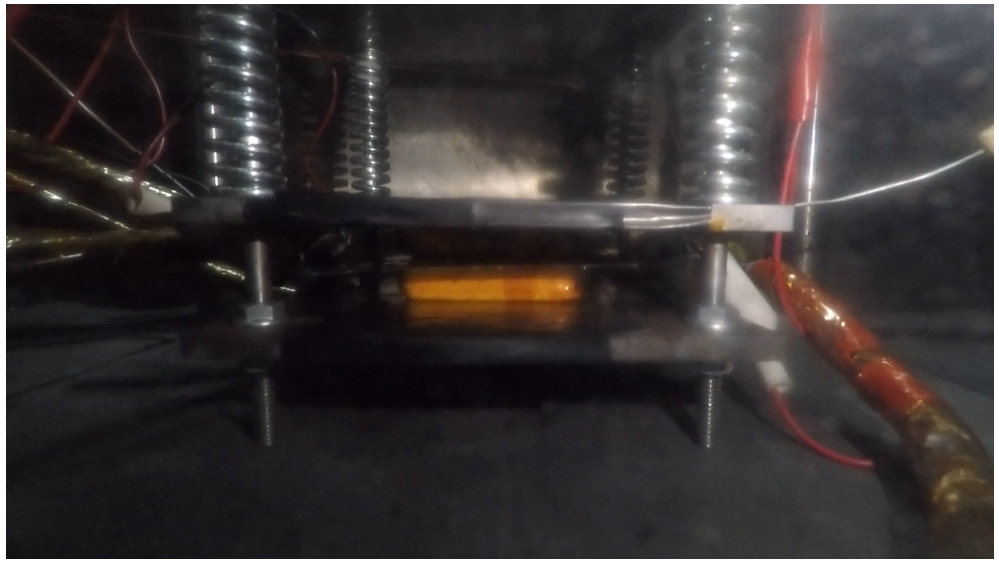
Internal Shorting of AFBs – Videos



Case 1



Case 2



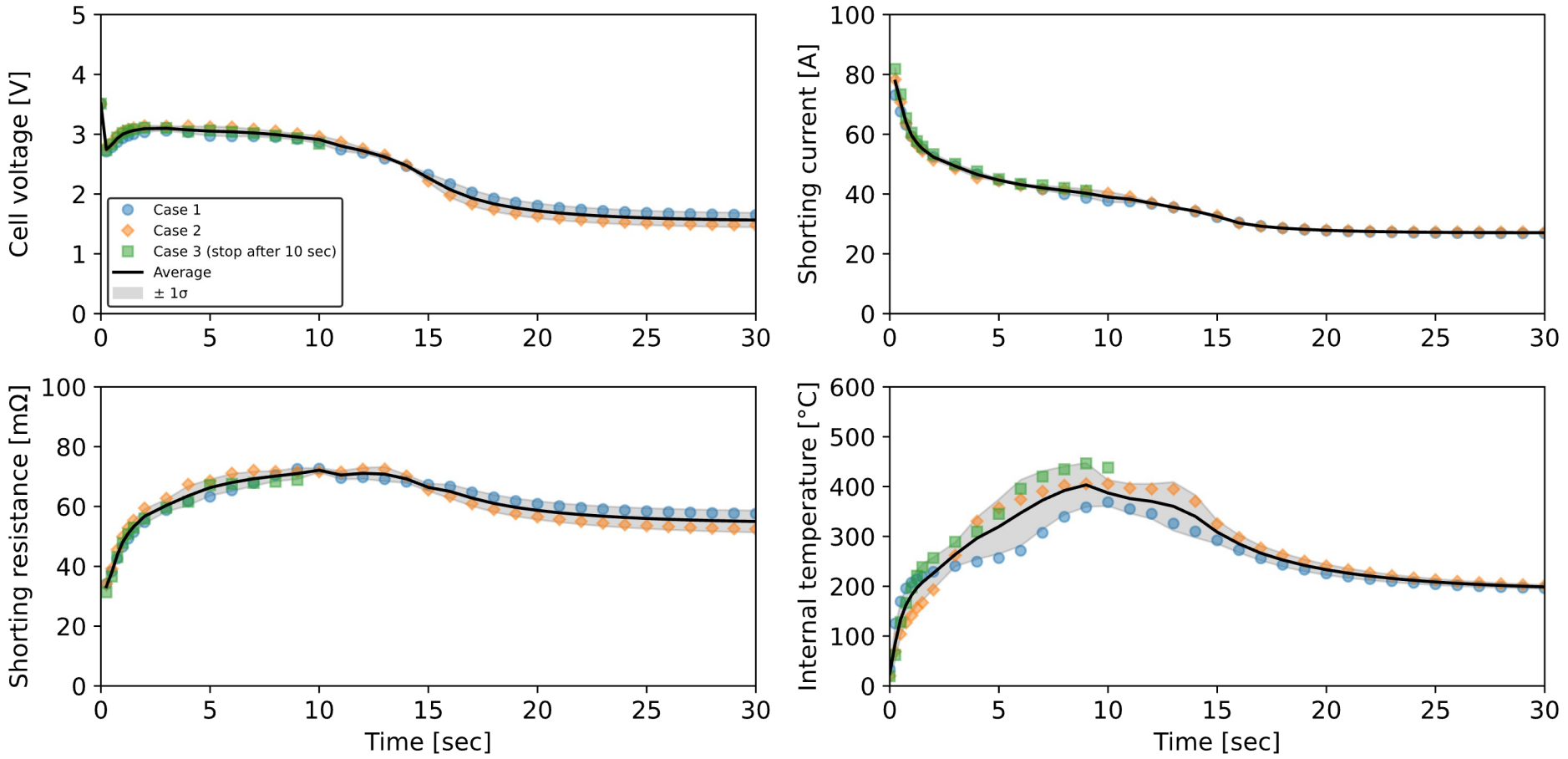
Case 3

- 3 NMC811/LHCE/Li Metal cells
- All cells catch fire at ~2.6 s.

No Fire of Anode-Free Batteries with LFP Cathode

LFP/LHCE/Anode-free undergoes internal shorting:

- There is no fire in all 3 cases

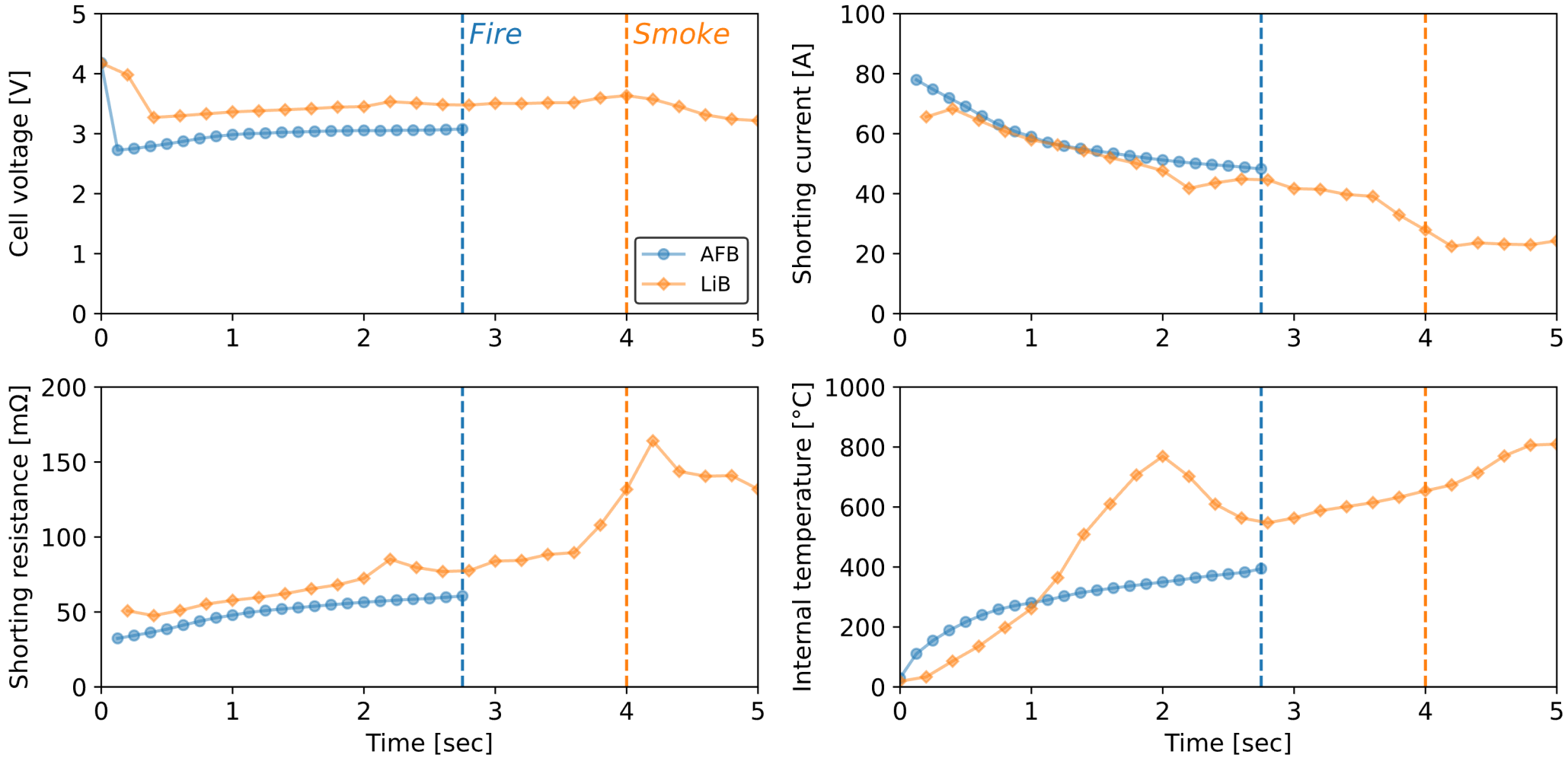


Combustion = Heat + Fuel + Oxygen

Fire: complete combustion

Smoke: incomplete combustion

Anode-Free Battery vs. LiB



Combustion = Heat + Fuel + Oxygen

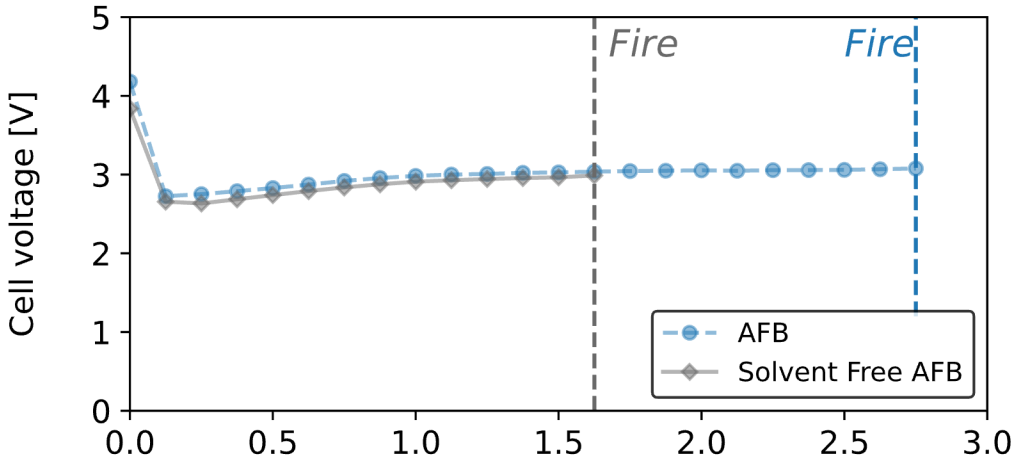
Fire: complete combustion

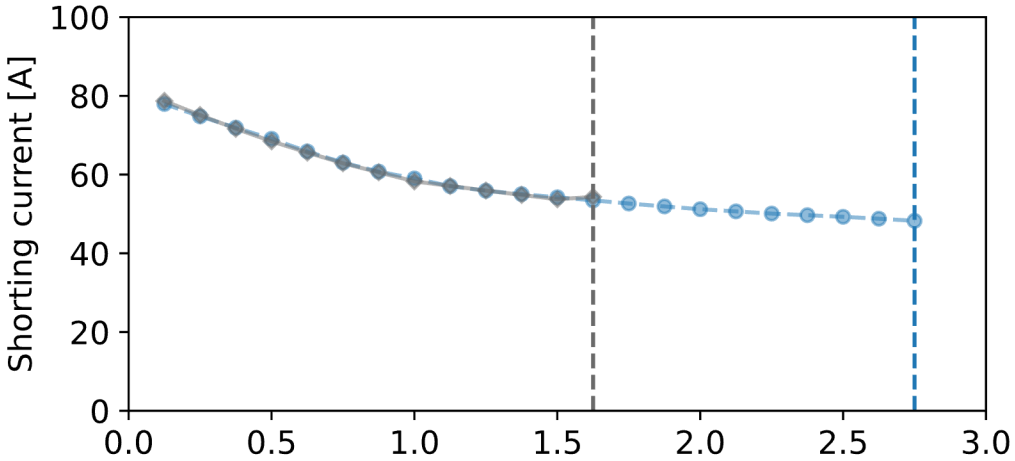
Smoke: incomplete combustion

Li metal is highly reactive

carbonates more difficult to burn

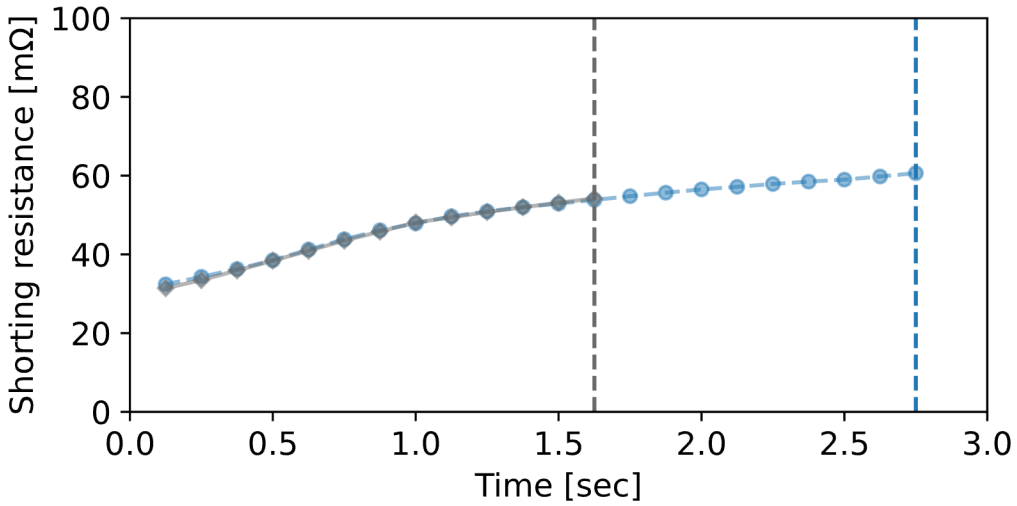
Violent Fire of Anode-Free Batteries w/o Liquid Electrolyte

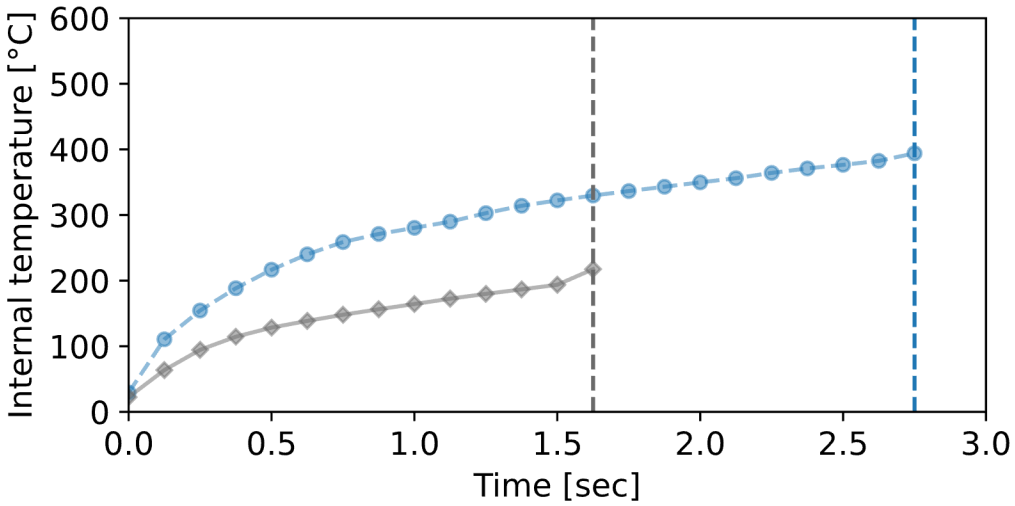






AFB (3.6sec)



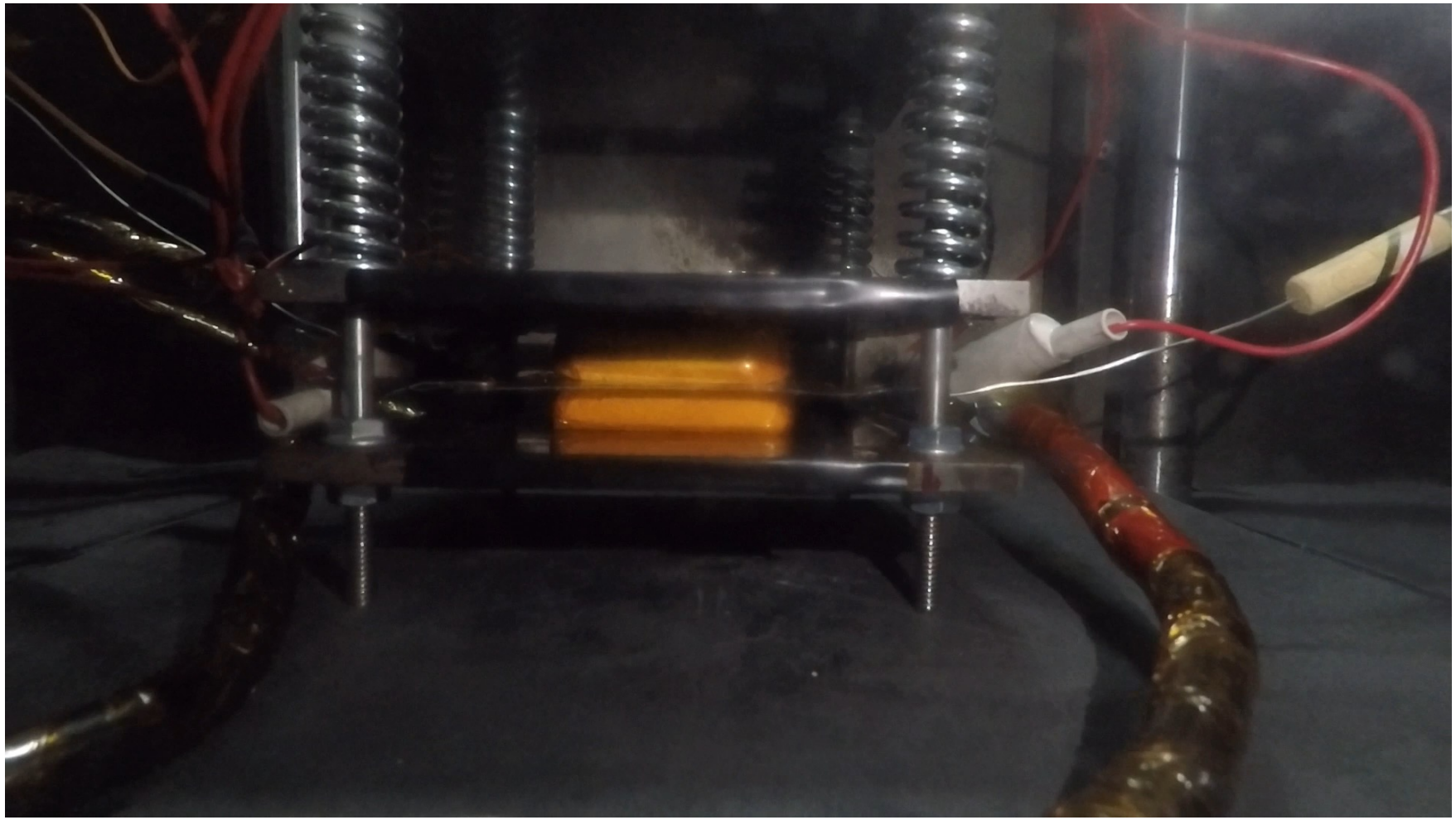




Solvent-free AFB (2.25sec)

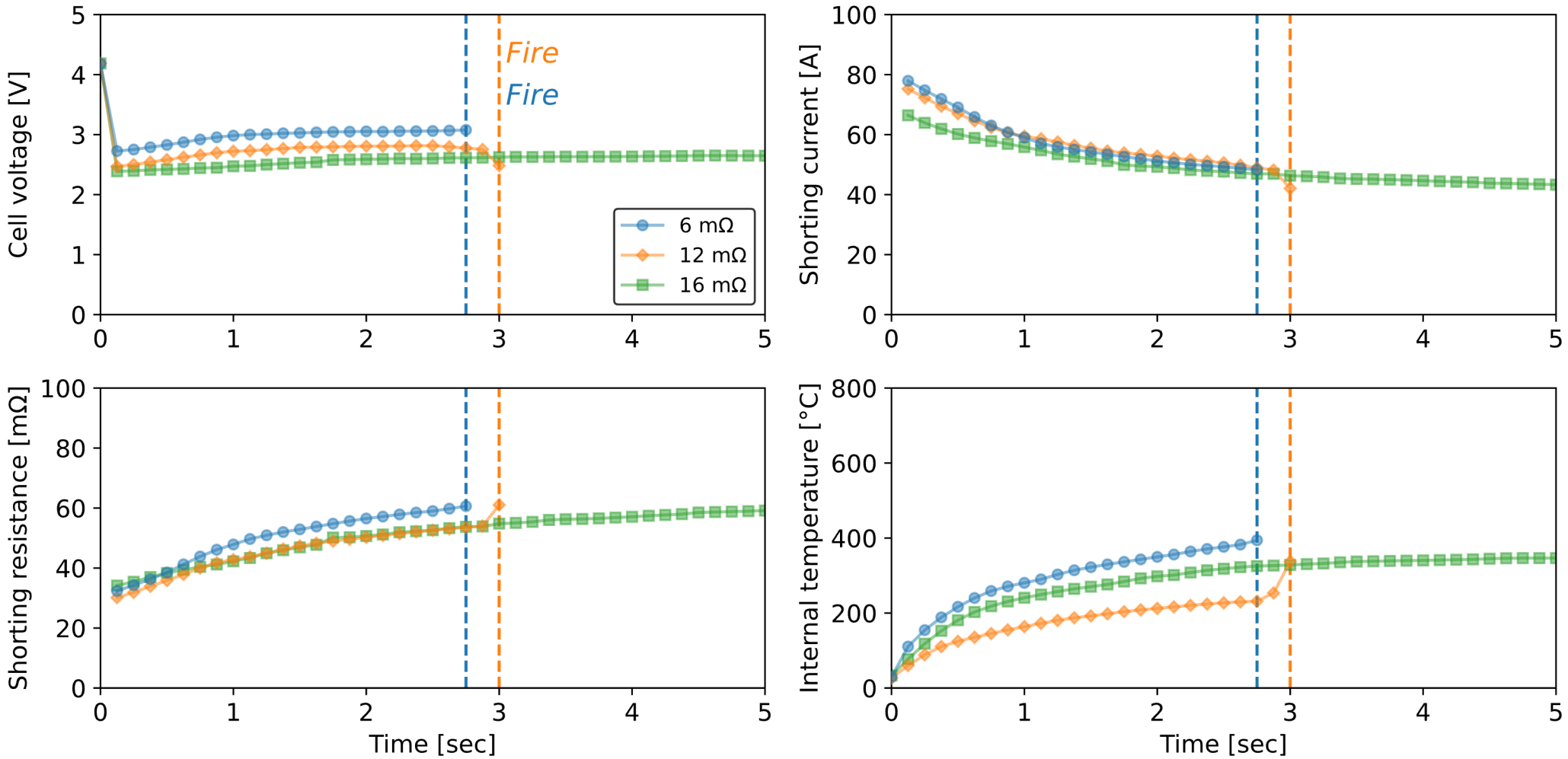
- A mock solid cell: liquid solvents evaporated under vacuum overnight.
- Ignition of the solvent-free cell was sooner than that w/ LHCE (1.6 vs. 2.6 sec).
  - Due to facile O_2 transport from O2-releasing cathode to Li metal anode thru open pores of a dry separator

Solvent-Free NMC/Li Metal – Video



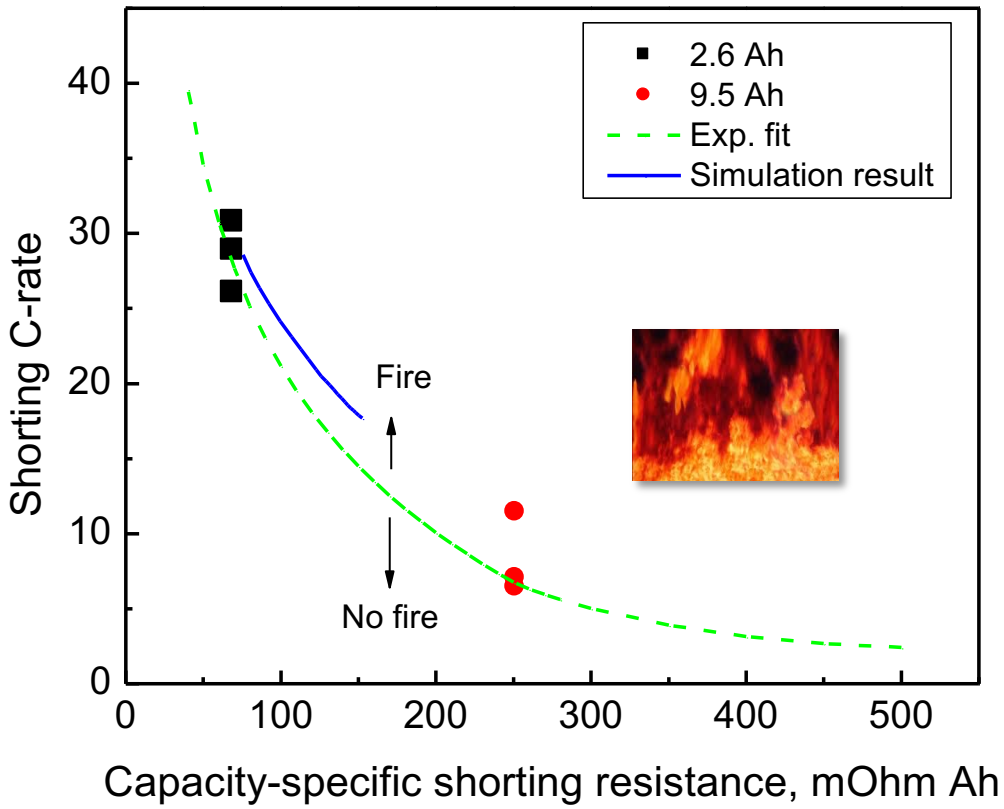
- Fire & explosion

Effect of Shorting Current



- There exists a threshold shorting current to trigger fires: ~70A or 27C of 2.6Ah cell

Safety Map



- Rate of thermal runaway:

$$\frac{dT}{dt} \sim \frac{ED}{c_p}\frac{1}{1/n} = \frac{n*ED}{c_p}$$

where *n* is the shorting C-rate.

- Larger cells are more dangerous.
- For large-Ah cells, the threshold shorting current for fires can be as low as ~5C!

Fire is More Likely in ASSBs and Smoke is in LiBs

Liquid solvent combustion in LiBs:

$(C_3H_4O_3 + 2\ C_4H_8O_3) + 11.5\ O_2 \rightarrow 7\ CO_2 + 6H_2O \quad \Delta H \sim 2980$ kJ

Combustion heat: 259 kJ/mol O_2

Li combustion in ASSBs:

$Li + 0.25\ O_2 \rightarrow 0.5\ Li_2O \quad \Delta H \sim 297$ kJ

Combustion heat: 1190 kJ/mol of O_2 – 4.6x less O_2 than in LiBs

- In ASSBs to generate 91.85 J/cm^2 heat, there are sufficient fuel + sufficient O2 -> fires
- In LiBs to generate 93.69 J/cm^2 heat, there is sufficient fuel + inadequate O2 -> smokes

Closing Comments

- Battery resilience under extreme conditions has been lacking for 2 centuries ever since Volta invented the anode/electrolyte/cathode structure.
- Industry & academia must face basic questions: 1) why batteries refuse to accept energy when it is most needed in extreme cold; 2) why batteries require AC system in extreme heat, effectively “self-discharging”. The more volatile solvents we add, the higher self-discharge rate in hot weather; 3) replacing liquid electrolyte with more flammable Li metal does not yield better safety in ASSBs.
- Without solving these fundamental problems, there would be no BEV industry.
- #1 priority in ASSBs is to figure out how to make them safe.
- Fire is most likely consequence of Li metal battery internal shorting.
- Fires from Li metal batteries occur in the time scale of 1-3 seconds, making pack-level safety engineering virtually in vain.全固态电池的最大头痛是秒级起火

Acknowledgements

Thank you for your attention

