

Energy Storage Safety and Reliability Thermal Runaway Database Development Hsin Wang¹, Lianshan Lin¹, Srikath Allu¹ Loraine Torres-Castro², Yuliya Preger², Valerio De Angelis **Development of Thermally Sensitive Paint** Hsin Wang¹, Beth Armstrong¹, Chanaka Gamalalaralage¹ Michael Starke¹ ¹Oak Ridge National Laboratory ²Sandia National Laboratories

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



Team Members - ORNL



Hsin Wang

Material Science and Technology Division Material Scientist, Testing



Beth Armstrong

MSTD Ceramist, Paint Development

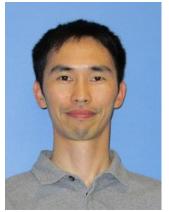


Srikanth Allu

Computational Science & Engineering Modeling & Simulation CAK RIDGE

Jianlin Li

Electrification & Energy Infrastructure Battery Research



Lianshan Lin

MSTD Mechanical, Database



Michael Starke

Electrification & Energy Infrastructure Battery Management System



Chanaka Gamaralalage

MSTD **Chemist, Paint Development**



Isabella Fishman

Northwestern University **DOE SULI Student, Battery Testing**





Collaboration: Sandia Laboratories and Others

Sandia Laboratories: Protocols development, parallel testing database development

Collaborators: Loraine Torres-Castro, Josh Lamb, Yuliya Preger and Valerio De Angelis

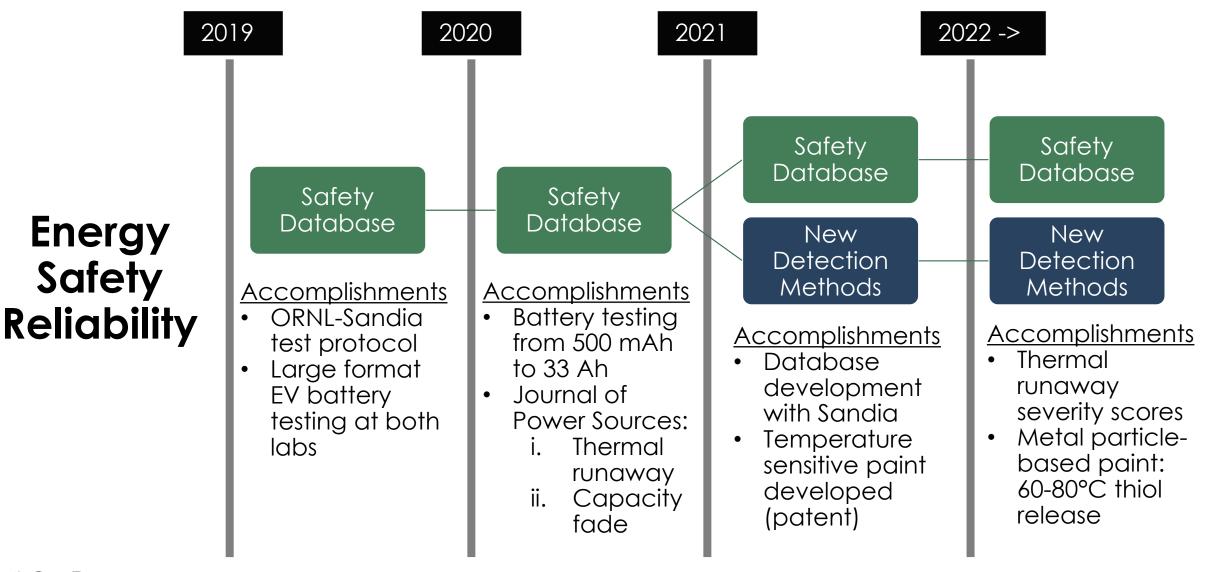
University of Tennessee: Accelerating Rate Calorimetry (ARC), thermal runaway reactions and propagation

Collaborator: Professor Peng Zhang @ UT Space Institute Tullahoma TN

LG&E KU: Technology Research and Analysis Department, Kentucky's first and largest utility-scale energy storage system. On-site lithium-ion battery temperature monitoring directly supports the E.W. Brown Solar facility



Project History and Progression



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Safety Database

Thermal Runaway Severity

Project Goal: Develop a thermal runaway database to rank/predict hazard severity



Mechanical Induced Short Circuit

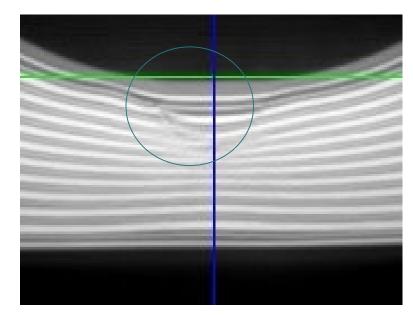
- Mechanically induced internal short circuit
 - Nail penetration
 - Single-side indentation
 - Pinch test (two indenters)
 - Pinch-torsion, indent-torsion

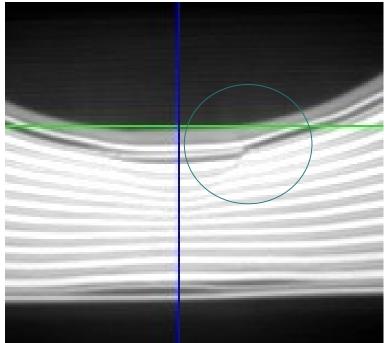
Real-time Monitoring:

– Load, displacement, V_{OC} and temperature

Post-mortem Examination:

- X-ray computed tomography (XCT)
- Open cell examination







ORNL and Sandia Testing Facility: Large Format Cells



Nissan Leaf Cell in Sandia Test Chamber



Nissan Leaf Cell After Indentation



Extracting Li-ion Cells from Electrical Vehicles at ORNL (Chevy VOLT, Nissan Leaf and FORD Focus EV)



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Li-ion Cells: Disassembled EVs and Commercial Sources

Large-format Prismatic Cells Tested at ORNL and Sandia









2017 Chevy VOLT (26 Ah) 2013 Nissan Leaf (33 Ah)

Commercial NMC Cells (10 Ah) Commercial LFP Cells (10 Ah)



10 NMC Cells (5 SOC x 2) after Testing Left to right: 0% SOC -> 100% SOC

10 LFP Cells (5 SOC x 2) after Testing Left to right: 0% SOC -> 100% SOC



Updated ORNL-Sandia Test Procedures and Standards

Internal Short-ciruit Induced Thermal Runaway

Mechanical abuse (indentation)

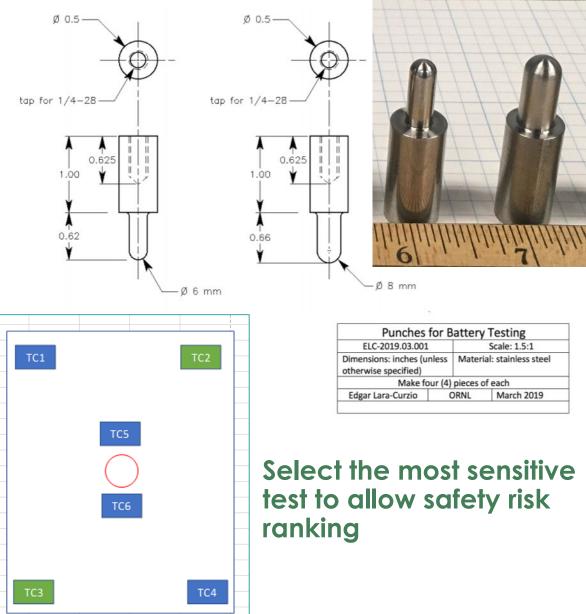
Updated Test Protocols:

- 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
- 6 mm punch (most sensitive, small contact)
- 0.05 inch per minute compressive loading
- 25 mV V_{oc} drop

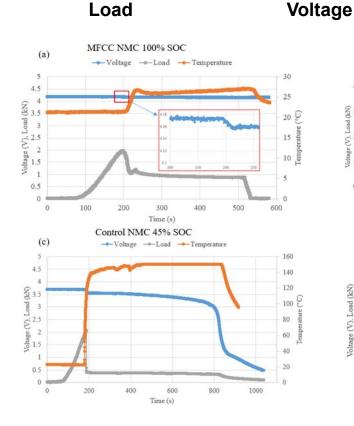
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- Hold the punch after short circuit
- Temperature measurement:
 - 5 mm from the indenter
- At cell corners when possible CAK RIDGE

Thermocouple Locations on Large-format Cells



Thermal Runaway Risks for Li-ion Batteries (ORNL-Sandia)

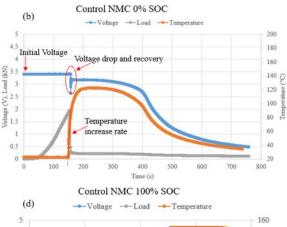


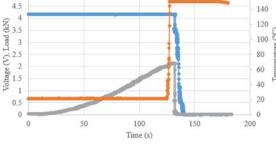
Small Cells Testing at ORNL: SOC: 20%, 40%,60% 80%,100% Capacity at 500, 1500, 200 mAhr Number of Cells: 4 cells/condition

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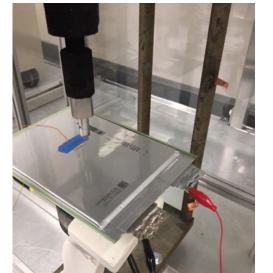
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Temperature





<u>ESS Batteries at Various SOCs:</u> Sandia: 30%, 50%, 75%, 100% ORNL: 20%, 40%,60% 80%,100%



Test Data and Cell Information:

- Cell Capacity
- Loading curve: before & after short
- Cell Voltage: drop and response
- Cell Temperature vs. Time
- Open cell voltage
- Anode thickness
- Cathode thickness
- Separator thickness
- C/2 Charge curve
- 1C discharge curve

Cell Name	Chemistry	Capacity (mAH)	Sample Number
Commercial LCO	LiCoO ₂	500	15
Commercial LCO	LiCoO ₂	1500	10
Commercial LCO	LiCoO ₂	2000	15
Commercial LCO	LiCoO ₂	6400	13
Control NMC	LiNiMnCoO ₂ (811)	5200	12
Metallized Film Current Collector (MFCC) NMC	LiNiMnCoO ₂ (811)	5200	10
Commercial LFP	LiFePO ₄	10000	16
Commercial NMC	LiNiMnCoO ₂	10000	14

Acronyms for cathode chemistry: lithium cobalt oxide (LCO); lithium nickel manganese cobalt oxide (NMC); lithium iron phosphate (LFP)

Thermal Runaway Severity: EUCAR vs Test Data-driven Severity Levels

EUCAR Severity Levels

Hazard Level	Description	Classification Criteria & Effect
0	No effect	No effect. No loss of functionality.
1	Passive protection activated	No defect; no leakage; no venting, fire, or flame; no rupture; no explosion; no exothermic reaction or thermal runaway. Cell reversibly damaged. Repair of protection device needed.
2	Defect/Damage	No leakage; no venting, fire or flame; no rupture; no explosion; no exothermic reaction or thermal runaway. Cell irreversibly damaged. Repair needed.
3	Leakage ∆mass < 50%	No venting, fire, or flame; no rupture; no explosion. Weight loss < 50% of electrolyte weight (electrolyte = solvent + salt).
4	Venting ∆mass ≥ 50%	No fire or flame; no rupture; no explosion. Weight loss ≥ 50% of electrolyte weight (electrolyte = solvent + salt).
5	Fire or Flame	No rupture; no explosion (i.e., no flying parts).
6	Rupture	No explosion, but flying parts of the active mass.
7	Explosion	Explosion (i.e., disintegration of the cell).

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ORNL-Sandia Test Data Based Severity Levels

Hazard Severity Level	Description	
1 (VL, 0-10)	Very low, instant local Joule heating, detectable voltage drops	
2 (L, 10-25)	Low, localized heating, small voltage drops and recovery	
3 (M, 25-75)	Moderate, localized heating spread, significant voltage drops, continued discharge after recovery	
4 (H, 75-90)	High, heating due to chemical reactions, cell puff and gas release, voltage drop to close zero	
5 (VH, 90-100)	Very high, heating spread to the cell, heavy smoke and possible fire, voltage drops to zero	

Calculation of Thermal Runaway Severity Score

SOC

(%)

Battery Capacity

(mAH)

Observed

Severity Level (OHS)

Low

Low

Low

Low

Low

Low

Moderate

Moderate

Moderate

Moderate

Low

Moderate

Moderate

Moderate

Moderate

Very High

Very High Very High

Moderate

Moderate

Moderate

Moderate

Very Low

Very Low

Very Low

Very Low

Very Low Very High

Very High

High

Moderate

Moderate

Moderate

Low

Moderate

Moderate

Moderate

Moderate

Moderate

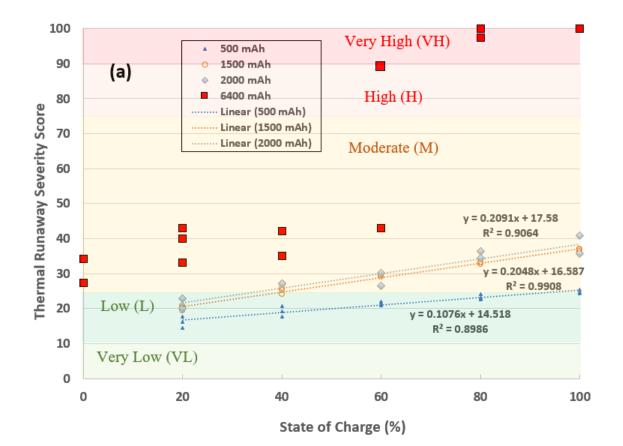
Moderate

Moderate

Severity Score Calculation Based on Temperature and	Voltage	Test Name	Calculated Severity Level (CHS 5-100)
$\int 5, if Max Temperature < 40 ^{\circ}C$		LCO 500mAh1-20SOC	14.4
		LCO 500mAhl-40SOC	17.6
$WA * \left(\frac{Max Temperature}{160}\right)^{0.25}$		LCO 500mAh1-60SOC	22.0
$WA + \begin{pmatrix} \\ \\ \\ 160 \end{pmatrix}$		LCO 500mAh1-80SOC	24.2
(Temperature Increase Rate)		LCO 500mAh1-100SOC	24.3
$\begin{cases} \min\{ +wB * \left(\frac{Temperature Increase Rate}{200}\right) \end{cases}$	(1)	LCO 1500mAh1-20SOC	20.7
		LCO 1500mAh1-40SOC	25.2
+wC * wCap * wSOC * Voltage Drop Score		LCO 1500mAhl-60SOC	29.0
$+cOffset, 100\}$		LCO 1500mAh1-80SOC	32.8
100, if Max Temperature > 160 °C		LCO 1500mAh1-100SOC	36.7
t 100, ij Max Temperature > 100 C		LCO 2000mAhl-20SOC	22.8
		LCO 2000mAhl-40SOC	27.1
Voltage Drop Score=		LCO 2000mAhl-60SOC	26.6
		LCO 2000mAhl-80SOC	36.3
		LCO 2000mAh1-100SOC	35.7
ر 1, if (Voltage Range)/(Initial Voltage) < 0.2		Soteria-Control-100SOC	100.0
, Voltage Range, Final Voltage Change		Soteria-Control-80SOC	100.0
2, if $\frac{Voltage Range}{Initial Voltage} > 0.5$ and $\frac{Final Voltage Change}{Initial Voltage} < 0.2$		Soteria-Control-60SOC	100.0
Initial Voltage Initial Voltage		Soteria-Control-40SOC	57.9
$\begin{cases} 3, if \frac{Voltage \ Drop \ in \ 2 \ Seconds}{Initial \ Voltage} < 0.4 \ and \ \frac{Final \ Voltage \ Change}{Initial \ Voltage} > 0.7 \end{cases}$		Soteria-Control-20SOC	40.3
5		Soteria-Control-10SOC	46.4
4, if $\frac{Voltage Drop in 2 Seconds}{Initial Voltage} \ge 0.4 and \frac{Final Voltage Change}{Initial Voltage} > 0.7$		Soteria-Control-0SOC	27.1
4, If $\underline{\qquad}$ Initial Voltage ≥ 0.4 and $\underline{\qquad}$ Initial Voltage ≥ 0.7		Soteria-MFCC-100SOC	5.0
		Soteria-MFCC-80SOC	5.0
$5, if \frac{Voltage Range}{Initial Voltage} > 0.7 and \frac{Final Voltage Change}{Initial Voltage} > 0.7 and \frac{Voltage Drop in 5 Seconds}{Initial Voltage} > 0.7$		Soteria-MFCC-60SOC	5.0
C ⁺ , Initial Voltage Initial Voltage Initial Voltage		Soteria-MFCC-40SOC	5.0
		Soteria-MFCC-20SOC	5.0
	(2)	LCO- 6400mAh-100SOC	100.0
	(-)	LCO- 6400mAh-80SOC	100.0
		LCO-6470mAh-60SOC	89.1
wA = 2.0*cScale, $wB = 3.0$ *cScale, $wC = 2.0$ *cScale	(3)	LCO-6270mAh-40SOC	35.1
		LCO-6500mAh-20SOC	43.0
	(\mathbf{A})	LCO-6560mAh-0SOC	34.3
wCap = Battery Capacity/10000	(4)	LFP 10Ah-0SOC	13.8
		LFP 10Ah-40SOC	27.1 33.2
wSOC = Battery SOC/100	(5)	LFP 10Ah-60SOC	
where Dattery beer 100		LFP 10Ab-80SOC	39.2
		LFP 10Ah-100SOC NMC 10Ahr-0SOC	44.8 37.1
cScale = 95/6, $cOffset = 5$ -cScale	(6)		25.3
* OAK RIDGE	× /	NMC 10Ah-20SOC NMC 10Ahr-40SOC	25.3 55.0
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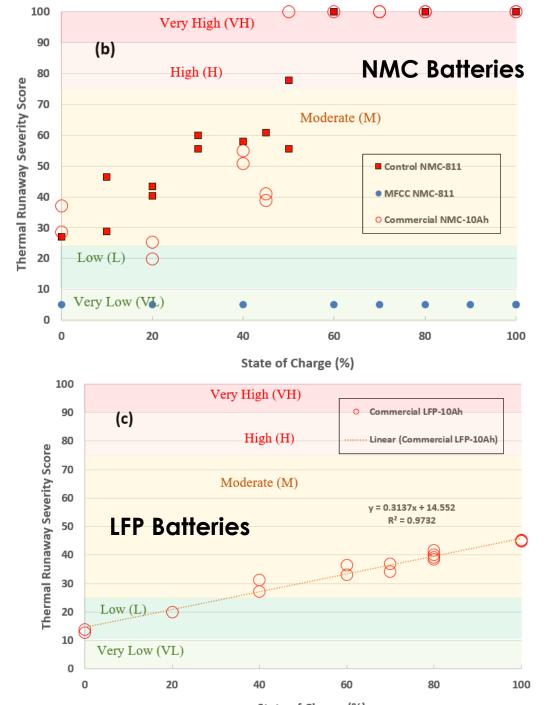
Results: Linear Change vs "Step Change"



LCO Batteries: 500 mAh to 6400 mAh

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State of Charge (%)

Thermal Runaway Severity Calculation Workflow

Format	ted data file in 'e			Calculation file	
File Home Insert	t Draw Page Layout Formulas Data		₽ ℃ ℃ ® ~ ≂	formatData-2022-newscript&5-100.xlsm 👻	Search (Alt+Q)
AE6	Necess	ary columns	File Home Insert Draw	Page Layout Formulas Data Review View	Developer Help
Time Lo		IMNOP Time Temperature	· 112 · · · · · · · · · · · · · · · · ·	$\times \checkmark f_x$	CapacitySOC
1 Time (sec) Penetrator	r Force (N) Cell Voltage (V) Displacement (mm)	Time (sec) TC1 (°C) TC2 (°C) TC3 (°C) TC4 (°C)	A	B C D	E F G H J
2 0 -4	4.19911968 3.452	0 22.8256	1 Sorteria-100SOC-cell1	-	Je heating, no internal discharge – 1 4960 100
	4.17687858 3.448	0.099 22.82095	2 Sorteria-100SOC-cell2 3 Sorteria-Control-100SOC-cell1		Jle heating, no internal discharge – 1 4960 100 pouch, smoke, gas release, fire – 7 5190 100
	4.50159864 3.448	0.2 22.81805	4 Sorteria-Control-100SOC-cell2		pouch, smoke, gas release, fire – 7 5190 100 Risk Analysis pouch, smoke, gas release, fire – 7 5190 100
	4.37704848 3.448 -5.3823462 3.448	0.299 22.77973	5 LCO-LP-6400mAh-100SOC-cell1		pouch, smoke, gas release, fire – 7 6400 100
	-5.3823402 3.448 4.09681062 3.448	0.433 22.77025	6 LCO-LP-6400mAh-100SOC-cell2	Processing Physical effect, rupture of	pouch, smoke, gas release, fire – 7 6400 100
	4.05081002 5.448	0.598 22.76464	7 LCO-LP-6400mAh-80SOC-Cell3		pouch, smoke, gas release, fire – 7 6400 80 Run
	4.07456952 3.449	0.7 22.79483	8 LCO-LP6400mAh-80SOC-cell4		
	4.17687858 3.45	0.799 22.78554	9 Soetria-80SOC-cell3 10 Sotteria-Control-60SOC-cell1		
	4.26139476 3.449	0.899 22.78264	11 Soetria-Control-45SOC-cell1		pouch, smoke, gas release, fire – 7 5190 60 COOC Illing), rupture of pouch, gas release – 6 5190 45 COOCE
	3.77653878 3.448	1 22.75069	12 Sorteria-control-40SOC-cell2		Iling), rupture of pouch, gas release - 6 5190 40
	3.73205658 3.448	1.1 22.7716	13 Sorteria-control-20SOC-cell1		lling), extended joule heating, local reactions - 5190 20
14 0.66 -2	2.31752262 3.448	1.2 22.78147	14 Soteria-control-30SOC-cell2		Iling), extended joule heating, local reactions - 5190 30
15 0.744	-3.4251294 3.448	1.299 22.82618	15 Soteria-control-30SOC-cell1 16 Soteria-control-10SOC-cell1		Iling), extended joule heating, local reactions – 5190 30 lioule heating, local reactions (limited spread) 5190 10
16 0.84 -3	3.30947568 3.448	1.4 22.84184	16 Soteria-control-10SUC-cell1 17 Soteria-Control-0SOC-cell1		I joule heating, local reactions (limited spread) 5190 10 I joule heating, local reactions (no spread) – 3 5190 0
17 1.017 -4	4.50604686 3.448	1.499 22.83546	18 Soteria-SCC-90SOC-cell1		Je heating, no internal discharge – 1 5180 90
18 1.063	-4.4704611 3.448	1.599 22.82211	19 Soteria-SCC-80SOC-cell1		Je heating, no internal discharge – 1 5180 80
19 1.121 -4	4.05232842 3.448	1.699 22.80528	20 Soteria-SCC-60SOC-cell1		ule heating, no internal discharge – 1 5180 60
	4.37260026 3.449	1.798 22.83256	21 Soteria-SCC-20SOC-5180mAh		Ile heating, no internal discharge – 1 5180 20
	3.37175076 3.447	1.899 22.85287	22 0F-1 C0-6490mAb-6080C		Lioule beating local reactions (limited spread) 6/00 60
	4.19911968 3.452 4.17687858 3.448	1.999 22.86563 2.132 22.80817	Juccer Summary	0	
	CommandButton3 Private Sub CommandButton3_Click() Dim ofOlder As Object Dim ofOlder As Object Dim iAs Integer 'Fhysical effect, rupture of pouch, smoke, gas relev	✓ Click ase, fire - 7	E ∽ C ~ B ~ = File Home Insert Draw	Page Layout Formulas Data Review Vie	Y 1, 4
	'No effect, local heating, internal discharge - 2	the worksheet	F25 • :	× √ f _x 40	Severity score
	'No effect, instant local Joule heating, no interna:	l discharge – 1		ed Score	Observed Score Calculated Score Capacity SOC
	<pre>'clear all existing content sheetname = "Sheet1"</pre>			ect, instant local Joule heating, no internal discharge – 1	1.00 5.00 4960 100 20.3214 0.22156 15.7067
	<pre>strPath = Application.ActiveWorkbook.Path Set oFS0 = CreateObject("Scripting.FileSystemObject")</pre>	")		ect, instant local Joule heating, no internal discharge – 1	1.00 5.00 4960 100 20.1898 0.18107 15.7067
	<pre>Set oFolder = oFSO.GetFolder(strPath) i = 0</pre>			al effect, rupture of pouch, smoke, gas release, fire – 7 al effect, rupture of pouch, smoke, gas release, fire – 7	7.00 100.00 5190 100 31.1724 37.6766 49.305 7.00 100.00 5190 100 31.1724 40.3477 49.305
	<pre>strFolderExists = Dir(strPath + "\excel\", vbDirecto If strFolderExists = "" Then</pre>	pry)		al effect, rupture of pouch, smoke, gas release, fire – 7	7.00 100.00 5150 100 31.1724 40.3477 49.305
	MsgBox "data file doesn't exist!"		7 LCO-LP-6400mAh-100SOC-cell2 Physica	al effect, rupture of pouch, smoke, gas release, fire – 7	7.00 100.00 6400 100 31.1724 29.8941 101.333
	Exit Sub 'MkDir strPath + "\excel\"			al effect, rupture of pouch, smoke, gas release, fire – 7	7.00 100.00 6400 80 31.1724 29.5352 81.0667
	End If			al effect, rupture of pouch, smoke, gas release, fire – 7 al effect, rupture of pouch, smoke, gas release, fire – 7	7.00 97.48 6400 80 31.1724 28.5057 48.64 7.00 100.00 4960 80 31.1724 29.5128 62.8267
	Dim strFileName As String 'n = oFolder.Files.Count			al effect, rupture of pouch, smoke, gas release, fire – 7	7.00 100.00 5190 60 31.1724 25.5128 49.305
	n = Cells(Rows.Count, 1).End(xlUp).Row + 10 'rows or	f first column	12 Soetria-Control-45SOC-cell1 Physica	al effect (pouch swelling), rupture of pouch, gas release – 6	6.00 60.73 5190 45 31.1724 18.1999 22.1873
	For i = 1 To n			al effect (pouch swelling), rupture of pouch, gas release - 6	6.00 57.93 5190 40 31.1724 17.8647 19.722
	'For i = 13 To 25 strFileName = Cells(i, 1)			al effect (pouch swelling), extended joule heating, local reaction al effect (pouch swelling), extended joule heating, local reaction	
	If strFileName <> "" Then 'addTemperature			al effect (pouch swelling), extended joule heating, local reaction al effect (pouch swelling), extended joule heating, local reaction	
	<pre>strExcelFile = strPath + "\excel\" + strFile strState = Cells(1, 3)</pre>	eName + ".xlsx"	17 Soteria-control-10SOC-cell1 Moder	ate effect, extended joule heating, local reactions (limited sprea	4.00 46.36 5190 10 30.345 21.9142 4.9305
	'If Dir(strExcelFile) <> "" And Dir(strTemp) If Dir(strExcelFile) <> "" And strState = ")	File) <> "" Then		ate effect, extended joule heating, local reactions (no spread) –	
	Dim app As New Excel.Application			ect, instant local Joule heating, no internal discharge – 1 ect, instant local Joule heating, no internal discharge – 1	1.00 5.00 5180 90 20.9707 0.28818 14.763 1.00 5.00 5180 80 20.8322 0.21012 13.1227
	app.Visible = False 'Visible is False by Dim book As Excel.Workbook			ect, instant local Joule neating, no internal discharge – 1 ect, instant local Joule heating, no internal discharge – 1	1.00 5.00 5180 80 20.8322 0.21012 13.1227 1.00 5.00 5180 60 20.5409 0.22226 9.842
	Set book = app.Workbooks.Open(strExcelF:	ile)	22 Soteria-SCC-20SOC-5180mAh No effe	ect, instant local Joule heating, no internal discharge – 1	1.00 5.00 5180 20 19.9489 0.14925 3.28067
OAK RII	Set wsheet = book.Worksheets(sheetname) 'calculate risk score			al effect (pouch swelling), rupture of pouch, gas release – 6	6.00 89.10 6470 60 31.1724 31.8859 36.879
		(JUD).Row 'upbound of voltage column	Sheet1 Summary	(+)	

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Search Database by Battery and Abuse Test Metadata (Host: Sandia Labs)



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New Detection Methods

Thermally Sensitive Paint Development

(Seedling)

Project Goal: Thermal runaway avoidance. Early detection of thermal runaway on every cell and large surface area



Indirect Large Area Temperature Monitoring

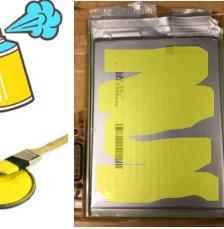
Temperature-Sensitive Paint for T_{Threshold} Monitoring Carriers for paint need to have the following features:

- ✓ Stay normal within battery operation temperature
- ✓ Release chemical/gas T > $T_{Threshold}$
- ✓ Non-line-of-sight (change of color is not an option)
- $\checkmark\,$ Detection via "smell" and gas detector



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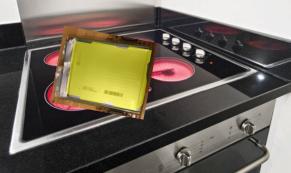
Li-ion Battery



Brush or Spray Paint



Overheating



Thermal Runaway



Heating

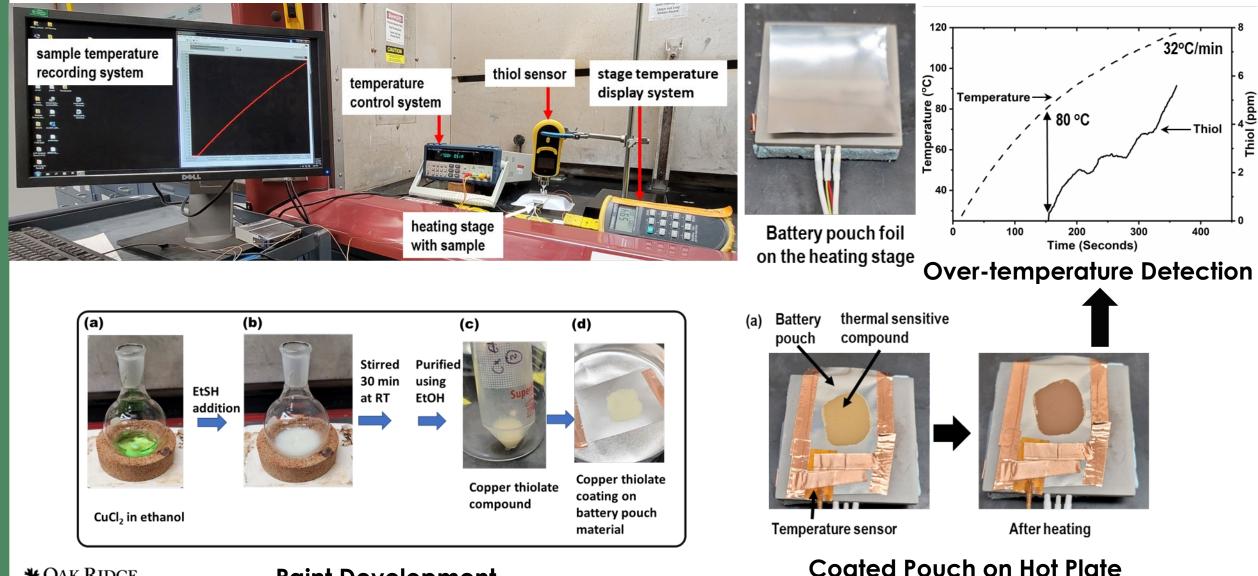




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(Web image)

Experimental Setup and Demonstration of Thiol Release



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Paint Development

Future Plan: ESS Reliability Safety Testing and Analysis Facility

Single Cells Database (ORNL-Sandia):

- > UL Standard, end-user upload
- > Machining learning, prediction of hazard severity

NHTSA Electrical Vehicles -> battery Packs, module and cell:

- > Thermal runaway testing
- > Thermal runaway propagation studies
- Modeling and Simulations of battery failure

Battery Safety Technology Development and Demonstration:

- > Thermal runaway warning system (paint development)
- > Gas detection, BMS/TMS control, prevention mechanisms (isolation,

***OAK RIDGE** lowering SOC, discharge)

Acknowledgements and Outputs

Project Supported by DOE EERE Office of Electricity (OE) (Dr. Imre Gyuk)

Publications, Patent, Presentation:

- 1. Tongxin Shan, Zhenpo Wang, Xiaoqing Zhu, Hsin Wang, Yangjie Zhou, Yituo Wang, Jinghan Zhang and Zhiwei Sun, "Explosion behavior investigation and safety assessment of large-format lithium-ion pouch cells", *Journal of Energy Chemistry*, doi.org/10.1016/j.jechem.2022.04.018, April 19, 2022 Impact factor =11.62
- 2. Wei Li, Bobing Xin, Thomas R. Watkins, Yong Xia, Hsin Wang, Juner Zhu, "Mechanical damage of prismatic Lithium-ion cells subject to bending: tests, model, and detection", *EcoMat*, revised, <u>doi.org/10.1002/eom2.12257</u>, pp1-16, 2022 Impact factor =12.213
- 3. Srikanth Allu, Jean-Luc Fattebert, Hsin Wang, Srdjan Simunovic, Sreekanth Pannala, and John Turner, **Book Chapter**: "Accelerating Battery Simulations by using High Performance Computing and Opportunities with Machine Learning", in *Modern Aspects in Electrochemistry Book Series*, Editor: Shriram Santhanagopalan, Springer, UK (2022)
- 4. L.S. Lin, J.L. Li, I. Fishman L. Torres-Castro, Y. Preger, V. De Angelis, J. Lamb, X.Q. Zhu, S. Allu and H. Wang, "Mechanically Induced Thermal Runaway Severity Analysis for Li-ion Batteries", *Journal of Energy Storage*, Submitted September 2022
- 5. Joshua Lamb, Sergiy Kalnaus and Hsin Wang, **Book Chapter**: "Experimental Simulations of Field Induced Mechanical Abuse Conditions", in *Modern Aspects in Electrochemistry Book Series*, Editor: Shriram Santhanagopalan, Springer, UK (2022)

One Provisional Patent Filed: ID 4373 "Temperature sensitive paint with gas and chemical release functions" by, BL Armstrong, CI Gamalarage, K. Buddett-Trofimov, GM Veith, H Wang

Invited talk: Battery & EV Congress 2022 (June 8-9, 2022 at the MSU Management Education Center, Troy, Michigan), Title: Thermal Runaway Risk of Li-ion Batteries Used in Electric Vehicles: Testing and Analysis by Hsin Wang et al



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