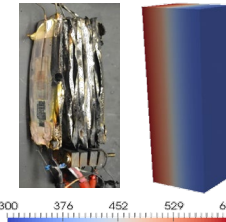
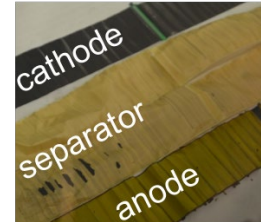
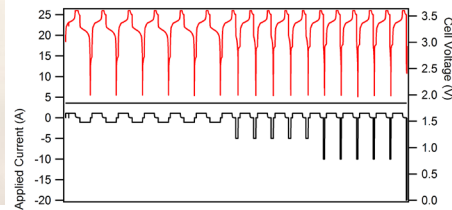


# Impact of Aging on the Safety of Lithium-ion Batteries



PRESENTED BY

Yuliya Preger

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DOE OE Energy Storage Peer Review  
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# Project objective and OE mission alignment



**OBJECTIVE:** Assess the impact of chemistry, aging level, and abuse technique on the abuse response of unused vs. aged cells

## SIGNIFICANCE

- Testing for battery safety standards + publications is typically done with unused cells, but cells are ‘unused’ for only a small fraction of their lifetime
- Understanding how the abuse response of aged cells differs from unused cells will enable the design of more effective energy storage failure mitigation systems, especially for second-life systems

## ALIGNMENT WITH CORE MISSION OF DOE OE

- Energy storage systems contribute to resilience, reliability, and flexibility of energy infrastructure
- Safety concerns are a major barrier to system deployment and collecting safety data for more relevant configurations will lead to improved system designs

# Gap: Standards only call for safety tests on unused cells



## Example Testing Report

Test	Unused Cell
Continuous charging at constant voltage	✓
External short circuit	✓
Free fall	✓
Thermal abuse	✓
Crush	✓
Forced discharge	✓
Forced internal short circuit	✓

Source: LG Chem 18650HG2, IEC Test Report issued under UL

# Gap: Standards only call for safety tests on unused cells



## Example Testing Report

Test	Unused Cell	Aged Cell
Continuous charging at constant voltage	✓	x
External short circuit	✓	x
Free fall	✓	x
Thermal abuse	✓	x
Crush	✓	x
Forced discharge	✓	x
Forced internal short circuit	✓	x

Source: LG Chem 18650HG2, IEC Test Report issued under UL

Failure mitigation mechanisms are developed based on the outcomes of these tests

# Influence of battery aging on safety is unclear



- More safe (due to capacity loss)?
- Less safe (due to materials/component instability)?
- Little difference?

# Previous work on safety of aged batteries



In 2022, we published the first comprehensive review of all public data on the safety of aged Li-ion batteries in collaboration with UL Electrochemical Safety Research Institute

## Key takeaways

- “Safety” depends on the metric and aging conditions
- Li plating lowers thermal runaway onset temperatures

## Identified areas with limited data

- Electrical and mechanical abuse response
- LFP cathodes
- Off-gassing\*
- Modules



### Perspective—On the Safety of Aged Lithium-Ion Batteries

Yuliya Preger,<sup>1,\*</sup> Loraine Torres-Castro,<sup>2</sup> Taina Rauhala,<sup>3,\*</sup> and Judith Jeevarajan<sup>3,\*</sup>

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<sup>3</sup>Electrochemical Safety Research Institute, Underwriters Laboratories Inc., League City, Texas 77573, United States of America

Concerns about the safety of lithium-ion batteries have motivated numerous studies on the response of fresh cells to abusive, off-nominal conditions, but studies on aged cells are relatively rare. This perspective considers all open literature on the thermal, electrical, and mechanical abuse response of aged lithium-ion cells and modules to identify critical changes in their behavior relative to fresh cells. We outline data gaps in aged cell safety, including electrical and mechanical testing, and module-level experiments. Understanding how the abuse response of aged cells differs from fresh cells will enable the design of more effective energy storage failure mitigation systems.  
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Manuscript submitted December 10, 2021; revised manuscript received January 19, 2022. Published March 4, 2022. *This paper is part of the JES Focus Issue on Women in Electrochemistry.*

High voltage and high energy density lithium-ion (Li-ion) batteries are increasingly used in many applications, including consumer electronics, electric vehicles, and grid-tied energy storage systems. However, with increasing energy density and installation size come heightened concerns about safety, including the risk of thermal runaway and severe fires.<sup>1–4</sup> Thermal runaway is traditionally defined as an accelerating release of heat inside a cell due to a

summarize critical parameters by which the safety of aged cells relative to fresh cells may be evaluated. We then identify aspects of aged battery safety that merit further exploration.

#### Current Status

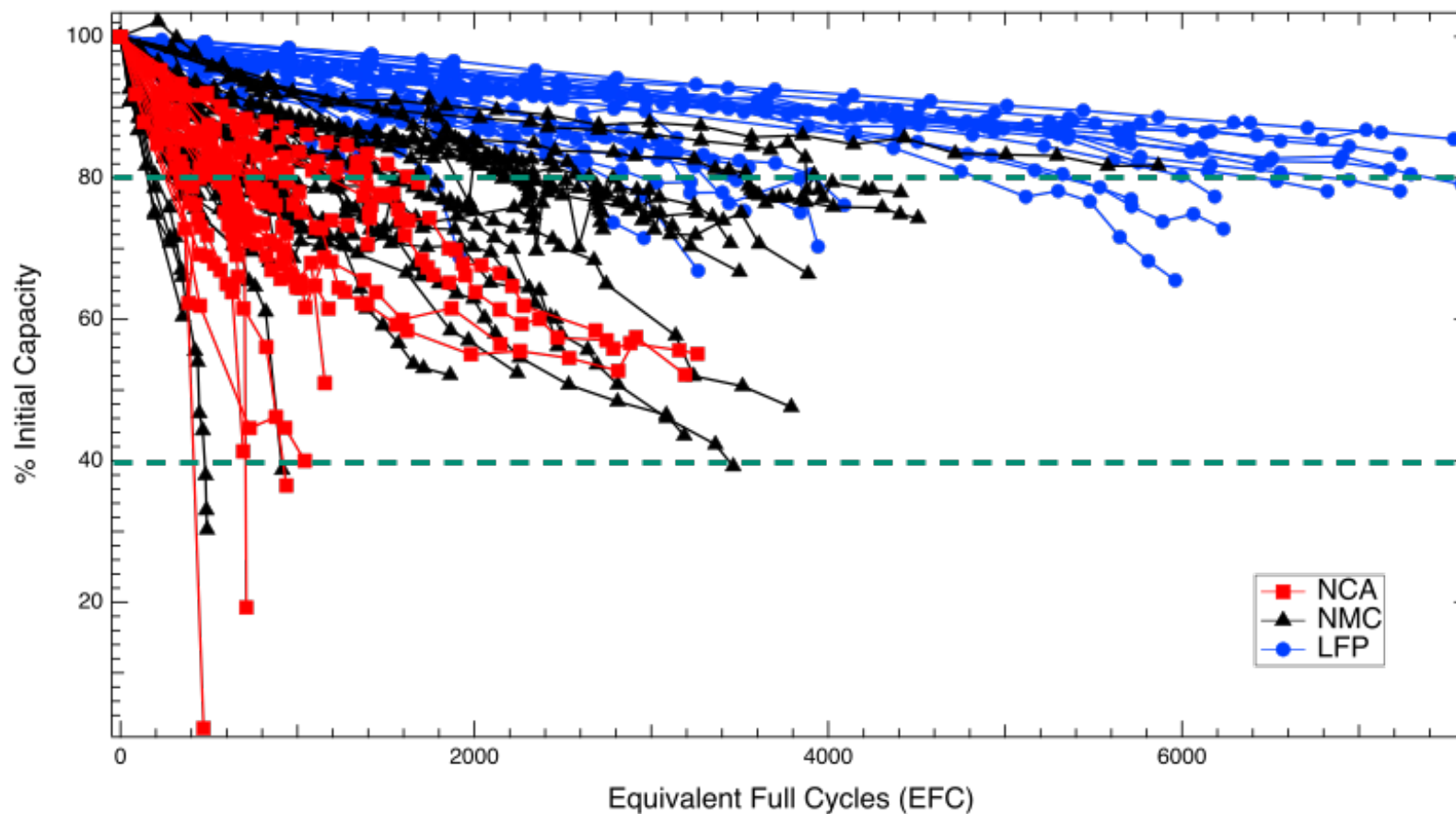
**Thermal abuse of aged cells.**—Batteries in fielded systems can



# Project methodology – Use cells from previous OE work on battery aging



Cells cycled for 7+ years at various conditions  
(full cycling history and materials characterization are available)



# Project testing matrix



Collaboration with Center for Solar Energy and Hydrogen Research in Germany (ZSW) allows us to broaden the matrix

Cell	SOH* %	Overcharge	Overdischarge	ARC	Nail penetration	Crush after overcharge	Experiments conducted
NCA-uncycled	100	3	3	2	3		ZSW
NCA-aged-80%	74-85	3	3	3	3		ZSW
NMC-uncycled	100	1	1	1		1	SNL
NMC-aged-70%	70-74	1	1	1		1	SNL
NMC-aged-40%	43	1	TBD	TBD		1	SNL
LFP-uncycled	100	1	1	1		1	SNL
LFP-aged-80%	80-83	1	1	1		1	SNL
LFP-aged-40%		TBD	TBD	TBD		TBD	SNL

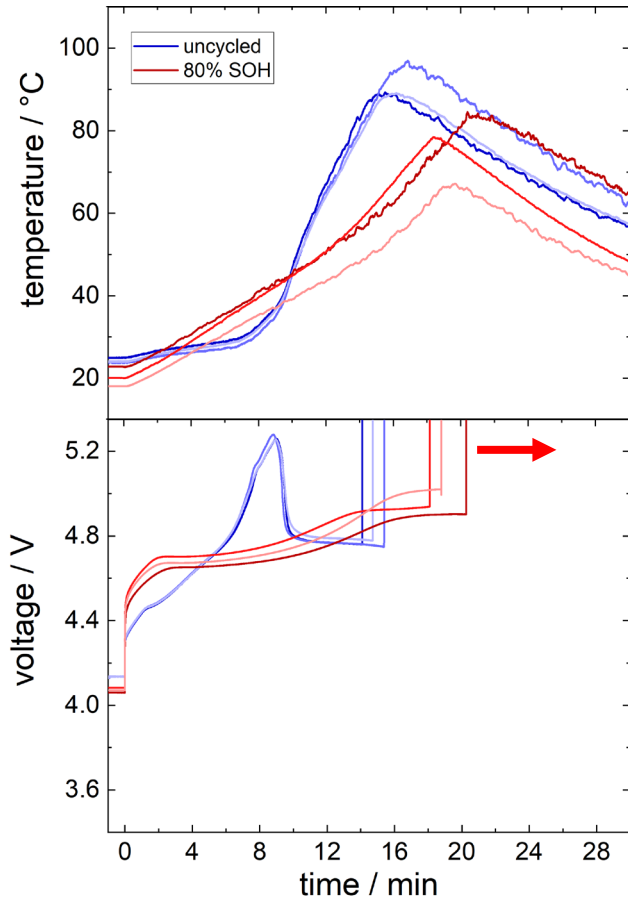
1. Does the impact of aging vary for **different abuse protocols**?
2. Does the safety of aged cells vary with **chemistry**?
3. Does the safety of aged cells vary for **different aging levels**?
4. How **reproducible** are the results?

\*avoid conditions with Li plating

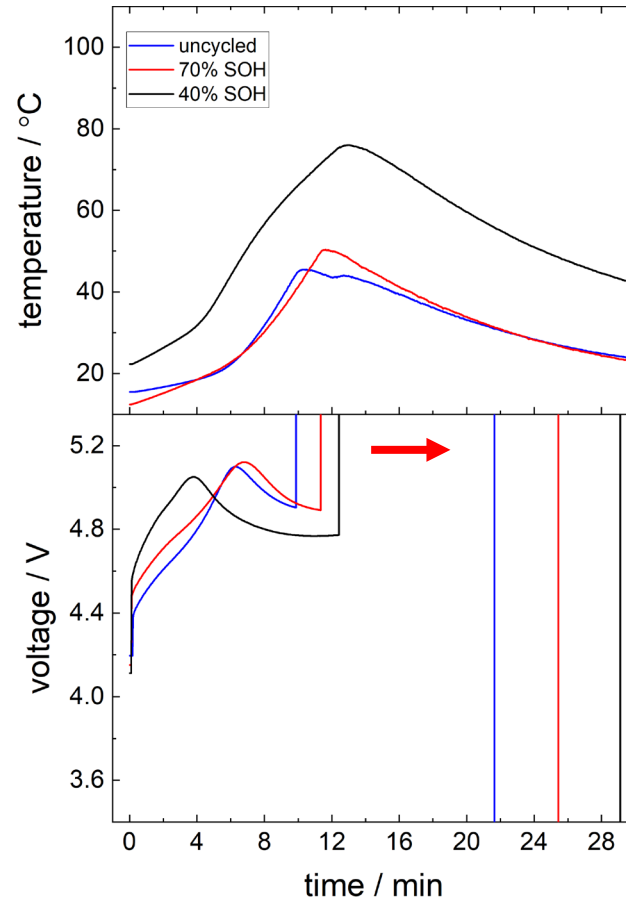
# 9 Impact of aging and chemistry on overcharge tolerance



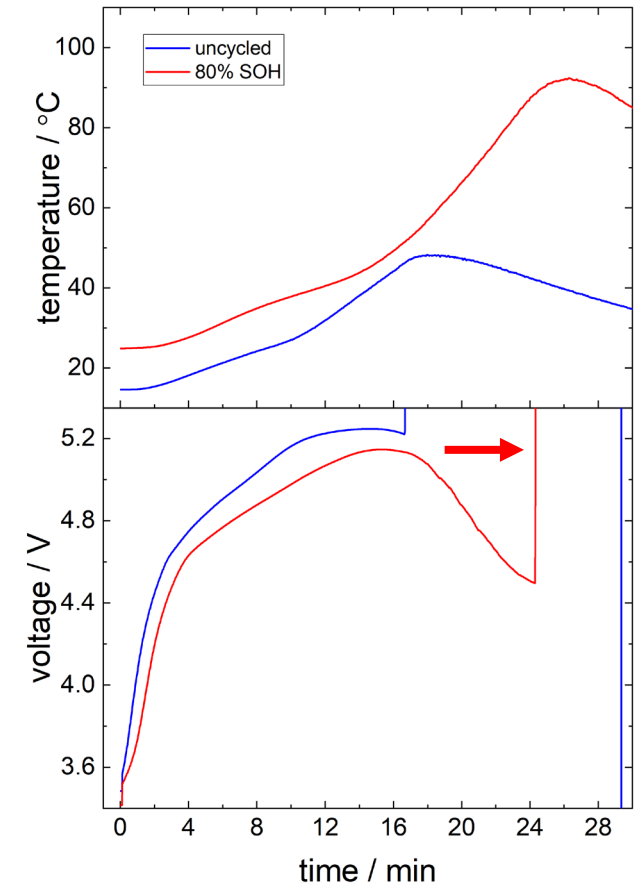
### NCA (ZSW)



### NMC (SNL)



### LFP (SNL)



Aged cells were **overcharged more** prior to CID activation (voltage spike), in contrast to previous literature. This highlights the sensitivity of abuse response to aging conditions.

# Overcharge visuals reveal another dimension of safety



## Uncycled LFP



### EUCAR Rating: 2

- CID activation
- Loss of functionality

## LFP – 80% SOH



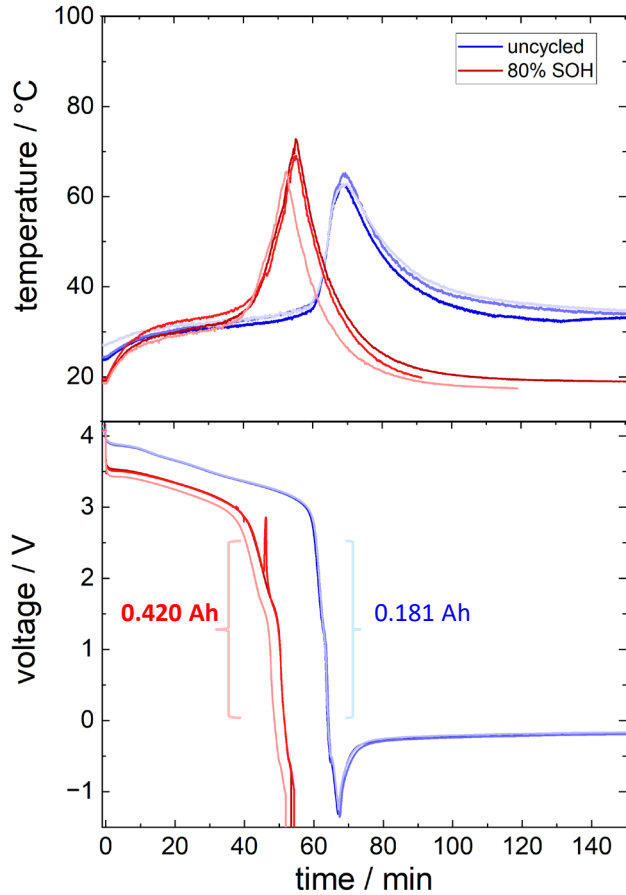
### EUCAR Rating: 3

- CID activation
- Loss of functionality
- **Electrolyte leakage**

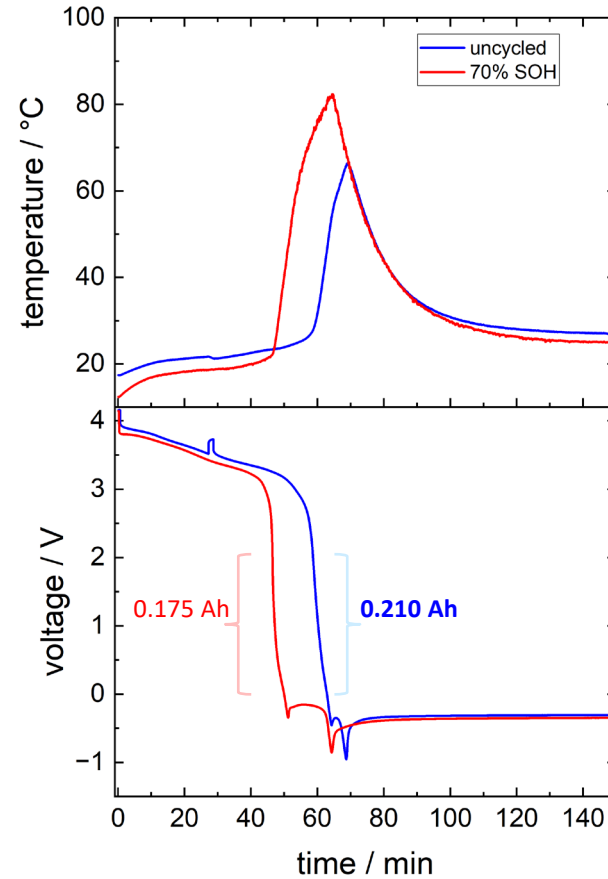
# Impact of aging and chemistry on overdischarge tolerance



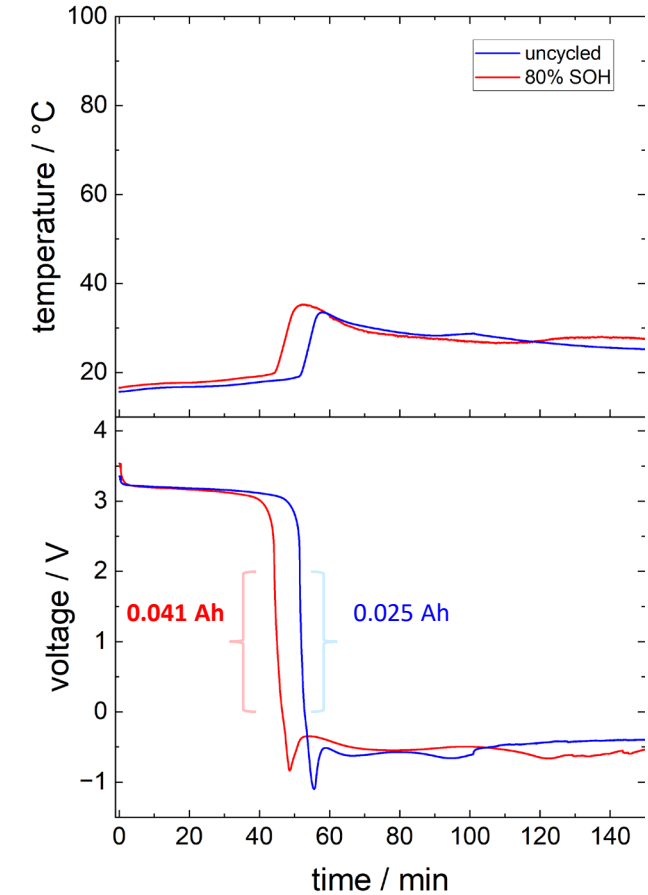
## NCA (ZSW)



## NMC (SNL)



## LFP (SNL)



Aged NCA and LFP cells were **overdischarged more** prior to dropping to 0 V

# Overdischarge visuals and standard hazard severity levels don't capture the differences



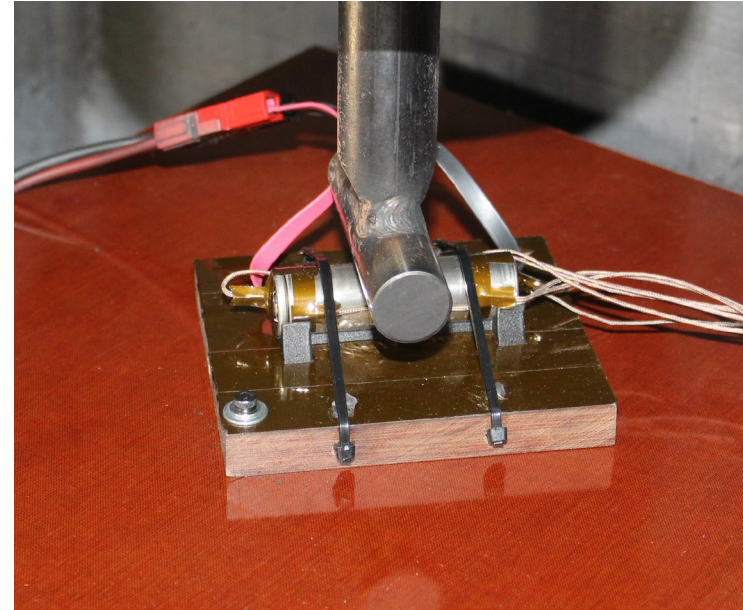
## Uncycled NMC



### EUCAR Rating: 2

- Loss of functionality
- No venting

## NMC – 70% SOH



### EUCAR Rating: 2

- Loss of functionality
- No venting

# Key takeaways



1. Does the impact of aging vary for **different abuse protocols**?  
Yes
2. Does the safety of aged cells vary with **chemistry**?  
Yes
3. Does the safety of aged cells vary for **different aging levels**?  
Yes
4. How **reproducible** are the results?  
Depends on the technique

## Future work

- Publication based on current testing matrix
- Materials characterization at 40% SOH
- More abuse tests as additional cells reach end-of-life

## Is an aged cell less safe than an uncycled cell?

There is no single answer. Depends on the metric, the cell, and the aging protocol.

**We know batteries can last a long time and degrade in different ways, but there has been limited testing to assess how their safety profiles change over time**

- Cycling study represents the broadest public work on post 80% Li-ion aging
- Previous review with UL represents the first comprehensive assessment of aged battery safety
- Current dataset with ZSW represents the broadest single dataset on the abuse of aged cells

**Results are relevant for anyone dealing with battery control or emergency response, e.g.,:**

- Battery management system tolerance for overcharge/discharge
- Thermal management in case of failure
- Second life battery policy questions

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## **Sandia team**

Abuse: Loraine Torres-Castro, Lucas Gray, Nathan Johnson, Jill Langendorf  
Cell aging: Reed Wittman, Chaz Rich

## **Perspective on safety of aged cells – UL Electrochemical Safety Research Institute**

Judy Jeevarajan, Taina Rauhala



## **Electrical abuse of aged cells – ZSW**

Thomas Waldmann, Max Feinauer, Christin Hogrefe, Gabriela Gerosa, Olaf Böse



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