



Impact of Aging on the Safety of Lithium-ion Batteries

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Background and Objective

- Problem:** Battery standards only require safety tests for fresh cells. It is unclear whether aging makes batteries more/less safe or if there is no difference. This is important for designing resilient energy storage systems with appropriate failure detection and mitigation.
- State of the field:** We previously completed the first comprehensive review of aged battery safety with UL Research Institutes (Preger et al. J. Electrochem. Soc., 2022, 169, 030507) and found that batteries aged under certain conditions consistently have a more severe thermal abuse response. We identified gaps in testing methods and breadth of chemistries evaluated.
- This work:** Evaluate the impact of different abuse techniques, aging level, and chemistry on the abuse response of aged cells relative to fresh cells.

OE Mission Alignment

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

Milestones

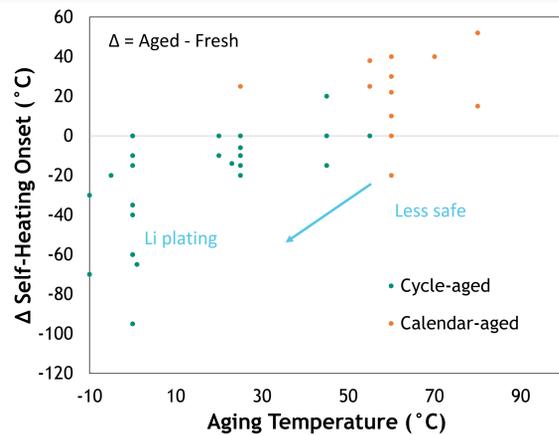
- Completed five different safety tests (calorimetry, overcharge, crush after over(dis)charge, nail penetration) for three lithium-ion battery cell types (LFP, NCA, NMC) for a total of 43 safety tests
- Publication: "Impact of Testing Method on Safety Assessment of Aged Li-ion Cells: Part II – Aged Cells Without Li Plating"

Methodology

Our previous review showed that the abuse response of batteries with Li plating is consistently worse than that of fresh cells (e.g., lower self-heating onset temperatures). Below, Li plating was caused by low aging temperatures, but it can also be caused by mnfg. defects or fast charging.

Example explosive failure caused by Li plating

In this work, we focused on cells with solid electrolyte interphase (SEI) formation as the main aging mechanism. This is the most common aging mechanism that lithium-ion batteries experience for most operating conditions. NMC and LFP cells were taken from SNL's 8+ year cycling study and NCA cells from ZSW.

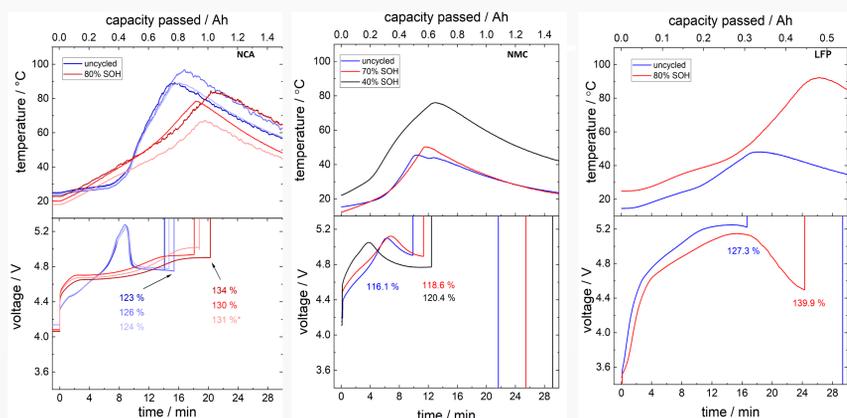


Cell name	Overcharge	Overdischarge	Accelerated Rate Calorimetry	Nail penetration	Crush after over(dis)charge
NCA-uncycled	3	3	2	3	
NCA-aged-80%*	3	3	2	3	
NMC-uncycled	1	1	1		1
NMC-aged-70%	1	1	1		2
NMC-aged-40%	1				1
LFP-uncycled	1	1	1		2
LFP-aged-80%	1	1	1		2

* % remaining capacity

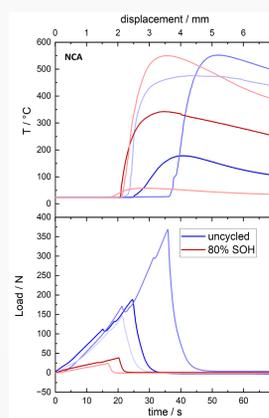
Overcharge

Aged cells tolerated more overcharge, but temperature rise varied.



Nail Penetration

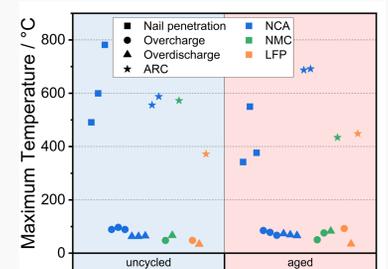
Aged cells required lower mechanical load to trigger failure (less safe), but temperature rise was lower (more safe).



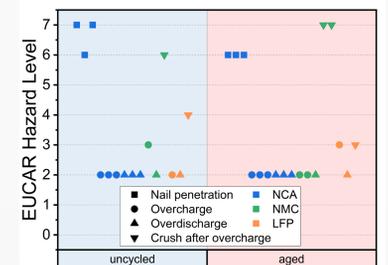
*Test is intended to simulate mechanical insult resulting in an internal short

All Tests

The max temperature was more strongly impacted by the safety test than the uncycled vs. aged state.



The EUCAR level (international battery safety standard) was generally unchanged between uncycled and aged cells.



Innovations

- Collected and published largest single public dataset on the abuse of aged Li-ion batteries under mild aging conditions that are relevant to real systems
- With SEI formation as the main degradation mechanism, uncycled and aged cells exhibited a similar magnitude of thermal runaway in response to abuse (e.g., temperature rise). However, in some cases, the sensitivity to triggering thermal runaway changed (e.g., later for aged cells during overcharging but earlier during nail penetration).

Impacts

- Informing standard committee discussions of energy storage safety, especially second-life systems
- Relevant for anyone dealing with energy storage control or emergency response (e.g., establishing battery management system guidance for over(dis)charge, thermal management in case of failure)