THERMAL PROPAGATION TOPICS

1. *Effect of Induced Metal Contaminants on Lithium-ion Cell Safety (Slides 2-18)*
2. *Detection of Cell Internal Shorts (Slides 19-26)*
3. *Industry Field Experience (Slides 27-37)*

Presented on behalf of OICA to the EVS GTR IWG

March 2018

EFFECT OF INDUCED METAL CONTAMINANTS ON LITHIUM-ION CELL SAFETY

Joint investigation between GM Global Battery Systems and GM China Science Lab

Presentation to EVS GTR IWG
March 2018

Based on material originally presented at:

Advanced Automotive Battery Conference, Advanced Automotive Battery Technology, Application & Market Symposium, Session 4 – Battery Abuse-Tolerance Design and Validation, June 19, 2015, Detroit, MI

KEY MESSAGES

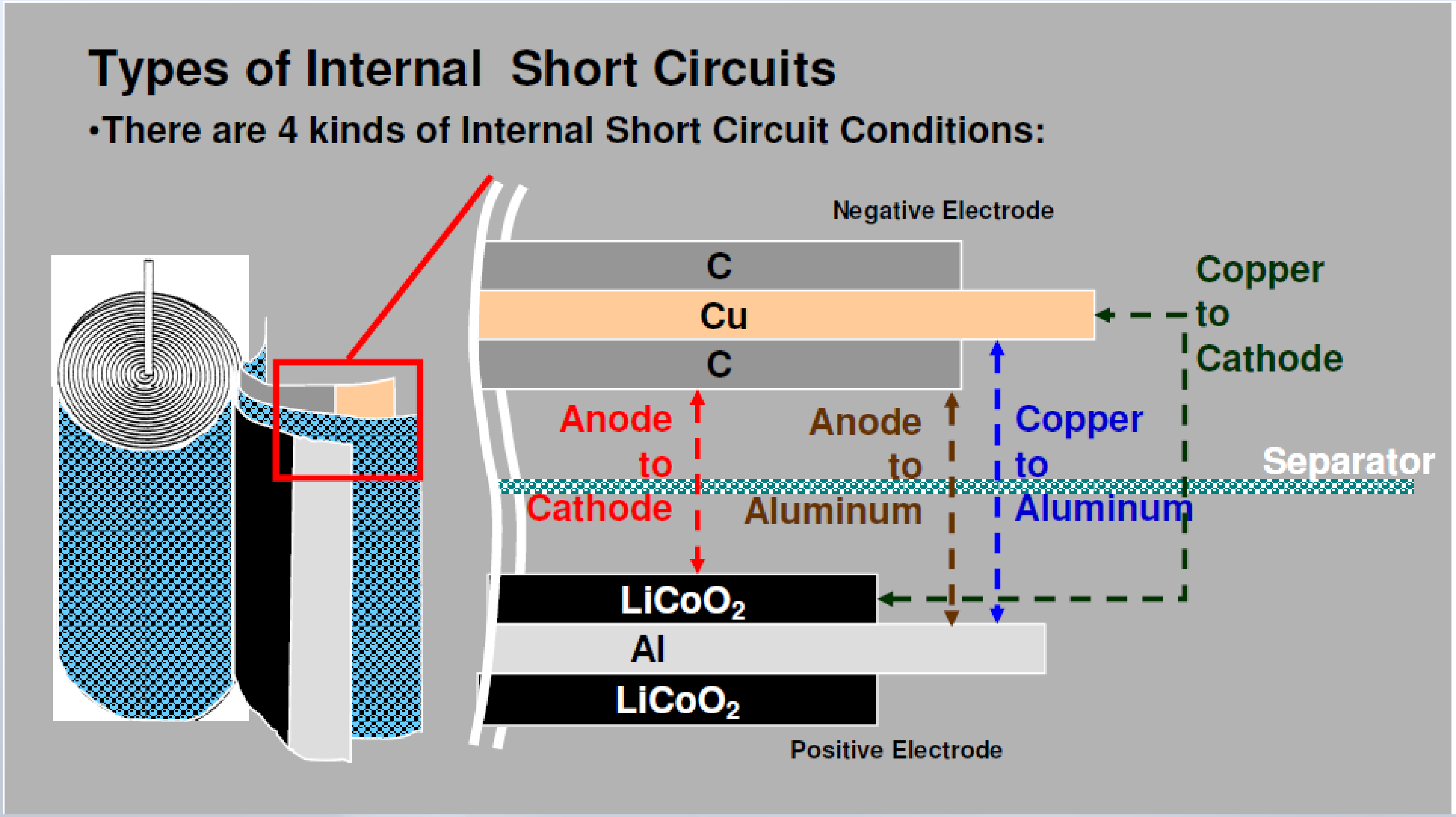
- Metal particle contamination does not necessarily result in catastrophic thermal events, even after cycling under compression.

- Careful cell design (chemistry, configuration) and manufacturing process steps will minimize risk that a severe internal short circuit event can occur.

EFFECT OF METAL PARTICLES IN LI-ION CELLS

- Problem Definition – Metal particles in Li-ion cells may pose a safety risk due to the potential formation of an internal short circuit.
  - How do metal particles cause short circuits in the cells?
  - Is the severity of the short circuit dependent on the location of the particle within the cell?
    - Separator poke-through versus dendrite formation
  - Is the severity of the short circuit dependent on the size of the particle?
    - At what minimum particle size will the effects caused by the particle be detected and the cell rejected in the manufacturing process?
  - Does the severity of the short circuit increase with cycling or storage?

TYPES OF INTERNAL SHORTS

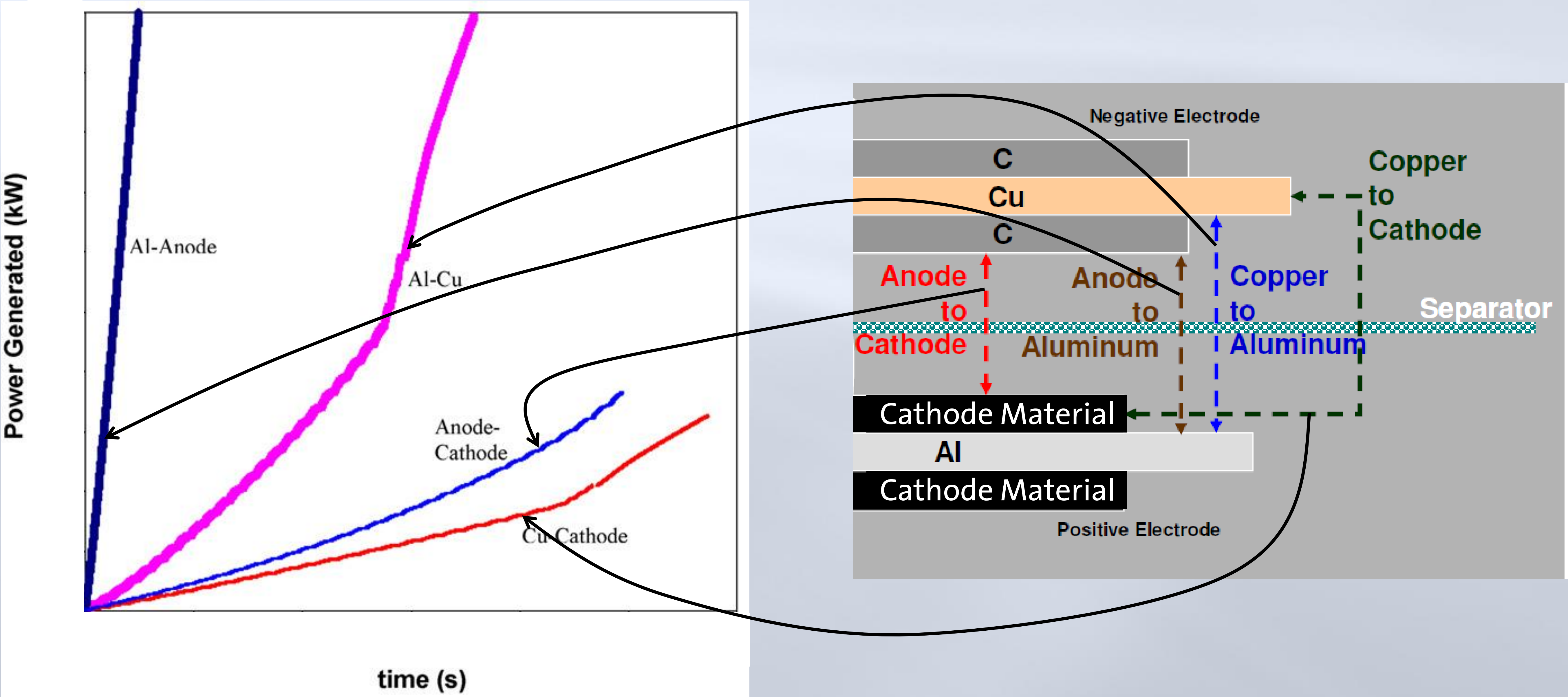


Types of Internal Short Circuits

- There are 4 kinds of Internal Short Circuit Conditions:

From "UL Transportation Tests and UL Lithium Battery Program Underwriter's Laboratory Inc. – General Experience and Status Update," November 11, 2008

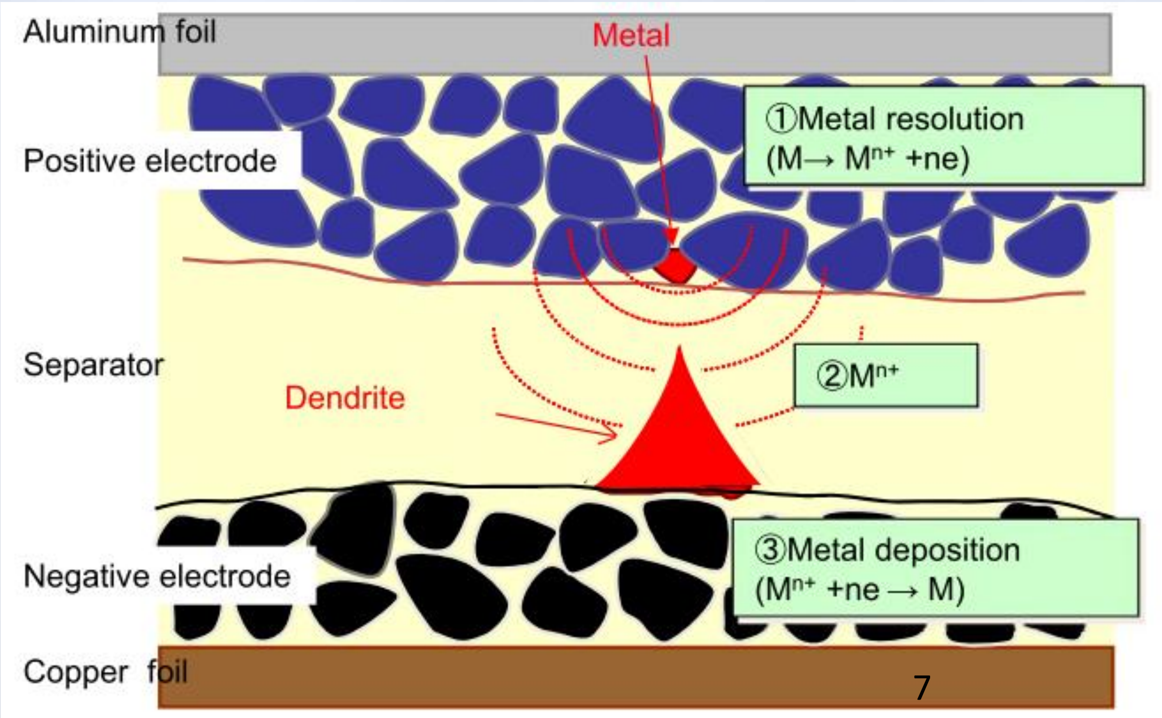
RELATIVE RESISTANCE OF ISC TYPE



Shriram Santhanagopalan, Premanand Ramadass, John (Zhengming) Zhang,
Analysis of internal short-circuit in a lithium ion cell,
Journal of Power Sources, Volume 194, Issue 1, 2009, Pages 550-557.

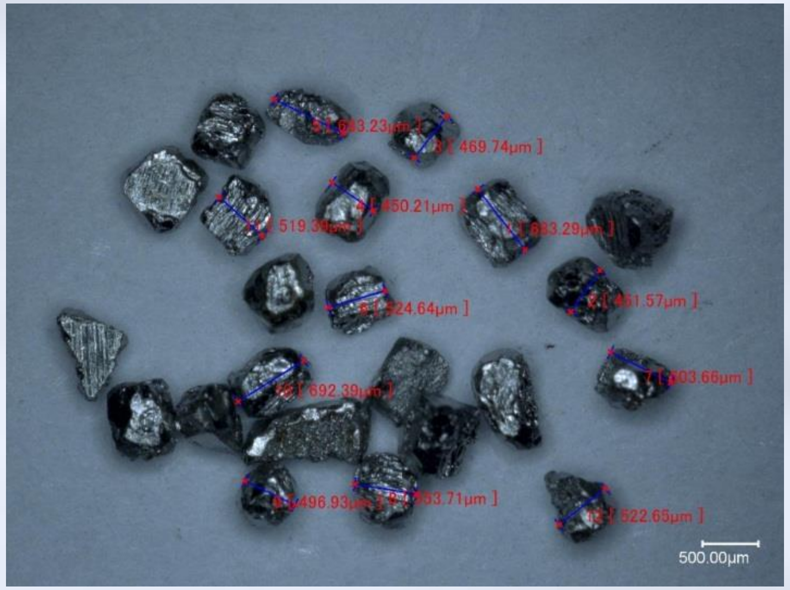
POTENTIAL METAL PARTICLE SHORTING MECHANISMS

- Separator Poke-through:
  - If the particle is large enough, it could rub-through or poke-through the separator and create an internal short circuit.
- Dendrite Formation:
  - If the particle is located on the surface of a charged positive electrode, it could undergo electrochemical dissolution, with subsequent plating of the metal onto the surface of the negative electrode.
  - If dendritic growth occurs, and the particle has enough mass, then these dendrites could grow through the separator and contact the positive electrode.

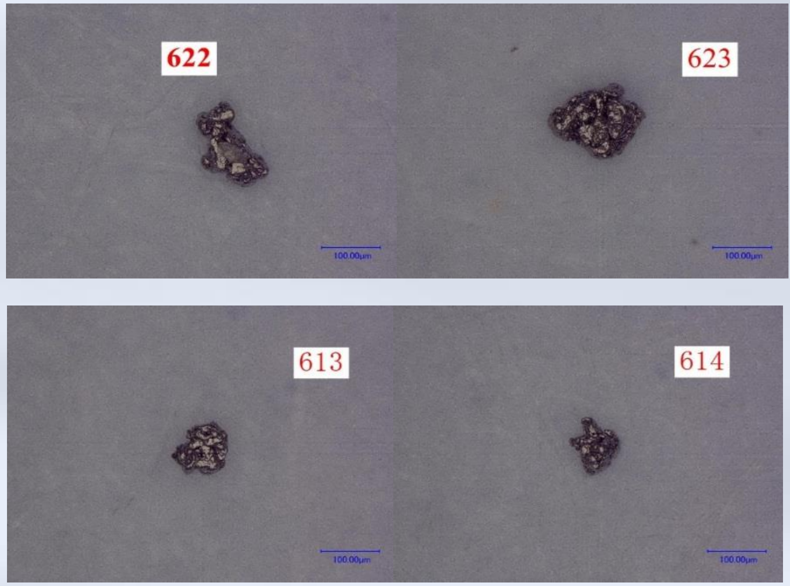


THE STUDY:

- Metal Particle Sizes
  - Run 1, 500-700 µm iron particles (ease of handling)
  - Run 2, 50-150 µm iron particles (low end of known contaminant sizes)

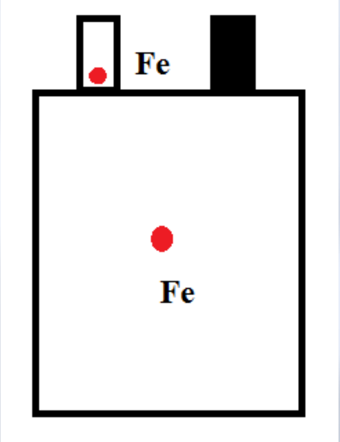


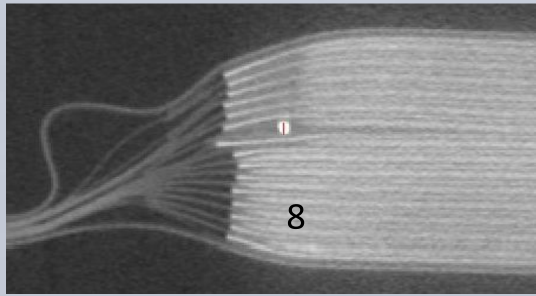
Run #1 Particles



Run #2 Particles

- Detection Methods and Tests
  - Hi-Pot test after electrode stack assembly
  - Self-Discharge (Delta-OCV) Check during Aging process step (50% SOC at 35°C for 7 days)
  - Cycle Life Test (100% DOD at 1C/1C rate and 35°C under compression)
  - Storage Test (100% SOC at 35°C under compression)
- The Cells Used
  - 1.4 Ah, multi-layer, Li-ion pouch cells (baseline and 1-particle cells, 3-6 of each type)
  - MCMB graphite and NMC, with uncoated 25 µm tri-layer separator and 1M $LiPF_6$ EC/DEC/EMC electrolyte
  - Fe particles placed in one of three locations: Anode Center, Cathode Center and Cathode Tab near the anode (see diagram and CT scan image)

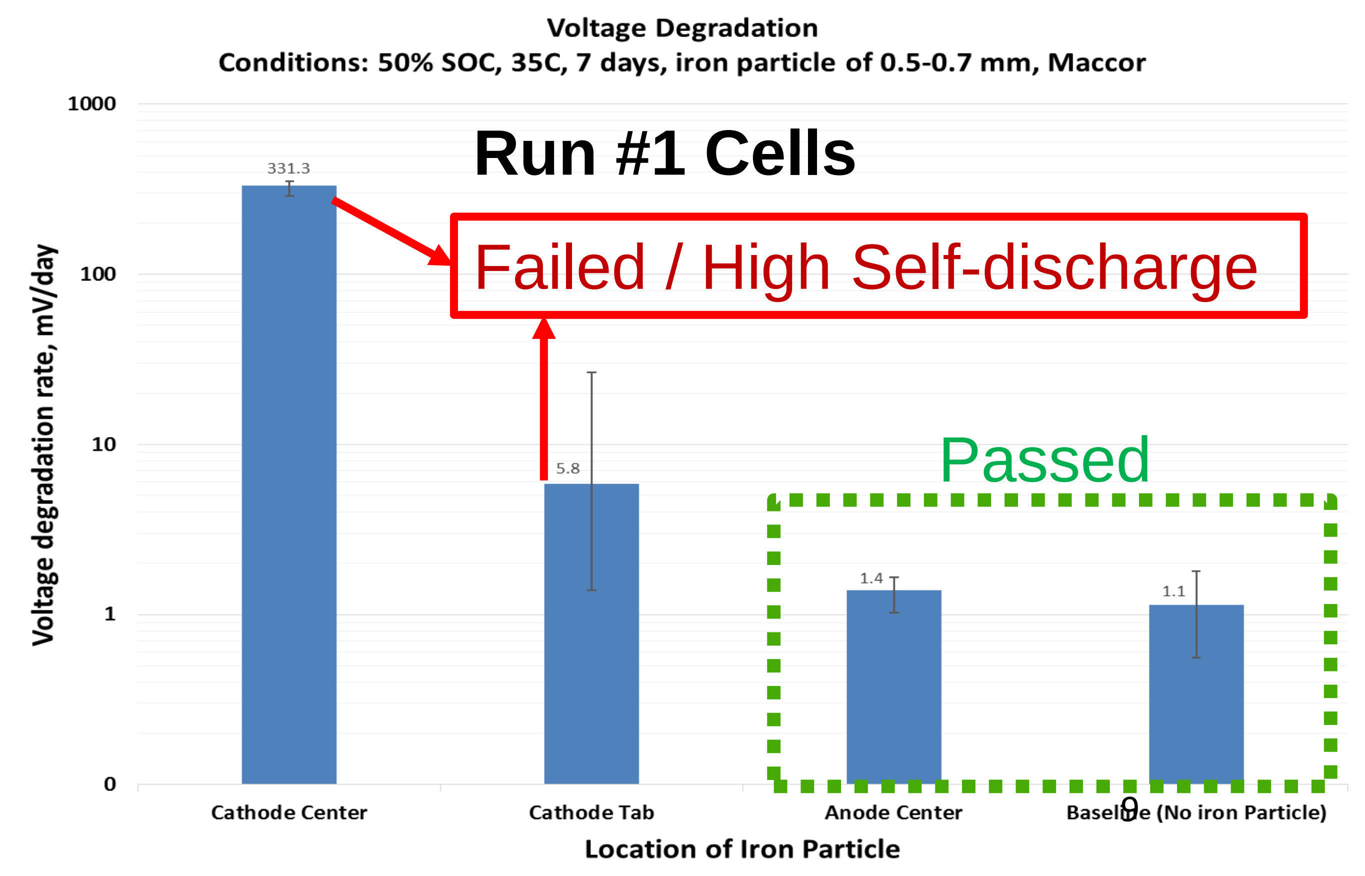




CELL MANUFACTURING QUALITY CHECKS

- All cells passed the Hi-Pot test after electrode stack assembly
- Only cells with large particles located on the cathode surface showed higher than normal self-discharge rates

Run	Iron Particle Size	Anode Center	Cathode Tab	Cathode Center	Baseline Cells
Run #1	> 500 μm	Pass Hi-Pot Pass self-discharge	Pass Hi-Pot Failed self-discharge	Pass Hi-Pot Failed self-discharge	Pass Hi-Pot Pass self-discharge
Run #2	100-150μm			Pass Hi-Pot Pass self-discharge	Pass Hi-Pot Pass self-discharge
	50-100 μm			Pass Hi-Pot Pass self-discharge	Pass Hi-Pot Pass self-discharge


Voltage Degradation
Conditions: 50% SOC, 35C, 7 days, iron particle of 0.5-0.7 mm, Maccor

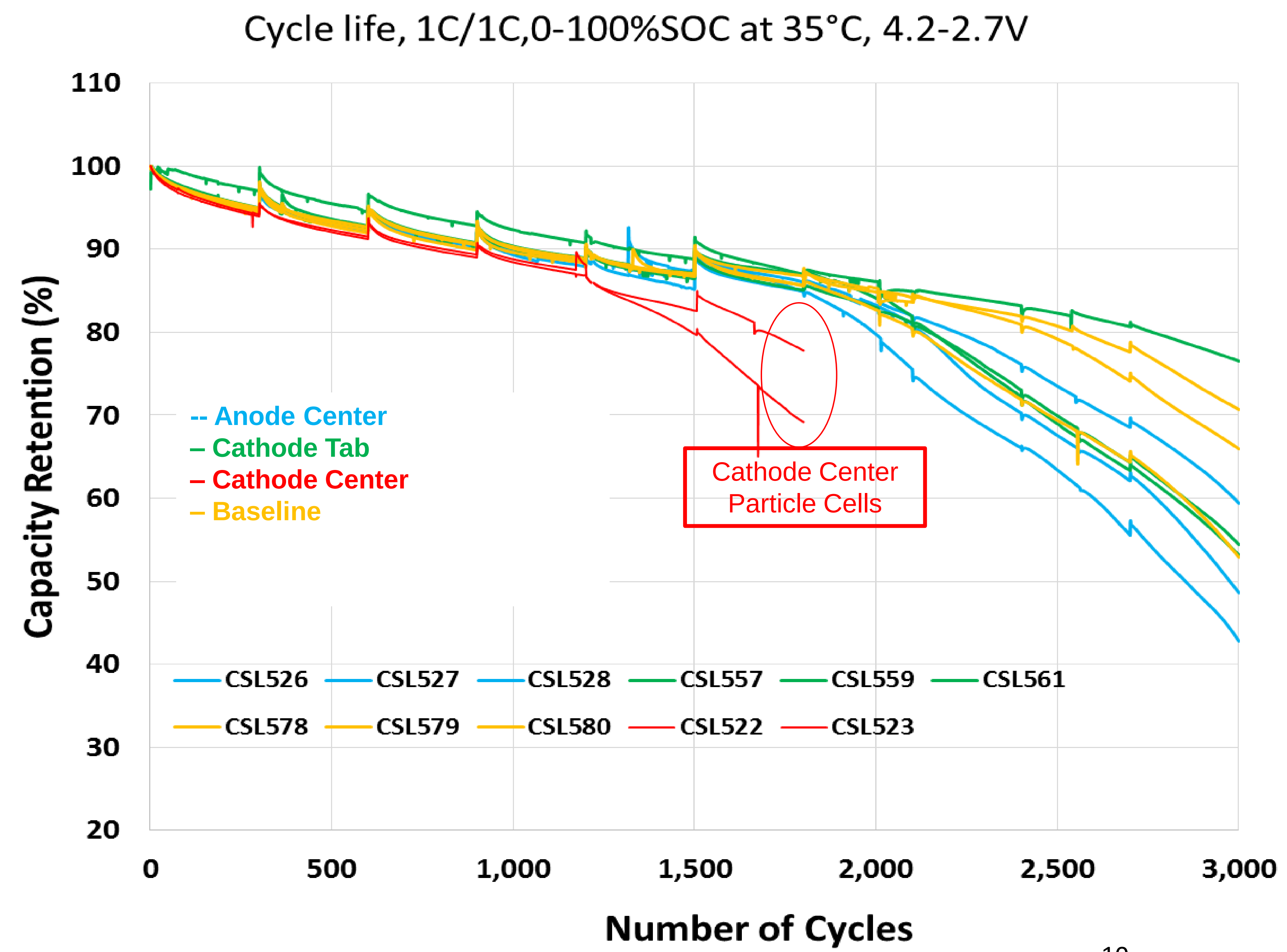
Run #1 Cells

Failed / High Self-discharge

Passed

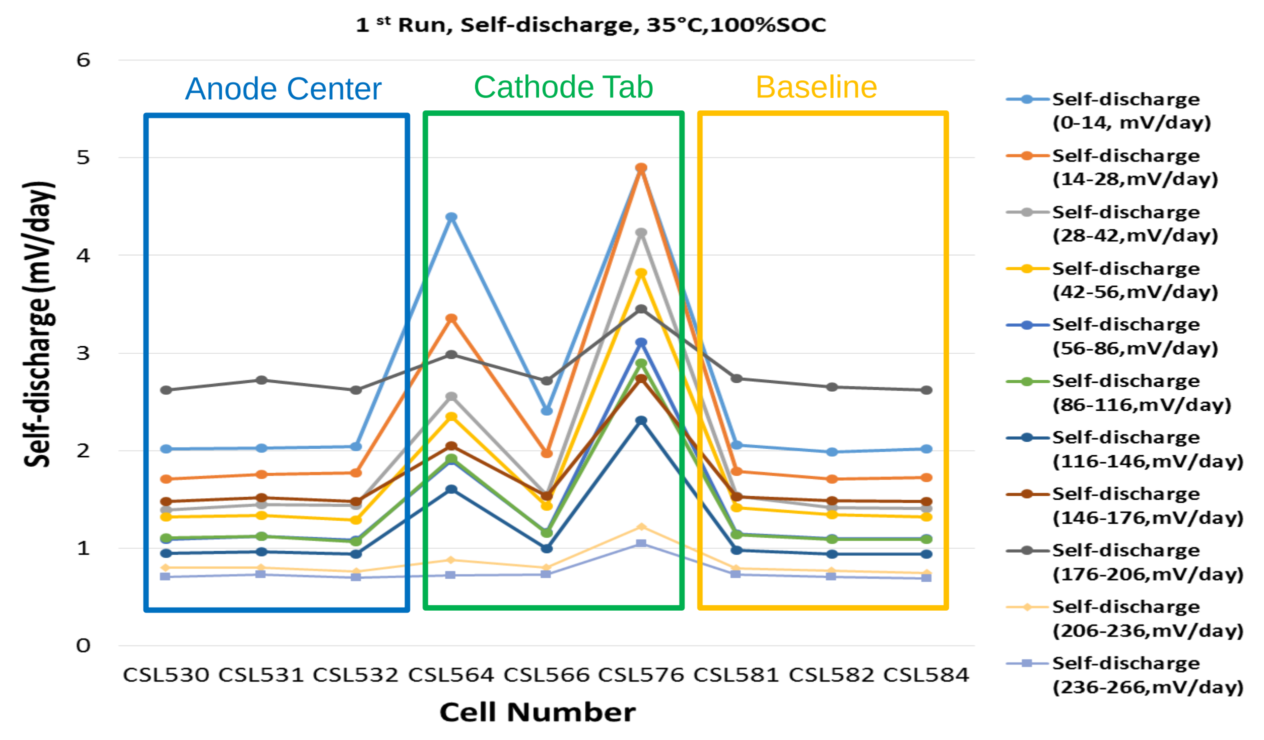
RUN #1 CELLS – CYCLE LIFE TEST

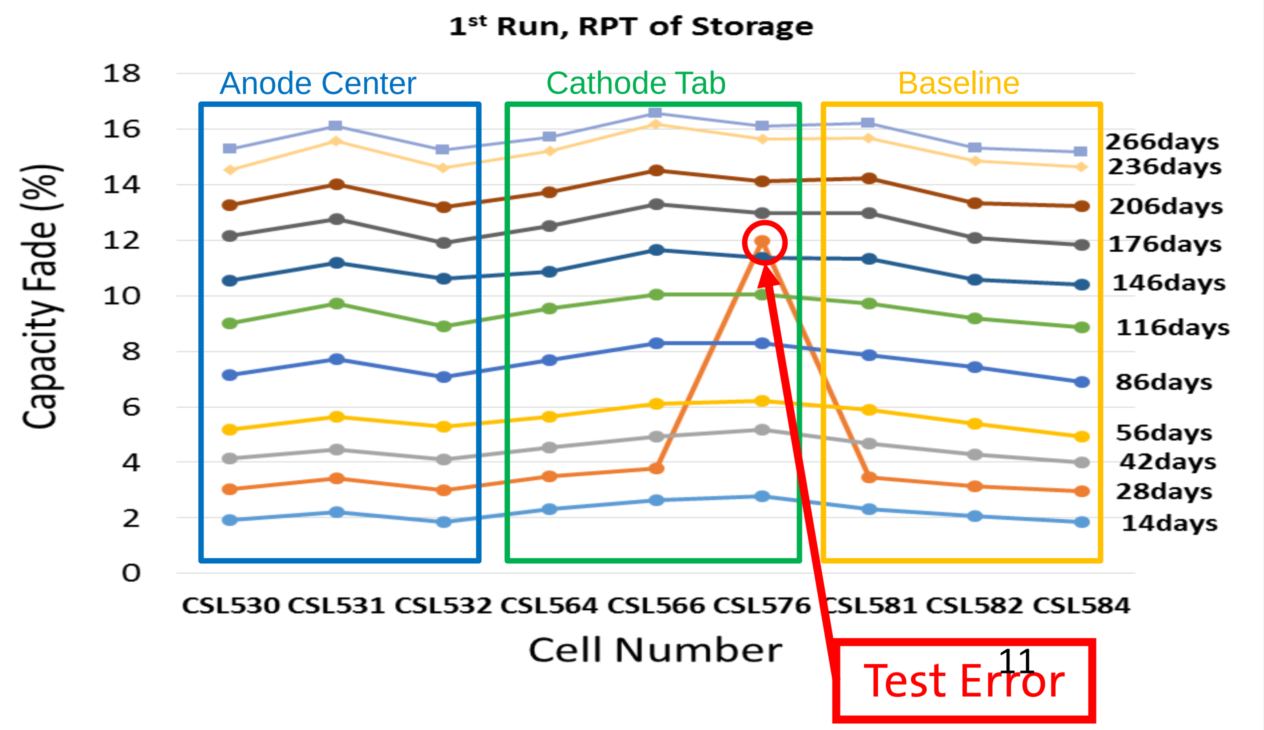
- Cathode Center particle cells showed a more rapid Ah capacity decline.
- Anode Center and Cathode Tab particle cells showed no significant difference compared to the Baseline cells.
- No cell venting occurred.



RUN #1 CELLS – STORAGE TEST

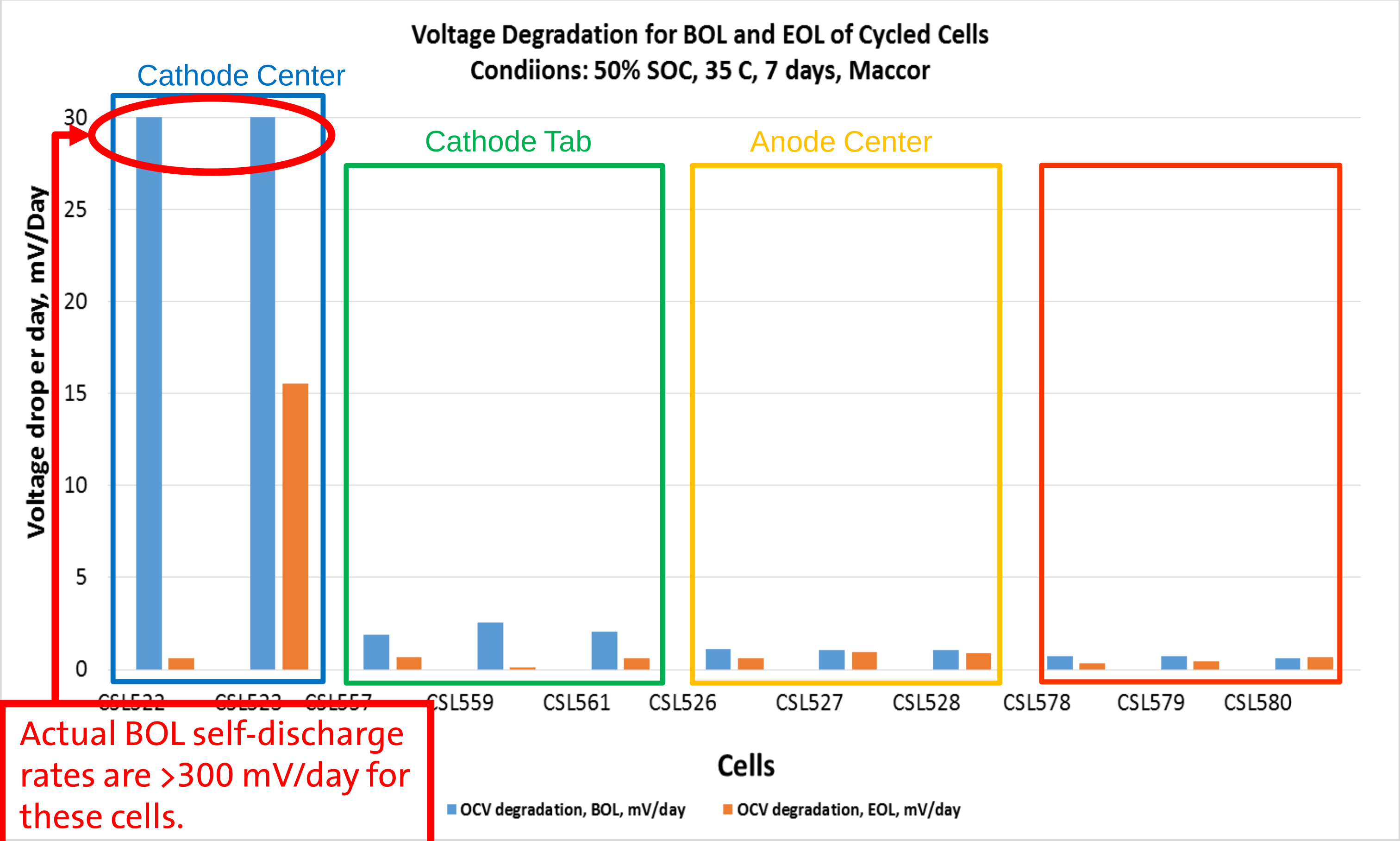
- Cathode Tab particle cells showed a higher voltage loss at each RPT.
- Anode Center particle cells showed no significant difference compared to the Baseline cells.
- Due to monthly RPT’s, all cells showed similar capacity loss.
- No cell venting occurred.
- Cathode center particle cells did not undergo this test due to their already high self-discharge rates.



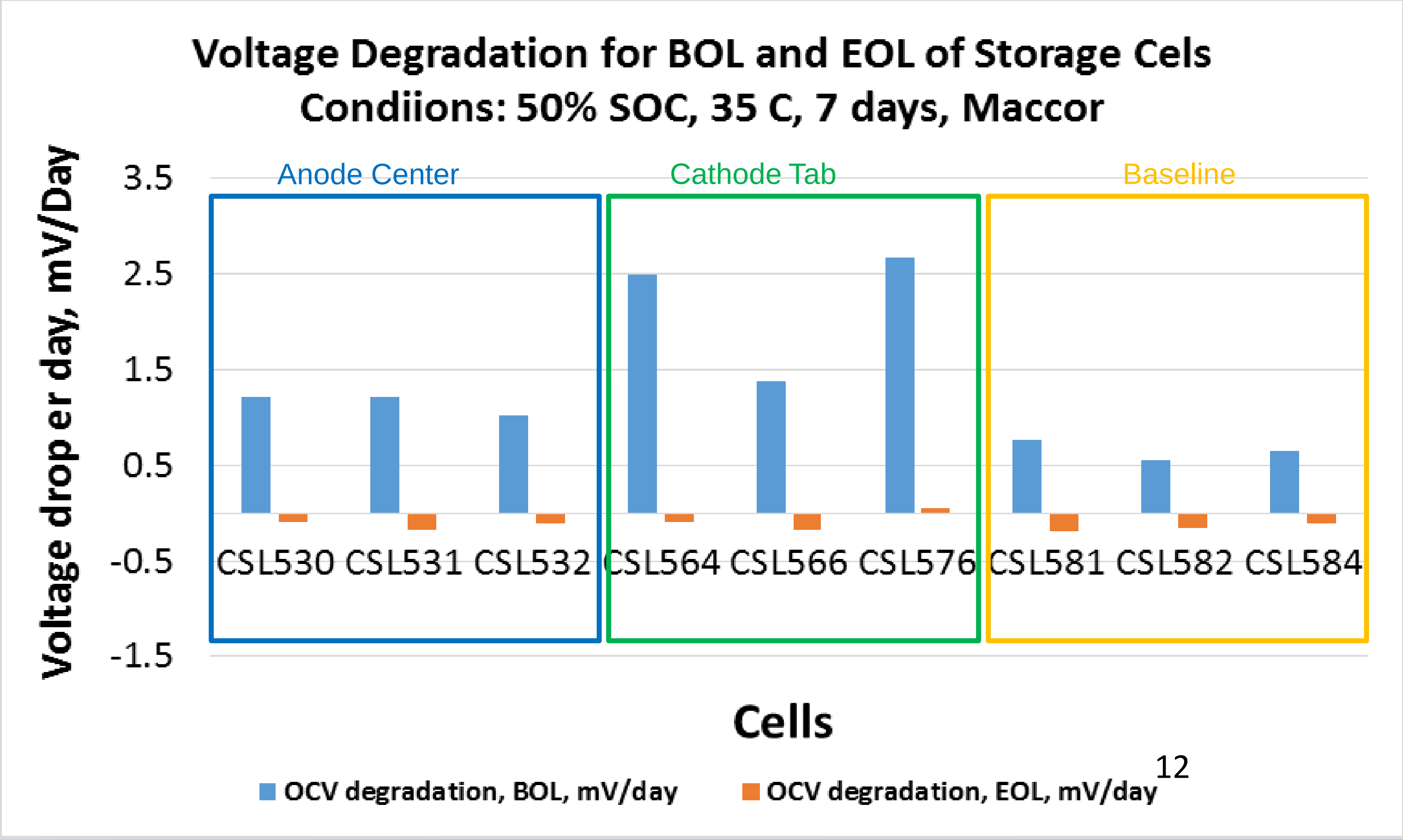


RUN #1 CELLS – SELF-DISCHARGE RATES AFTER CYCLING OR STORAGE TESTS

- In all cases, both the particle containing cells and the baseline cells showed reduced 7-day self-discharge rates after their cycling or storage tests.

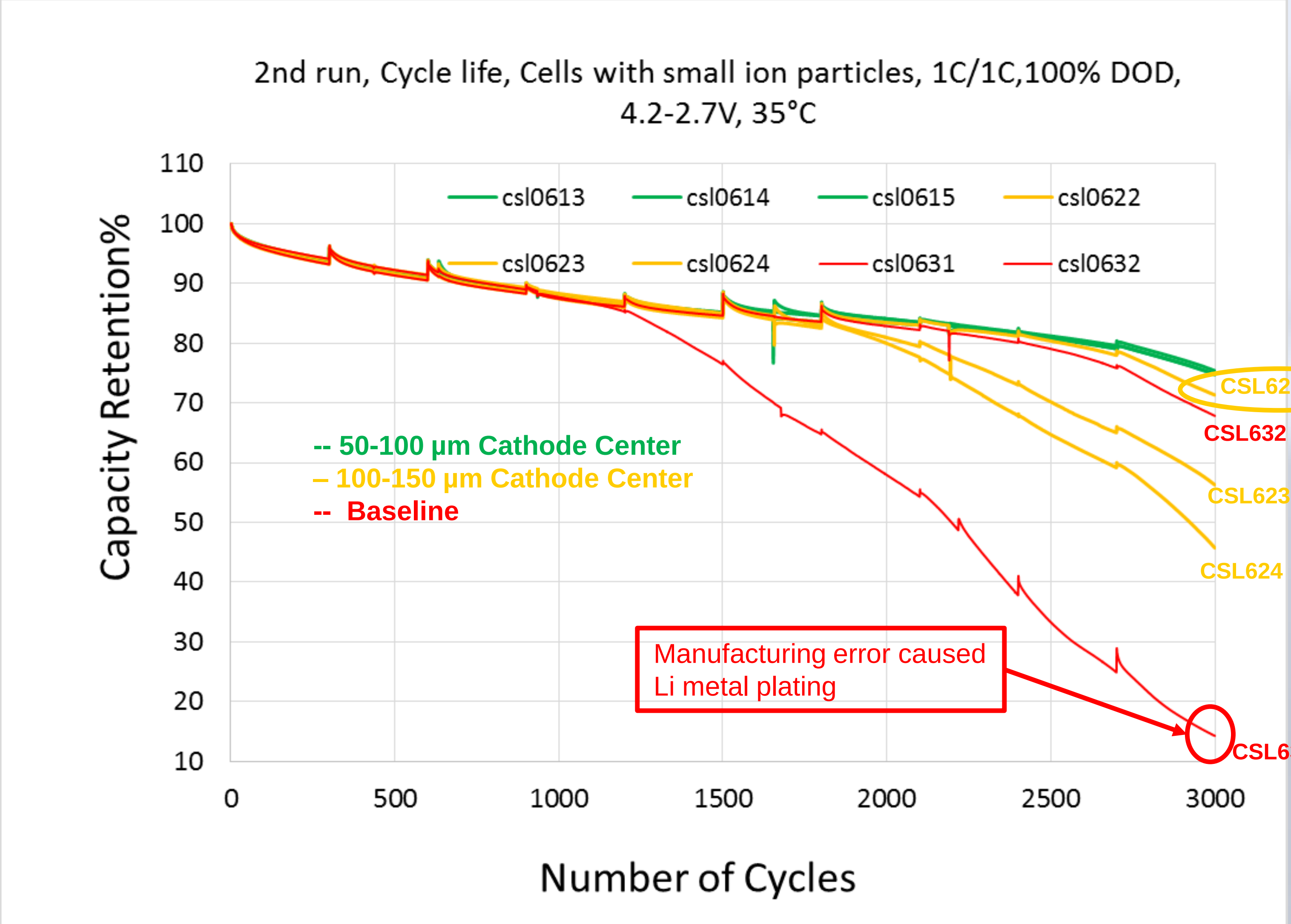


Actual BOL self-discharge rates are >300 mV/day for these cells.

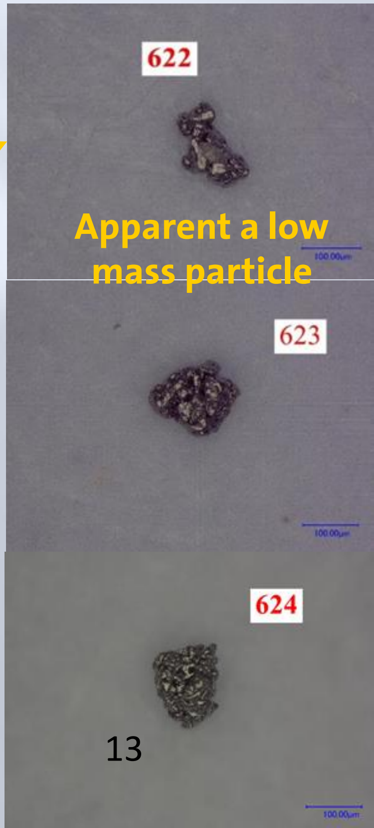


RUN #2 CELLS – CYCLE LIFE TEST

- 100-150 µm particles appear to the minimum size that causes premature cycle life failure.
- No cell venting occurred



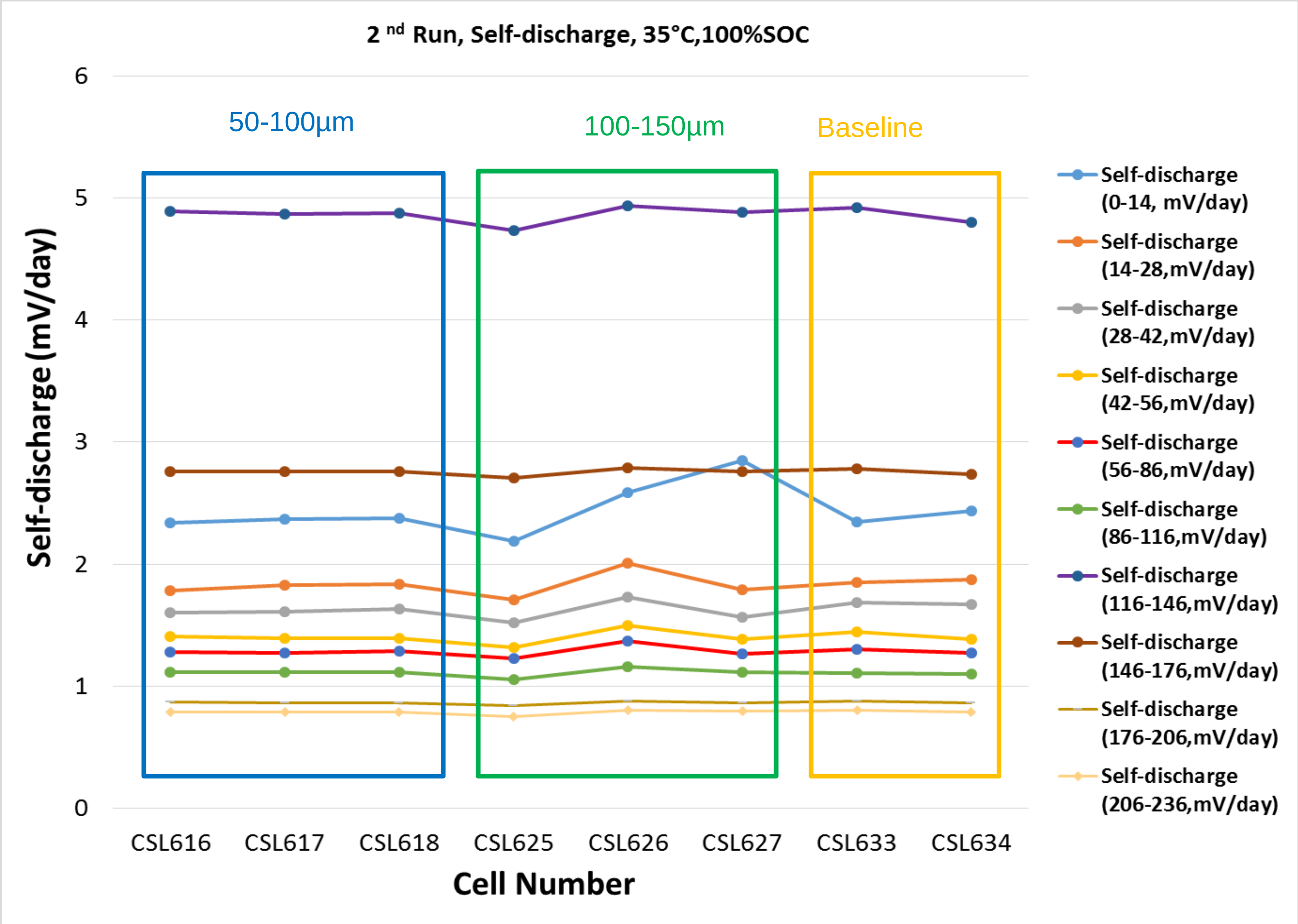
Manufacturing error caused Li metal plating

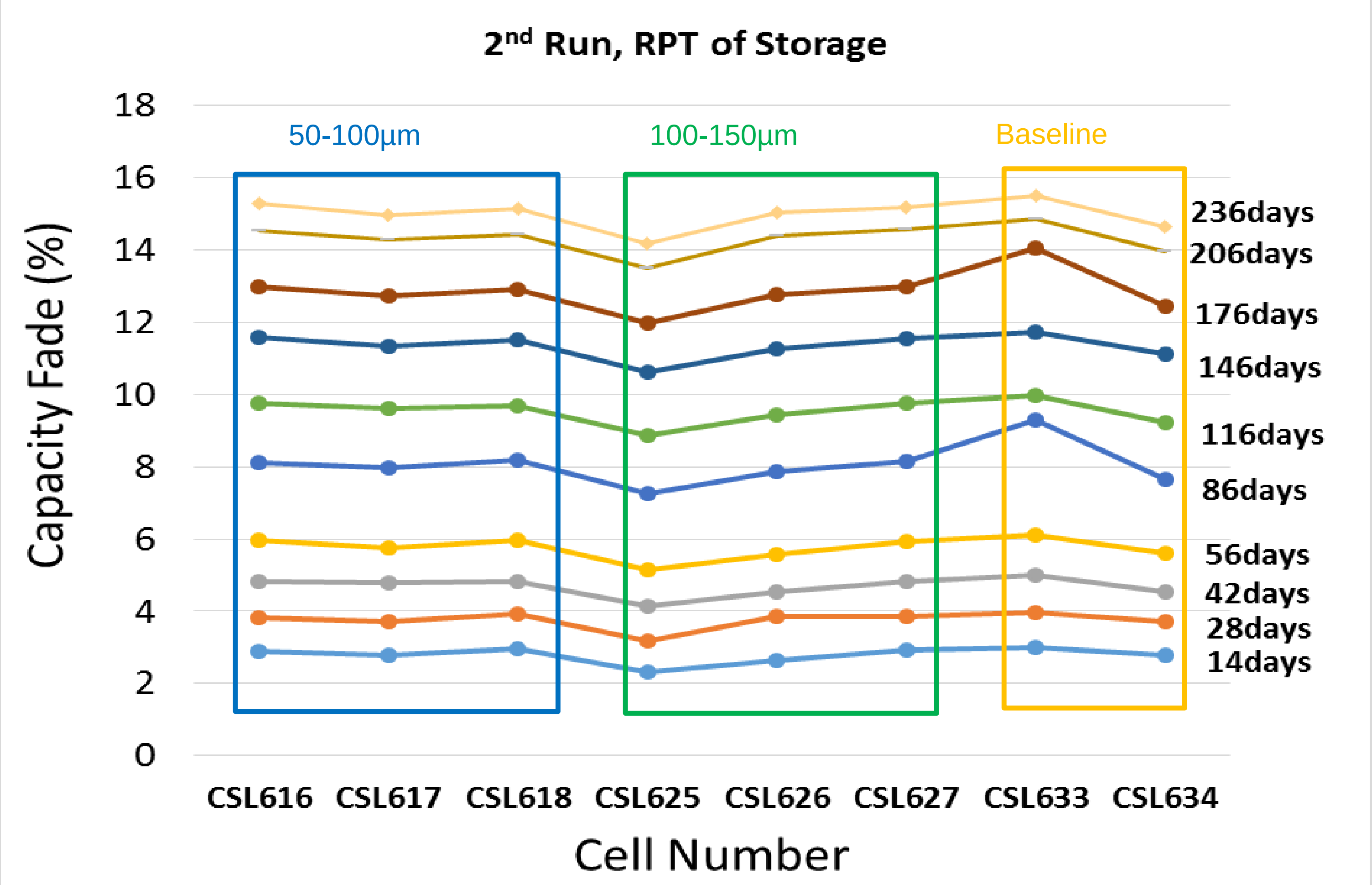


Apparent a low mass particle

RUN #2 CELLS – STORAGE TEST

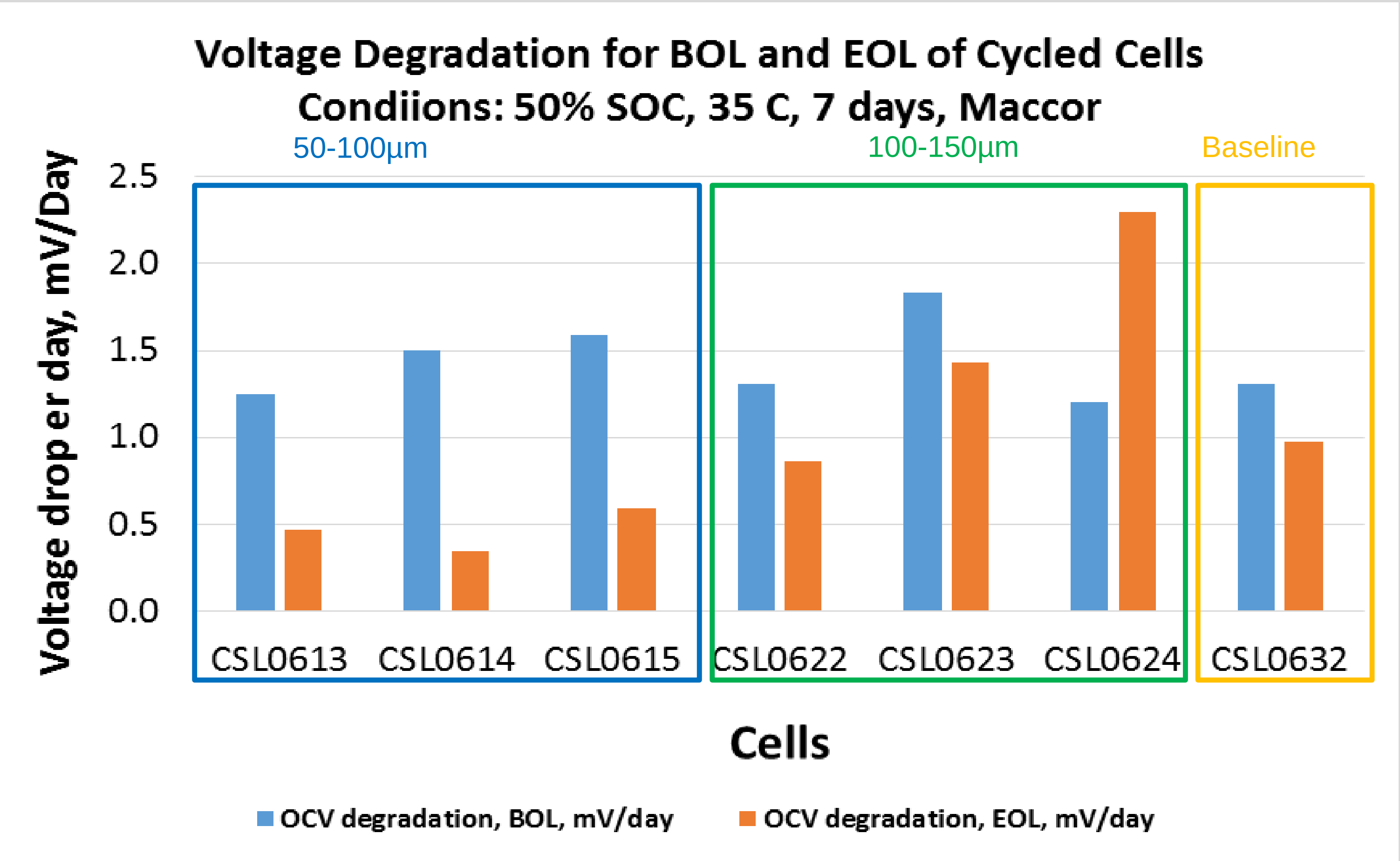
- For cells with particles <150 µm, no significant self-discharge rates or capacity loss differences were seen between them and the Baseline cells.

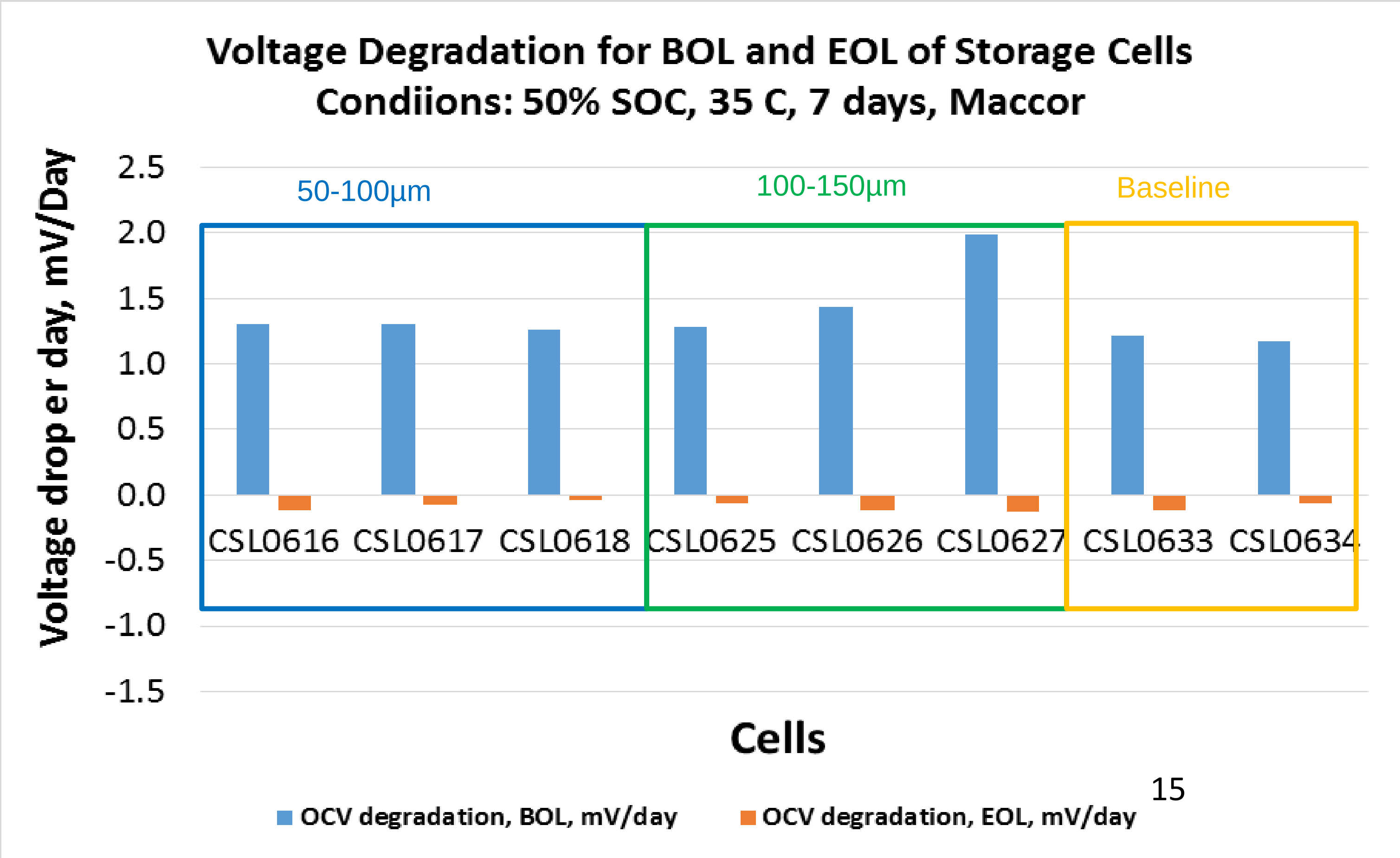




RUN #2 CELLS – SELF-DISCHARGE RATES AFTER CYCLING OR STORAGE TESTS

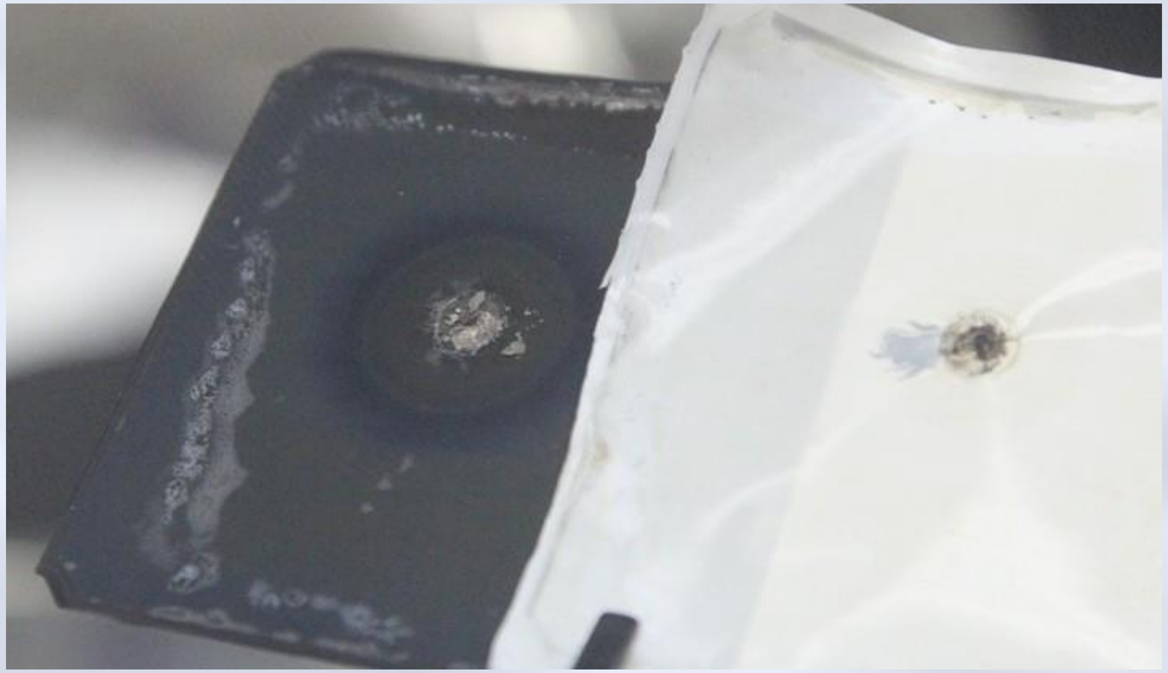
- In almost all cases, both the particle containing cells and the baseline cells showed reduced 7-day self-discharge rates after their cycling or storage tests.





POST-TESTING TEARDOWN

- All particle containing and Baseline cells were examined post-test.
  - 7-day Self-Discharge test and teardown to confirm presence of the particle and root cause of failure.
  - Evidence of Fe dendrites found on separator and anode surface for all Cathode Center and Cathode Tab cells. (No particle left on cathode surface).
  - Li metal plating also found on anode surface surrounding the Fe dendrite growth (worse for large particle cells, not seen in <100 μm size particle cells).
  - Original particles found in all Anode Center cells.



TEST RESULT SUMMARY:

Run	Iron Particle Size	Particle Location	7-day Aging OCV Check	Cycling vs. Baseline Cells	Storage vs. Baseline Cells
Run #1	>500 μm	Cathode Center	Exceeded 2 mV/day Limit	More rapid capacity fade	*Not Run*
		Cathode Tab	Exceeded 2 mV/day Limit	No Difference	Greater Self-discharge
		Anode Center	Passed	No Difference	No Difference
Run #2	100-150 μm	Cathode Center	Passed	Slightly more rapid capacity fade	No Difference
	50-100 μm	Cathode Center	Passed	No Difference	No Difference

CONCLUSIONS:

- Particles much larger than the separator’s thickness (20-28 times) did not push through to create an internal short, even after cycling under compression.

- Metal particles on the negative electrode (anode) did not cause internal cell shorting.

- Only metal particles initially located on the positive electrode, if of sufficient size and mass, caused internal cell shorting.

- Large metal particles are detectable by self-discharge and capacity loss in the manufacturer’s Aging/Storage process step.

- Particles below 100 μm have limited or no effect, while particles near 150 μm did cause pre-mature cycle life failure.

Detection of Cell Internal Shorts

OICA Presentation to the EVS GTR IWG

March 2018

Key Messages

- Many internal shorts can be detected during manufacture and in usage
- Internal short behavior can often be measured and understood

Types of Shorts

- Immediate
  - Largely managed by cell design and manufacturing control
  - Possibly detectable during manufacturing process

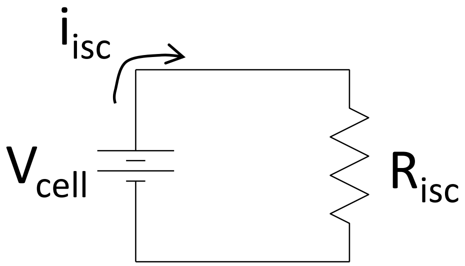
- Developing
  - Likely not possible to fully prevent
  - Possibly detectable during usage –
    - Requires appropriate cell measurements and diagnostic algorithms
    - Assumes that short develops over multiple cycles / days

Possible Detection Methods

- In manufacturing process
  - Self-discharge rate – monitor for values above a defined limit
    - Times, methods, limits vary by manufacturer
  - High voltage test prior to electrolyte added
- In vehicle
  - Cell voltage – monitor for low cell voltage
  - Cell to cell voltage difference – monitor for differences above a defined limit

Why Can These Methods Work?

- Simple circuit model

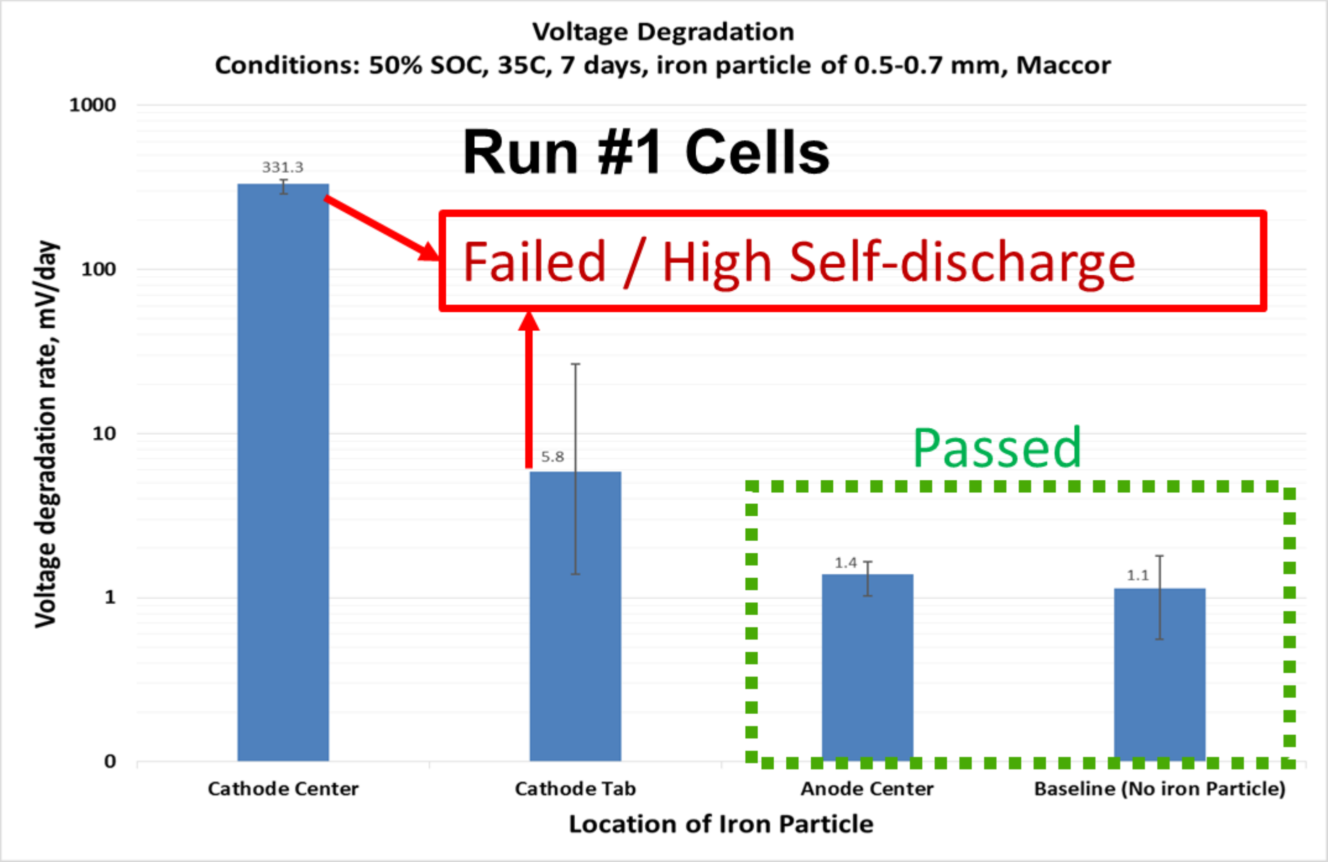


$$E_{dis} = \int V_{cell} \cdot i_{isc} \, dt$$

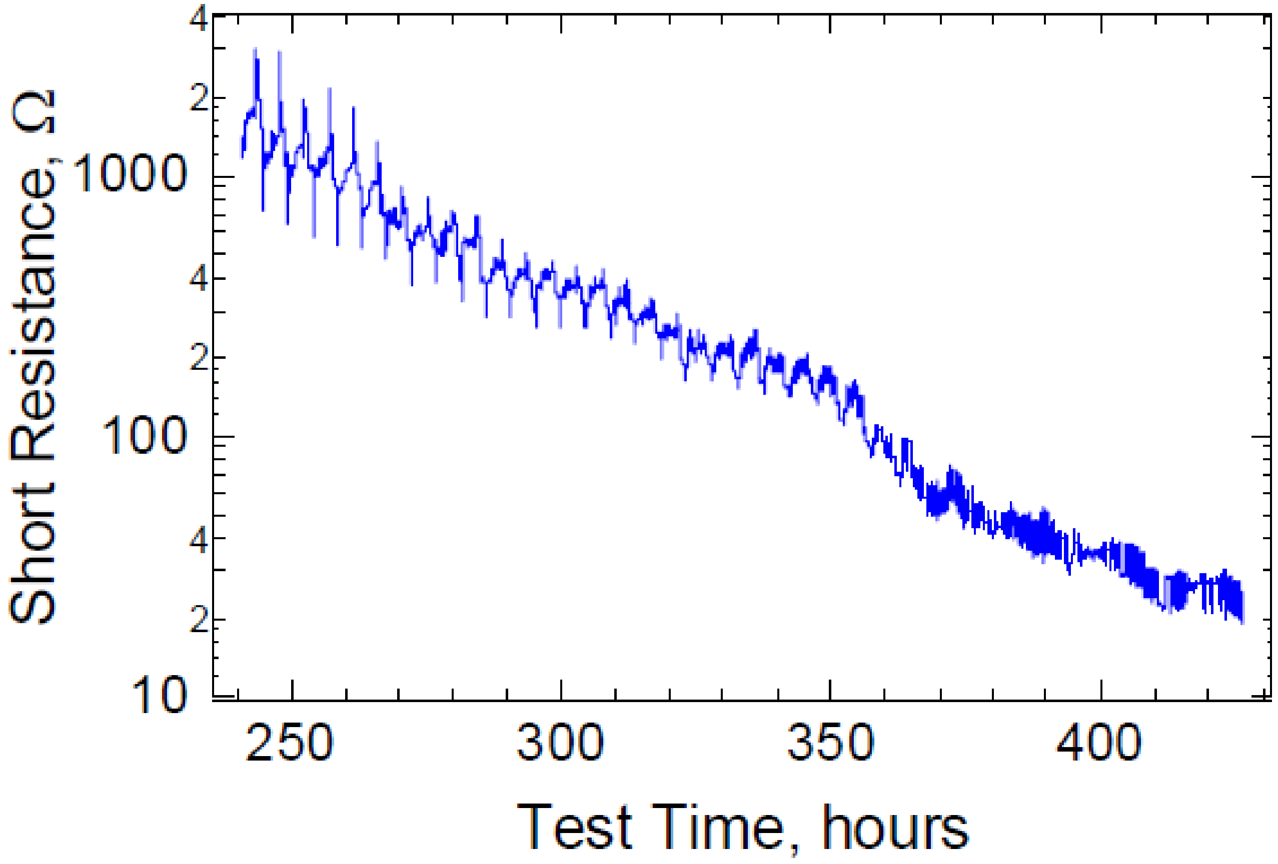
- Since stored energy is proportional to battery voltage, as energy is dissipated through resistance, battery voltage drops.
- Voltage reduction is observable.

Example of Manufacturing Process Detection

- Voltage degradation monitored for a period of time
- Measured degradation compared to acceptable limit values



Internal Short Resistance Behavior In Use



- Resistance reduces over time
- Cell energy (∴voltage) is reducing throughout time
- As energy loss integrates over time, can reach detectable level prior to short circuit at critical level

McCoy, C., Sriramulu, S., Stringfellow, R., Ofer, D. & Barnett, B. Lithium-Ion Battery Safety: Detection of Developing Internal Shorts and Suppression of Thermal Runaway. 46th Power Sources Conference, 2014.

Critical Internal Short Resistance

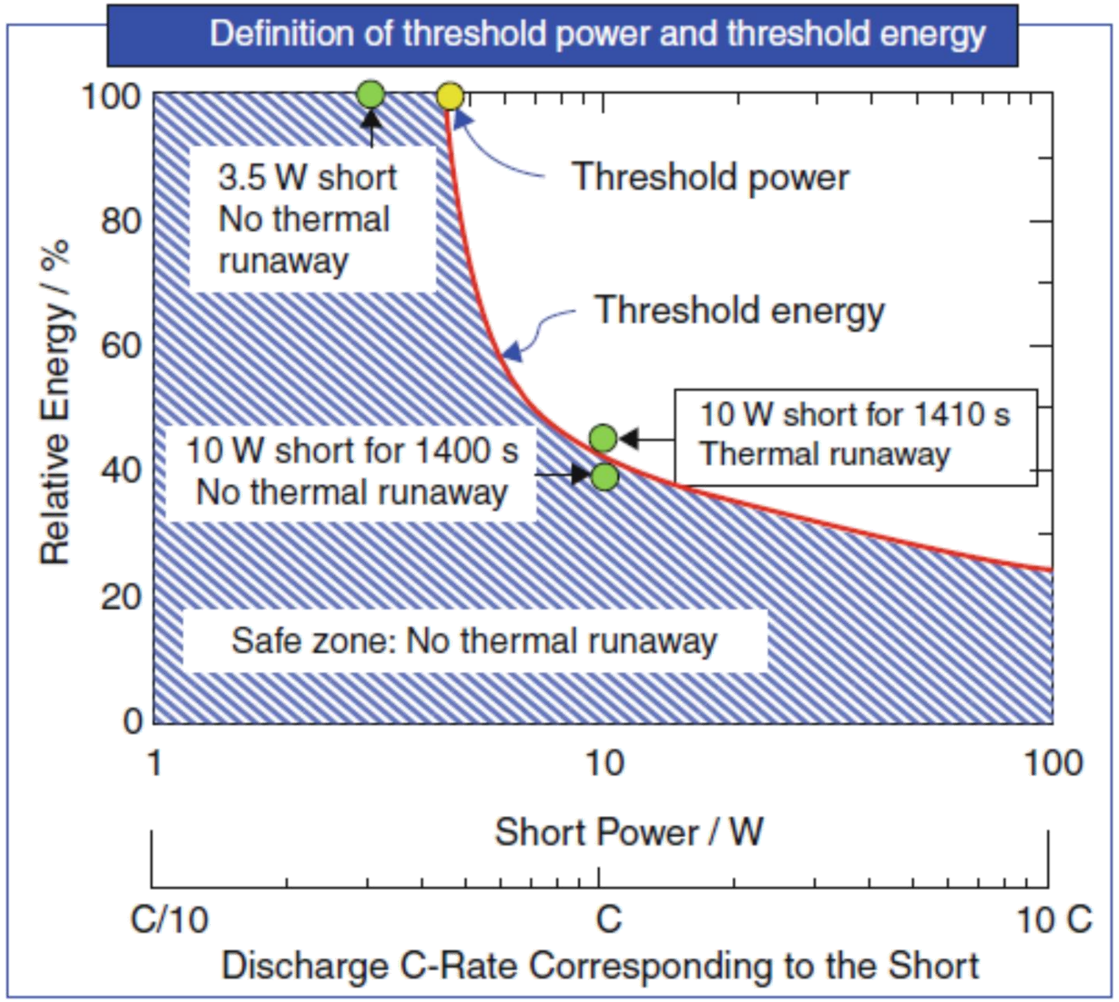


Fig. 9.9 The Safe Zone construct

Barnett B., Ofer D., Sriramulu S., Stringfellow R. (2013) Lithium-Ion Batteries, Safety. In: Brodd R. (eds) Batteries for Sustainability. Springer, New York, NY

- Depending on cell chemistry, cell design, and application, there exists a threshold between thermal runaway and no thermal runaway

Industry Field Experience

Lithium Ion Battery Internal Short

Presentation to EVS GTR IWG

March 2018

Key Messages

- Industry has extensive field experience with lithium ion cells
- There have been no known incidents of internal short circuits resulting in cell thermal runaway

General Motors Experience

Lithium ion cells in field since 2010

Multiple vehicle applications

GM battery cell varieties

- Chevrolet Volt
  - Construction type: Pouch
  - Cathode material:
    - 50% LMO / 50% 111 NMC
    - 30% LMO / 70% 442 NMC
    - 532 NMC
- Spark EV
  - Construction type: Pouch
  - Cathode material:
    - LFP *(limited volume)*
    - 30% LMO / 70% 442 NMC
- Bolt
  - Construction type: Pouch
  - Cathode material:
    - 622 NMC
- Mild Hybrid
  - Construction type: Cylindrical
  - Cathode material:
    - 111 NMC
- Strong Hybrid
  - Construction type: Prismatic can
  - Cathode material:
    - 442 NMC

Chemistry Description

- Cathodes
  - LMO - lithium manganese oxide
    - $LiMn_2O_4$
    - Sometimes called Manganese Spinel or Li Manganese Spinel
  - NMC – lithium nickel manganese cobalt oxide
    - $Li(Ni_xMn_yCo_z)O_2$
    - Numerical prefix refers to relative amount of each metal in the structure
  - LFP – lithium iron phosphate
    - $LiFePO_4$
- Anodes
  - Carbon
    - Mixtures of various types of carbons (hard and soft) and/or graphites (artificial and natural with an amorphous carbon coating).

GM estimated vehicle volumes

- Volt Gen 1 (and related vehicles): ~ 90k
- Volt Gen 2 (and related vehicles): ~ 45k
- Spark EV: ~ 7k
- Bolt: ~ 25k

Represents nearly 50 million cells

Known Internal Short Induced Thermal Events

- NONE

Possible internal short frequency

- Varies somewhat by cell type and manufacturer
- Overall GM experience shows ~2-5 events per million cells for detected cell internal short in customer vehicles

Ford Motor Company Experience

Ford Battery Cell Varieties

- Focus Electric
  - Construction Type: Pouch cell
  - Cathode Material: 622 NMC
  - Anode Material: Carbon

- Fusion / Mondeo / Lincoln MKZ Hybrid
  - Construction Type: Aluminum Can
  - Cathode Material: 111 NMC
  - Anode Material: Carbon

- Fusion Energi
  - Construction Type: Aluminum Can
  - Cathode Material: 111 NMC
  - Anode Material: Carbon

- C-Max Hybrid
  - Construction Type: Aluminum Can
  - Cathode Material: 111 NMC
  - Anode Material: Carbon

- C-Max Energi
  - Construction Type: Aluminum Can
  - Cathode Material: 111 NMC
  - Anode Material: Carbon

Ford Motor Company EVs by Model Year	Approximate Sales Volume
2012-2017 Ford Focus Electric (BEV)	10,500
2013-2017 Ford Fusion / C-Max / Mondeo / Lincoln MKZ Hybrid (HEV)	313,000
2013-2017 Ford Fusion / C-Max Energi (PHEV)	90,000

Approximately 35 Million Cells and no
documented thermal events due to internal short