Presentation ID 701

Thermal Runaway Studies: Development of Coatings for Over-Temperature Warning and Database of Hazards Risk Ranking

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  Oak Ridge National Laboratory

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OE ESS Project No. 1 : Thermal Runaway Detection Method Thermally Sensitive Paint Development

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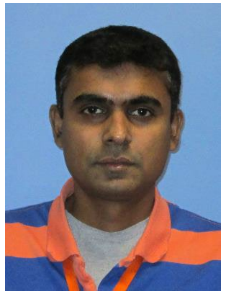

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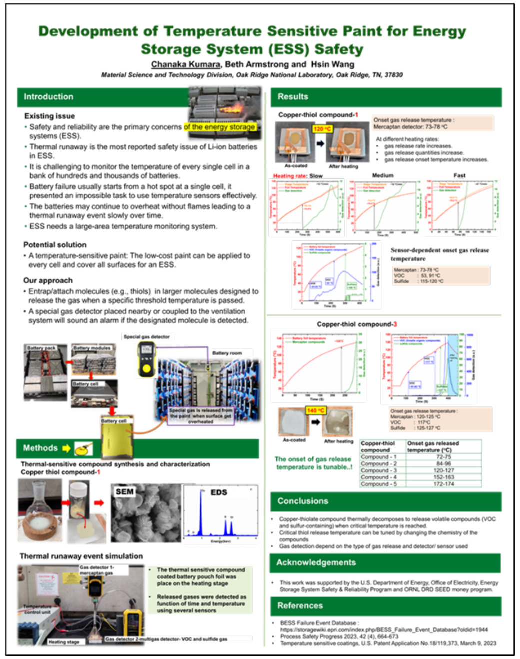

OE ESS Project No. 2 : Thermal Runaway Severity Safety Database (With Sandia National Lab)

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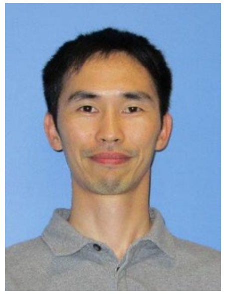

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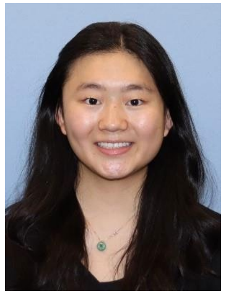

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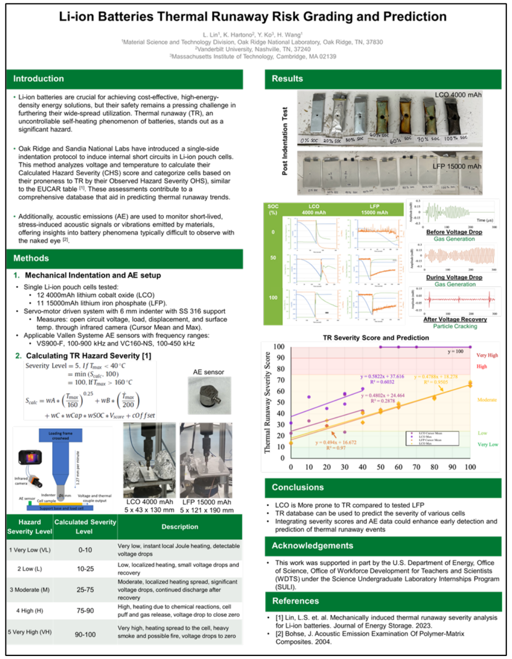

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Developing early warning system for energy storage system (ESS) safety

Existing issue

- Safety and reliability are the primary concerns of the ESS.
- Battery failure usually starts from a hot spot at a single cell, it presented an impossible task to use temperature sensors effectively.
- The batteries may continue to overheat without flames.

Potential solution

- A temperature-sensitive paint: The low-cost paint can be potentially applied to every cell and cover all surfaces for an ESS.

Approach

- Entrap/attach molecules (e.g., thiols) in larger molecules designed to release the gas when a certain threshold temperature is passed.
- A special gas detector placed nearby or coupled to the ventilation system with ppm level sensitivity will sound an alarm of the potential danger.

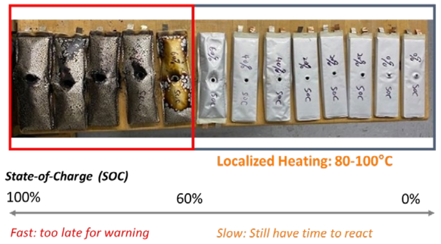
April 2019


Cause of APS battery explosion that injured 9 first responders detailed in new report

July 2021


Tesla 'big battery' fire fuels concerns over lithium risks

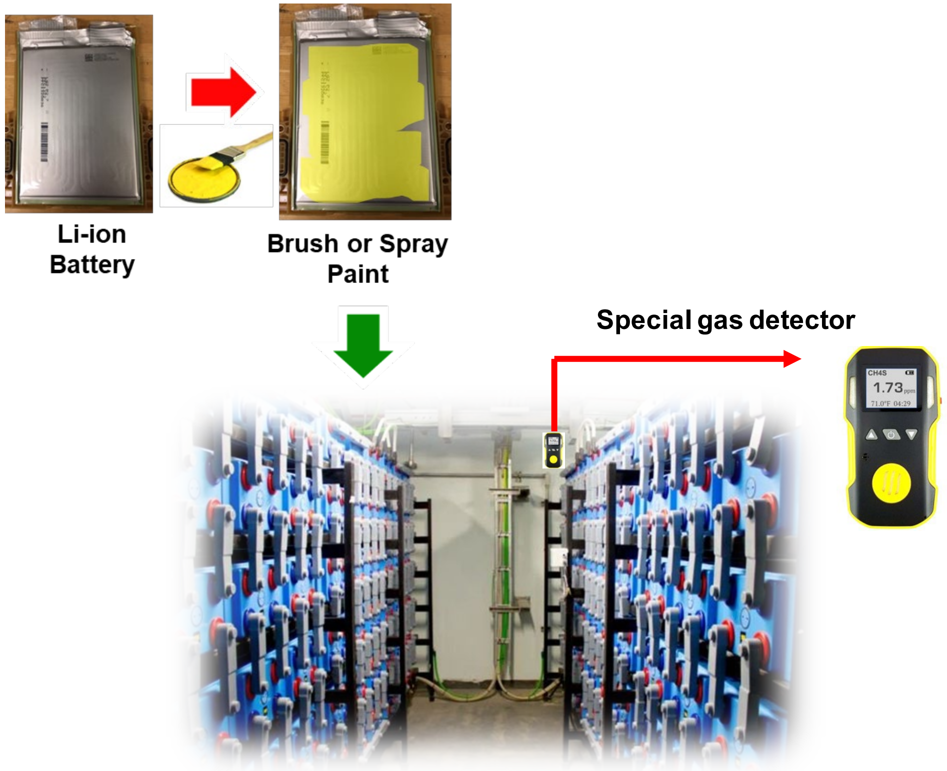
Latest incident comes as utilities around the world increasingly rely on lithium-ion to store renewable energy



Thermally sensitive paint development

Temperature-sensitive paint for $T_{Threshold}$ monitoring

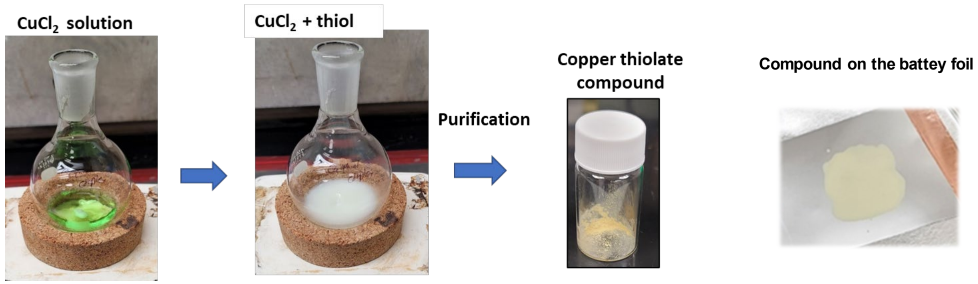
- Stays normal within battery operation temperature
- Release chemical/gas $T > T_{Threshold}$
- No-line-of-sight
- Detection via "smell" and gas detector



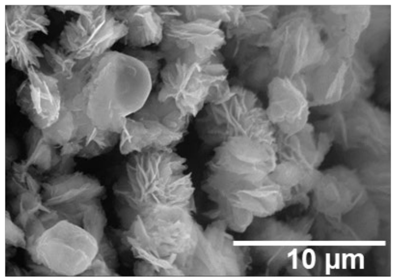
Special gas is released from the paint when the battery surface get overheated

- Use of sulfur containing molecules
  - Smell easily recognized
  - Existing sensor technology
  - Chemically or physically bonded to another molecule
  - Releases the gas at a certain threshold temperature
- Advantages include:
  - large area coverage
  - remote detection
  - designable temperature ranges

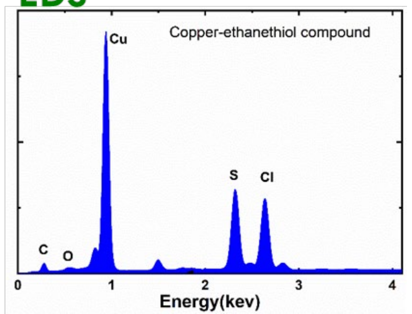
Thermal-sensitive compound synthesis demonstrated using a variety of organometallic compounds



SEM

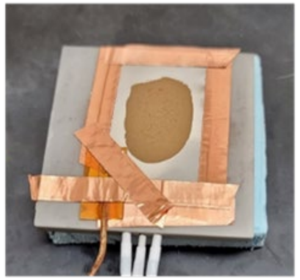


EDS



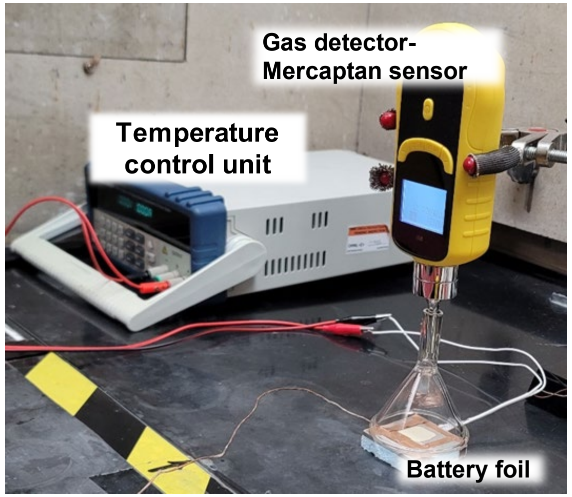
Heating rate affects thiol release rate and thiol temperature onset

As-coated

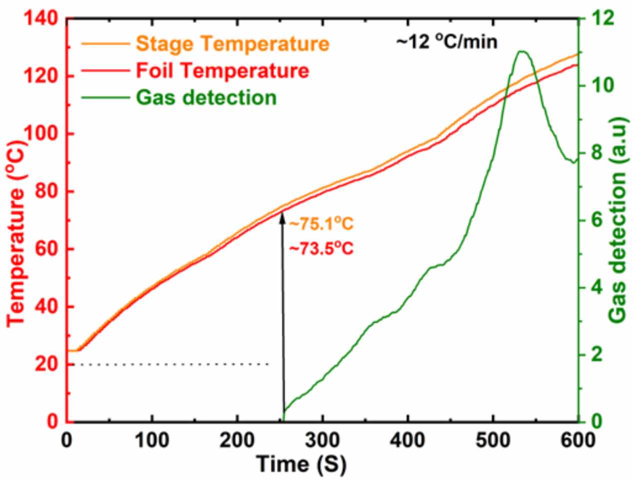


After heating

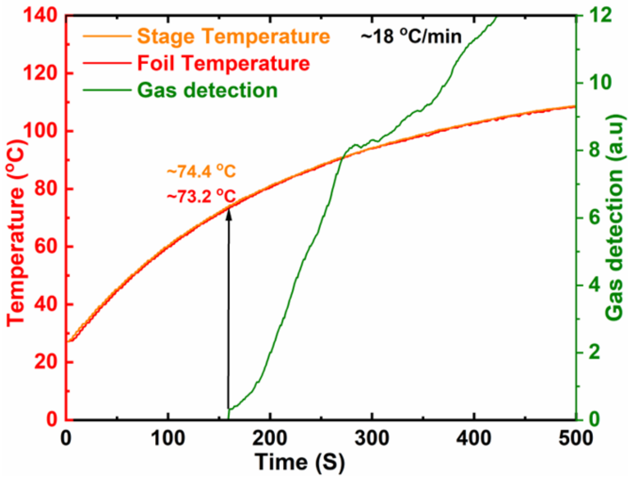
Detector 1- SKY : Mercaptan sensor



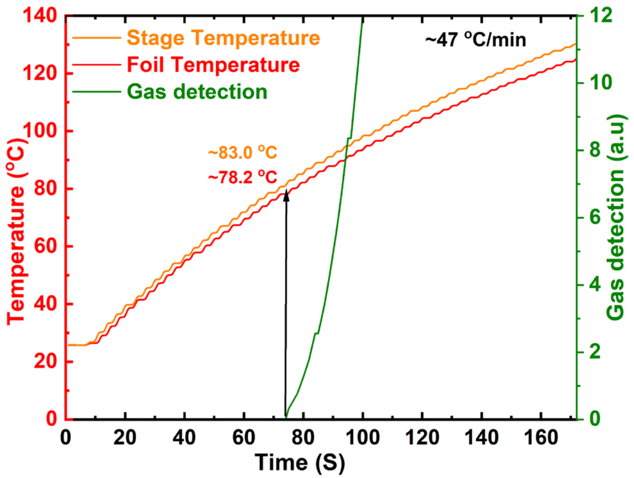
Heating rate: Slow



Medium



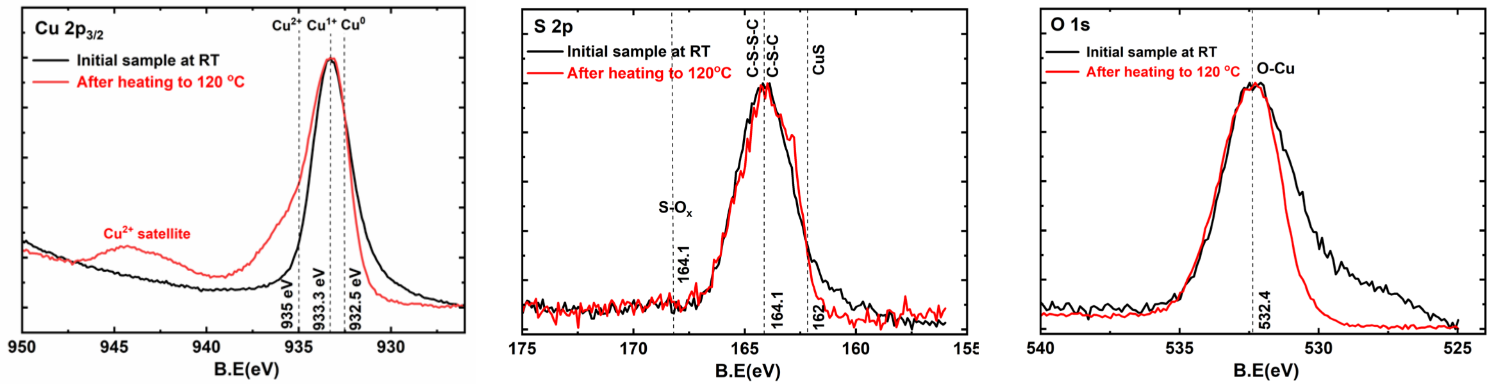
Fast



At different heating rates:
-thiol release rate increases
-gas release quantities increase
- thiol release onset temperature increases (thermal inertia)

The chemical composition changes as the sample heating

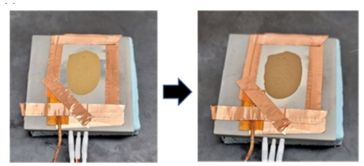
XPS analysis: After heated to 120 °C (1 cycle)



- The oxidation state of copper is in transition from Cu^{+1} to Cu^{+2}.
- Not much change to S or O after heating.
- Sulfur content decreases while oxygen content increases after heating.

XPS composition

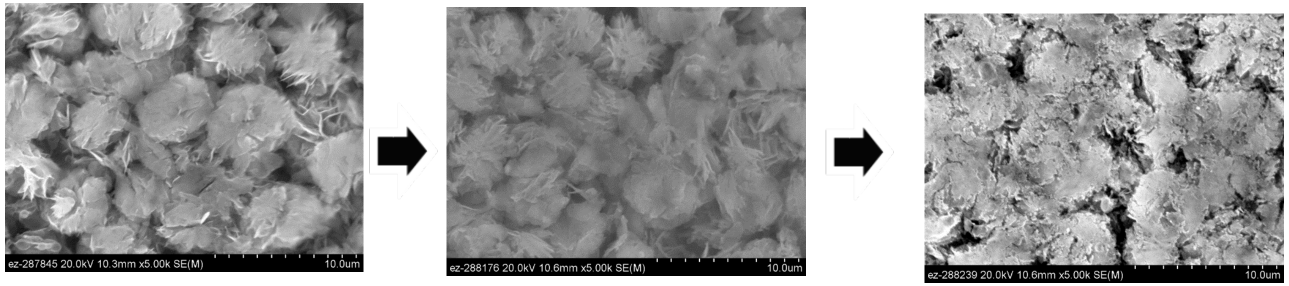
Surface composition (at. %, relative)					
	C	Cl	Cu	**O**	**S**
Initial	46	12	21	**11**	**11**
After heating	41	14	20	**19**	**6**



As- coated → After heating

EDS analysis

Initial → After heated to 120 °C (heating 1) → after heated to 120 °C (heating 6 times)



EDS composition

Element	at.% (relative)		
	Initial	Cycle 1	Cycle 6
S	**27**	**23**	**12**
Cu	67	72	59
O	**6**	**6**	**29**

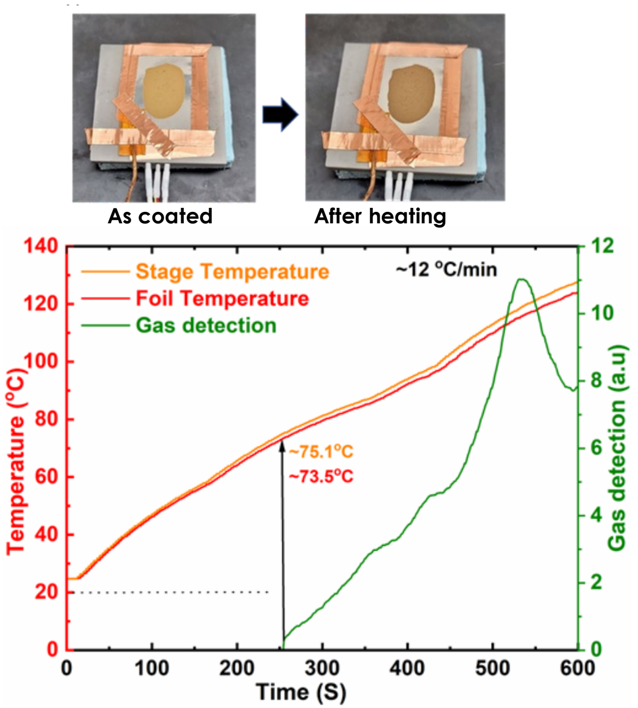
- Sulfur content decreased as sample heating, due to the release of sulfur compounds.
- Oxygen content increases as the sample continues heating due to sample oxidation.

The onset gas release temperature is tunable!

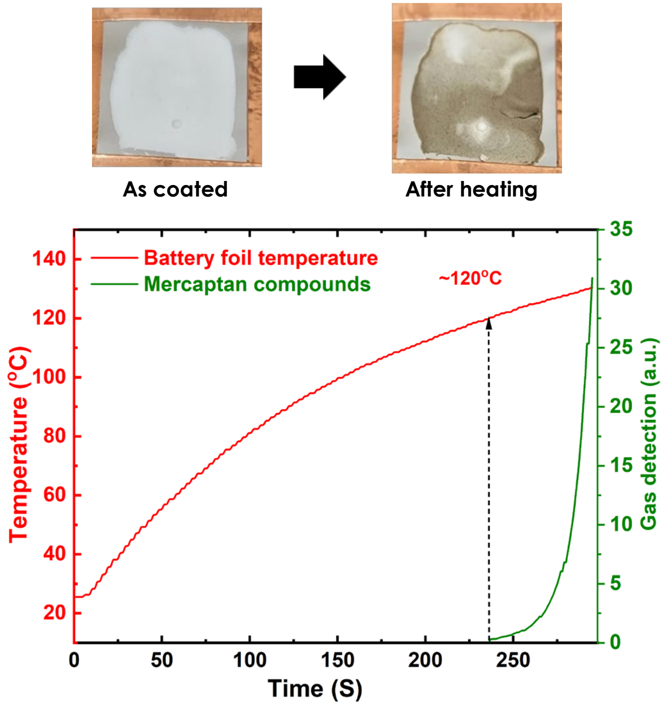
Copper-thiol compounds	Onset gas released temperature (°C)
Compound - 1	**70-75**
Compound - 2	84-96
Compound - 3	**120-127**
Compound - 4	152-163
Compound - 5	172-174

Different organometallic thiol compound were synthesized using different thiol groups (R-SH)

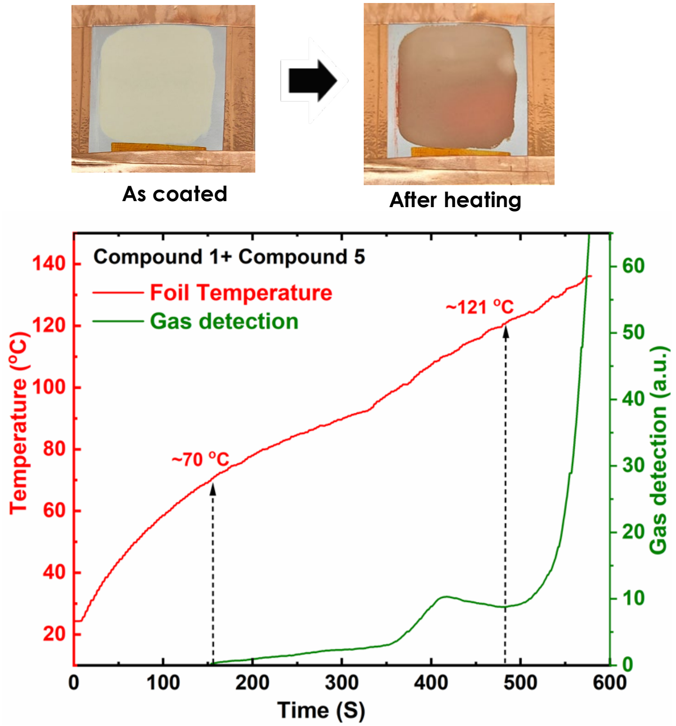
Compound -1: ~73 °C



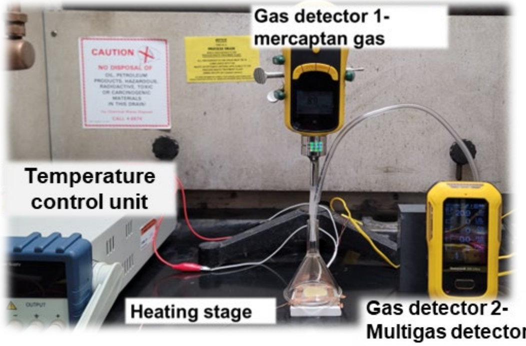
Compound -3: ~120 °C



Compound 1+3 mixture: ~70 °C and ~120 °C



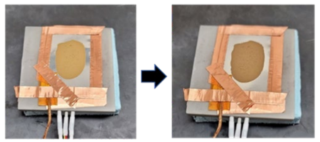
Detector dependent responses



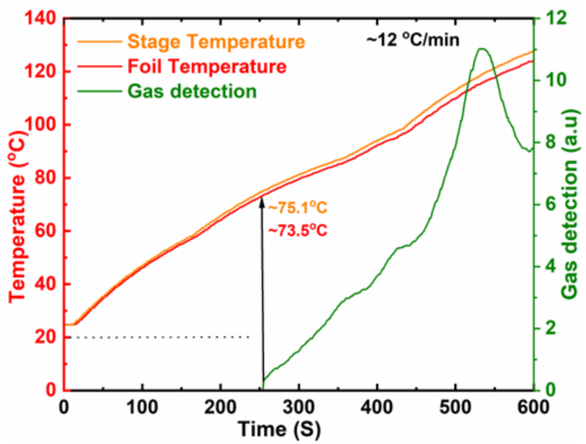
Detector 1-SKY : Mercaptan sensor

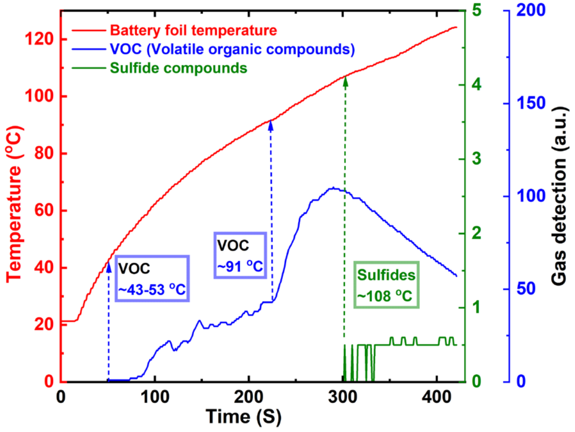
Detector 2-Honeywell : VOC and sulfide sensor

Compound-1:
~73 °C



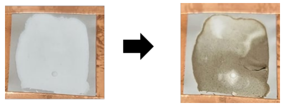
As- coated　After heating



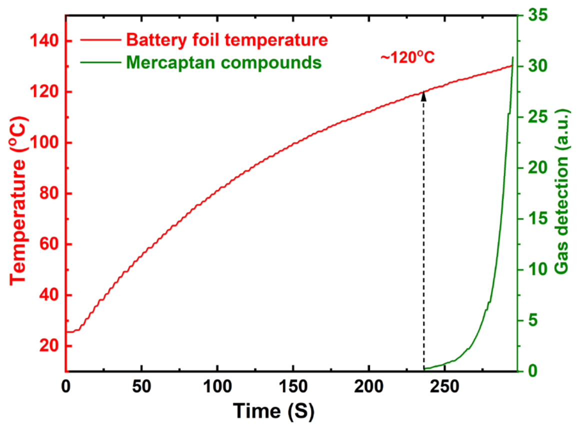


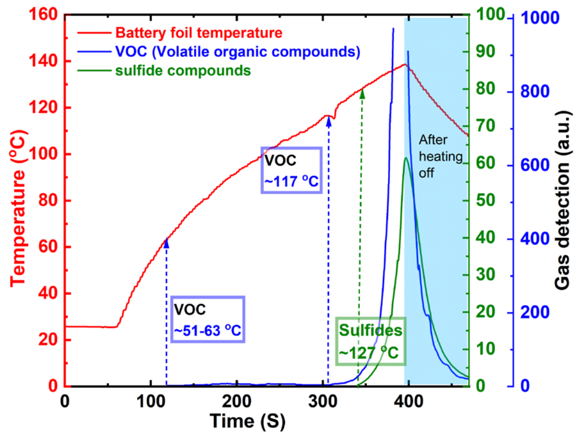
Onset gas release temperature :
Mercaptan : 73-78 °C
VOC : 53, 91 °C
Sulfide : 115-120 °C

Compound-3:
~120 °C



As coated　After heating





Onset gas release temperature :
Mercaptan : 120-125 °C
VOC : 117°C
Sulfide : 125-127 °C

Onset gas release temperature and associated signal intensities vary depending on the detector/ sensor used

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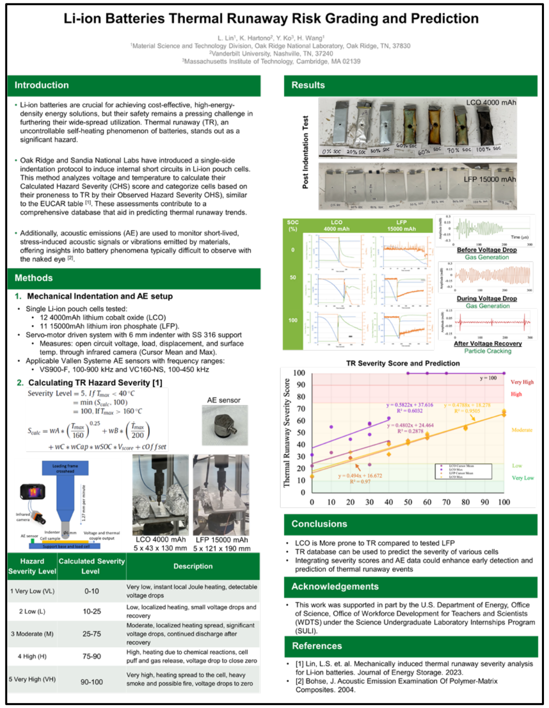
OE ESS Project No. 2 With Sandia Thermal Runaway Severity Safety Database

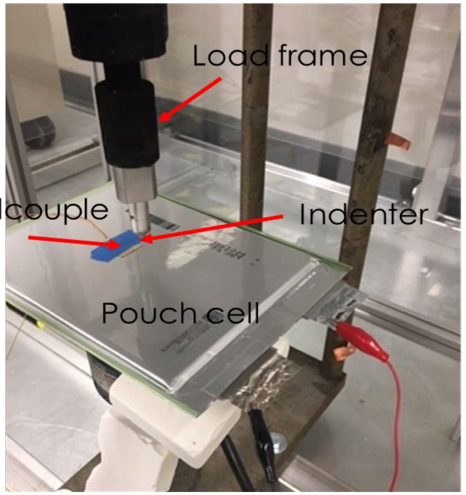
ORNL- Mechanically Induced Thermal Runaway Test

- **Mechanically simulated internal short circuit**
  - Nail penetration
  - **Single-side indentation**
  - Pinch test (two indenters)
  - Pinch-torsion, indent-torsion
- **Real-time Monitoring:**
  - Load, displacement, V_{OC} , temperature and acoustic emissions (AE)
- **Post-mortem Examination:**
  - X-ray computed tomography (XCT)
  - Open cell examination
- **Goal:** build cell thermal runaway database, rank and predict hazard severity



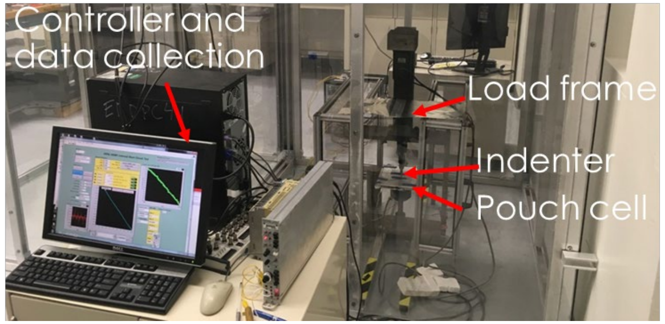
Mechanical abuse test protocol developed by ORNL and Sandia

- Cycle cell 3-5 times at C/2 between 3.0-4.2V to determine SOC and discharge to test SOC
- Hydraulic or servo-motor driven load frame
- Ø6 mm indenter (most sensitive, small contact)
- 0.05 inch/minute compressive loading
- 25 mV V_{oc} drop to stop the loading
- Hold the punch after short circuit
- Temperature measurement:
  - 5 mm from the indenter
  - At cell corners when possible

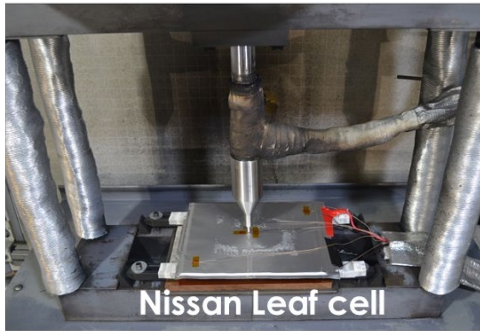


Test conducted at ORNL and SNL using the same protocol will validate the repeatability and reproducibility of the data

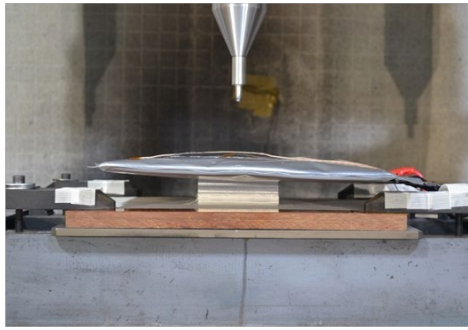
ORNL test chamber



Sandia test chamber



Nissan Leaf Cell After Indentation



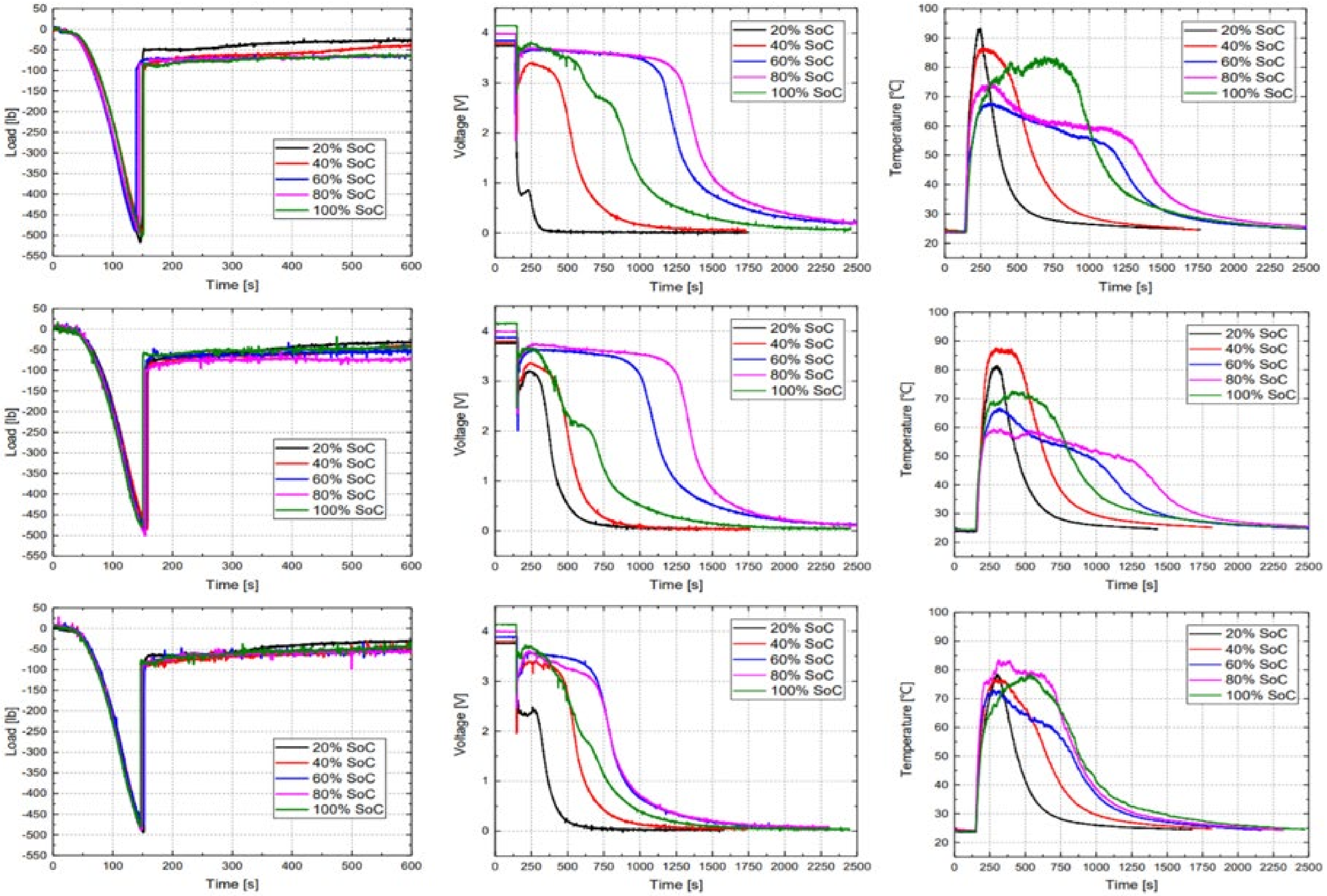
Real-time monitoring of battery voltage and temperature at TR

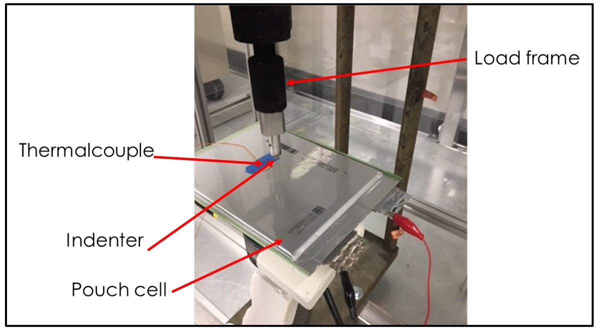
Load | Voltage | Temperature

500 mAh

1500 mAh

2000 mAh





- The different battery has a different thermal runaway signatures.
- V, T along with SOC and cell capacity will be used for thermal runaway severity calculation

Example of Traditional Data Analysis

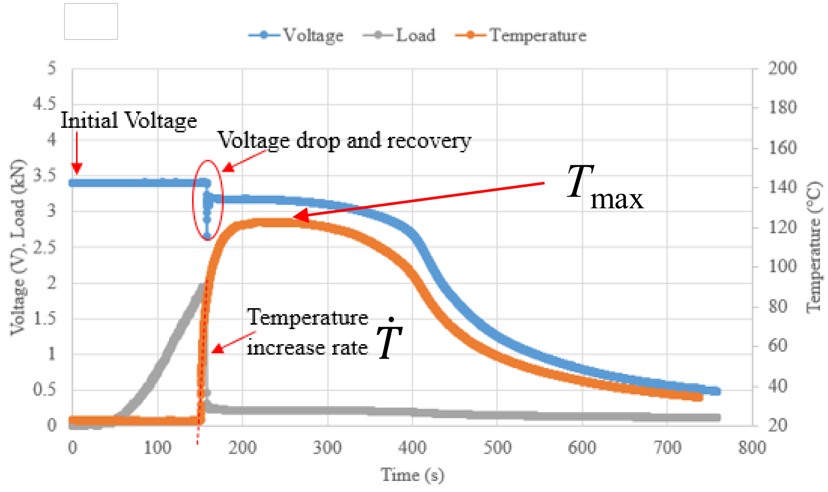
Cell Capacity (mAh)	500	500	500	500	500
SOC %	20%	40%	60%	80%	100%
Test Cell Capacity (mAh)	100	200	300	400	500
Voc (V)	3.75	3.784	3.861	3.991	4.147
V drop Initial (V)	0.25	2.284	0.351	3.581	3.955
V at 300 sec (V)	0.0183	0.095	0.407	0.15595	0.033569
Sumof V*Δt (V-Sec)	120.63	110.47	220.09	77.176	29.462
Load at failure (lb)	-338	-337.52	-345.7	-355.16	-353.82
Load during hold (lb)	-81.79	-88	-131.6	-170.04	-147.09
Temp Max	79.83	78.055	82.93	81.913	86.655
Sum of ΔT*Δt (K-Sec)	6685.3	8093.482	10168.27	14668.71	17089.57
Time to reach Tmax (sec)	62.57	33.6	61.2	60.8	57.8

Calculation of Thermal Runaway Score

Severity Level $= 5$, If $T_{max} < 40$ °C

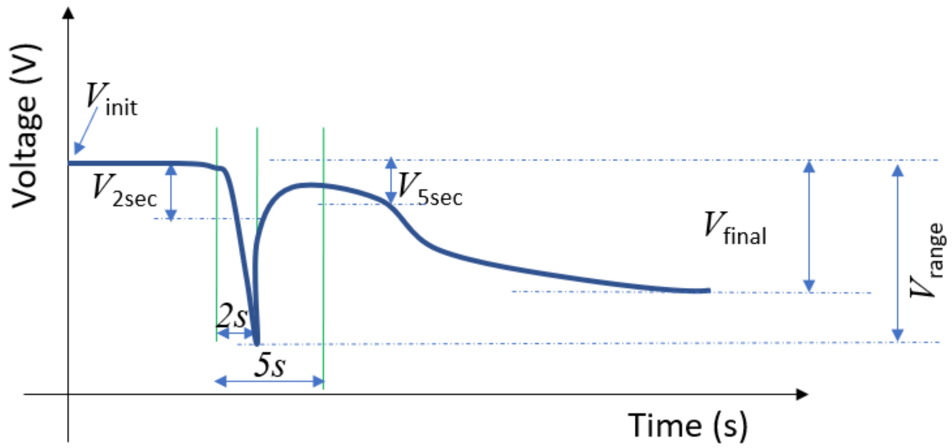
$= \min(S_{calc}, 100)$

$= 100$, If $T_{max} > 160$ °C



$$S_{calc} = wA * \left(\frac{T_{max}}{160}\right)^{0.25} + wB * \left(\frac{\dot{T}_{max}}{200}\right) + wC * wCap * wSOC * V_{score} + cOffset$$

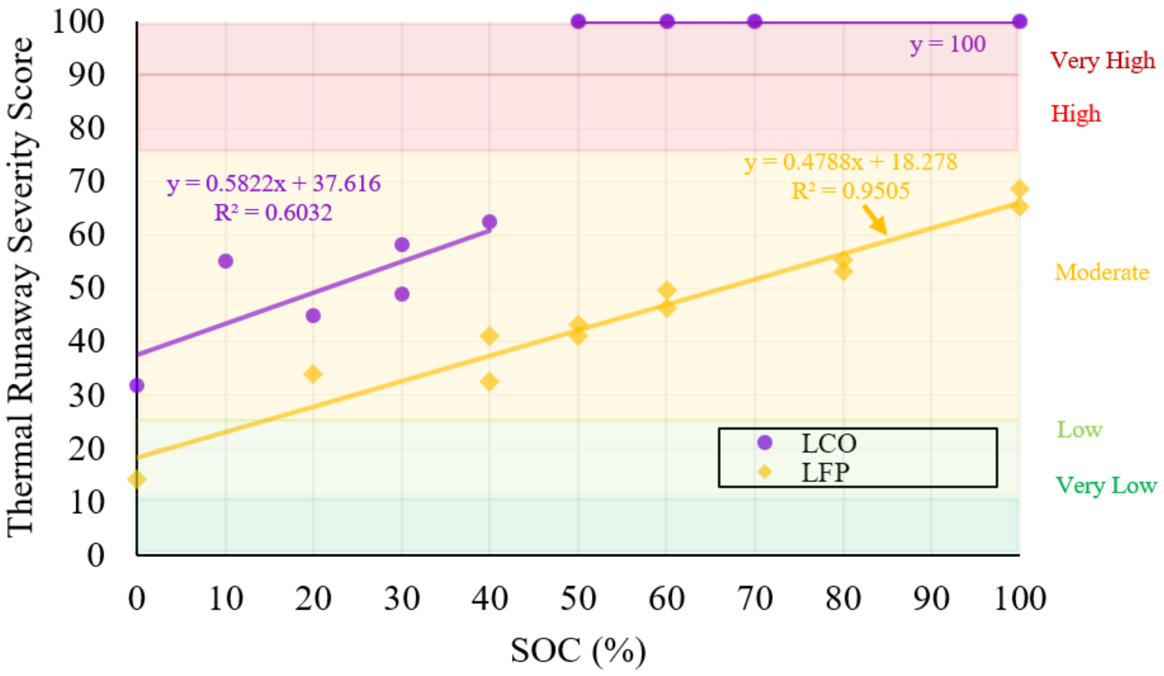
V_{score}
=1, if $V_{range}/V_{init} < 20\%$
=2, if $V_{range}/V_{init} > 50\%$ and $V_{final}/V_{init} < 20\%$
=3, if $V_{2sec}/V_{init} < 40\%$ and $V_{final}/V_{init} < 20\%$
=4, if $V_{2sec}/V_{init} \geq 20\%$ and $V_{final}/V_{init} < 70\%$
=5, if $V_{5sec}/V_{init} > 95\%$

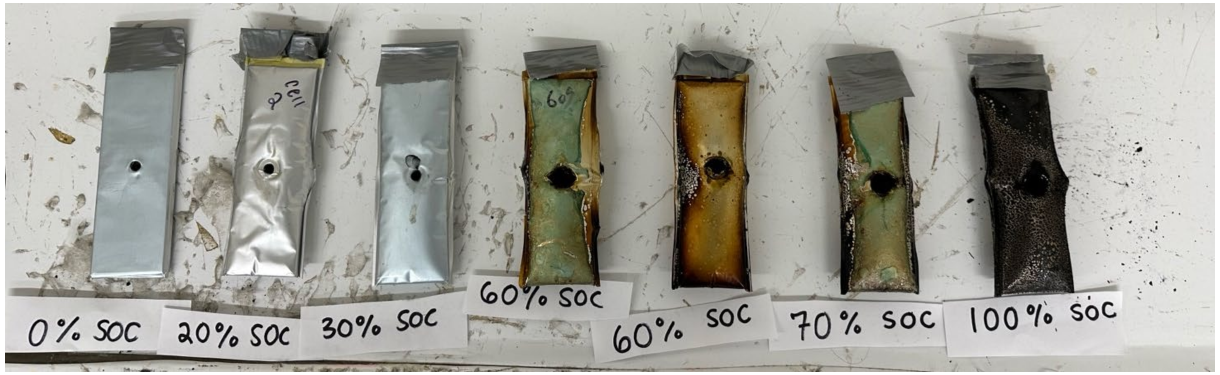


Inputs: Cell capacity (mAh), SOC (%), Voltage-time series, Temperature-time series.
Output: Thermal runaway severity score 5~100.

1. L. Lin, et al. Mechanically induced thermal runaway severity analysis for Li-ion batteries. Journal of Energy Storage, 2023, 61. Jg., S. 106798.
2. L. Lin, et al. Dataset of Mechanically Induced Thermal Runaway Measurement and Severity Level on Li-ion Batteries. Data in Brief (2024): 110609.

Thermal Runaway Severity Grading

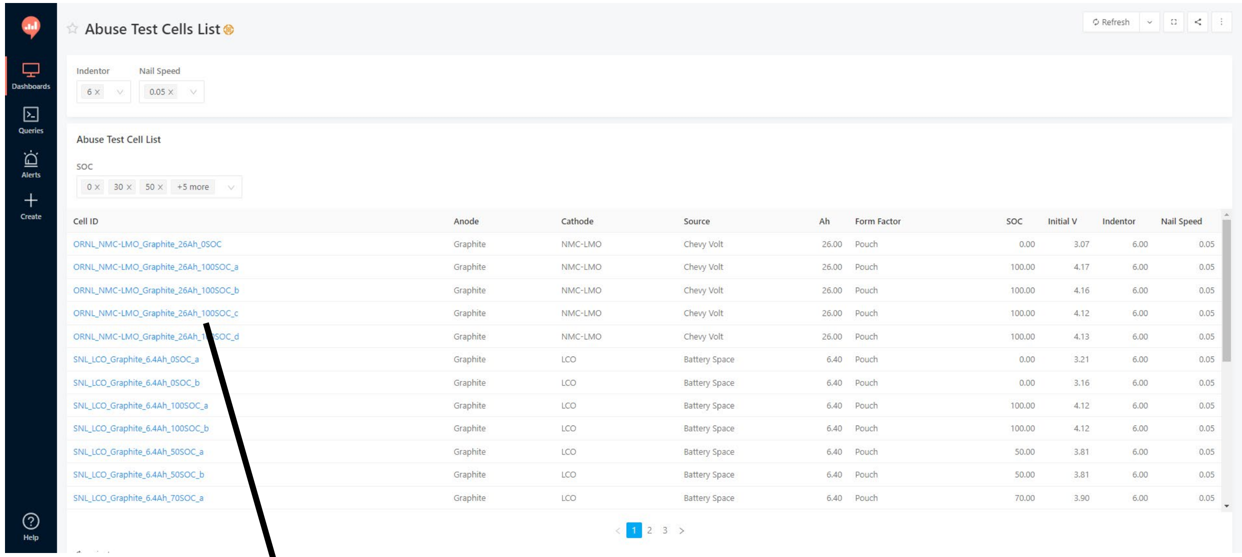


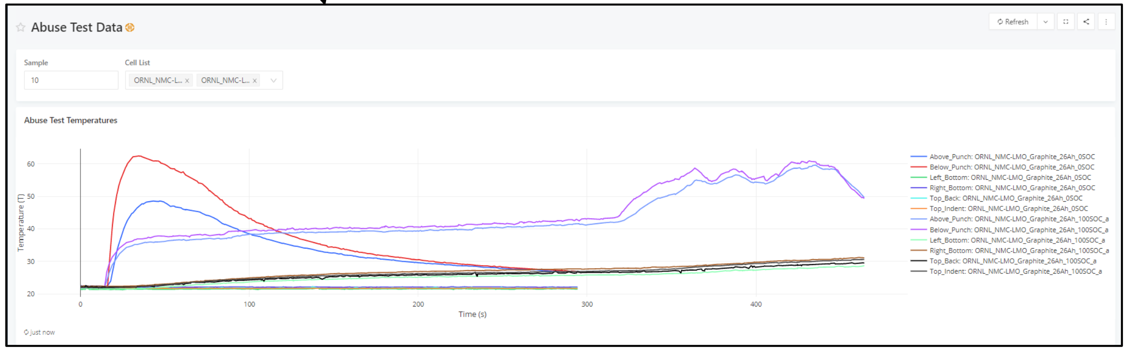


LCO 4000 mAh

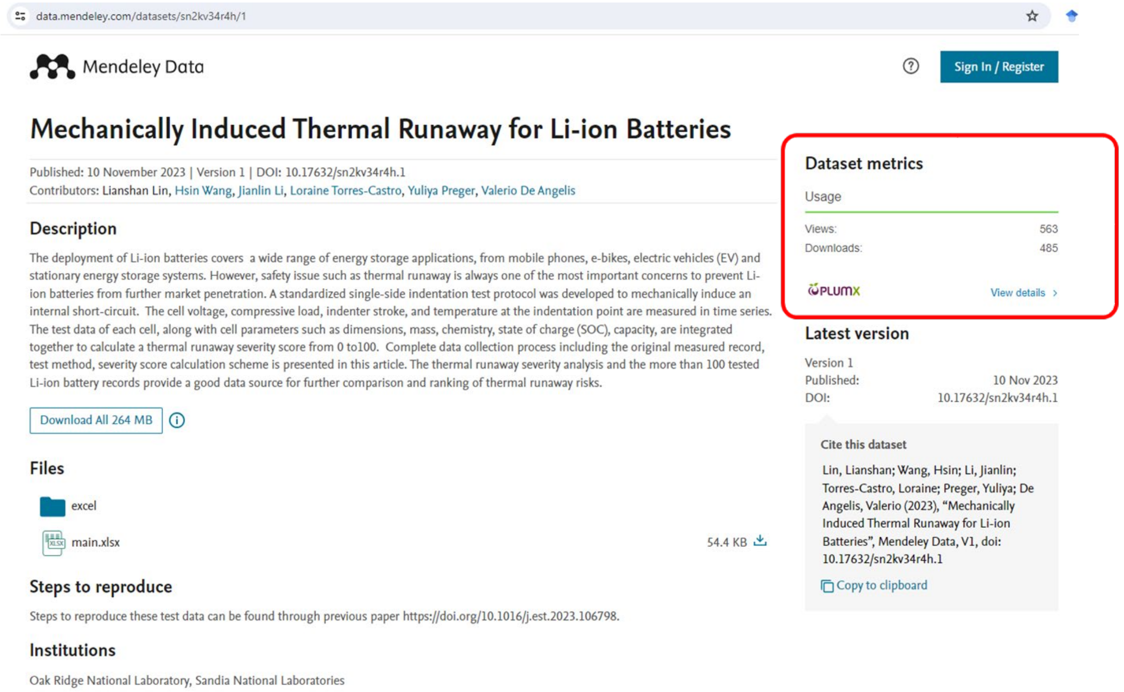
LFP 15000 mAh

Database of Battery Abuse Test (Host: Sandia Labs)



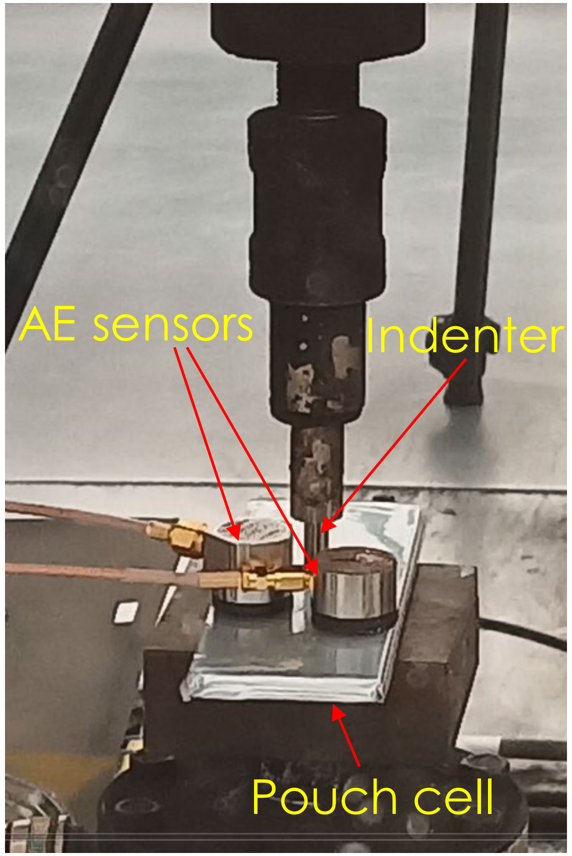


Original Datasets Shared to Public (Mendeley Data)

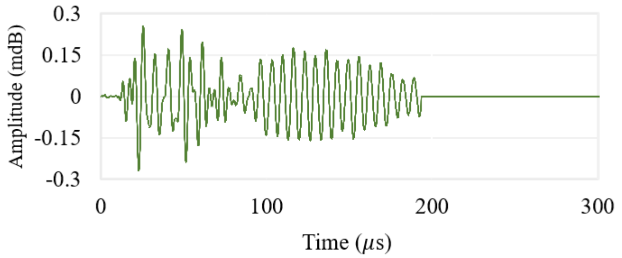


https://data.mendeley.com/datasets/sn2kv34r4h/1

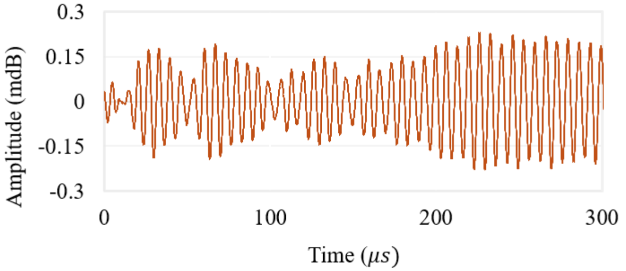
Real-Time acoustic emission monitoring



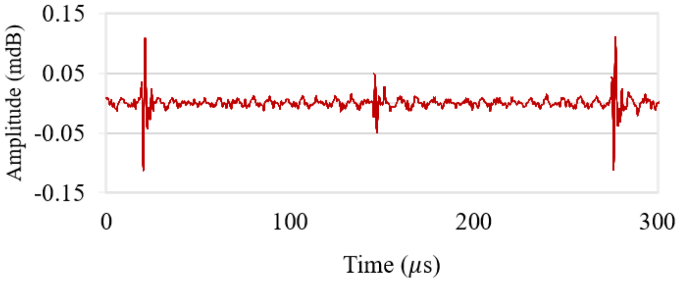
pre-Internal Short circuit (ISC)



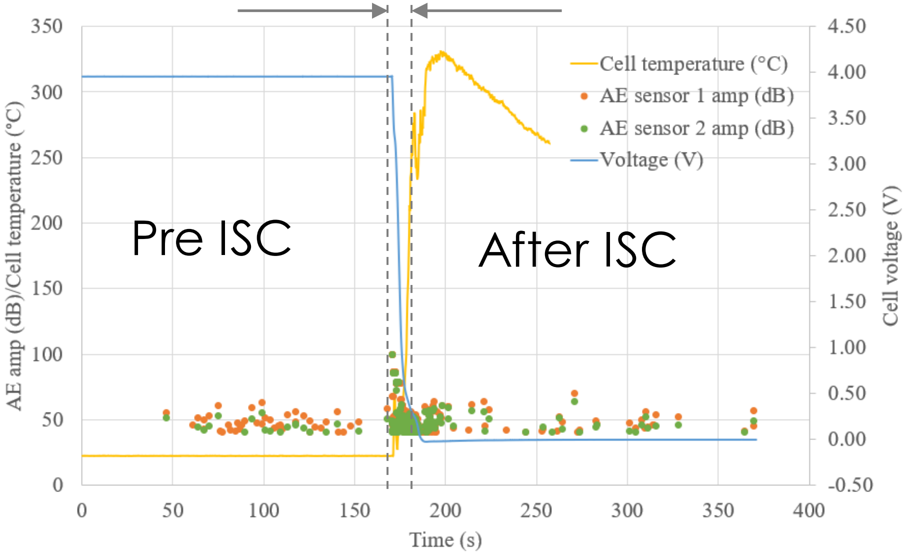
During ISC



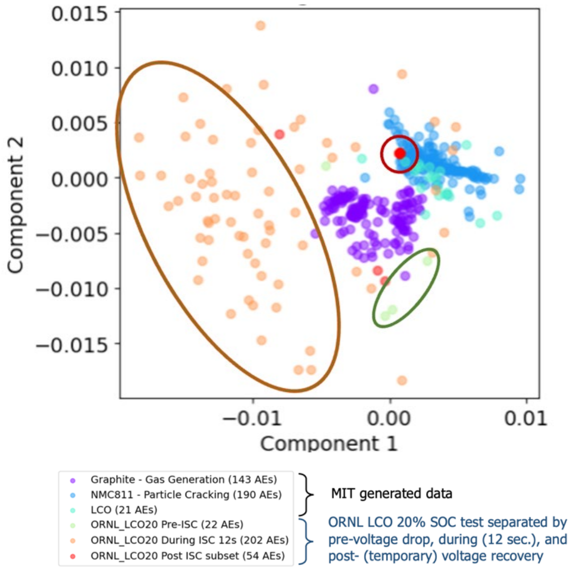
After ISC (gas releasing)



During ISC



Acoustic emissions amplitude, voltage and temperature for LCO 4000 mAh, SOC 70%



In cluster plot, axes represent a complex mix of frequency and time content (similar to PCA). Each point represents one emission – closer points represent more similar waveforms.

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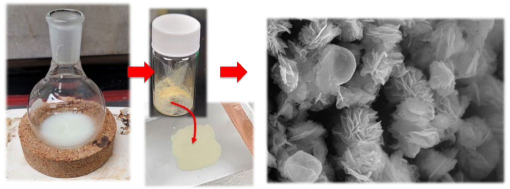
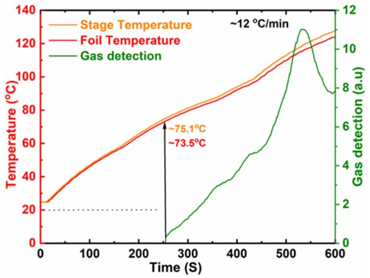
Conclusions

- Thermal sensitive copper–thiol compounds were synthesized



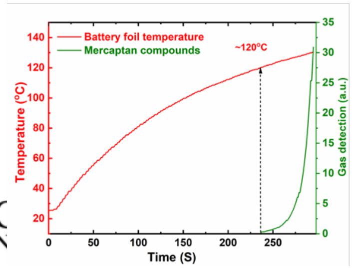
- Compound thermally decomposes to release volatile compounds when critical temperature is reached.

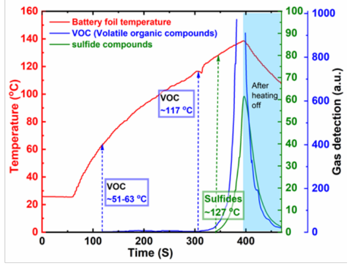


- Critical thiol release temperature can be tunable

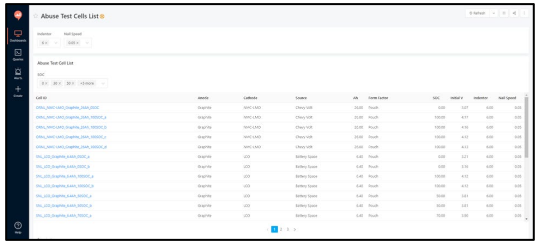
Copper-thiol compound	Onset gas released temperature (°C)
Compound - 1	72-75
Compound - 2	84-96
Compound - 3	120-127
Compound - 4	152-163
Compound - 5	172-174

- Gas detection depend on the type of gas release and sensor

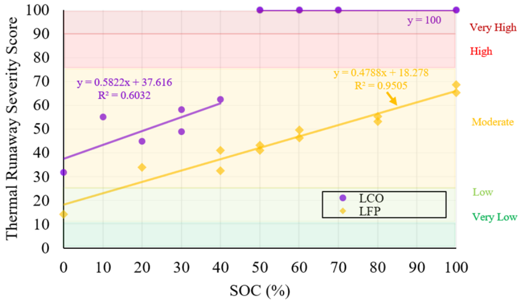


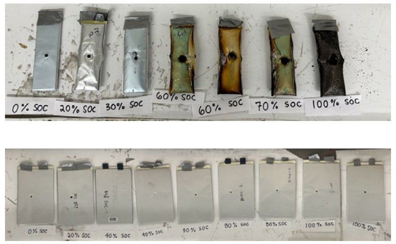


- TR database can be used to predict the severity of various cells

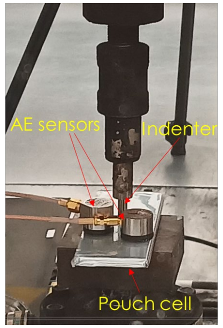


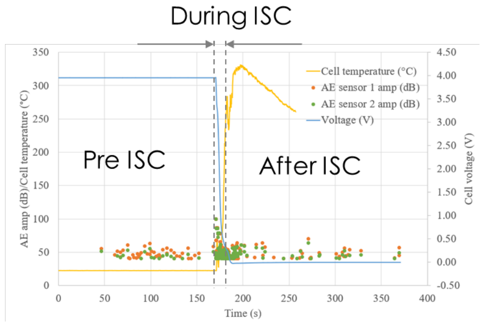
- LCO is More prone to TR compared to tested LFP





- Integrating severity scores and AE data could enhance early detection and prediction of thermal runaway events





Publications and communications

- L.S. Lin, J.L. Li, I.M. Fishman, L. Torres-Castro, Y. Preger, V. De Angelis, J. Lamb, X.Q. Zhu, S. Allu, H. Wang, Mechanically induced thermal runaway severity analysis for Li-ion batteries, *Journal of Energy Storage*, 2023, 61,106798
- Lianshan Lin, Jianlin Li, Isabella M. Fishman, Loraine Torres-Castro, Yuliya Preger, Valerio De Angelis, Irving Derin, Xiaoqing Zhu, Hsin Wang, *Data in Brief*, 2024,55,110609
- Patent Application: Temperature sensitive coatings, 8/119,373, March 9, 2023
- *Manuscript ready to submit: "Temperature Sensitive Copper Thiolate Compounds for Energy Storage Systems safety "* (2024)
- Invention discloser (ORNL ID 81955144) submitted on July 5th 2024

Collaborations and recent activates

Internal: ORNL Chemical Science Division for further characterization

External: Power Sources Technology Group, Sandia National Laboratory: for repeatability, reproducibility, and potential application for larger system

- Hsin wang visited SNL on May 7, 2024
- Sandia Labs tested ORNL's thermally sensitive coating using multiple gas sensors

Presentation

- Invited talk: Development of Temperature Sensitive Paint and Battery Management System for Energy Storage System Safety, 48th International Conference and Expo on Advanced Ceramics and Composites (ICACC) 2024, Daytona Beach, FL

Thank you

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- Sandia National Laboratory

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