Advancing safety in energy storage systems through pre- and post- incident gas monitoring

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Energy Storage Safety and Reliability Forum
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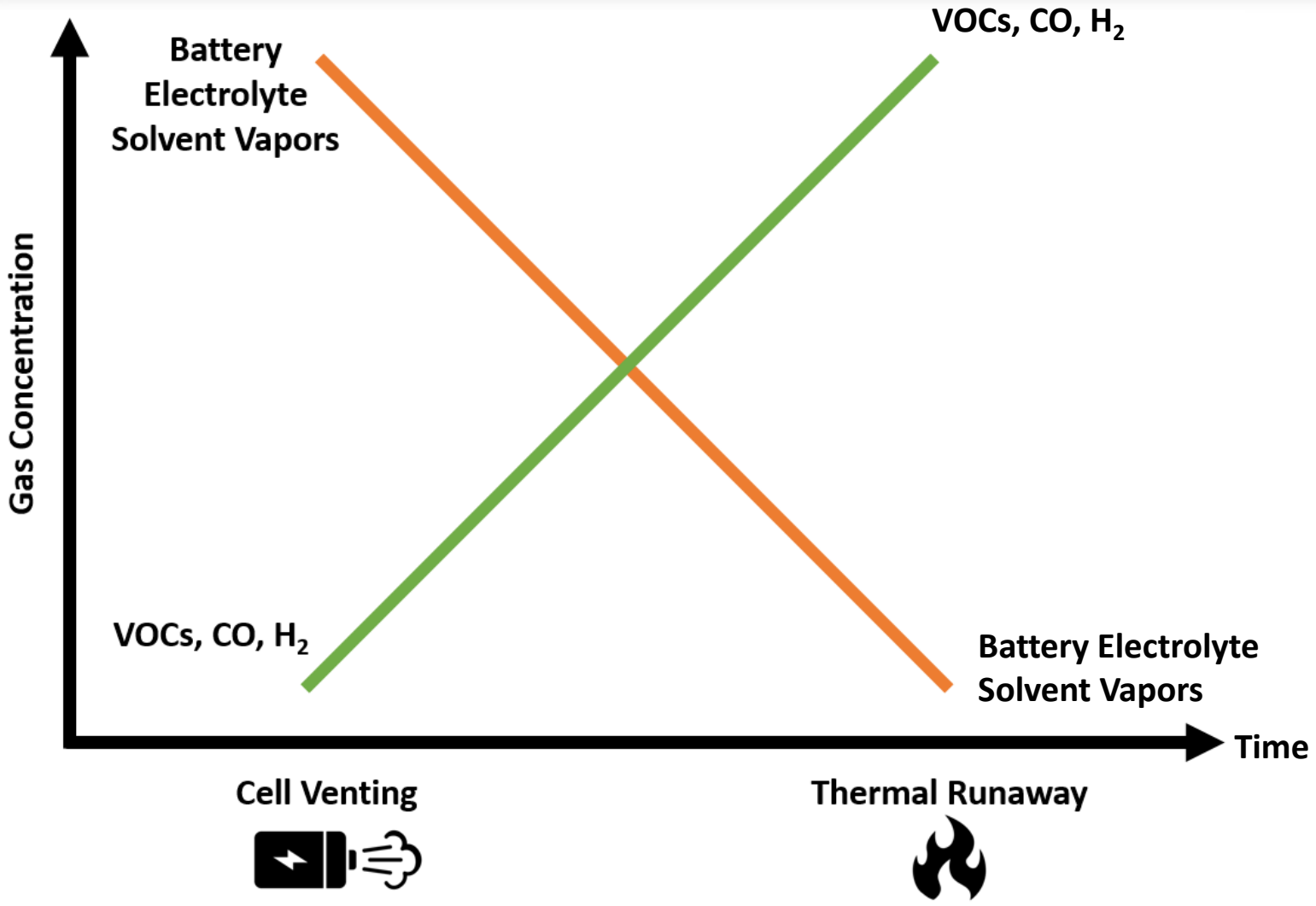
Gas production characteristics of Li-ion



Two stage gas release

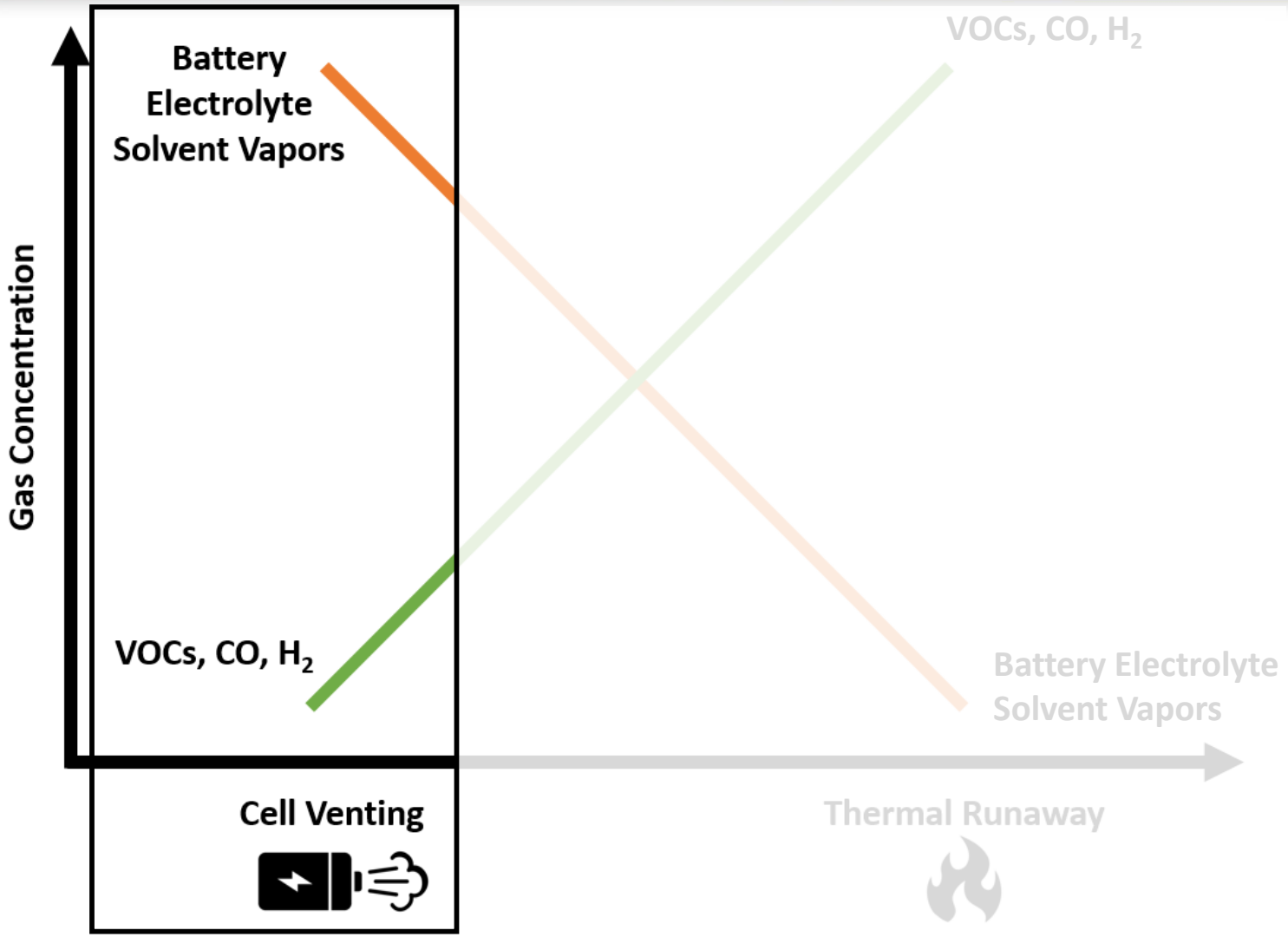
First stage:

- Initial cell venting
- Results from battery electrolyte solvent degradation (gas formation)
- Degradation stems from battery abuse, including thermal, electrical, and mechanical abuse
- Initial cell venting occurs, on average, 8 minutes prior to thermal runaway

Second stage:

- Thermal runaway
- Extreme temperature spike, often exceeding 1000°C
- Fire and smoke are emitted from the battery
- Risk of failure propagation to surrounding cells is likely

Gas production characteristics of Li-ion



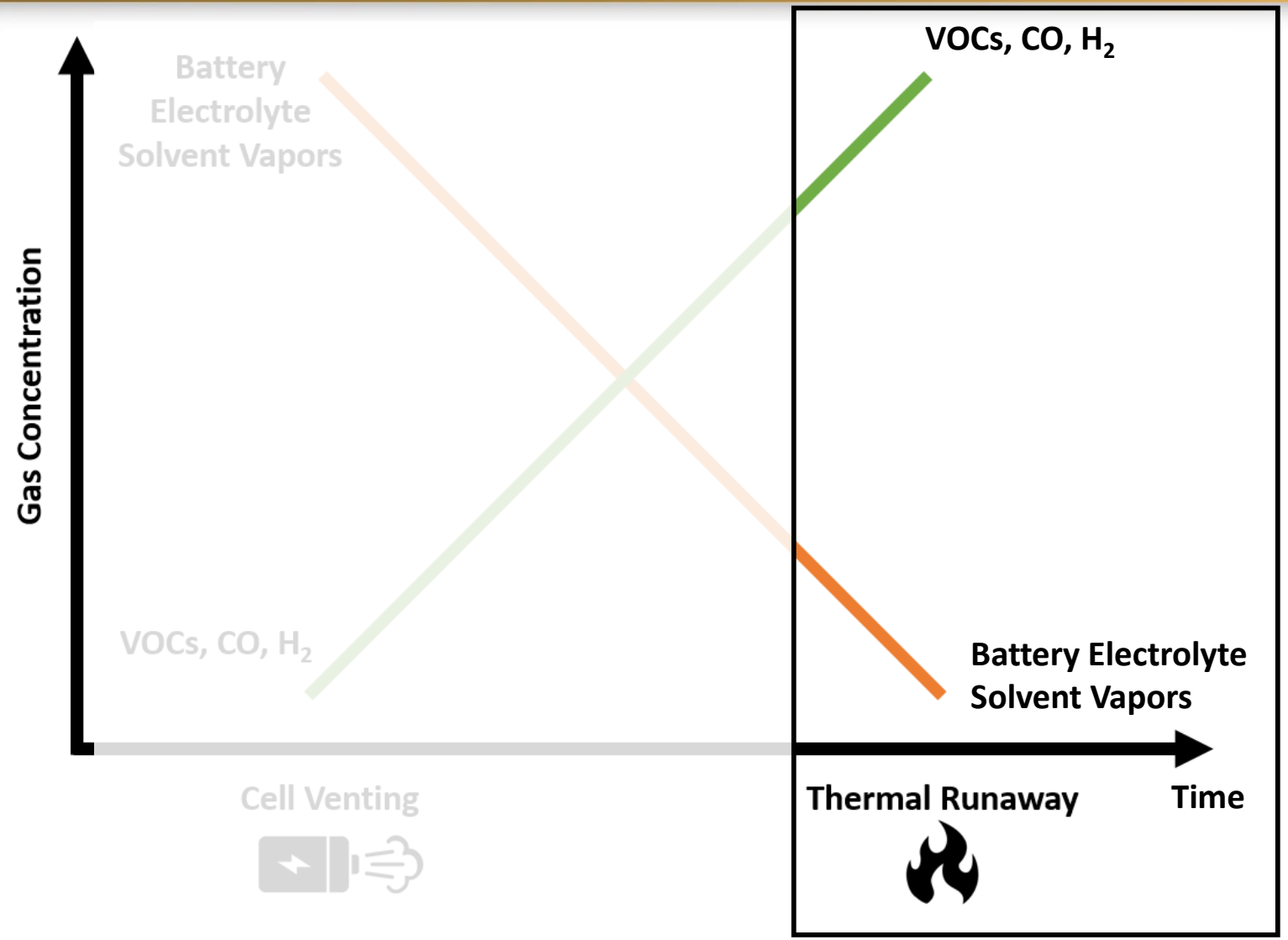
Two stage gas release

First stage:

- Gas composition is predominantly battery electrolyte solvent vapors (BESV) and water vapor[1]
  - BESV = EMC, DMC, DEC, EC,PC, etc.
  - Volatile carbonate liquid solutions
- Trace volatile organic compounds (VOCs), CO, and H_2
- Occurs, on average, 10 minutes prior to thermal runaway
- Gas generation is typically 1 – 2 orders of magnitude less than second stage, both in rate and total quantity of gas generated
  - 15-150 ppm/sec generation rate
  - 0.5 – 3.0 Liters gas production

[1] Essl, C.; Golubkov, A.W.;Fuchs, A. Influence of Aging on the Failing Behavior of Automotive Lithium-Ion Batteries.Batteries2021,7, 23. https://doi.org/10.3390/batteries7020023

Gas production characteristics of Li-ion



Two stage gas release

Second stage:

- Gas composition is predominantly CO, H_2, and CO_2, and VOCs[1]
- Trace BESV
- Fire and smoke are emitted from the battery
- Risk of failure propagation to surrounding cells is likely

[1] Essl, C.; Golubkov, A.W.;Fuchs, A. Influence of Aging on the Failing Behavior of Automotive Lithium-Ion Batteries.Batteries2021,7, 23. https://doi.org/10.3390/batteries7020023

First stage gas composition

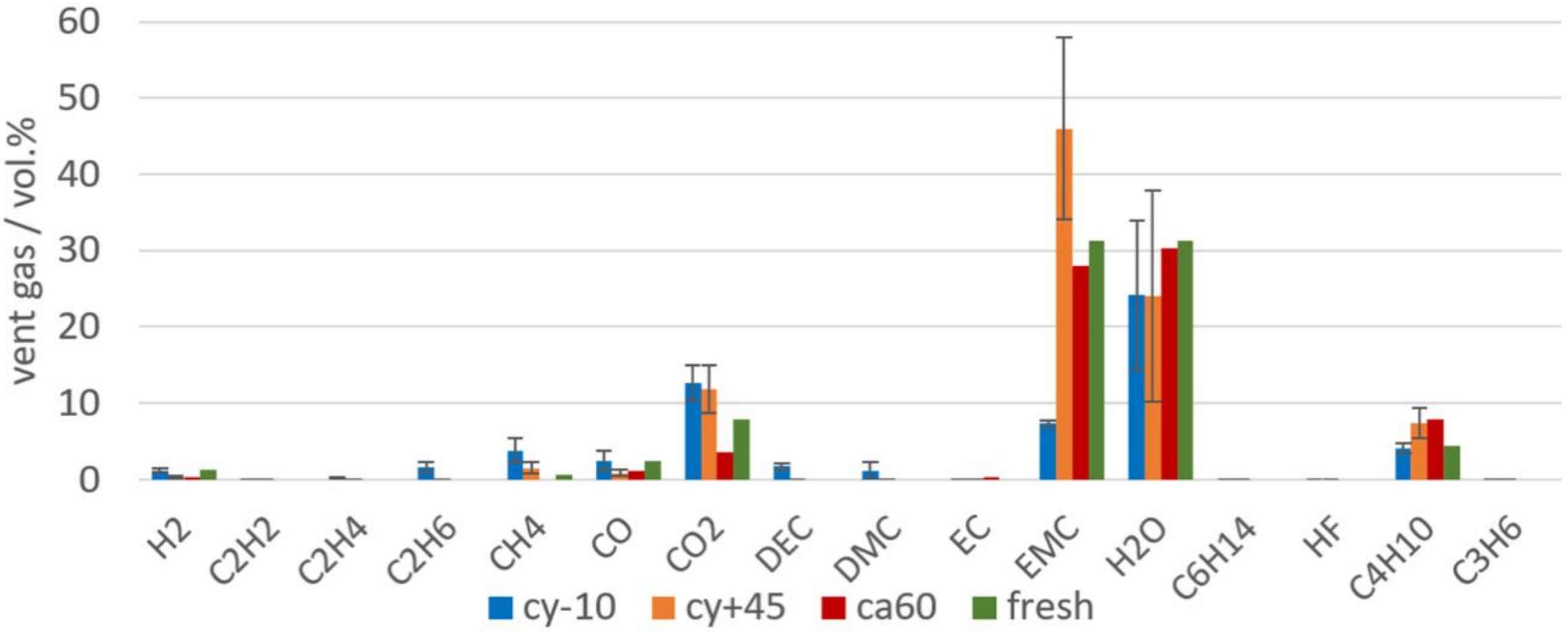


Figure 1. Gas species as a function of volume % in the initial cell venting of a 41 Ah NMC lithium-ion battery during an overheating test.[2]

[2] Essl, C.; Golubkov, A.W.;Fuchs, A. Influence of Aging on the Failing Behavior of Automotive Lithium-Ion Batteries.Batteries2021,7, 23. https://doi.org/10.3390/batteries7020023; Figure 5b

Second stage gas composition

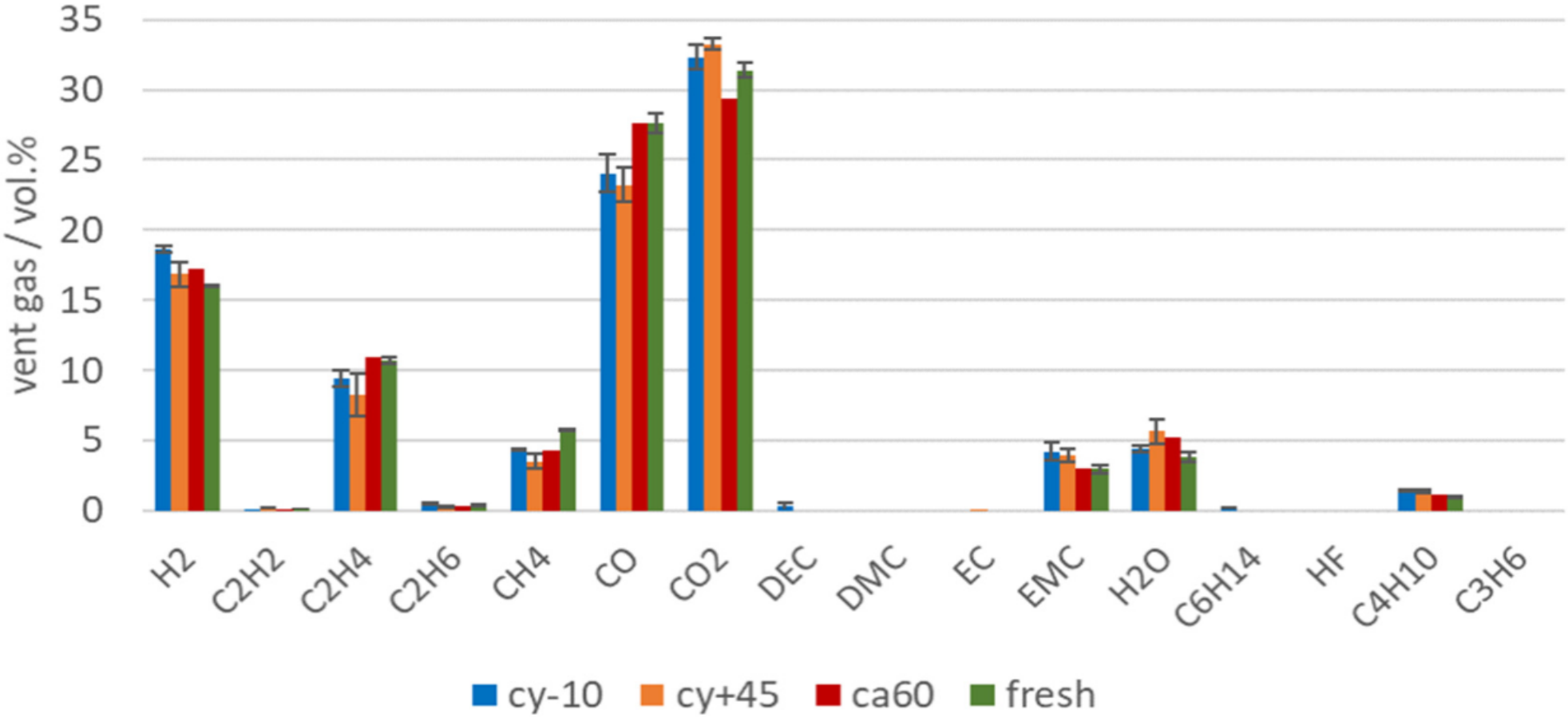


Figure 2. Gas species as a function of volume % in the second venting (thermal runaway) of a 41 Ah NMC lithium-ion battery during an overheating test.[3]

[3] Essl, C.; Golubkov, A.W.;Fuchs, A. Influence of Aging on the Failing Behavior of Automotive Lithium-Ion Batteries.Batteries2021,7, 23. https://doi.org/10.3390/batteries7020023; Figure 6

Initial cell venting in regulations

Definition (per NFPA 855):

- Off-gas event: The event in which the cell case vents due to a rise in internal pressure of the cell.

UL 9540A

<u>UL 9540A Cell level test measures venting separate from thermal runaway:</u>

7.3.1.8 The temperature at which the cell case vents due to internal pressure rise shall be documented. ← **off-gas event**

7.3.1.9 The temperature at the onset of thermal runaway shall be documented. ← **thermal runaway**

Application-Focused Testing

- Gas analyses of battery failures are not often performed with application-specific conditions

- Testing batteries where
  - Widely used batteries are failed,
  - Batteries are placed within representative volumes (racks for stationary ESS),
  - Industry gas monitoring solutions are used,
  - Gas monitoring solutions are placed in realistic scenarios,
  - Air flow conditions are realistic

Generates very valuable comparative data on which available solutions can provide the best warning of lithium-ion battery failures.

Application-Focused Testing

Test conditions

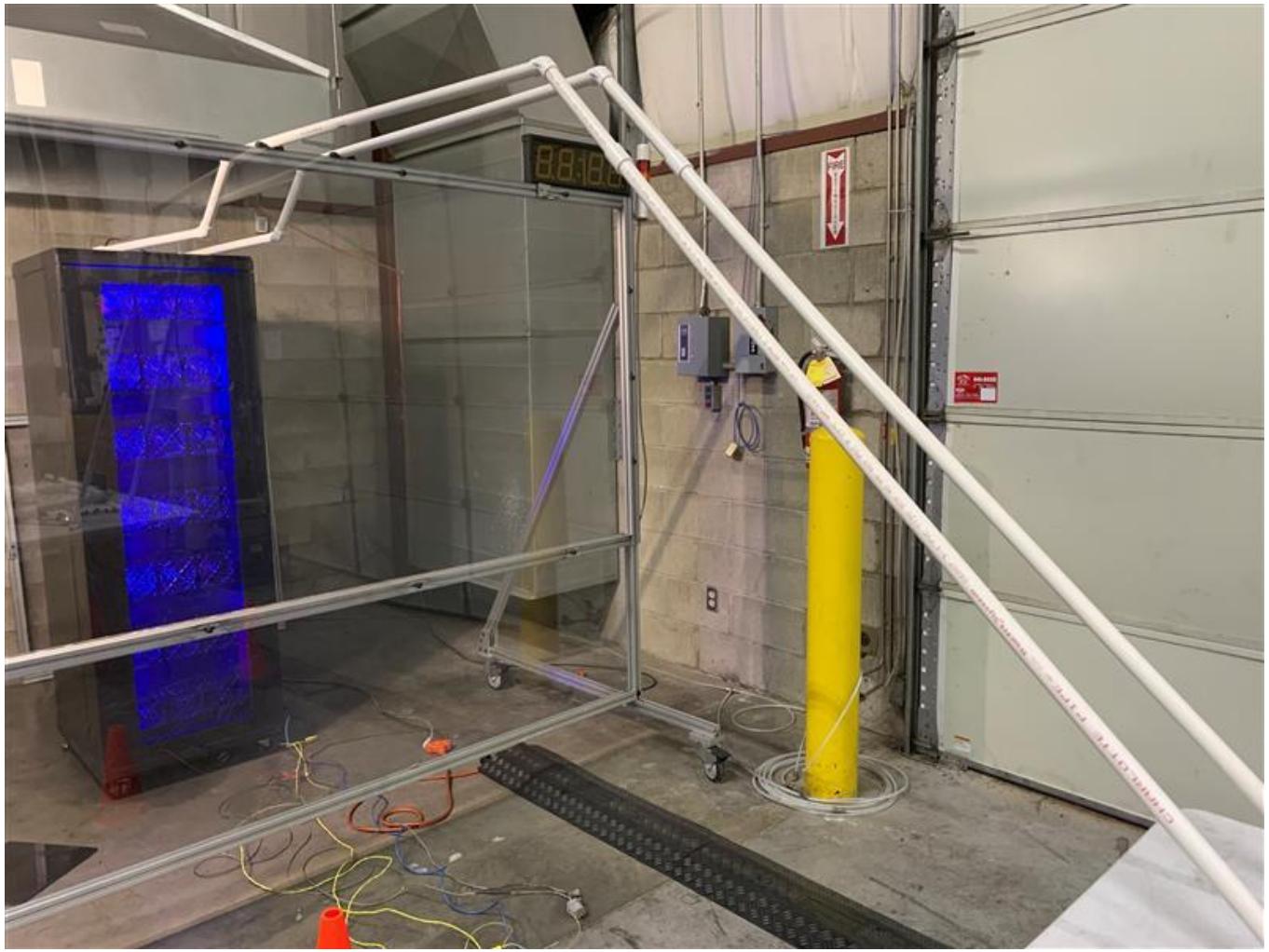
- Gas detectors are placed on aspirating pipe
- Battery is failed within representative volume
- Gas detectors are placed in realistic positions
- Aspirating pipe is placed on top of rack
- Rack has mock battery modules and module fans for forced air convection

Cell tested

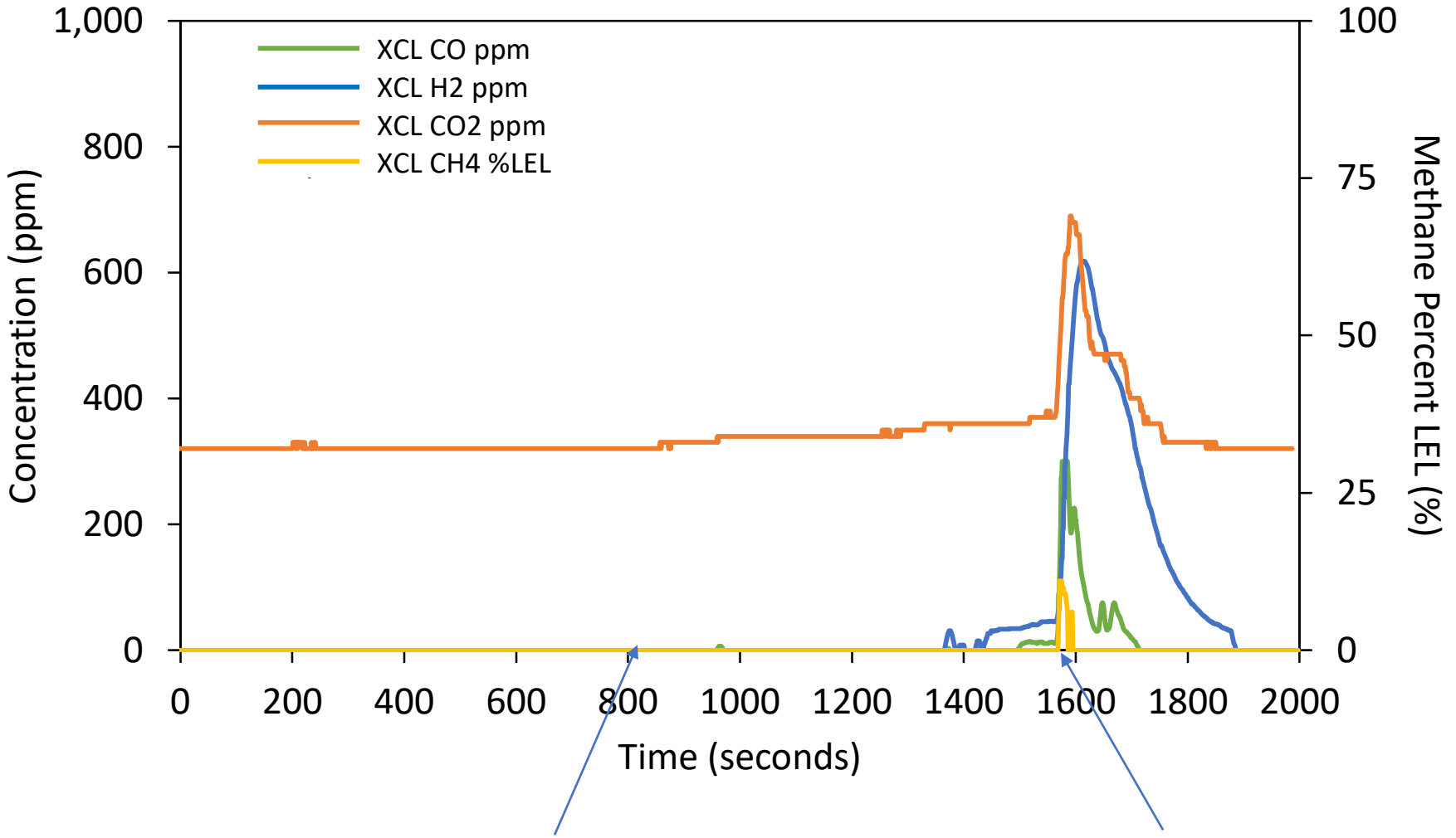
- Form factor: Prismatic
- Chemistry: $LiFePO_4$ (LFP)
- Capacity: 280 Ah
- Failure mode: Overcharge

Gas detectors tested

- Li-ion Tamer
- XCL H_2 ppm
- XCL CO ppm
- XCL CO_2 ppm
- XCL CH_4 %LEL



Gas Monitor Responses



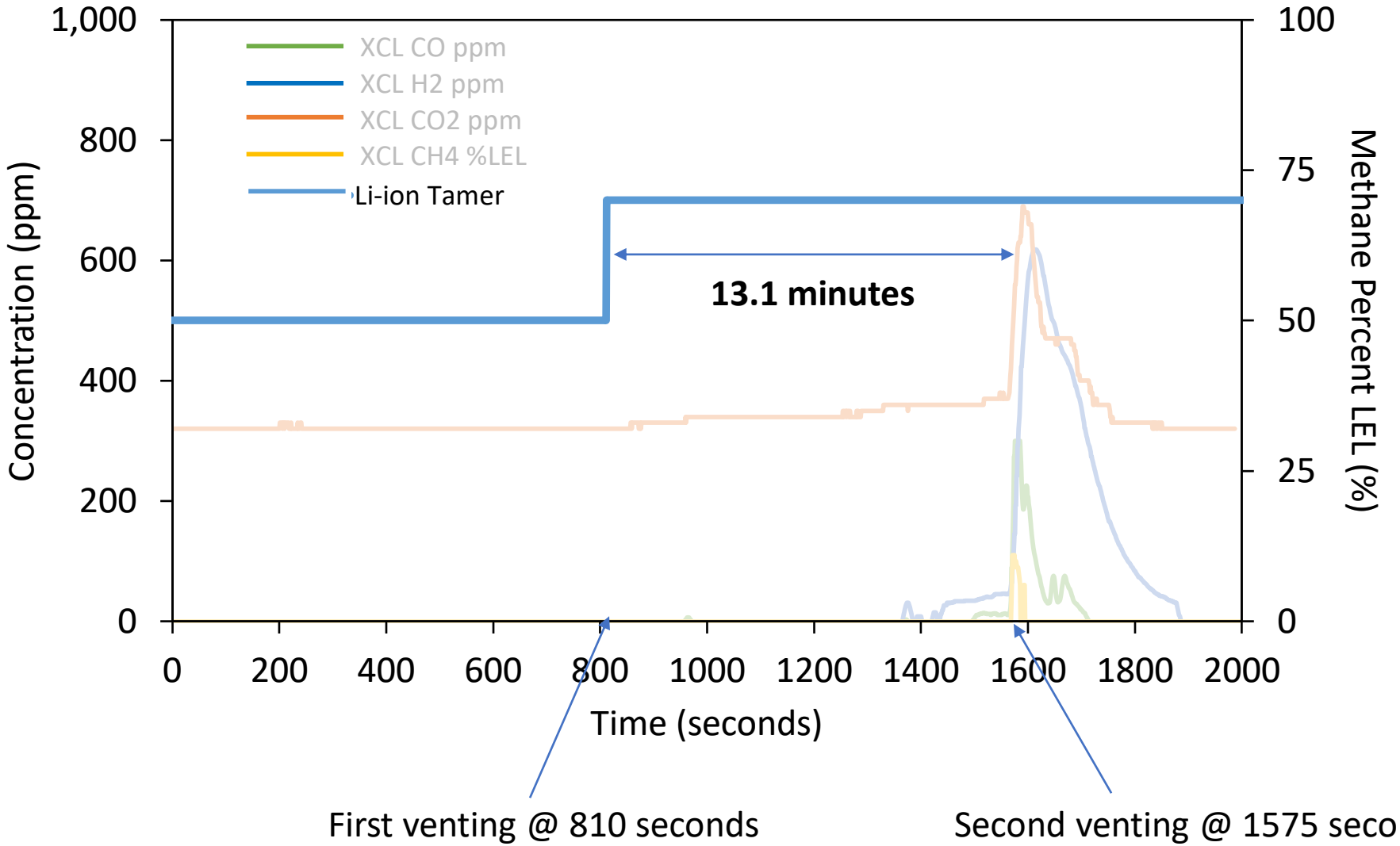
CO Monitor
Peak response: 300 PPM
First venting response: No
Second venting response: Yes

H_2 Monitor
Peak response: 600 PPM
First venting response: No
Second venting response: Yes

CO_2 Monitor
Peak response: 670 PPM (320 PPM ambient)
First venting response: No
Second venting response: Yes

CH_4 Monitor
Peak response: 10% LEL
First venting response: No
Second venting response: Yes

Gas Monitor Responses



Li-ion Tamer response

First venting response: Yes

Second venting response: Yes

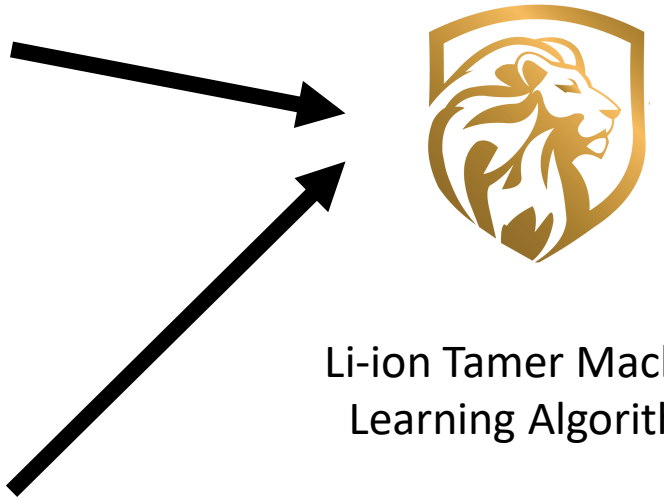
Li-ion Tamer responds immediately to first venting

Li-ion Tamer provides 13.1 minutes of early warning!

Li-ion Tamer operation theory

Battery Failure Tests with Application-Specific Conditions

Events which should not trigger sensor



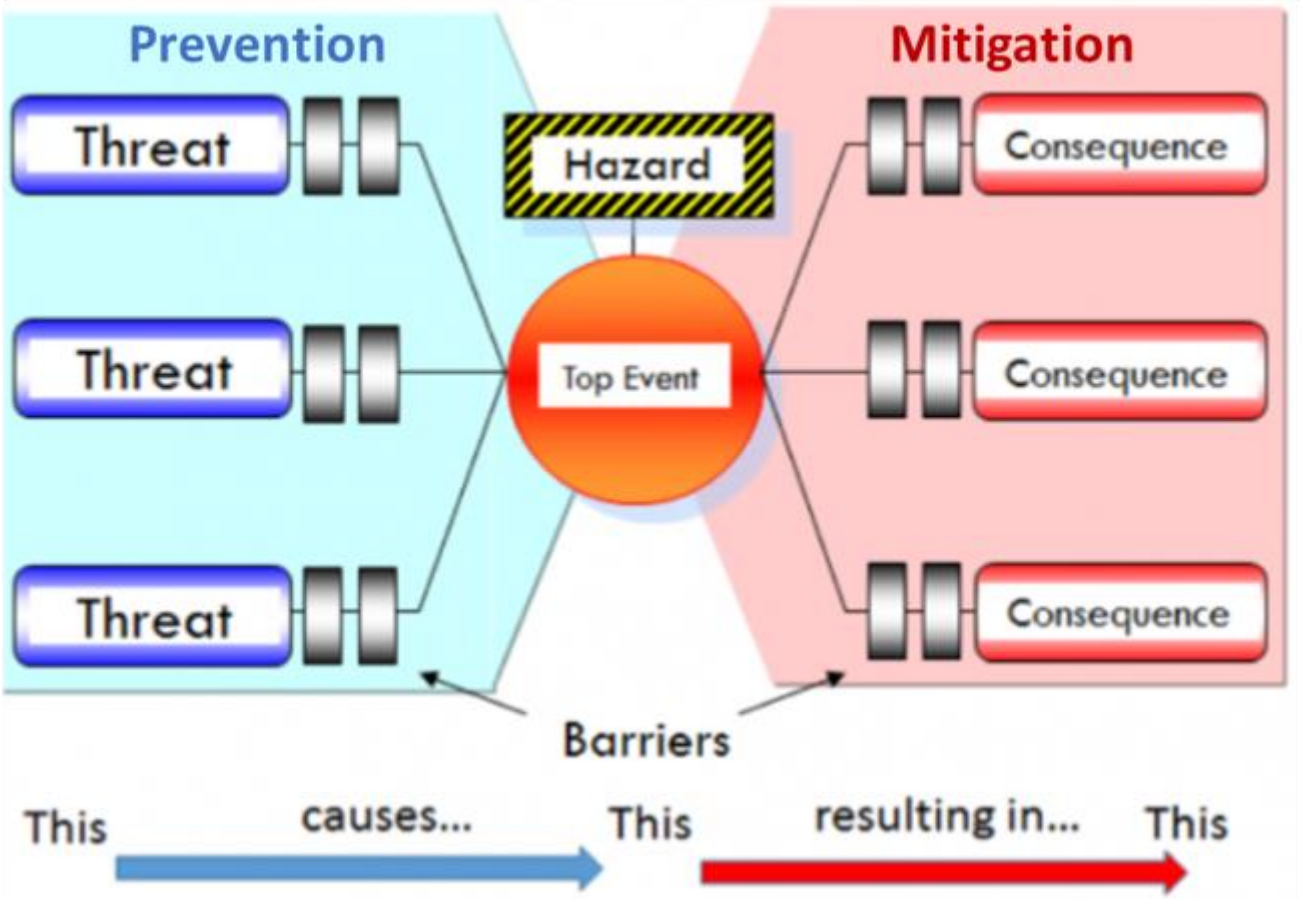
Li-ion Tamer Machine Learning Algorithm

Event Detection Algorithm

Metal-oxide based gas sensor
Li-ion Tamer event detection algorithm is based on actual battery failure scenarios
Detection threshold is rate-of-change based
Event detection algorithm returns to normal state when gas is no longer present
Detection principle: monitor for gas before dilution/dispersion through localization

Hazard Mitigation Analysis

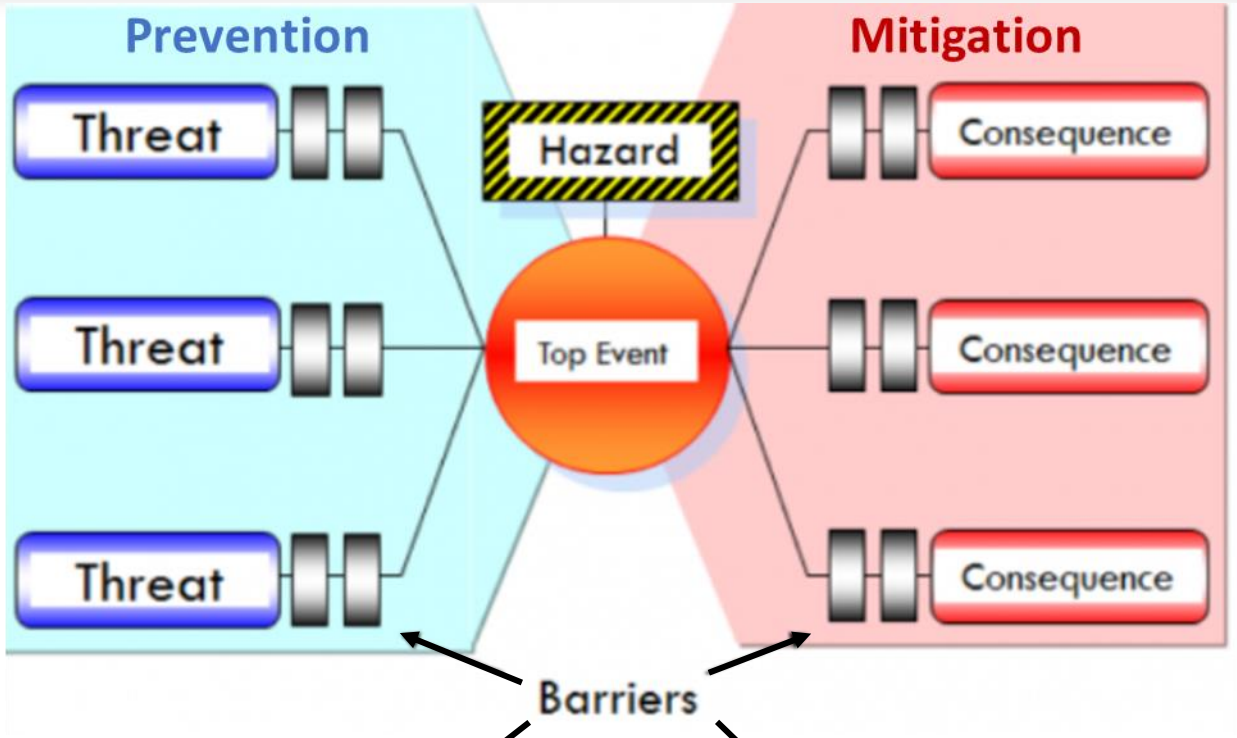
- NPFA 855, Section 4.1.4 requires an HMA
- Reference HMA available in EPRI's "Energy Storage Reference Fire Hazard Mitigation Analysis"[4]
- Bow tie analysis
- Prevention and Mitigation
- Identify barriers on both sides
- Gas risks identified in both Threat and Consequence pathways
- General need for situational awareness – Risk of gas inside container



[4] https://www.epri.com/research/products/000000003002017136

Gas Detection as Barriers

"..early [gas] detection, coupled with correct system shutdown measures **is an important safety barrier."**[5]



Gas detection as barriers:

Type of Gas Detection	Prevention	Mitigation
Conventional Gas Detection	✗	✓
Off-gas Detection	✓	✓

[5] B. Gully et al, "MARITIME BATTERY SAFETY JOINT DEVELOPMENT PROJECT - Technical Reference for Li-ion Battery Explosion Risk and Fire Suppression", DNV GL AS Maritime, Norway, 2019-1025, Rev. 4, Nov. 2019.

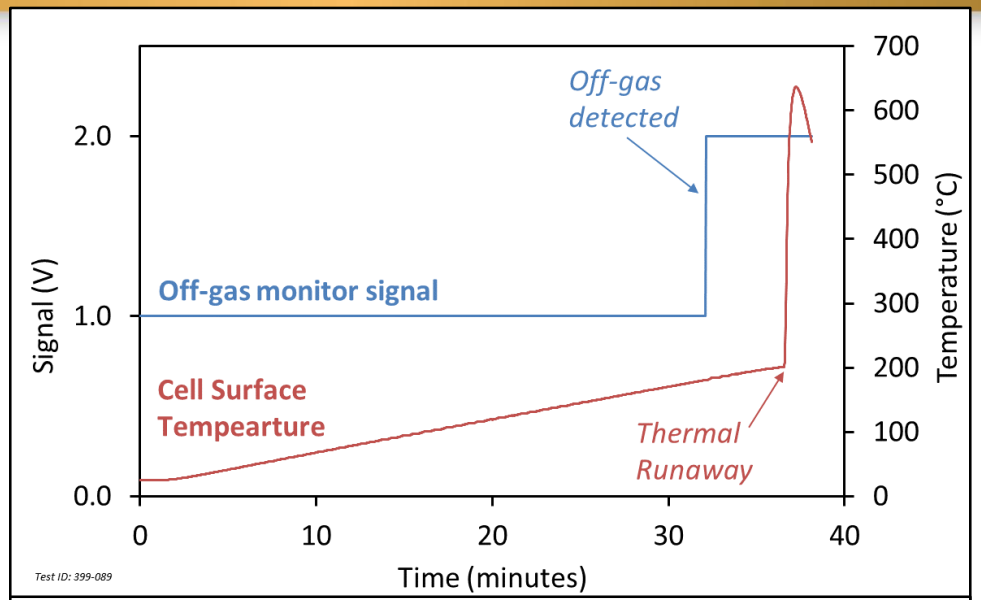
Li-ion Tamer is an Effective Barrier to Thermal Runaway

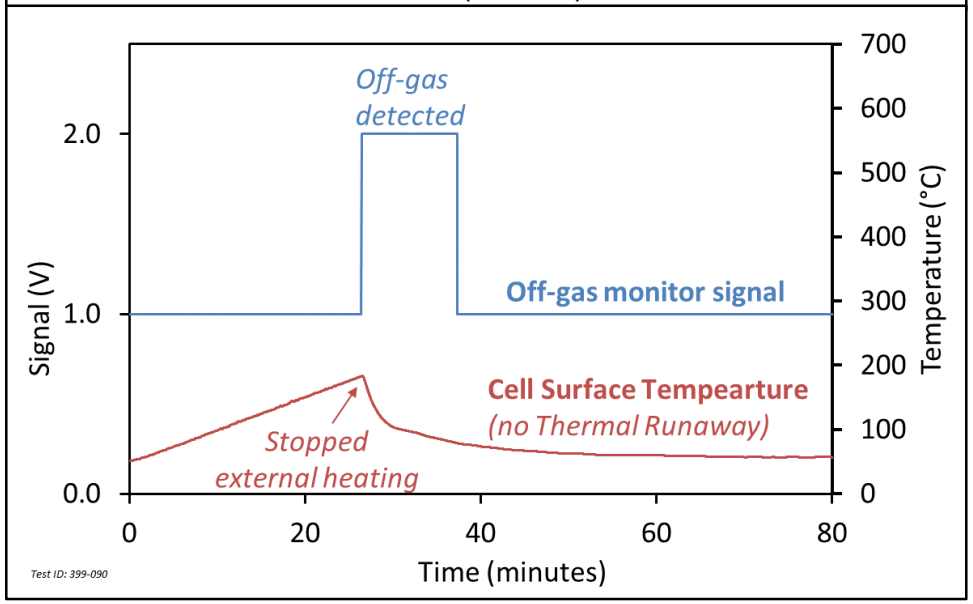
Test 1: Early Warning

- UL 9540A test method distinguishes between venting and thermal runaway
- Off-gas detection can provide early warning
- Independent of chemistry, capacity, and form factor

Test 2: Barrier to Thermal Runaway

- Off-gas monitoring can enable mitigation
- Isolate from charge/load when off-gas occurs
- Provides an effective barrier to thermal runaway





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