

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

Chanaka Kumara, Beth Armstrong , Lianshan Lin and Hsin Wang

- *Materials Science and Technology Division  
Oak Ridge National Laboratory*

ORNL is managed by UT-Battelle, LLC for the US Department of Energy



*This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division*

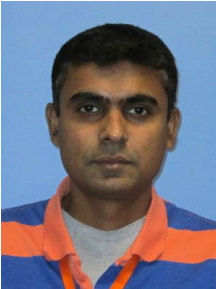
# OE ESS Project No. 1 : Thermal Runaway Detection Method Thermally Sensitive Paint Development



Hsin Wang  
MSTD  
Material Scientist, Testing



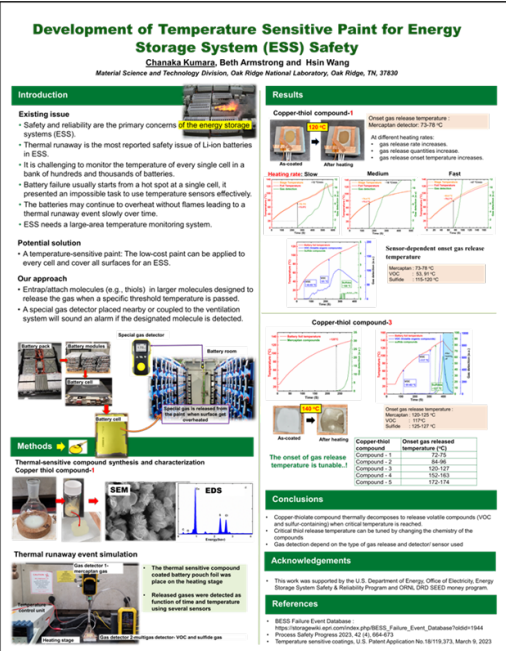
Beth Armstrong  
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Chemist, Paint Development



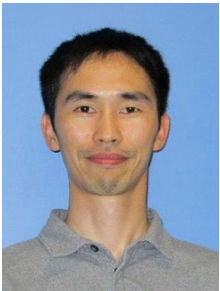
Seokhoon Jang  
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# OE ESS Project No. 2 : Thermal Runaway Severity Safety Database (With Sandia National Lab)



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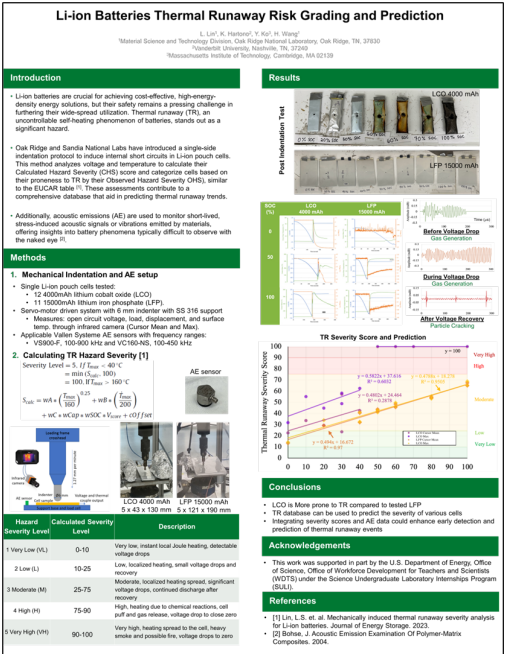
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Kathleen Hartono  
DOE SULI Student,  
Chemical Eng., Battery Testing



# 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.



Home > Battery industry > Cause of APS battery explosion that injured 9 first responders detailed in...

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

April 2019



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



Thermal Runaway



State-of-Charge (SOC)

100% 60% 0%

Fast: too late for warning

Localized Heating: 80-100°C

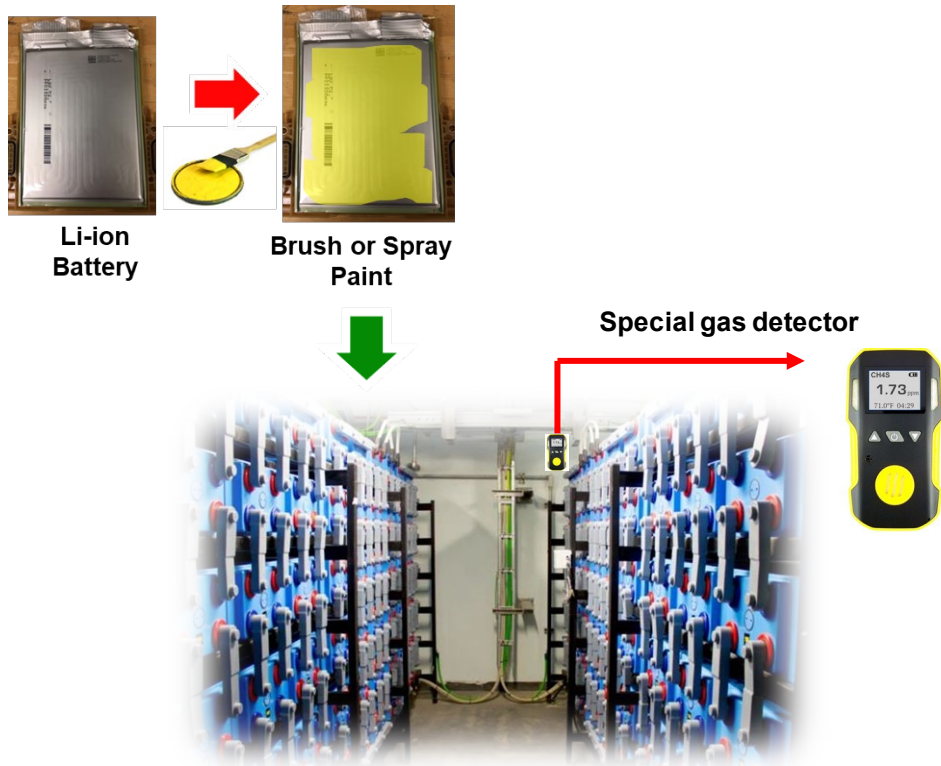
Slow: Still have time to react



# Thermally sensitive paint development

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

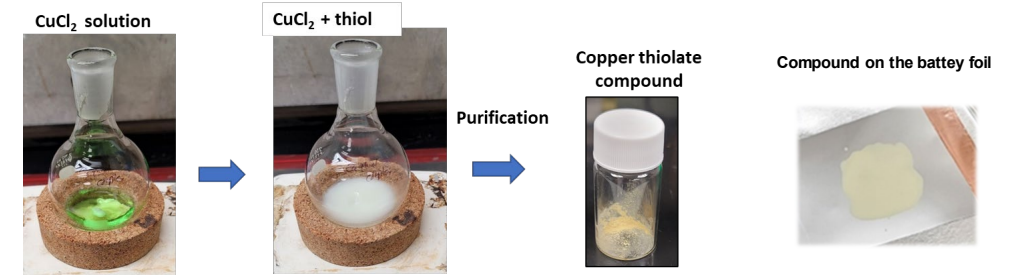
- Stays normal within battery operation temperature
- Release chemical/gas  $T > T_{\text{Threshold}}$
- No-line-of-sight
- Detection via “smell” and gas detector



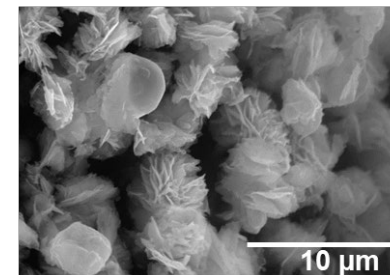
Special gas is released from the paint when the battery surface get overheated

- 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

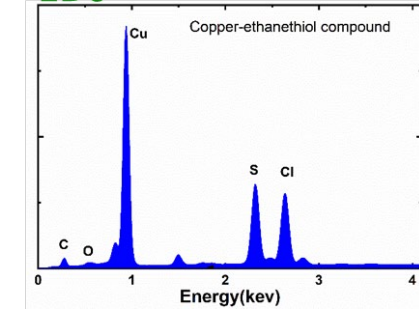
Thermal-sensitive compound synthesis demonstrated using a variety of organometallic compounds



SEM

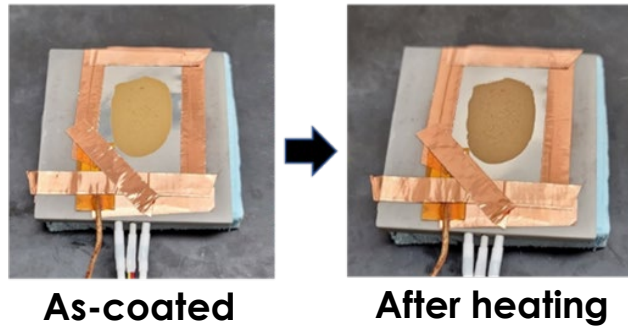
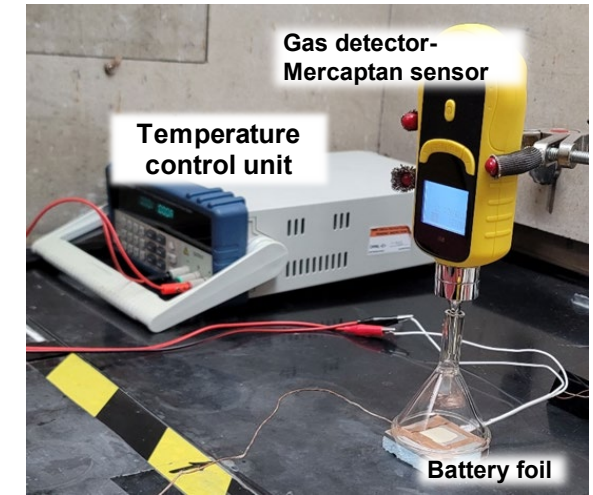


EDS

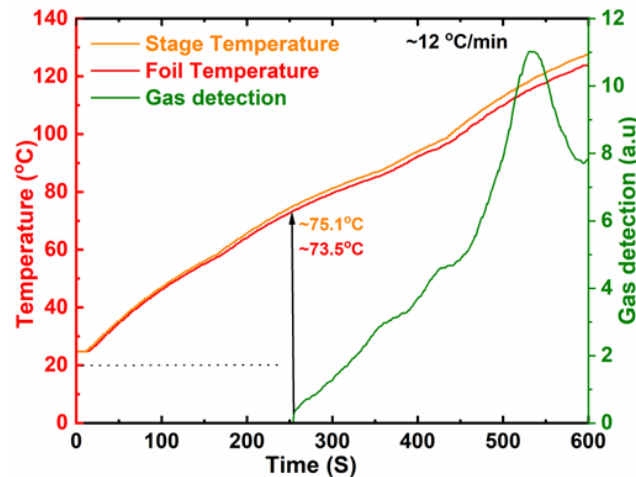


# Heating rate affects thiol release rate and thiol temperature onset

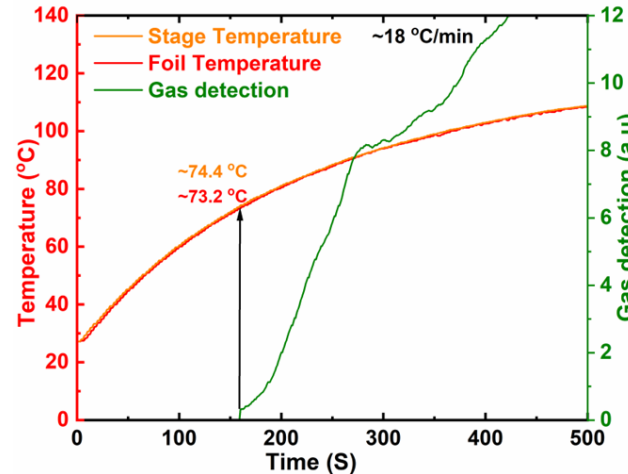
Detector 1- SKY :  
Mercaptan sensor



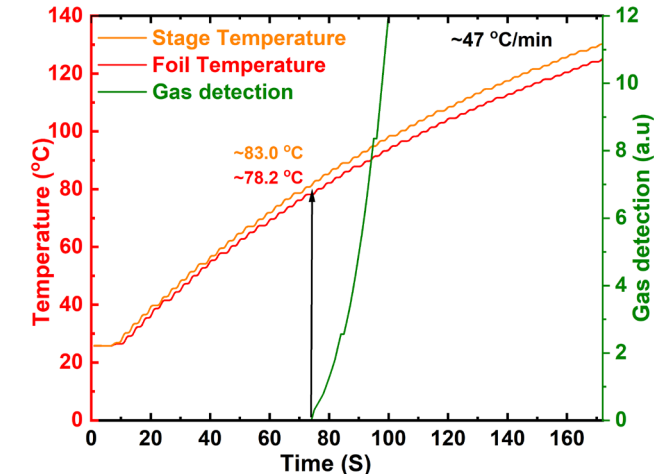
**Heating rate: Slow**



**Medium**



**Fast**

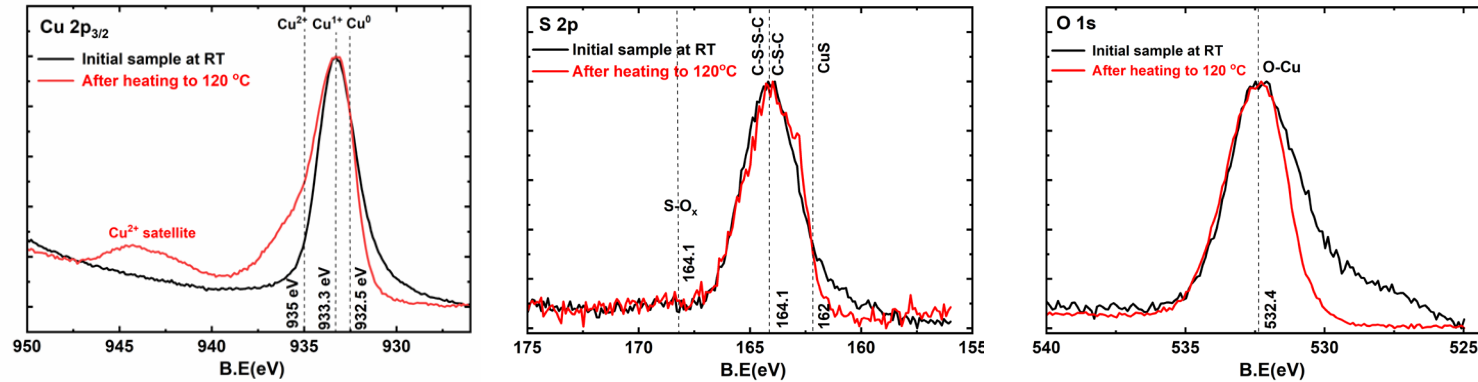


At different heating rates:

- thiol release rate increases
- gas release quantities increase
- thiol release onset temperature increases (thermal inertia)

# The chemical composition changes as the sample heating

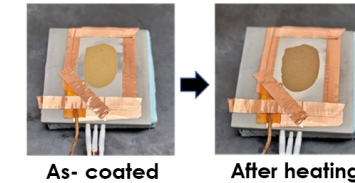
## XPS analysis: After heated to 120 °C (1 cycle)



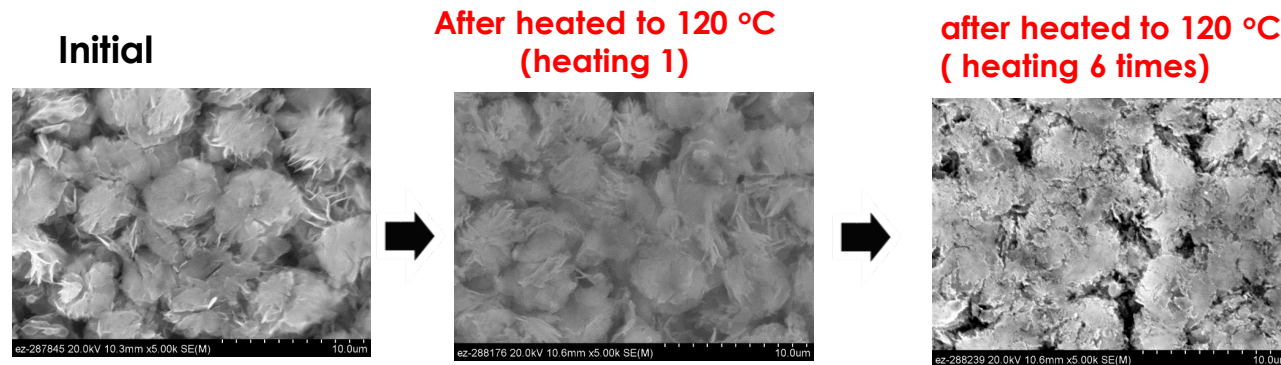
- The oxidation state of copper is in transition from Cu<sup>+1</sup> to Cu<sup>+2</sup>.
- Not much change to S or O after heating.
- Sulfur content decreases while oxygen content increases after heating.

## XPS composition

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



## EDS analysis



## EDS composition

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

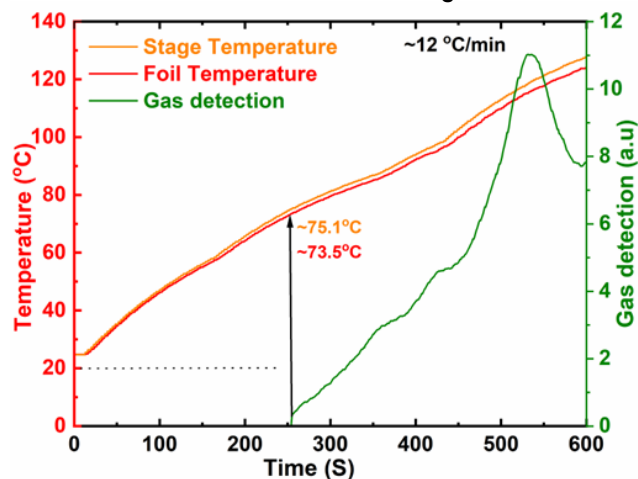
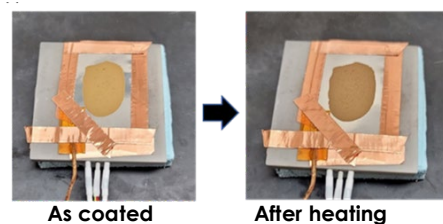
- Sulfur content decreased as sample heating, due to the release of sulfur compounds.
- Oxygen content increases as the sample continues heating due to sample oxidation.

# The onset gas release temperature is tunable!

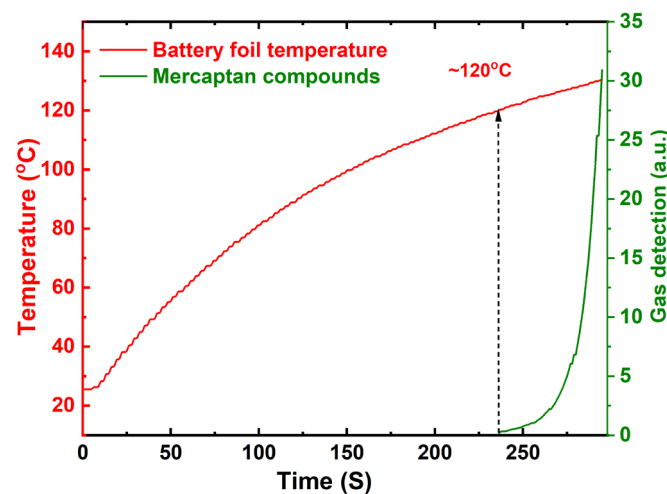
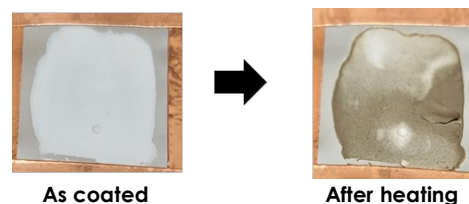
Copper-thiol compounds	Onset gas released temperature (°C)
<b>Compound - 1</b>	<b>70-75</b>
Compound - 2	84-96
<b>Compound - 3</b>	<b>120-127</b>
Compound - 4	152-163
Compound - 5	172-174

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

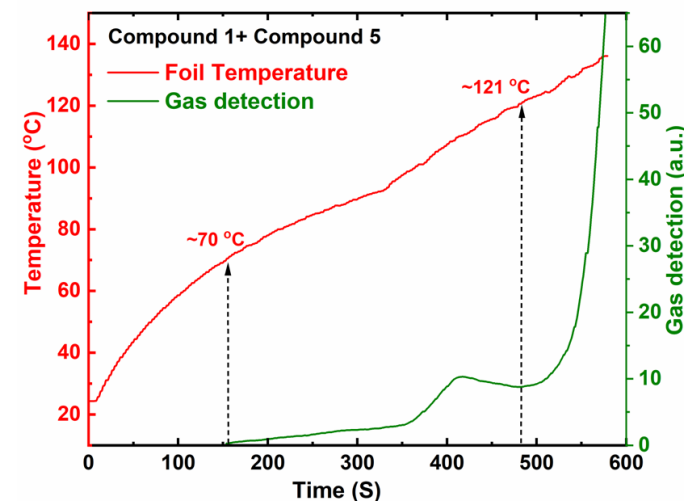
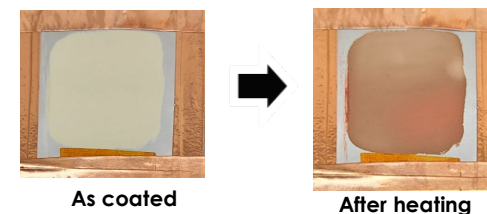
**Compound -1: ~73 °C**



**Compound -3: ~120 °C**



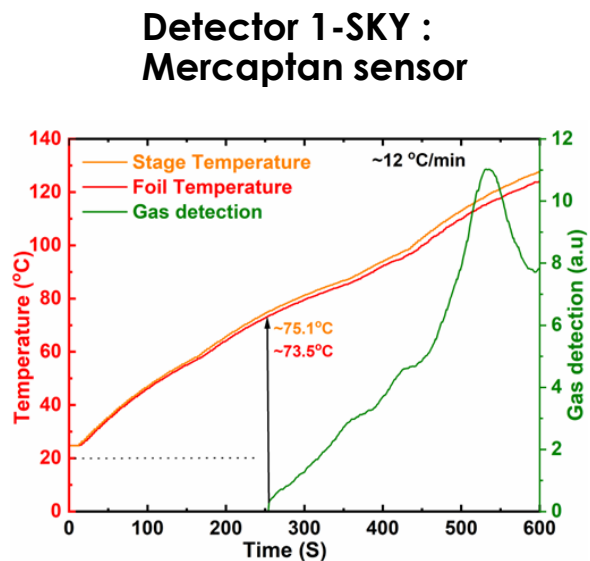
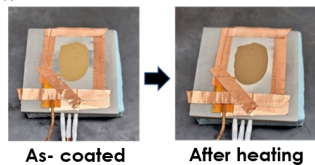
**Compound 1+3 mixture: ~70 °C and ~120 °C**



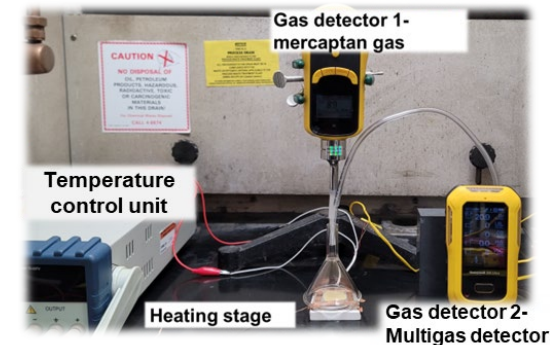
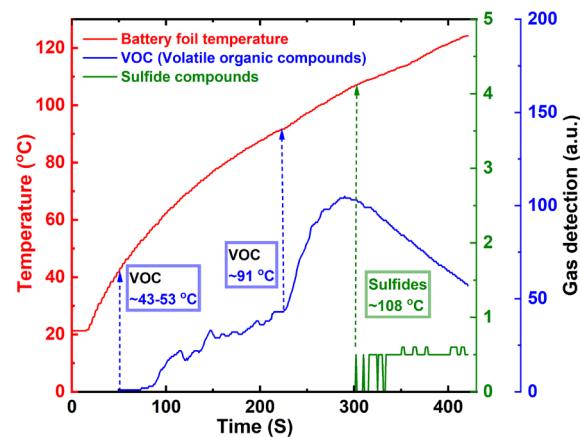


# Detector dependent responses

Compound-1:  
~73 °C



**Detector 2-Honeywell :  
VOC and sulfide sensor**



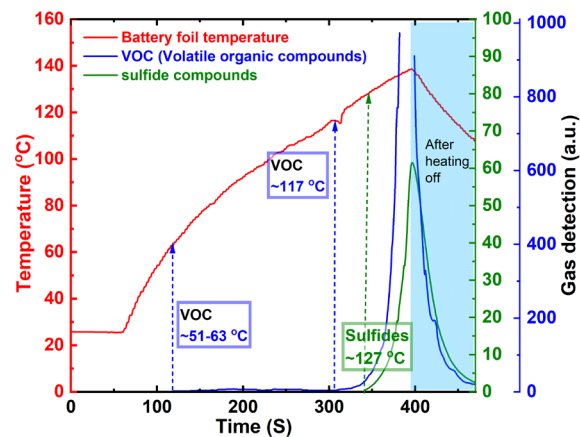
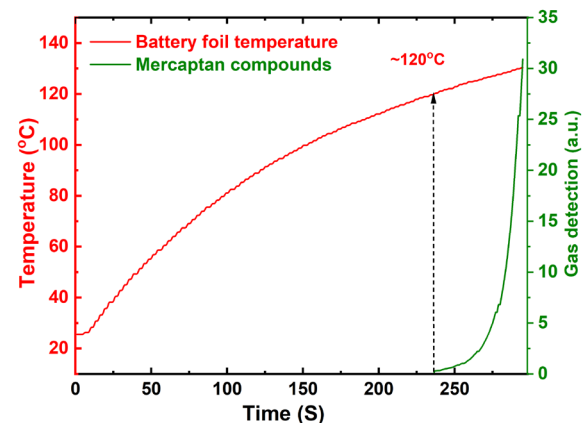
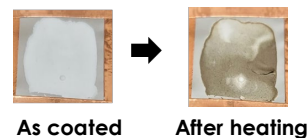
Onset gas release temperature :

Mercaptan : 73-78 °C

VOC : 53, 91 °C

Sulfide : 115-120 °C

Compound-3:  
~120 °C



Onset gas release temperature :

Mercaptan : 120-125 °C

VOC : 117 °C

Sulfide : 125-127 °C

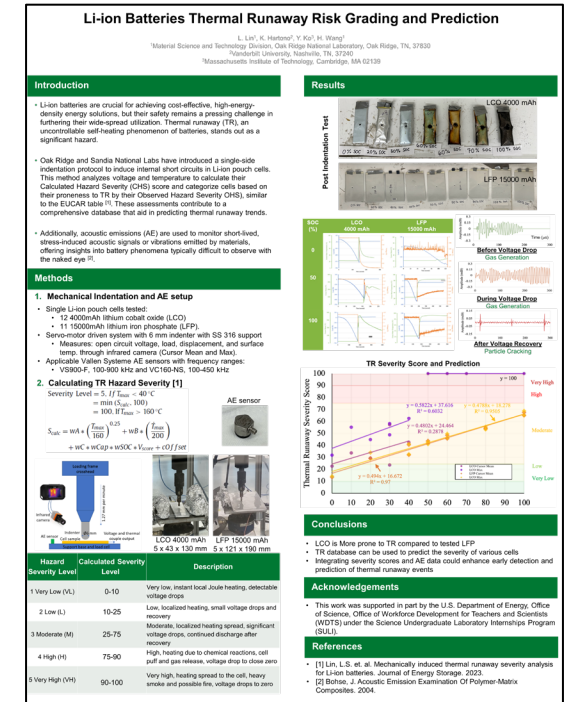
Onset gas release temperature and associated signal intensities vary depending on the detector/ sensor used



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

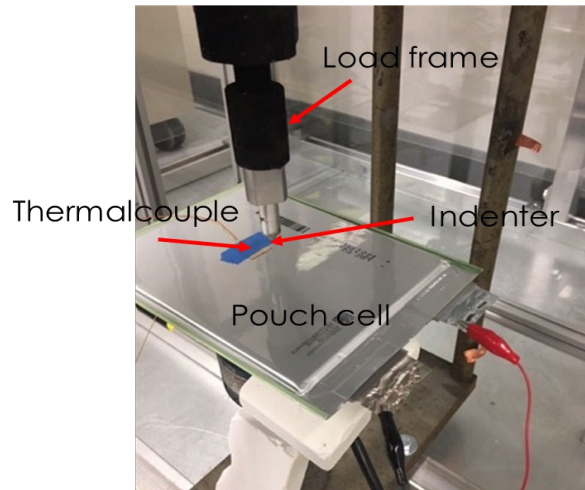
## ORNL- Mechanically Induced Thermal Runaway Test

- **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

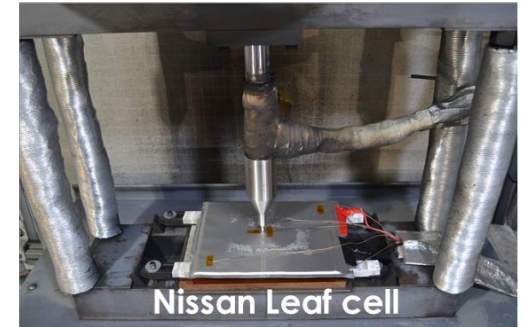


Test conducted at ORNL and SNL using the same protocol will validate the repeatability and reproducibility of the data

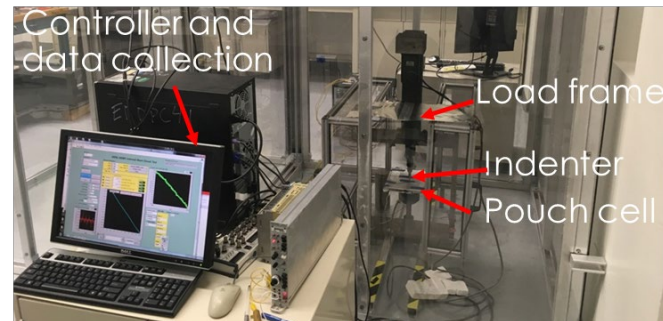
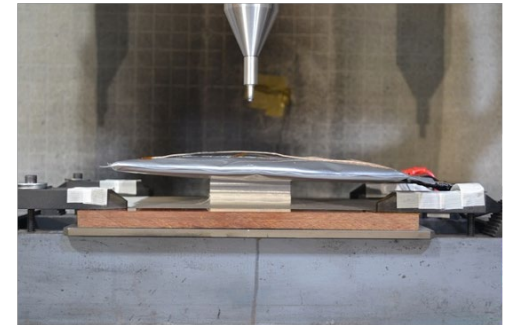
**ORNL test chamber**



**Sandia test chamber**

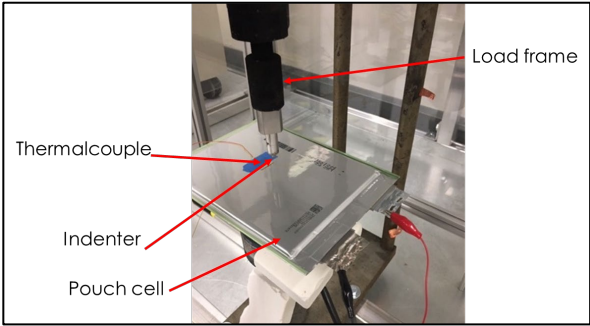
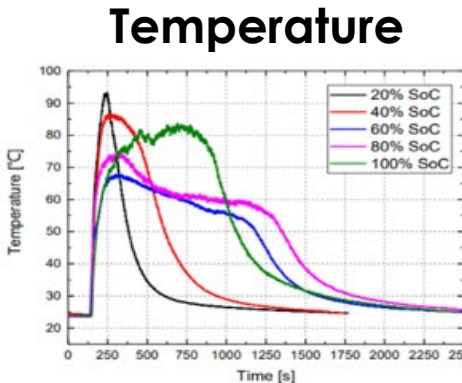
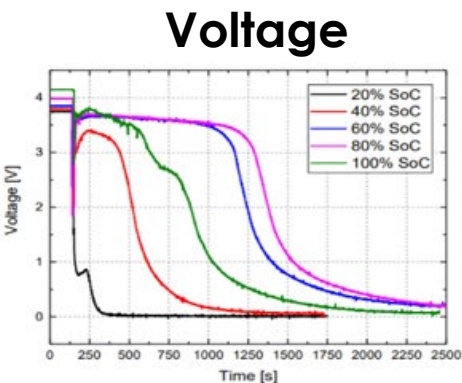
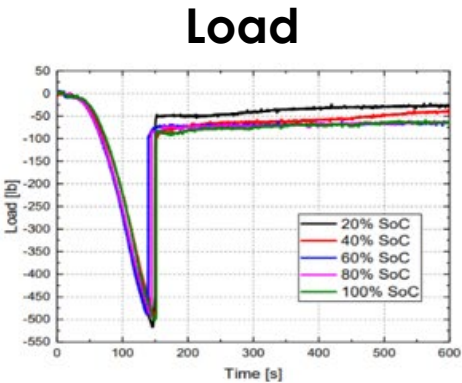


**Nissan Leaf Cell After Indentation**

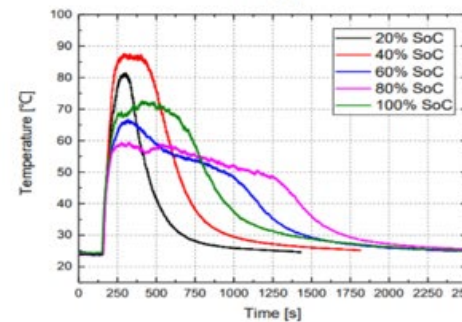
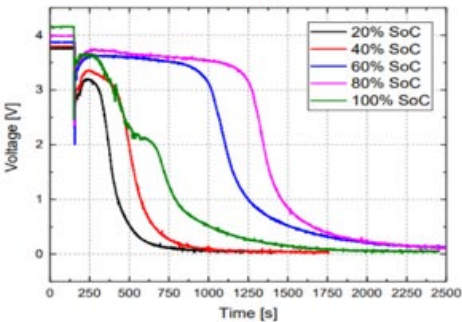
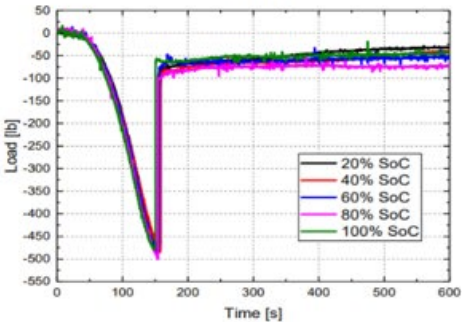


# Real-time monitoring of battery voltage and temperature at TR

500  
mAh

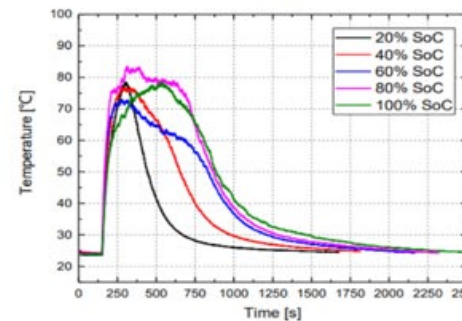
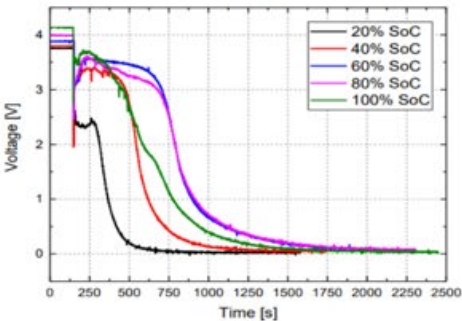
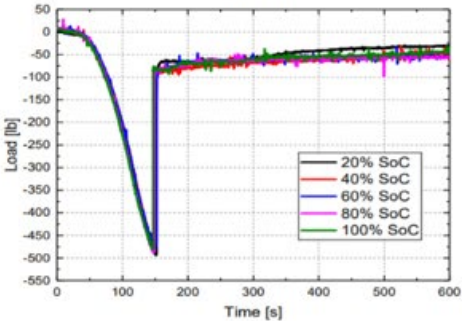


1500  
mAh



- 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

2000  
mAh



## 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
Sum of 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

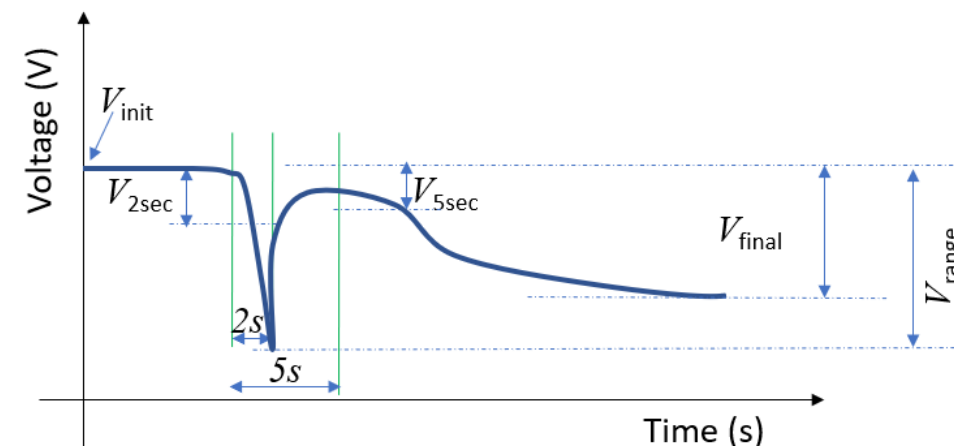
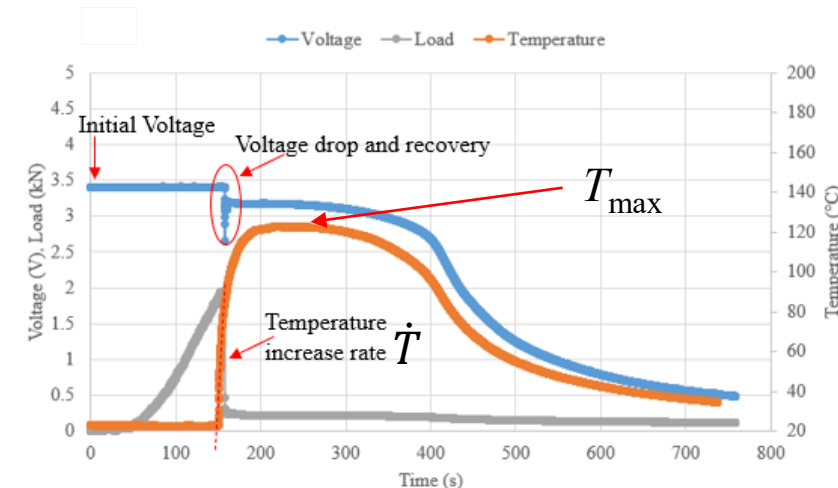
$$\begin{aligned} \text{Severity Level} &= 5, & \text{If } T_{\max} < 40 \text{ }^{\circ}\text{C} \\ &= \min(S_{\text{calc}}, 100) \\ &= 100, & \text{If } T_{\max} > 160 \text{ }^{\circ}\text{C} \end{aligned}$$

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

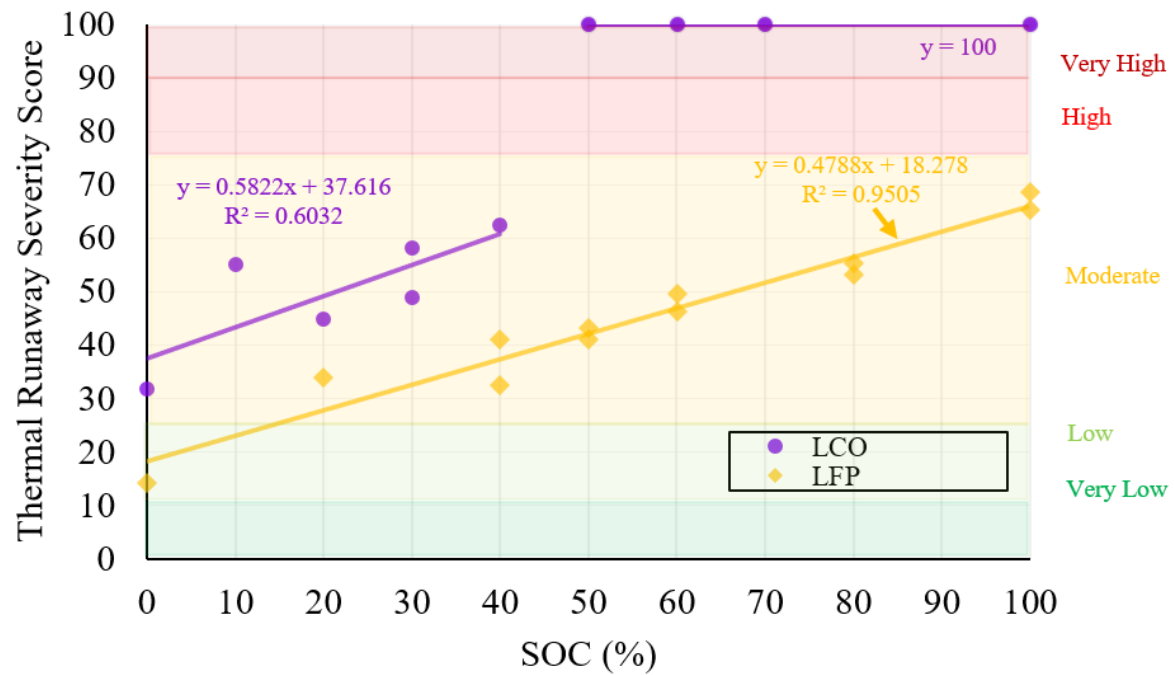
$$\begin{aligned} V_{\text{score}} &= 1, \text{ if } V_{\text{range}}/V_{\text{init}} < 20\% \\ &= 2, \text{ if } V_{\text{range}}/V_{\text{init}} > 50\% \text{ and } V_{\text{final}}/V_{\text{init}} < 20\% \\ &= 3, \text{ if } V_{2\text{sec}}/V_{\text{init}} < 40\% \text{ and } V_{\text{final}}/V_{\text{init}}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

Inputs: Cell capacity (mAh), SOC (%), Voltage-time series, Temperature-time series.

Output: Thermal runaway severity score 5~100.



# Thermal Runaway Severity Grading



LCO 4000 mAh



LFP 15000 mAh

# Database of Battery Abuse Test (Host: Sandia Labs)

Abuse Test Cells List

Indenter

Nail Speed

6 X

0.05 X

Abuse Test Cell List

SOC

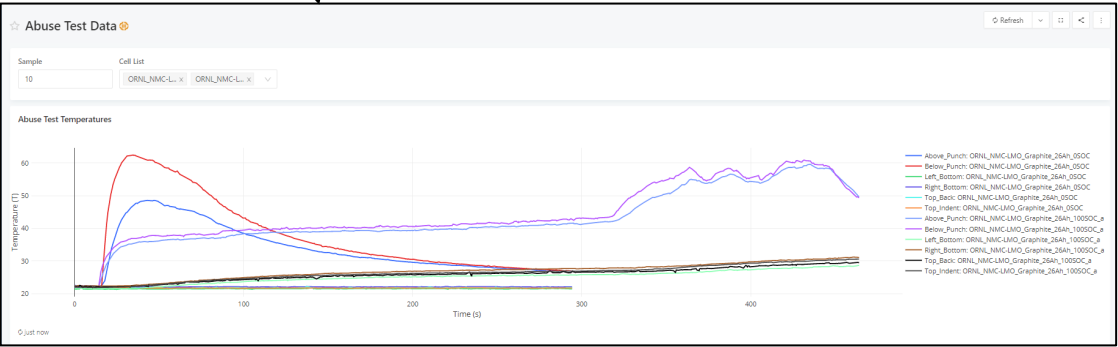
0 X

30 X

50 X

+5 more

Cell ID	Anode	Cathode	Source	Ah	Form Factor	SOC	Initial V	Indenter	Nail Speed
ORNL_NMC-LMO_Graphite_36Ah_050C	Graphite	NMC-LMO	Chevy Volt	26.00	Pouch	0.00	3.07	6.00	0.05
ORNL_NMC-LMO_Graphite_36Ah_10050C_a	Graphite	NMC-LMO	Chevy Volt	26.00	Pouch	100.00	4.17	6.00	0.05
ORNL_NMC-LMO_Graphite_36Ah_10050C_b	Graphite	NMC-LMO	Chevy Volt	26.00	Pouch	100.00	4.16	6.00	0.05
ORNL_NMC-LMO_Graphite_36Ah_10050C_c	Graphite	NMC-LMO	Chevy Volt	26.00	Pouch	100.00	4.12	6.00	0.05
ORNL_NMC-LMO_Graphite_36Ah_10050C_d	Graphite	NMC-LMO	Chevy Volt	26.00	Pouch	100.00	4.13	6.00	0.05
SNL_LCO_Graphite_6.4Ah_050C_a	Graphite	LCO	Battery Space	6.40	Pouch	0.00	3.21	6.00	0.05
SNL_LCO_Graphite_6.4Ah_050C_b	Graphite	LCO	Battery Space	6.40	Pouch	0.00	3.16	6.00	0.05
SNL_LCO_Graphite_6.4Ah_10050C_a	Graphite	LCO	Battery Space	6.40	Pouch	100.00	4.12	6.00	0.05
SNL_LCO_Graphite_6.4Ah_10050C_b	Graphite	LCO	Battery Space	6.40	Pouch	100.00	4.12	6.00	0.05
SNL_LCO_Graphite_6.4Ah_5050C_a	Graphite	LCO	Battery Space	6.40	Pouch	50.00	3.81	6.00	0.05
SNL_LCO_Graphite_6.4Ah_5050C_b	Graphite	LCO	Battery Space	6.40	Pouch	50.00	3.81	6.00	0.05
SNL_LCO_Graphite_6.4Ah_7050C_a	Graphite	LCO	Battery Space	6.40	Pouch	70.00	3.90	6.00	0.05



# Original Datasets Shared to Public (Mendeley Data)

data.mendeley.com/datasets/sn2kv34r4h/1

Mendeley Data

Published: 10 November 2023 | Version 1 | DOI: 10.17632/sn2kv34r4h.1

Contributors: Lianshan Lin, Hsin Wang, Jianlin Li, Loraine Torres-Castro, Yuliya Preger, Valerio De Angelis

Mechanically Induced Thermal Runaway for Li-ion Batteries

The deployment of Li-ion batteries covers a wide range of energy storage applications, from mobile phones, e-bikes, electric vehicles (EV) and stationary energy storage systems. However, safety issue such as thermal runaway is always one of the most important concerns to prevent Li-ion batteries from further market penetration. A standardized single-side indentation test protocol was developed to mechanically induce an internal short-circuit. The cell voltage, compressive load, indenter stroke, and temperature at the indentation point are measured in time series. The test data of each cell, along with cell parameters such as dimensions, mass, chemistry, state of charge (SOC), capacity, are integrated together to calculate a thermal runaway severity score from 0 to100. Complete data collection process including the original measured record, test method, severity score calculation scheme is presented in this article. The thermal runaway severity analysis and the more than 100 tested Li-ion battery records provide a good data source for further comparison and ranking of thermal runaway risks.

Download All 264 MB

Files

excel

main.xlsx

54.4 KB

Steps to reproduce

Steps to reproduce these test data can be found through previous paper <https://doi.org/10.1016/j.est.2023.106798>.

Institutions

Oak Ridge National Laboratory, Sandia National Laboratories

Dataset metrics

Usage

Views: 563

Downloads: 485

View details

Latest version

Version 1

Published: 10 Nov 2023

DOI: 10.17632/sn2kv34r4h.1

Cite this dataset

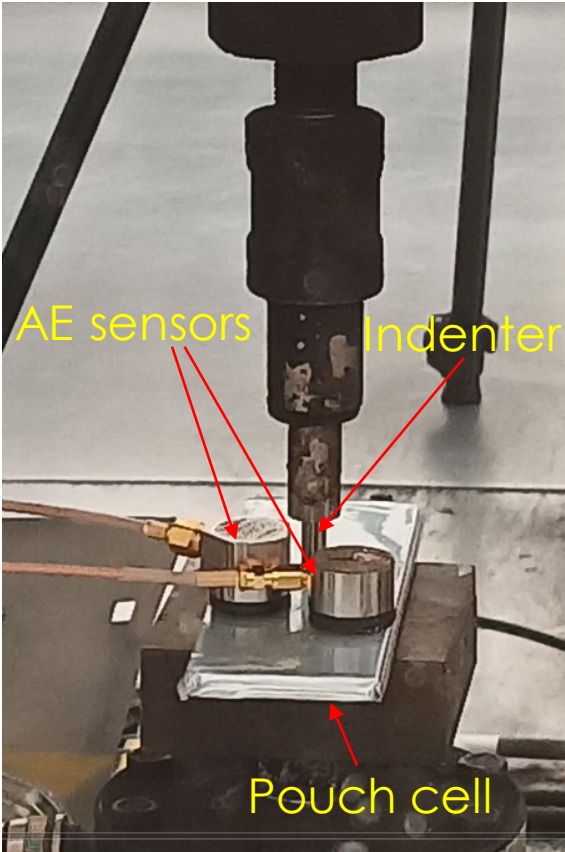
Lin, Lianshan; Wang, Hsin; Li, Jianlin; Torres-Castro, Loraine; Preger, Yuliya; De Angelis, Valerio (2023), "Mechanically Induced Thermal Runaway for Li-ion Batteries", Mendeley Data, V1, doi: 10.17632/sn2kv34r4h.1

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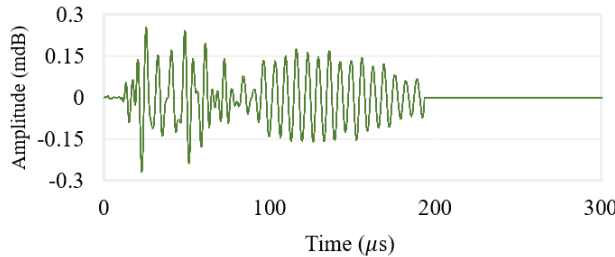
<https://data.mendeley.com/datasets/sn2kv34r4h/1>



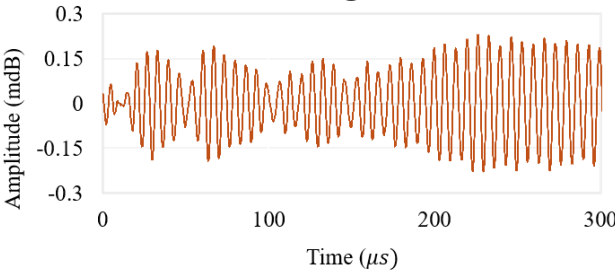
# Real-Time acoustic emission monitoring



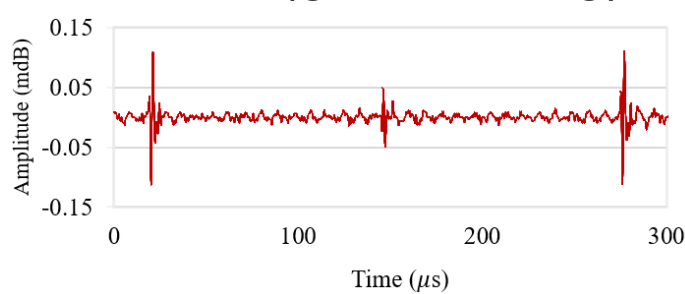
pre-Internal Short circuit (ISC)



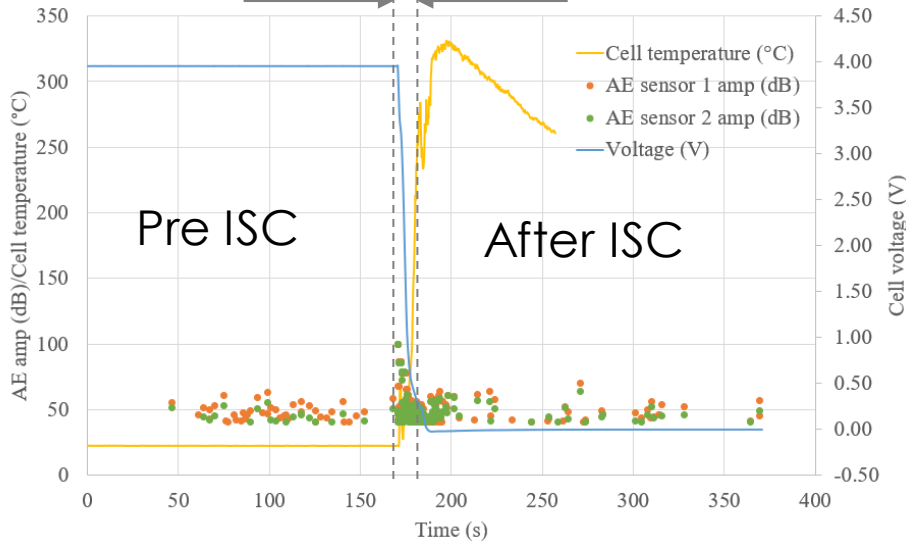
During ISC



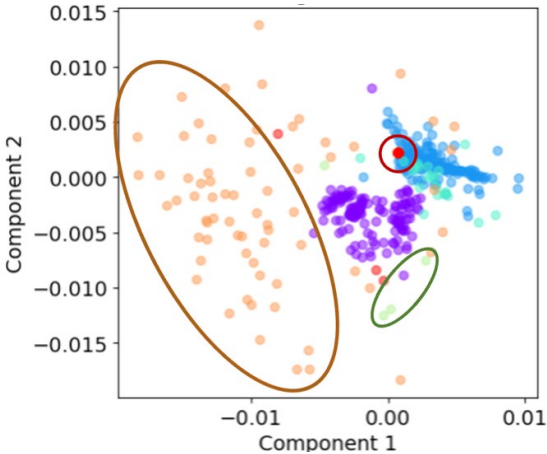
After ISC (gas releasing)



During ISC



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

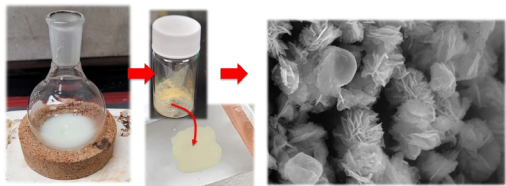


In cluster plot, axes represent a complex mix of frequency and time content (similar to PCA). Each point represents one emission – closer points represent more similar waveforms.

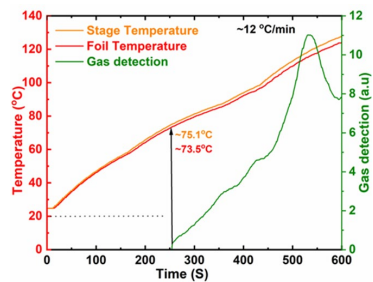
- Graphite - Gas Generation (143 AEs)
  - NMC811 - Particle Cracking (190 AEs)
  - LCO (21 AEs)
  - ORNL\_LCO20 Pre-ISC (22 AEs)
  - ORNL\_LCO20 During ISC 12s (202 AEs)
  - ORNL\_LCO20 Post ISC subset (54 AEs)
- MIT generated data
- ORNL LCO 20% SOC test separated by pre-voltage drop, during (12 sec.), and post- (temporary) voltage recovery

# Conclusions

- Thermal sensitive copper–thiol compounds were synthesized



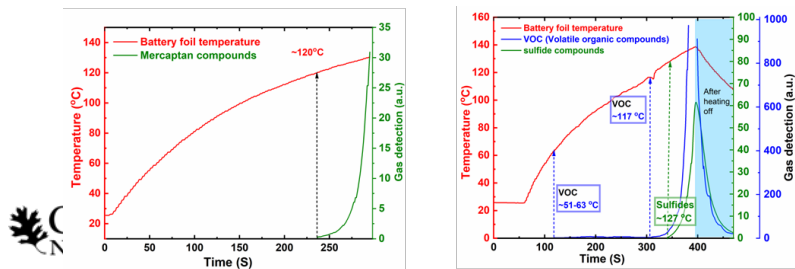
- Compound thermally decomposes to release volatile compounds when critical temperature is reached.



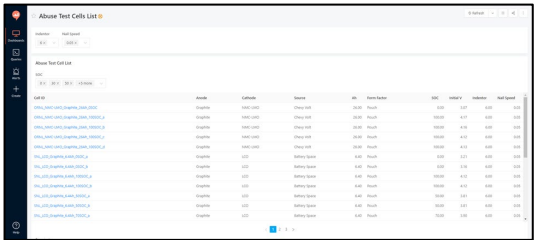
- Critical thiol release temperature can be tunable

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

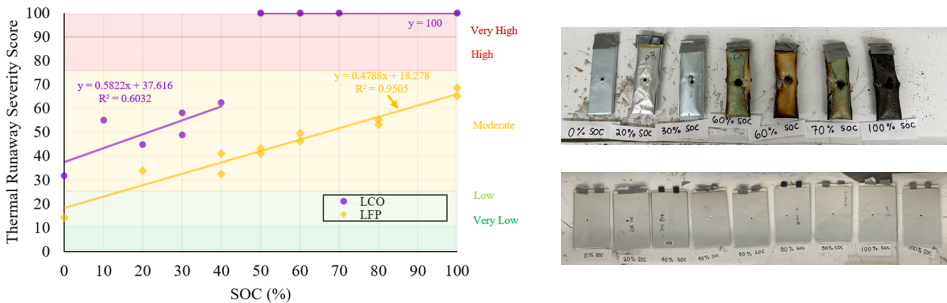
- Gas detection depend on the type of gas release and sensor



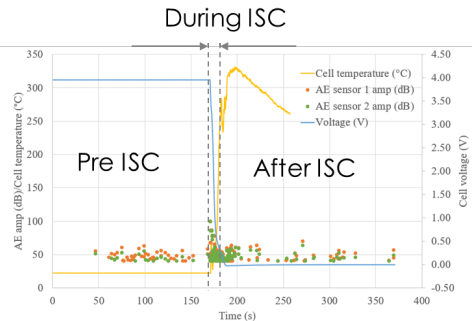
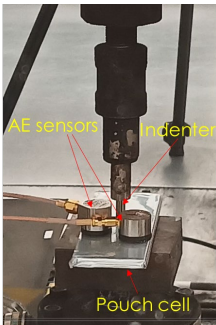
- TR database can be used to predict the severity of various cells



- 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 5<sup>th</sup> 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

## Acknowledgments

- ORNL DRD SEED money program
- Office of Electricity, Energy Storage System Safety & Reliability Program
- Sandia National Laboratory

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