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Study of Aging Effects on Safety of 18650-type LiCoOx Cells

Presented by:

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OUTLINE

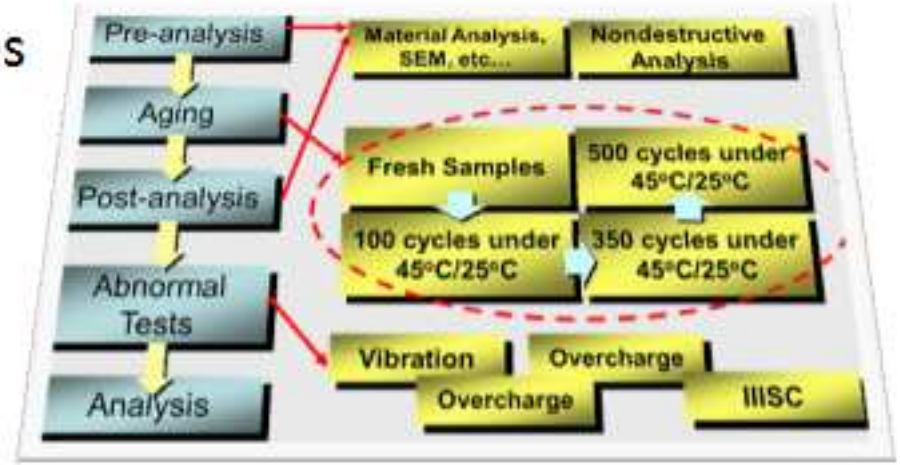
Introduction

Literature Overview

Study of Aging Effects on LIB Safety

- Electrochemistry Properties
- Thermal Stability
- Others

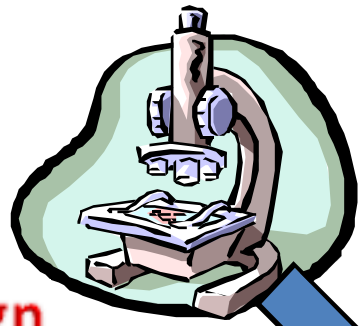
Summary



Root Causes of Safety Issues on LIBs

Manufacturing

- Uniformity of Product Quality
- Contamination
- Production Line Testing
- Out-going Quality Control



Design

- Construction Integrity
- Safety Function Design
- Material Properties

Use

- Mechanical Abuse
- Electrical Abuse
- Environmental Condition
- User Behaviors
- **Aging Effects**

The Safety Performance of a Lithium Ion Battery could change over time !

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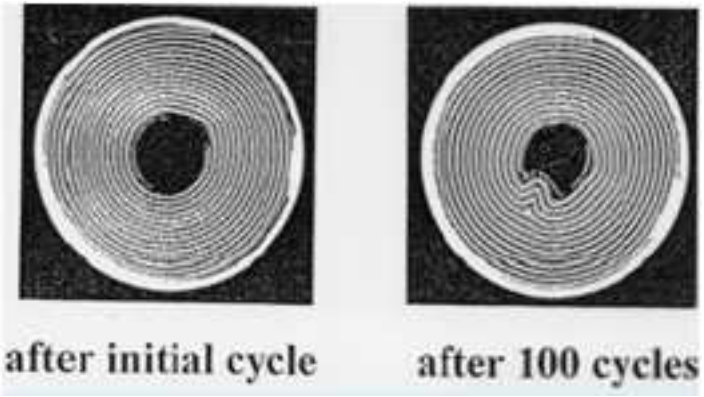
AGING EFFECT SHOULD NOT BE IGNORED!

- Most product defects can be detected by safety testing, production line testing and OQC screening

- Many battery incidents occur after the battery was used for some time, even under normal use conditions!

AGING EFFECTS ON LIB SAFETY ISSUE

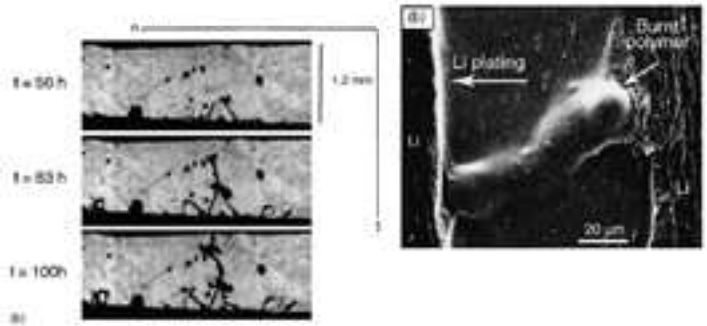
Mechanical Integrity



Source: Presentation Prof. T. Takamura “Carbon Material in Power Sources”. June 2005, ZSW Ulm

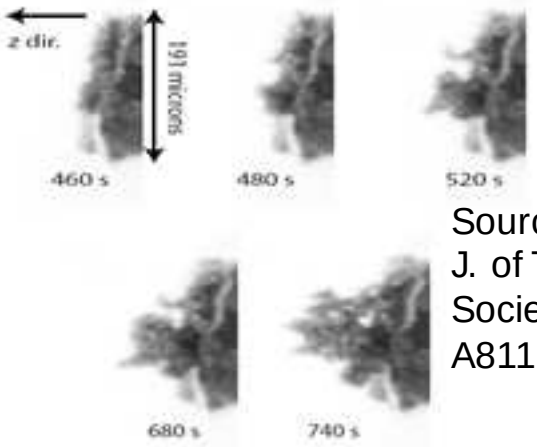
Lithium Plating & Dendrite Formation

Observed by SEM and conventional optical microscopy



Source: M. Rosso et al., Electrochimica Acta 51 (2006) 5334-5340

Observed by a Carl Seiss Stemi 2000-C optical microscope equipped with a Pix-eLink 623-C digital camera



Source: O. Crowther et al., J. of The Electrochemical Society, 155 (11) A806-A811 (2008)

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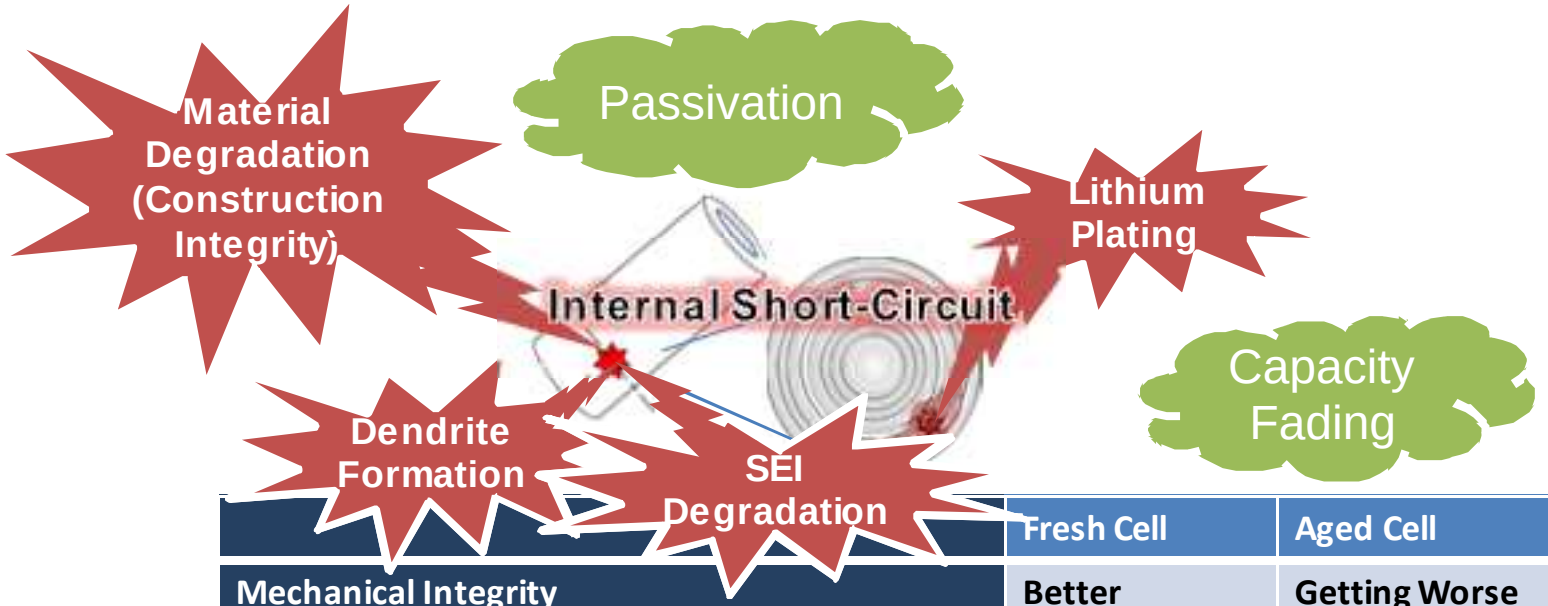
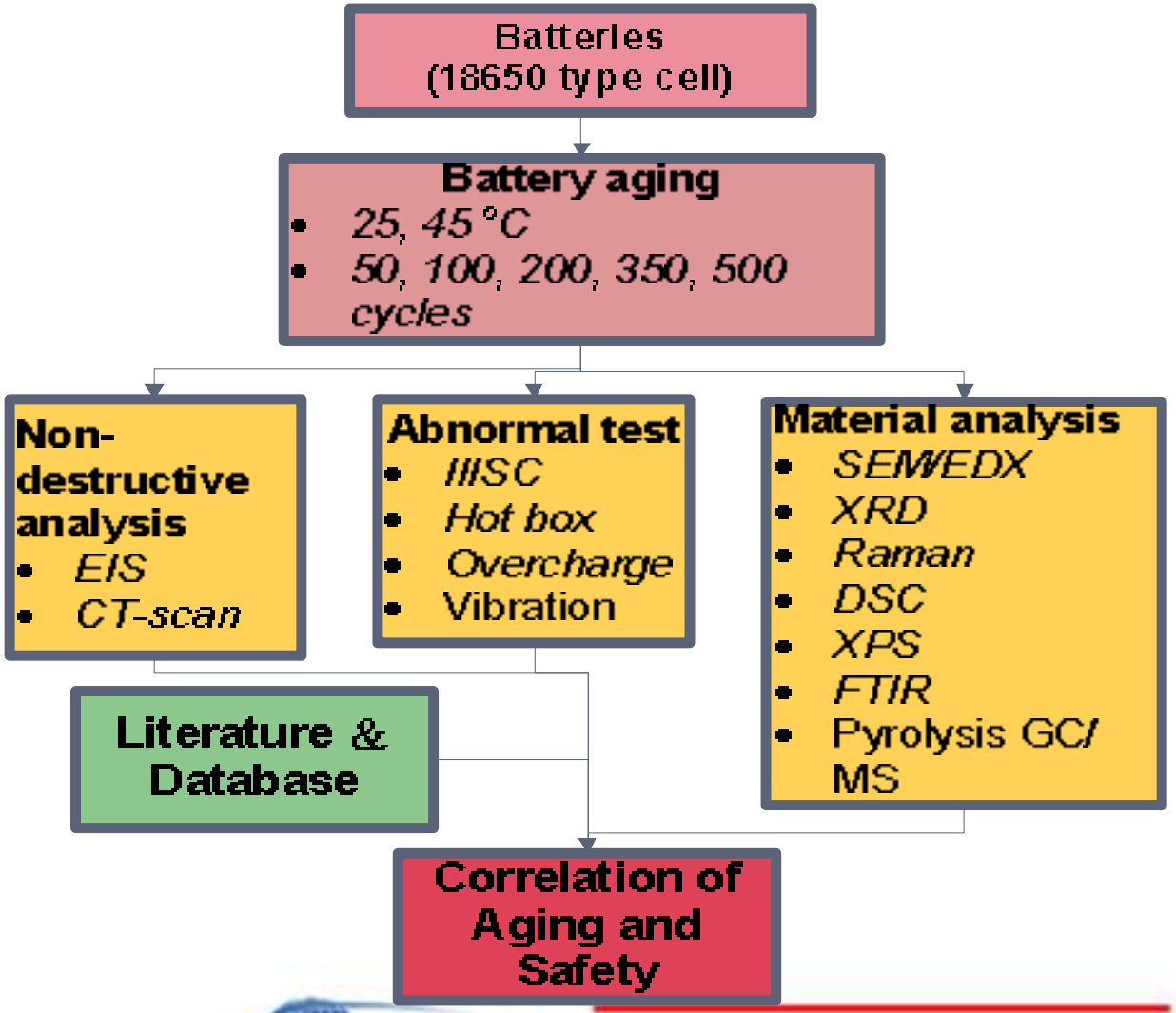
HYPOTHESES OF AGING EFFECTS



	Fresh Cell	Aged Cell
Mechanical Integrity	Better	Getting Worse
Activity of Material(s)/Component(s)	More active	Less active
Dendrite Formation & Lithium Plating	Not an issue	Potential concern
Thermal Stability of Material(s)/Component(s)	Good	Could be worse
Polarization Effect	Less concern	Potential concern
Risk of Electrolyte Leakage	No	Yes
Tolerance to Thermal Abusive Conditions	Good	Could be worse

STUDY OF LIB AGING EFFECT(S)



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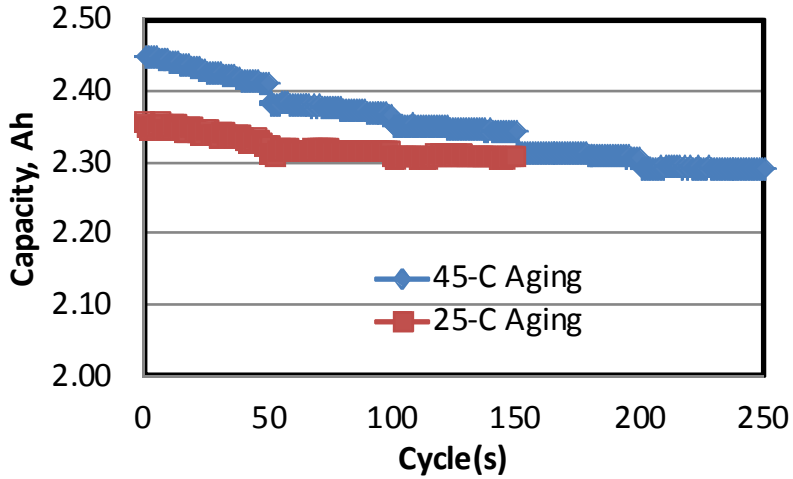
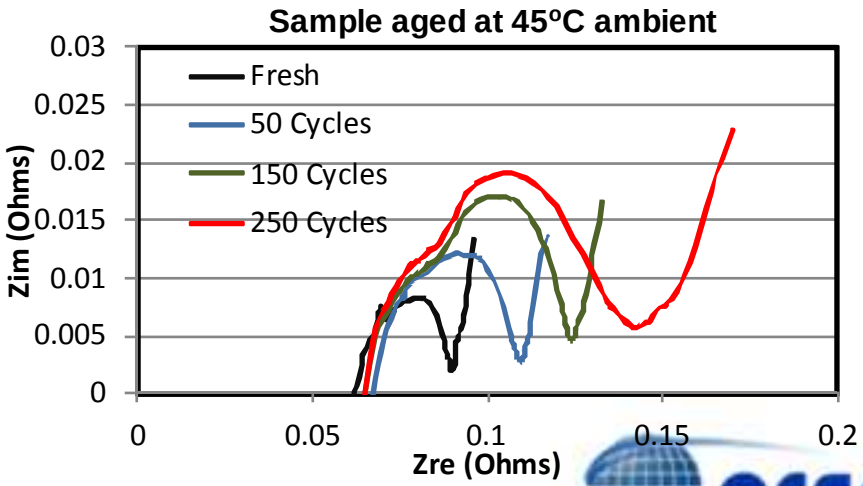
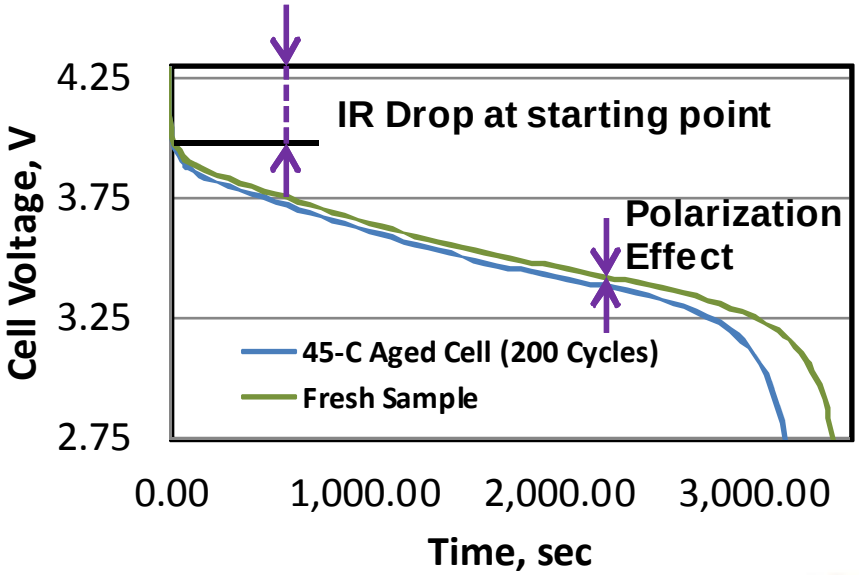
CAPACITY FADING & EIS







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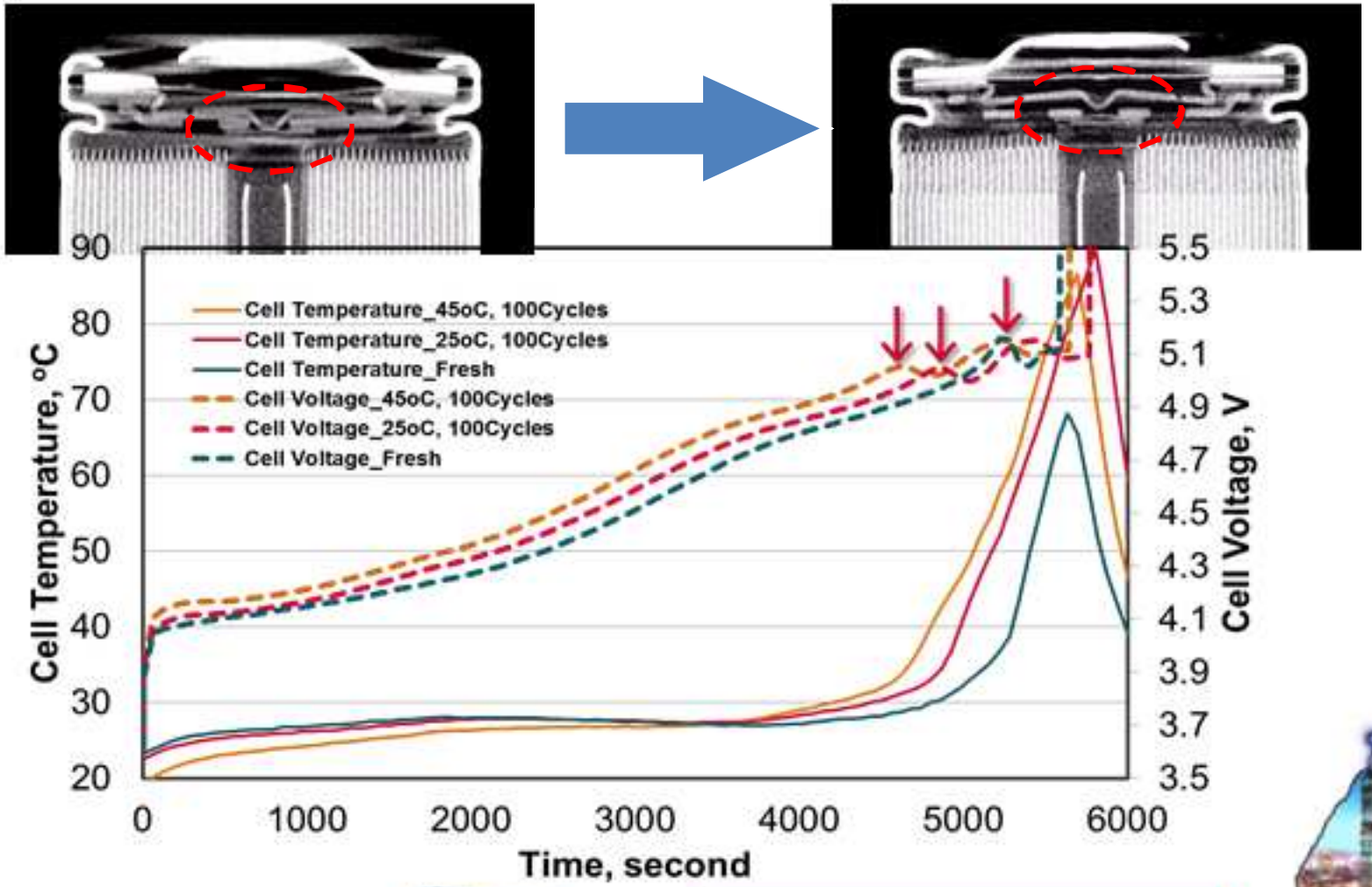
OVERCHARGE TEST



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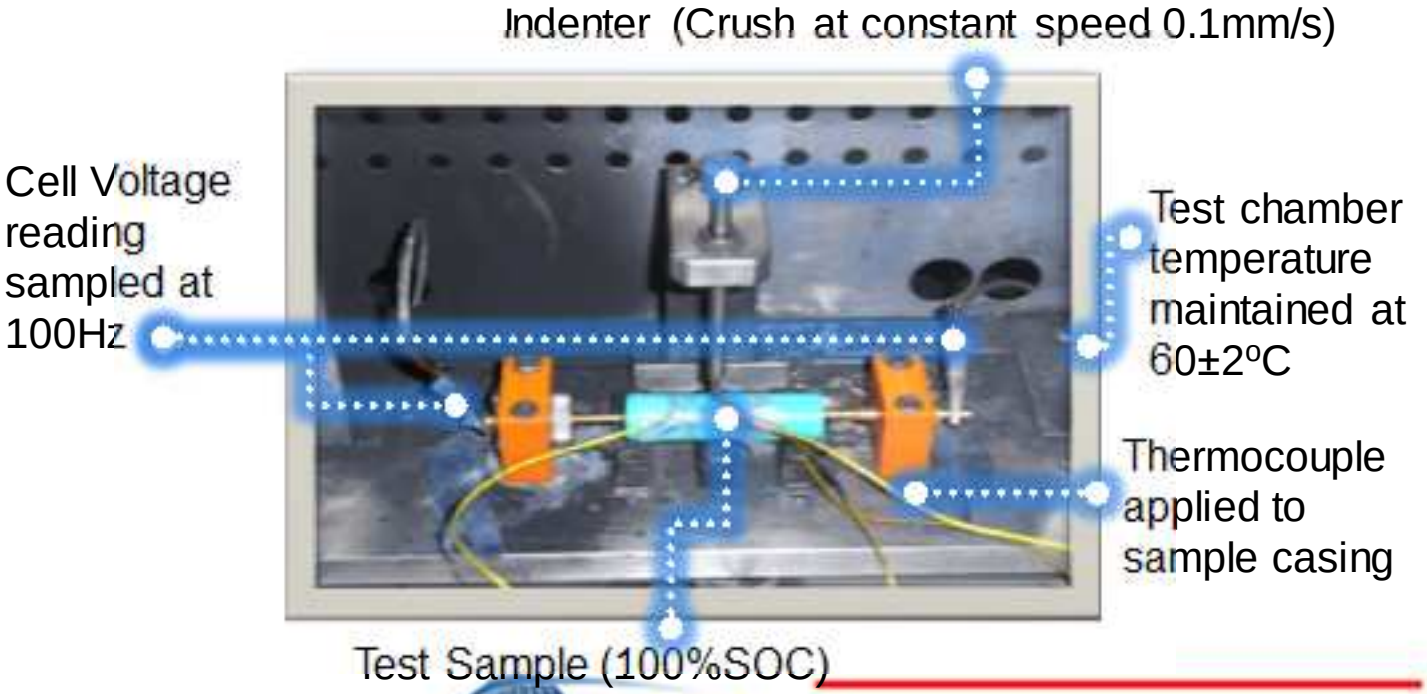
INDENTATION-INDUCED ISC (IIISC) TEST

Purpose:

- To investigate the “severity” of ISC event of the cell design
- To study how the “severity” changes on the identical cell design, but under different aging conditions

Test Method Overview



IIISC TEST (CONT.)

Cell aged at 45°C

Fresh Sample, 100% Fails IIISC Test (N=3)

50 Cycle Aged Sample, fails IIISC Test, but in different failure mode (i.e.. no sustained fire)

100 Cycle Aged Sample, 1 cell pass and 1 cell fail

200 Cycle Aged Sample, 1 cell pass and 1 cell fail

Cell aged at room temperature

Fresh Sample 100%, Fails IIISC Test (N=3)

50 Cycle Aged Sample, 100% Fails IIISC Test

100 Cycle Aged Sample, 1 cell pass and 1 cell fail

HOT BOX TESTING

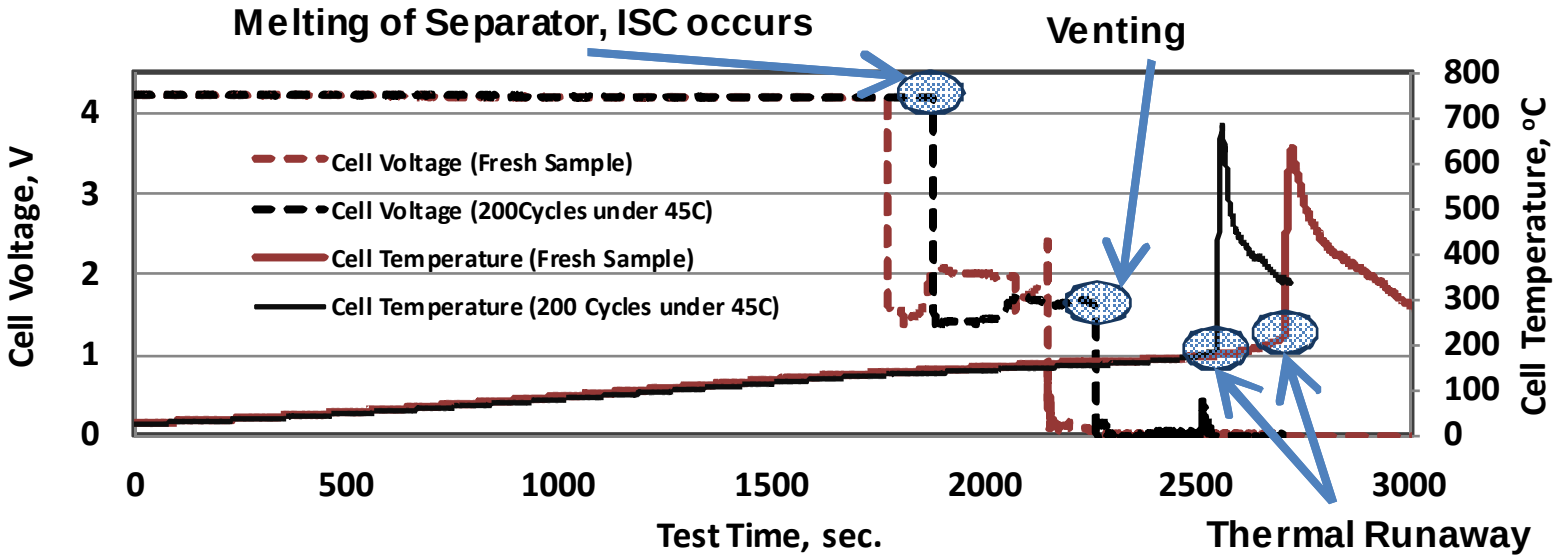
Purpose:

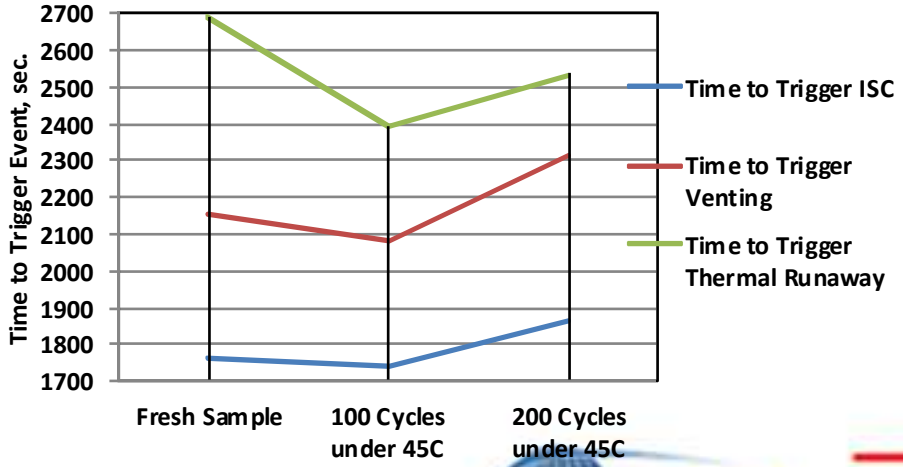
- To investigate cell behaviors under heating condition.
- To study the thermal stability of cells after being aged under different aging conditions.

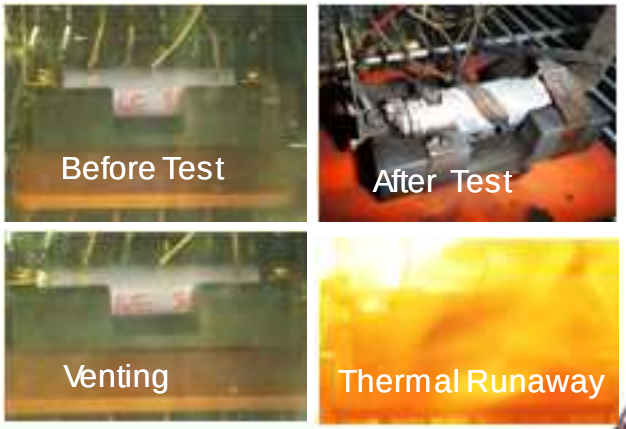
Test Method Overview:

- Test Sample: The test sample is charged to 4.25V using CC-CV standard charging protocol.
- Experimental:
  - Put test sample in oven with the thermal couple(s) attached on the cell casing.
  - Raise the temperature of the test sample at a rate of 5°C/min from room ambient (ex.25°C) to 180°C. Maintain the oven temperature at 180°C until the "final event" of the cell. The final event is usually the thermal runaway for LiCoO2-type cell.
  - Monitor the cell voltage and cell casing temperature while testing.

HOT BOX TESTING (CONT.)







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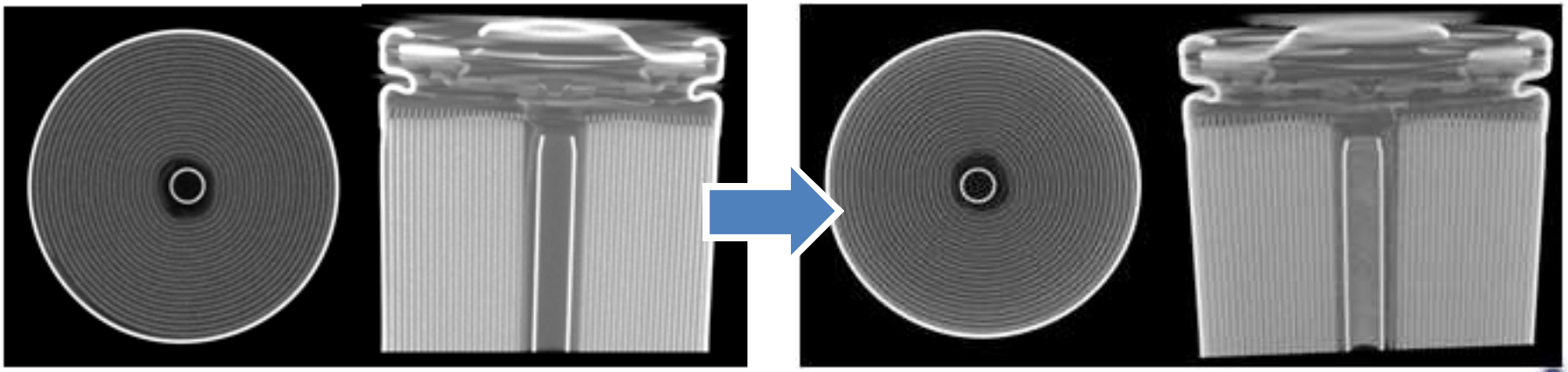
VIBRATION TEST & CONSTRUCTION INTEGRITY

	Fresh Sample		100 Cycles, 25°C		100 Cycles, 45°C		200 Cycles, 45°C	
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
	OCV/Mass	OCV/Mass	OCV/Mass	OCV/Mass	OCV/Mass	OCV/Mass	OCV/Mass	OCV/Mass
Before	4.213/45.81	4.209/45.90	4.198/45.78	4.208/45.88	4.208/45.98	4.214/45.79	4.210/45.90	4.203/45.88
After	4.213/45.81	4.209/45.90	4.198/45.78	4.208/45.88	4.208/45.98	4.214/45.79	4.209/45.90	4.203/45.88



Before Aging

After Aging (250 Cycles under 45°C)

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AGING EFFECT SUMMARY

Aging has potential unfavorable effect(s) to the thermal stability. The DSC data shows some exothermal reactions in aged samples can be triggered earlier than that of a fresh cell.

The polarization effects can be found in aged cells via overcharging test, which will usually lead to more heat generation. However, polarization is not the only source to generate heat, there could be also material decomposition and some unknown chemistry/electrochemistry reaction(s) that can lead to more heat release during overcharging.

The ISC can usually be triggered earlier under overcharging conditions for aged samples than fresh samples, which leads to safety concerns.

Fresh samples have higher failure rates than aged samples during IIISC tests.

Thermal Aging at 45°C will have more apparent aging effect(s) than cell aging at room ambient.

The XRD data indicates the bulk material composition of electrodes makes no difference between fresh and aged samples. However, the significant difference on interface of both anode and cathode materials can be observed via FTIR and Raman analysis. (It also matches to the electrochemistry behaviors of battery according to EIS profiles)

Lithium-ion Cells with hard metal casing (i.e.. 18650 type cells) usually have good construction integrity. There was no difference observed during vibration testing, and when observing 3D CT Scan images of fresh and aged samples.

FOLLOW UP AND FURTHER STUDY

Extend the aging effect study to different material design (ie. NMC, LPF) and different cell type (ie. Prismatic, Pouch type)

Study the aging effects on batteries with abuse aging conditions

Further study in Overcharging Test to single cell

Further study in Thermal Stability to the Component(s) in single cell

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