Study of Aging Effects on Safety of 18650-type $LiCoO_x$ Cells

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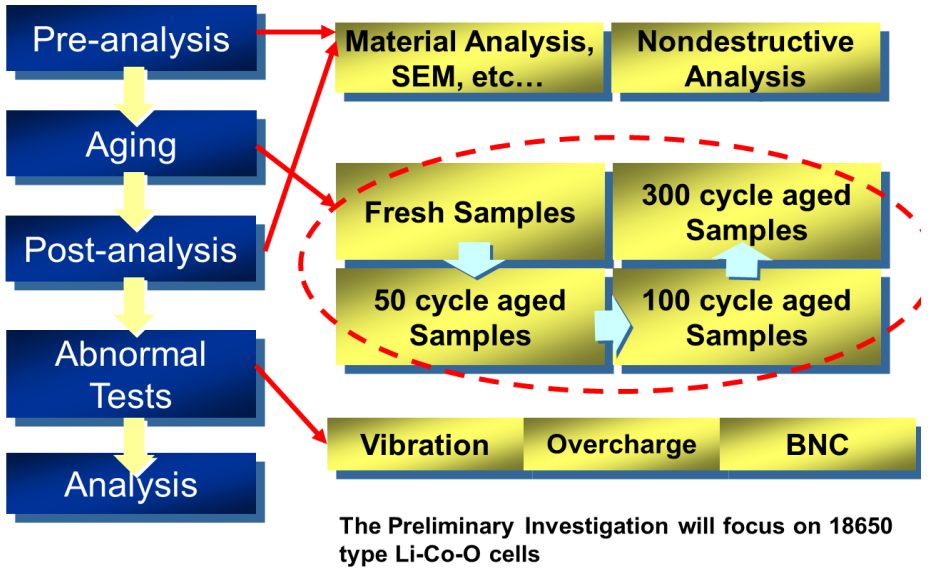
OUTLINE

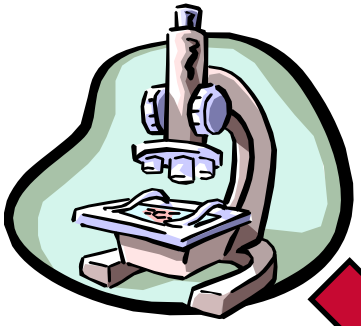
- Introduction
- Literature Overview
- Study of Aging Effects on LiB Safety
  - Electrochemistry properties of the cell
  - Thermal stability
  - Others
- Summary



Root Causes of LiB Safety Issues

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**

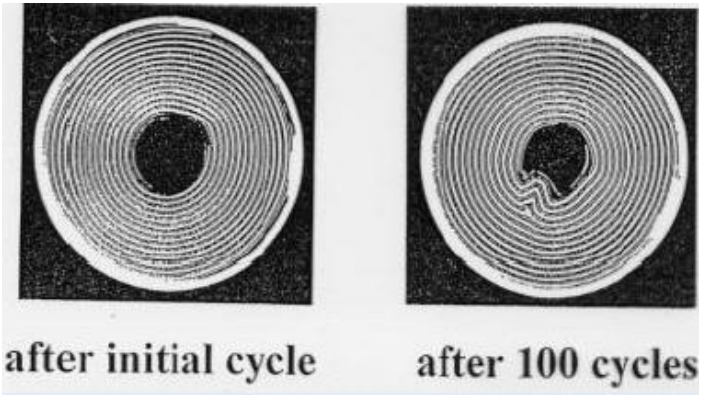
The Safety Performance of a Lithium Ion Battery could change over time !

Aging Effect should not be Ignored

- Most product defects can be detected by safety testing, production line testing and QC screening
- Many battery incidents occur after the battery was in use for some time, even under normal (anticipated) conditions.

AGING EFFECTS ON LIB SAFETY

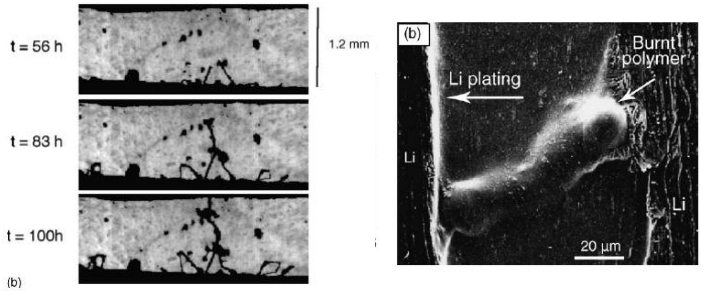
❑ Mechanical Integrity



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

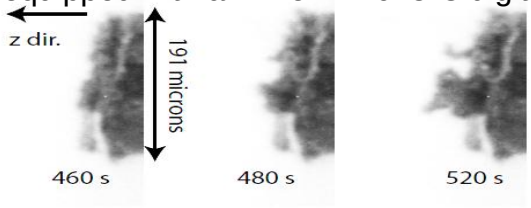
❑ Lithium Plating & Dendrite Formation

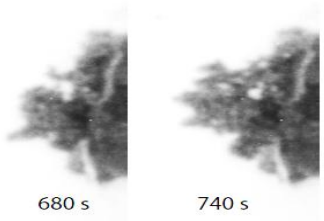
Observed by SEM and conventional optical microscopy



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

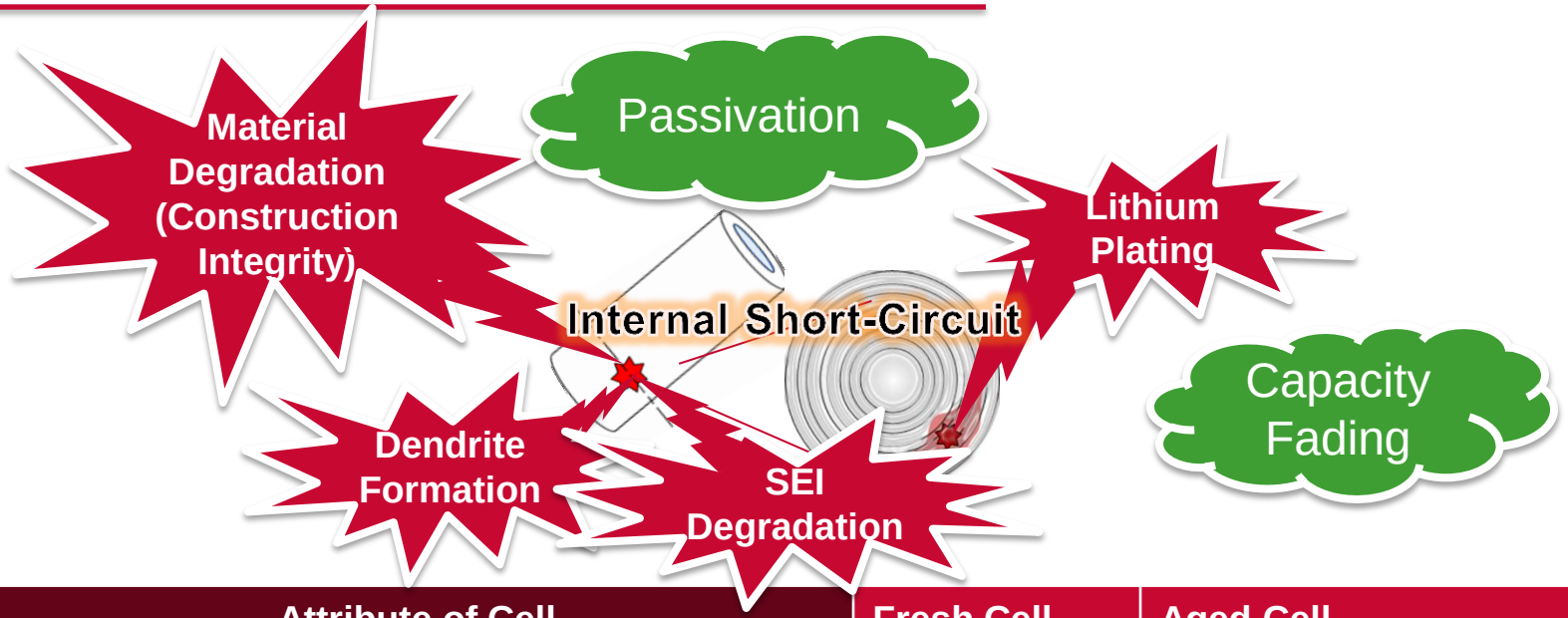
Observed by a Carl Seiss Stemi 2000-C optical microscope equipped with a Pix-eLink 623-C digital camera





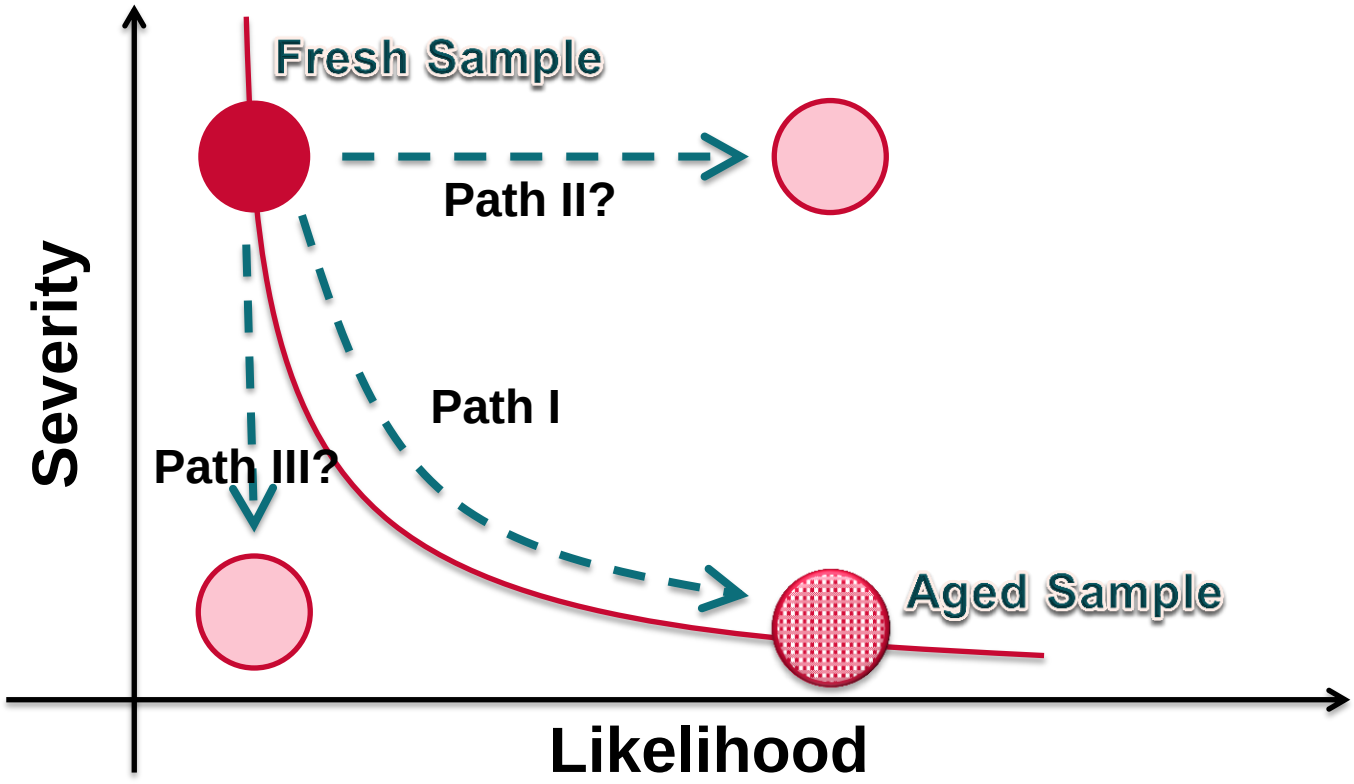
Source: O. Crowther et al., J. of The Electrochemical Society, 155 (11) A806-A811 (2008)

Hypothesis of Aging Effects



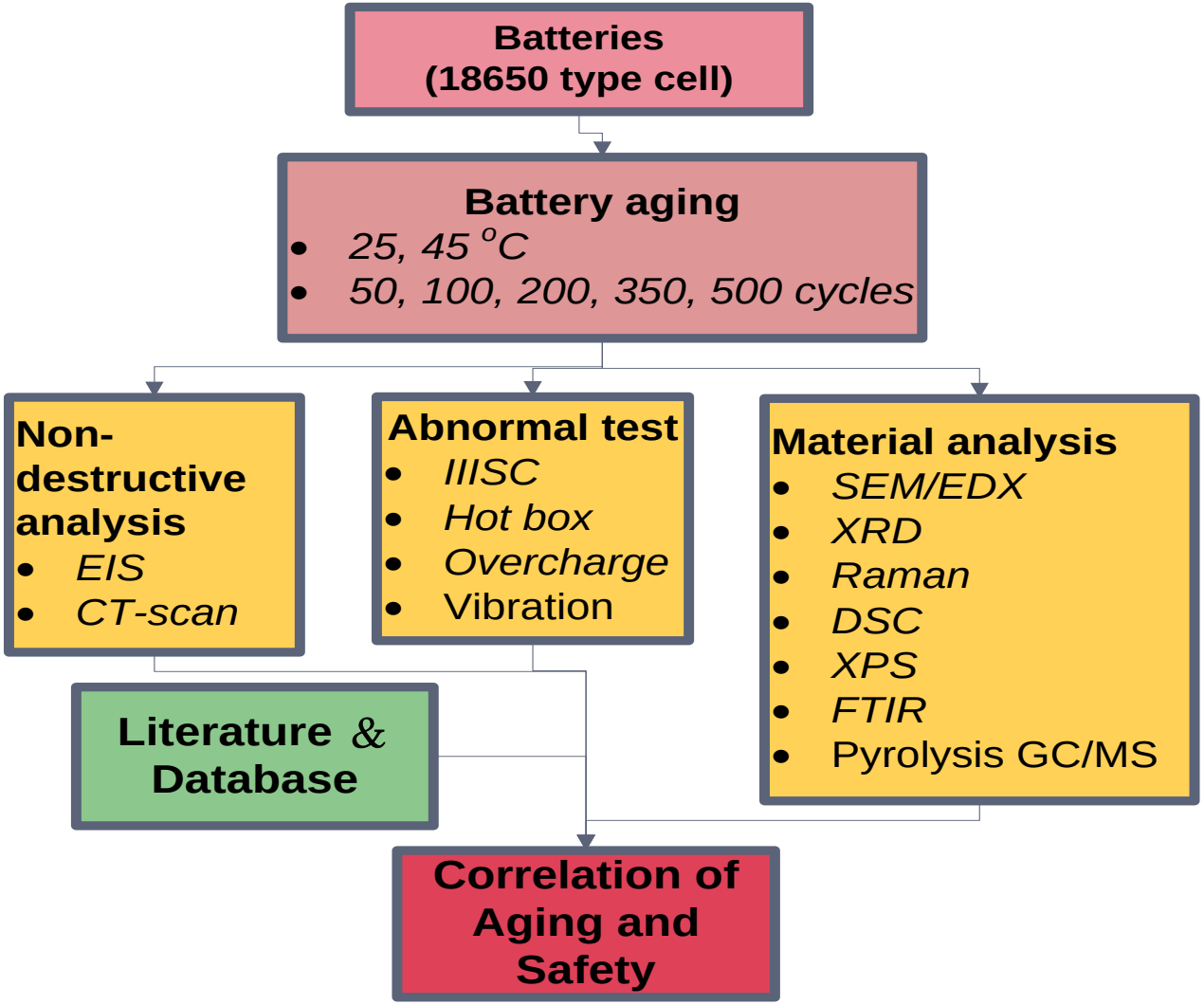
Attribute of Cell	Fresh Cell	Aged Cell
Mechanical Integrity	Better	Getting Worse
Activity of Material(s)/Component(s)	More active	Less active
Dendrite Formation & Lithium Plating	Not an issue	Potential concern
Thermal Stability of Material(s)/Component(s)	Good	Could be worse
Polarization Effect	Less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

Hypothesis of Aging Effects to battery Failures



Understand the Mechanism of Aging can help to understand the Battery Safety Behavior

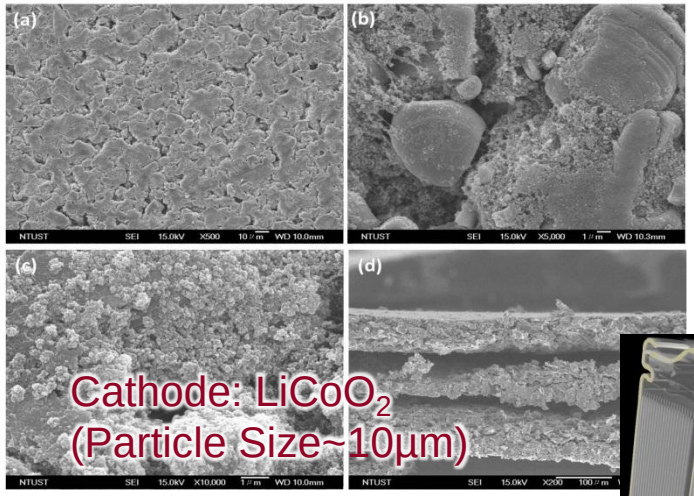
STUDY OF LIB AGING EFFECT(S)



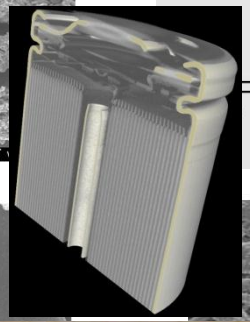
EXPERIMENTAL

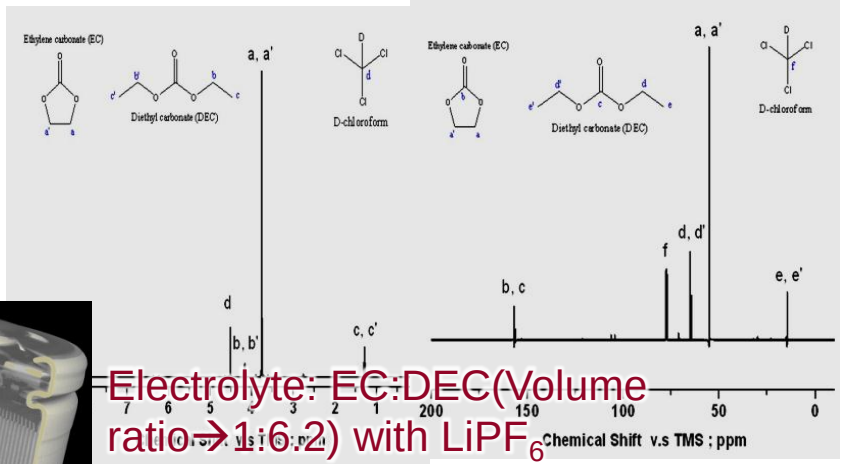
Technique		Purpose
Material Analysis	SEM	To observe the change of morphology of electrode surface, such as particle size, distribution of active material, binder, conductive carbon, coating layer, thickness and etc.
	EDX	To analyze the elements of battery materials (electrodes, separator) to obtain the composition change of battery materials
	XRD	Observe the crystal structural change of electrode
	FTIR	Analysis the surface chemistry, mainly SEI layer, of electrode
	DSC	Evaluate the change of thermal stability of the electrode materials
	Raman	Observe the structural change of electrode material
	XPS	Analyze the surface chemistry, mainly SEI layer, of electrode
	Pyrolysis GC/MS	Analyze the thermal decomposition mechanism for active materials
Non-destructive Test	EIS	Analyze the internal resistance change
	CT-Scan	Investigate the internal physical structure, such as valve, electrode packing and alignment
Abnormal Test	IIISC	Evaluate the battery behaviors when localized internal short circuit occurs.
	Vibration	Evaluate the battery behaviors change upon vibration after charging/discharging cycles
	Hot box	Evaluate thermal stability of battery with temperature
	Overcharge	Evaluate the battery behavior under overcharging condition

TEST SAMPLE – 18650 2800MAH CELL

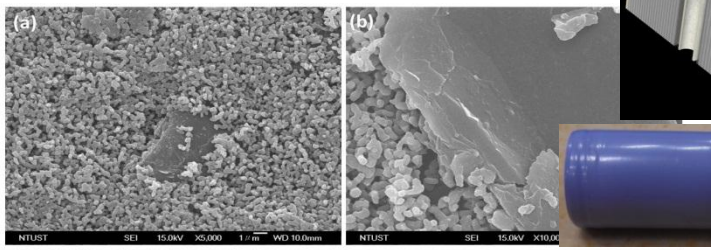


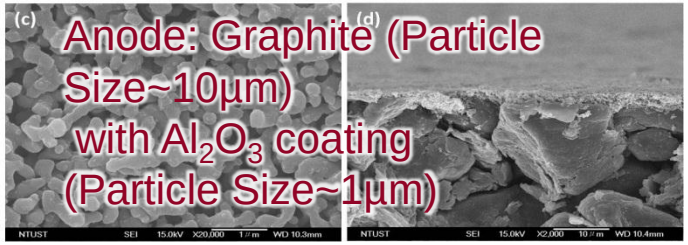
Cathode: $LiCoO_2$ (Particle Size~10μm)



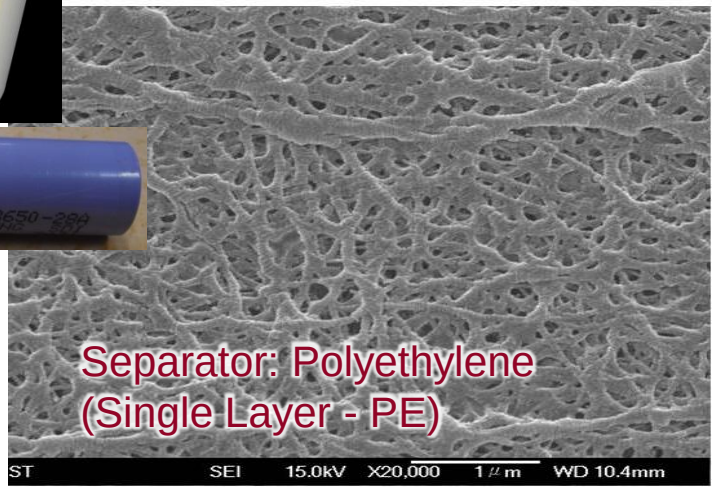


Electrolyte: EC:DEC(Volume ratio→1:6.2) with $LiPF_6$



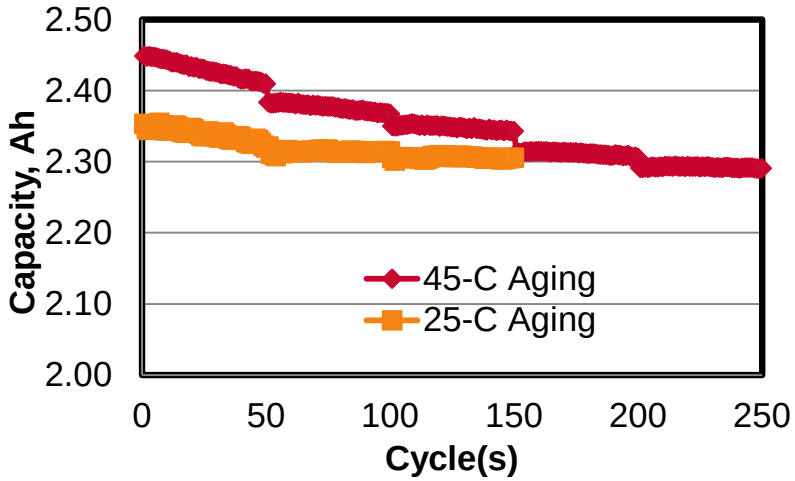


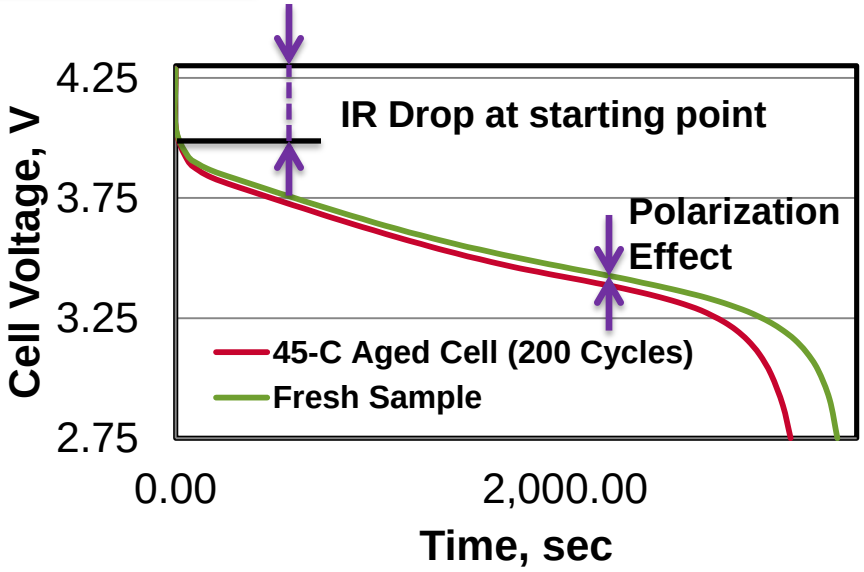
Anode: Graphite (Particle Size~10μm) with Al_2O_3 coating (Particle Size~1μm)

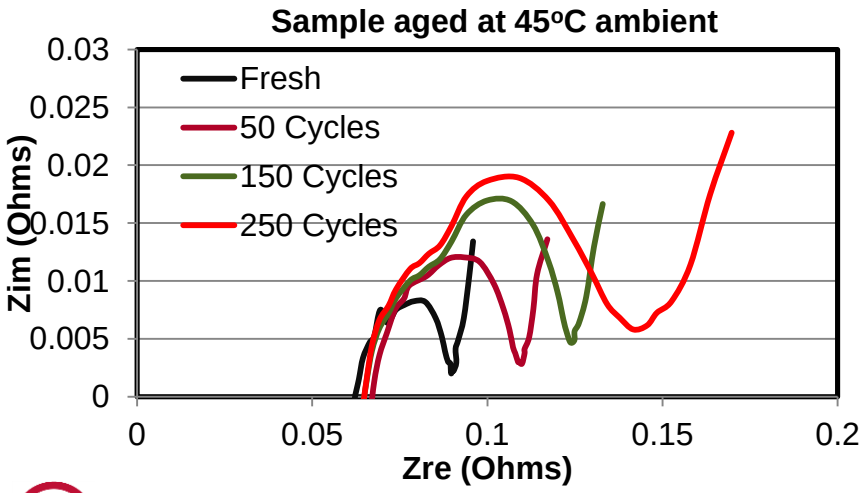


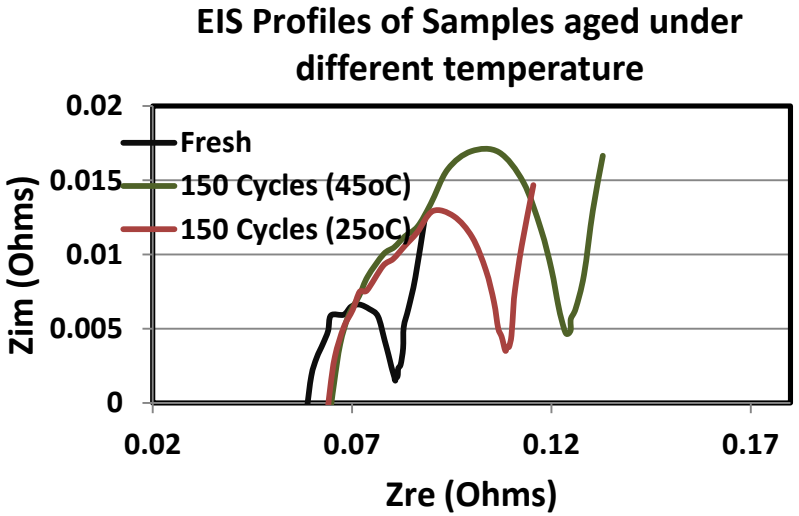
Separator: Polyethylene (Single Layer - PE)

CAPACITY FADING & EIS

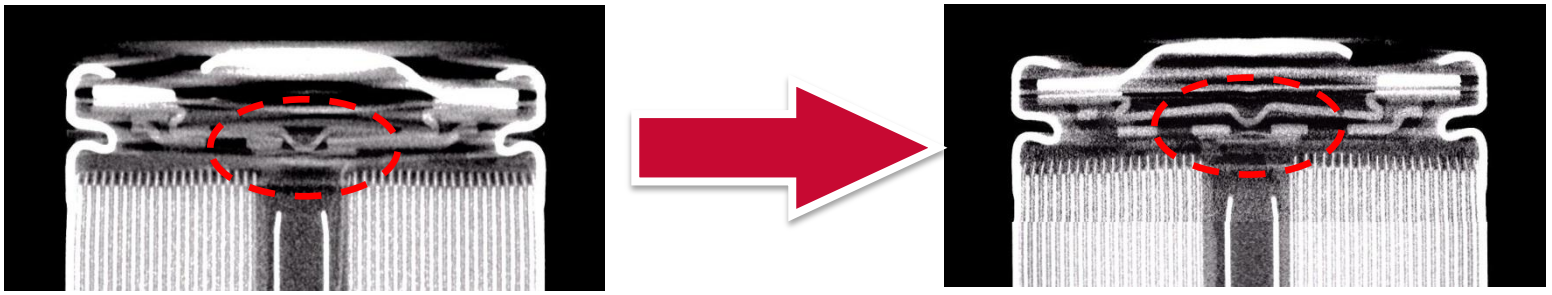


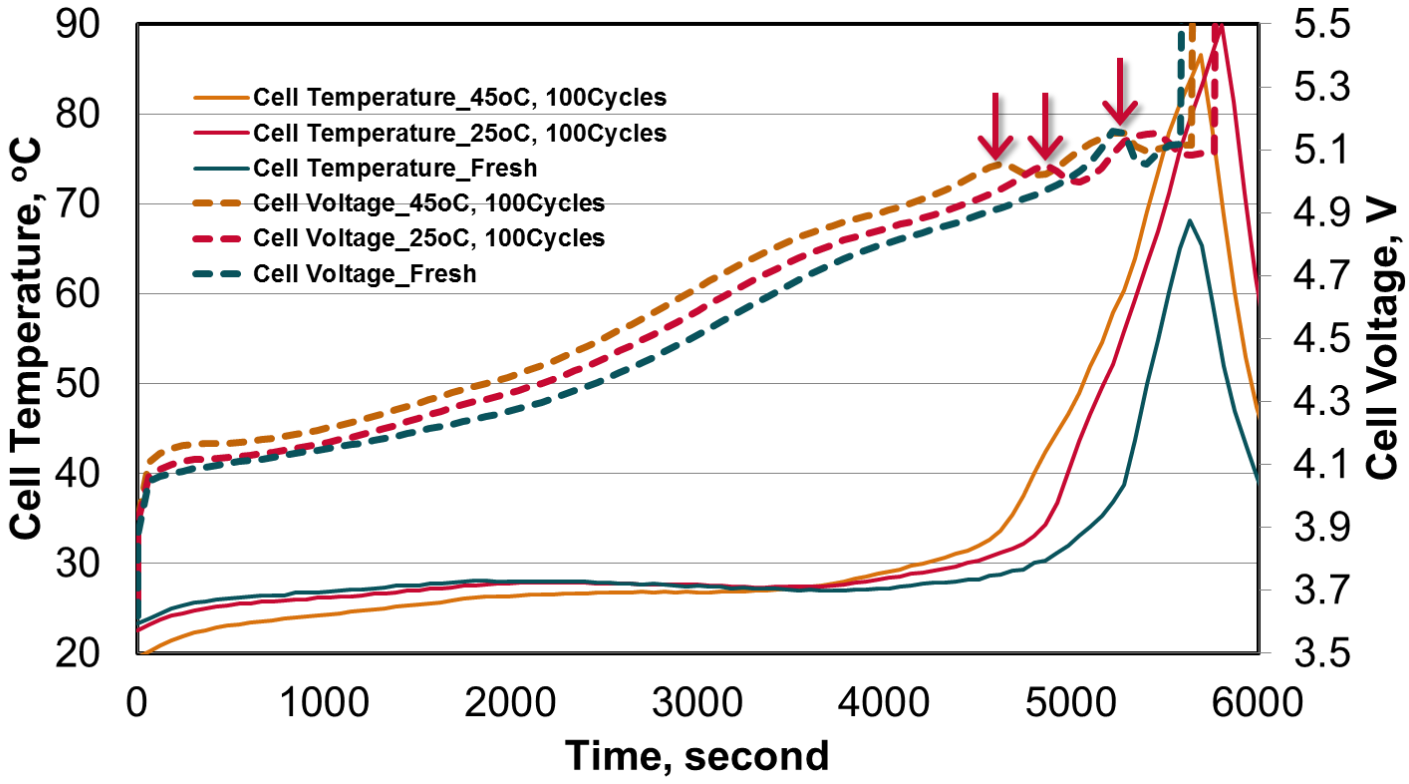




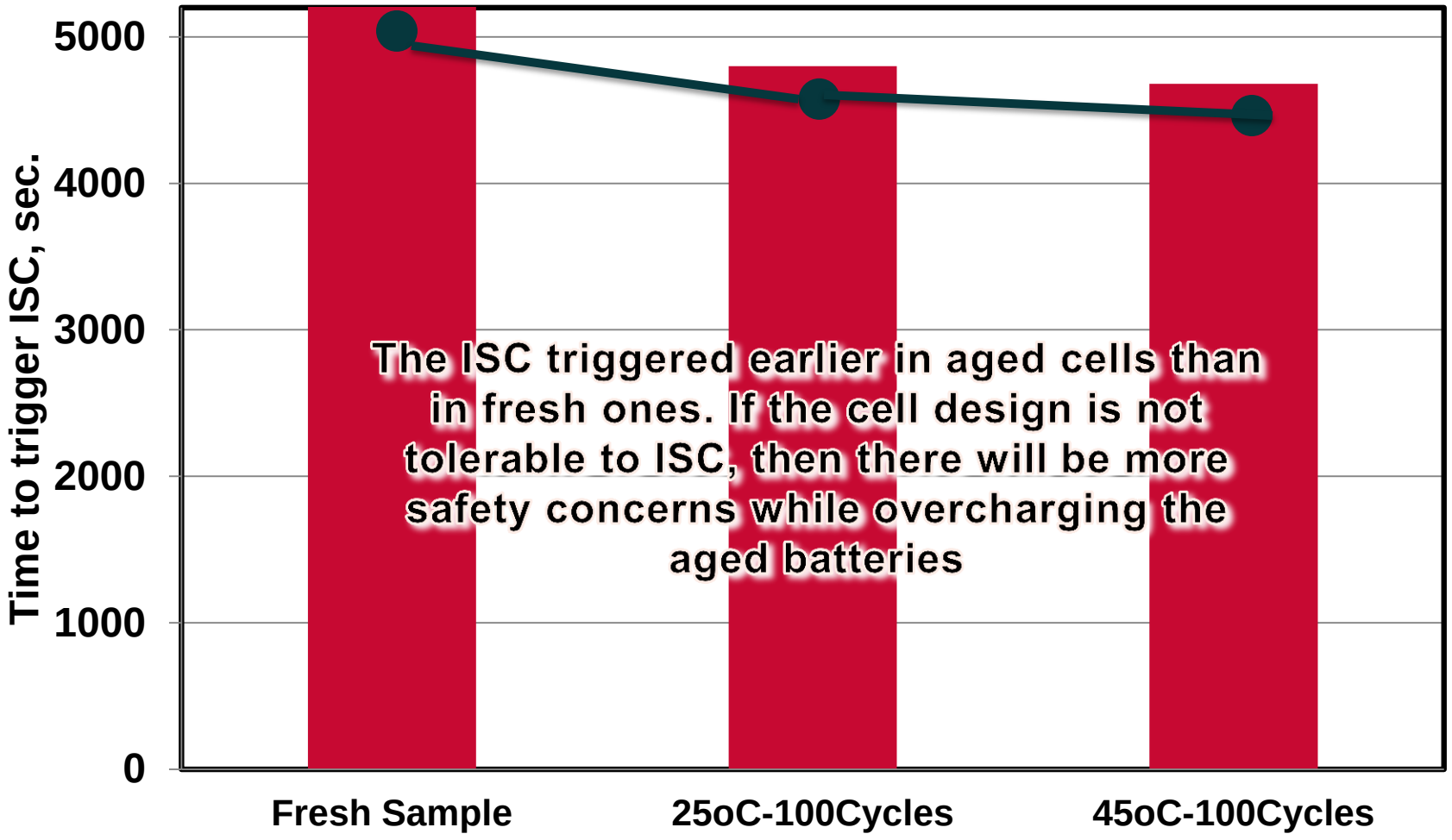


OVERCHARGE TEST



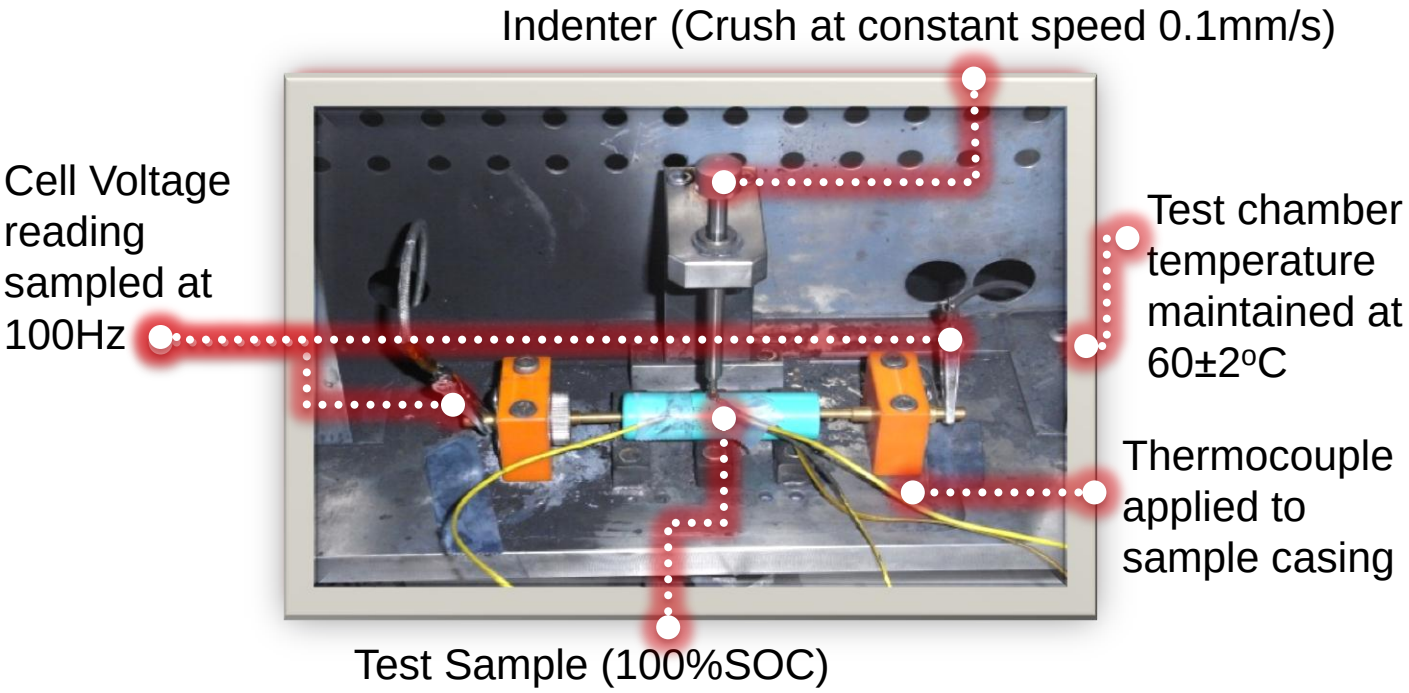


ISC TRIGGERED WHILE OVERCHARGING



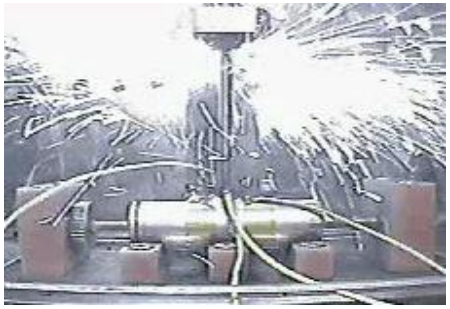
INDENTATION-INDUCED ISC (IIISC) TEST

- 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



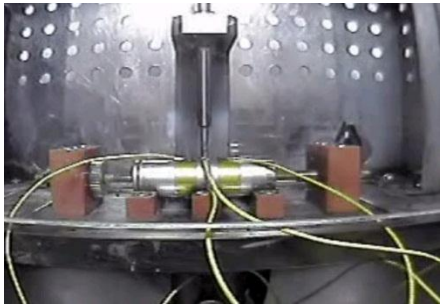
IIISC TEST, CELL BEHAVIOR

Cell aged at 45ºC

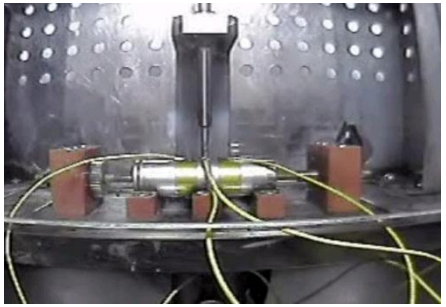


Fresh Sample, 100% Fails IIISC Test (N=3)

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

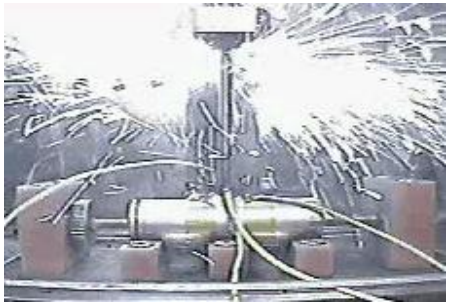


100 Cycle Aged Sample, 1 cell pass and 1 cell fail

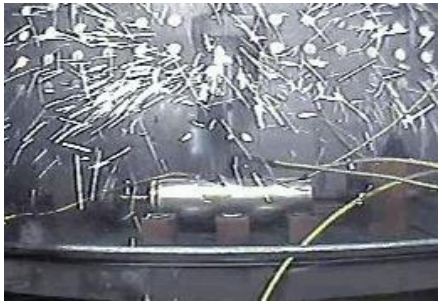


200 Cycle Aged Sample, 1 cell pass and 1 cell fail

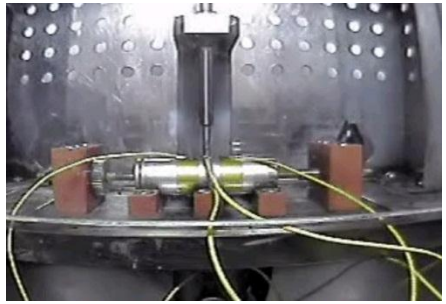
Cell aged at room temperature



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



50 Cycle Aged Sample, 100% Fails IIISC Test

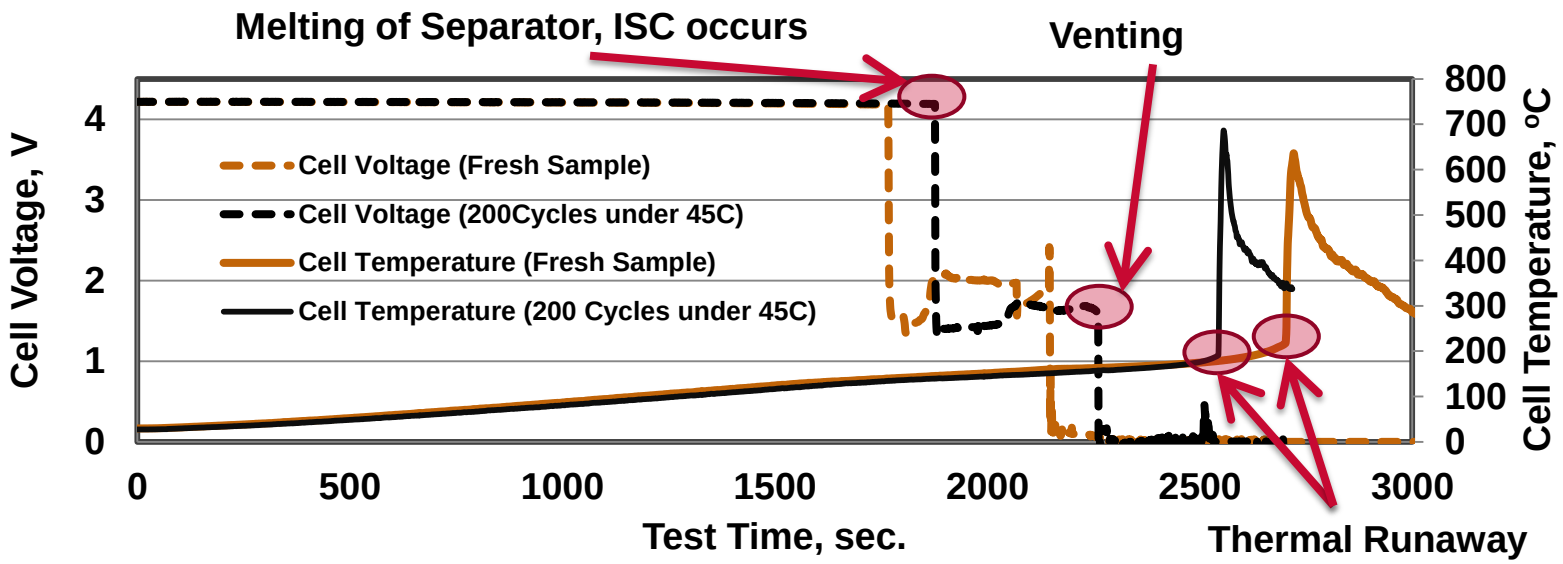


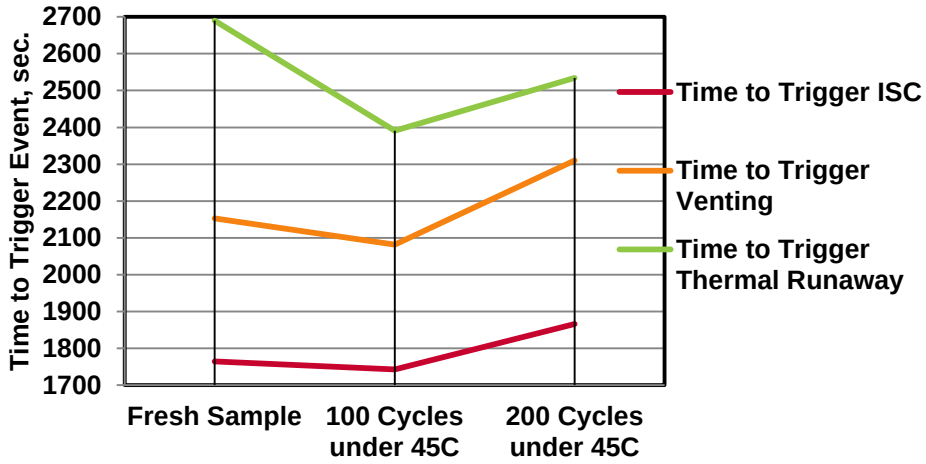
100 Cycle Aged Sample, 1 cell pass and 1 cell fail

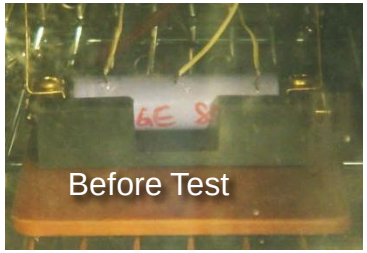
HOT BOX TESTING

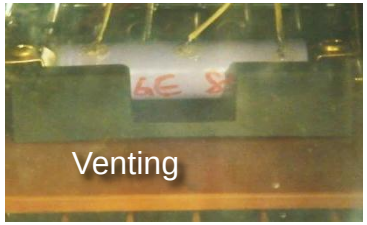
- Purpose:
  - To investigate cell behavior under heating conditions.
  - To study the thermal stability of cells after aging under different aging conditions.
- Test Method Overview:
  - Test Sample: The test sample is charged to 4.25V using CC-CV standard charging protocol.
  - Experimental:
    - 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 DATA



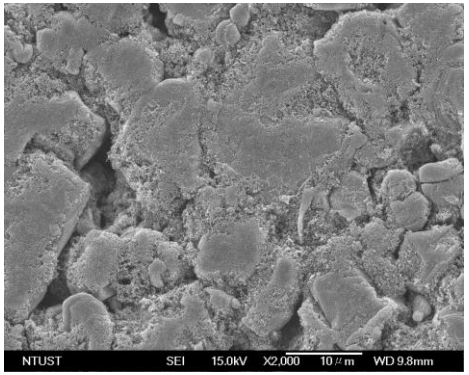




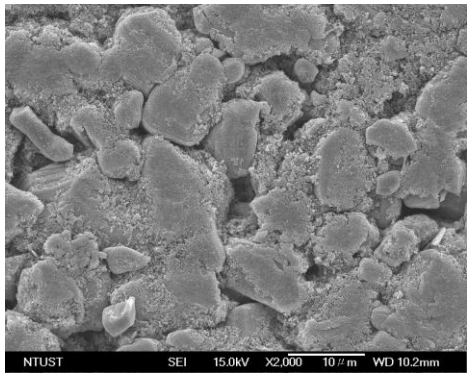


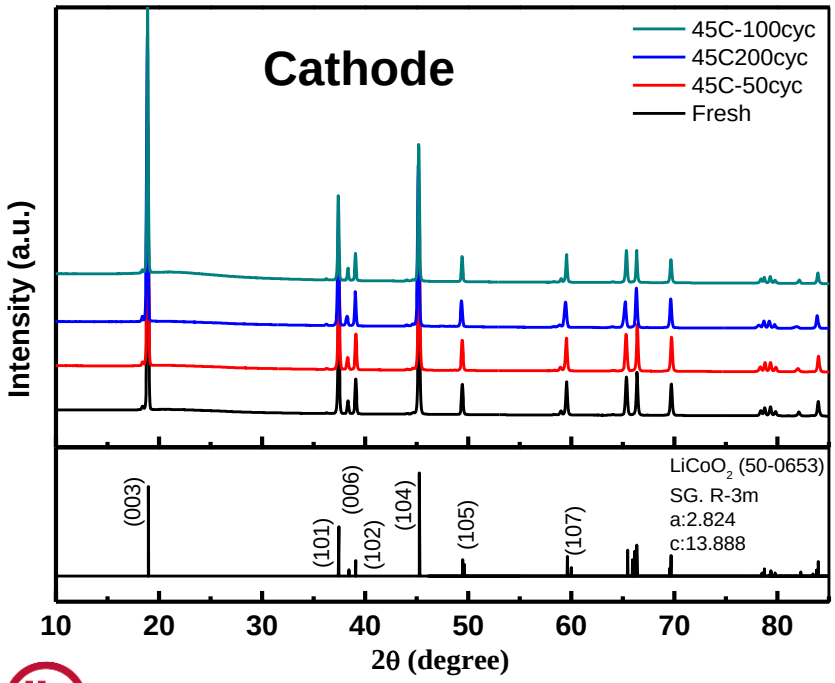
SEM AND XRD ANALYSIS

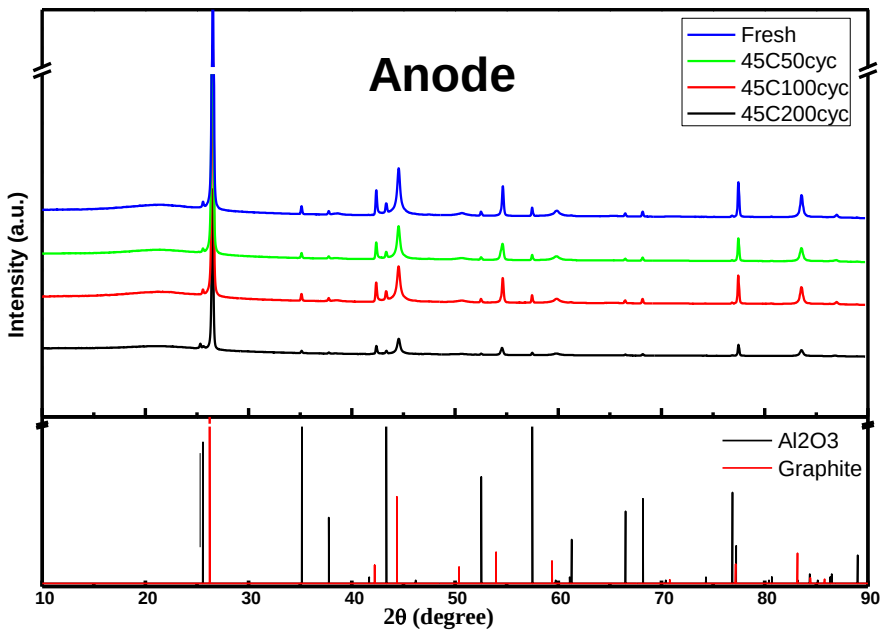
Fresh



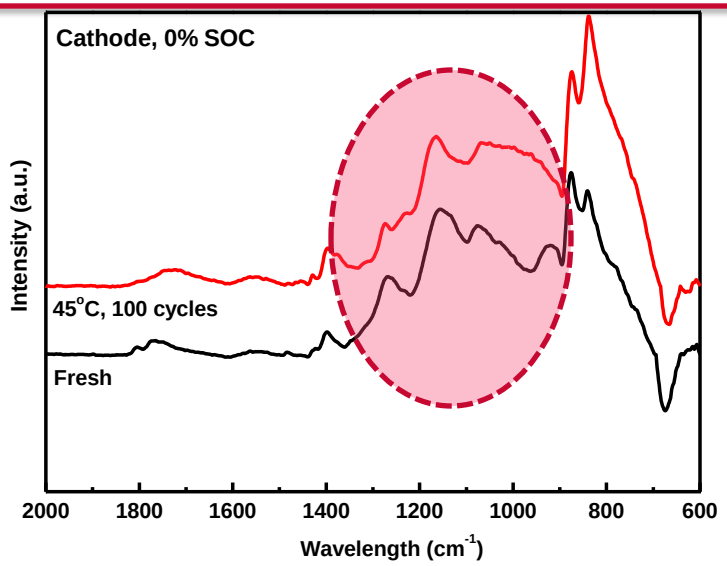
45ºC, 100 cycles

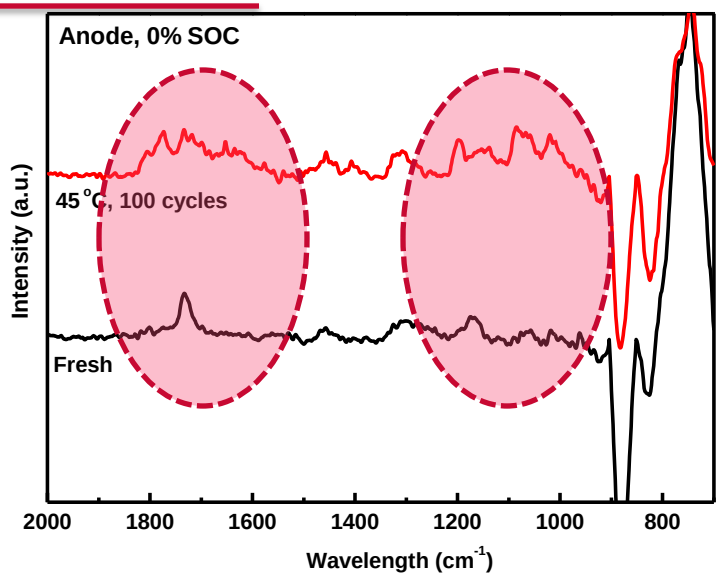


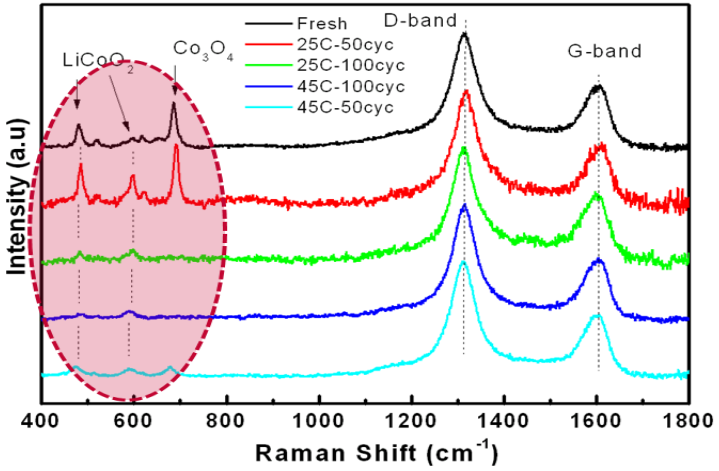


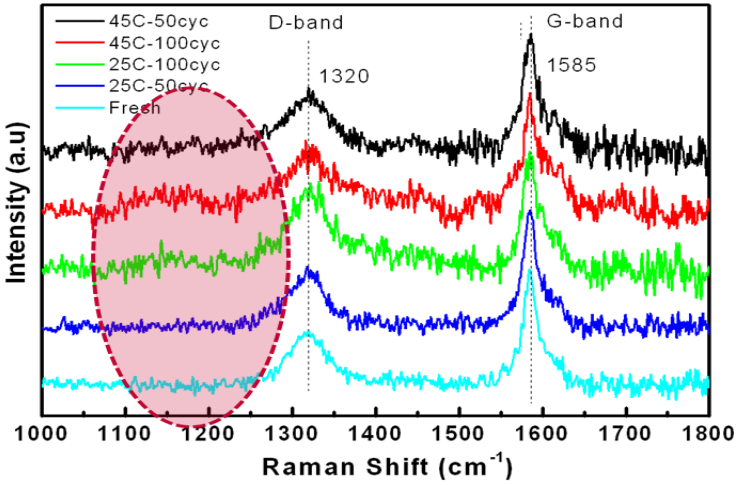


FTIR AND RAMAN ANALYSIS





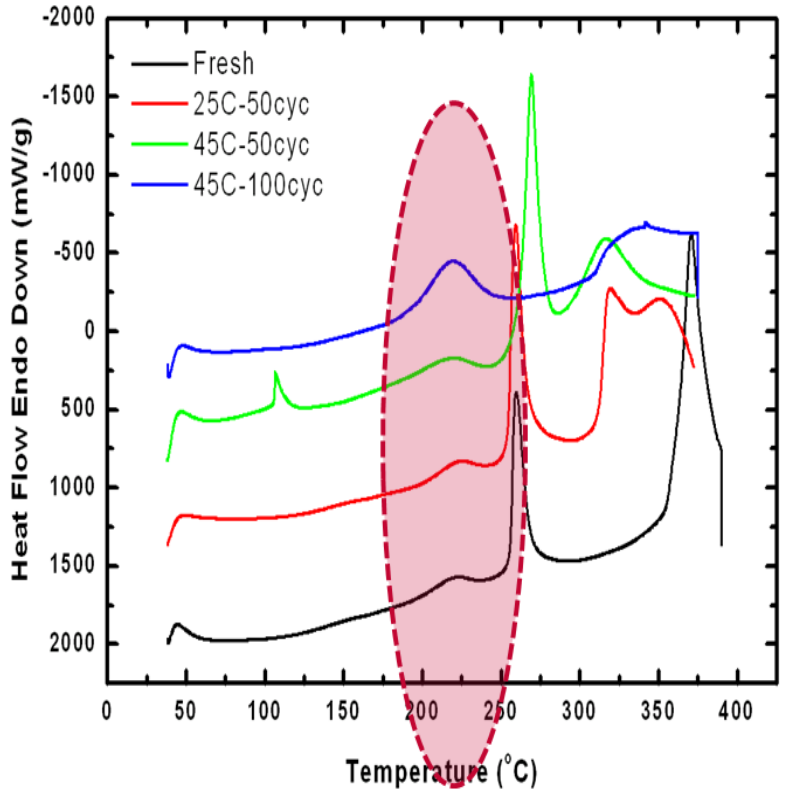




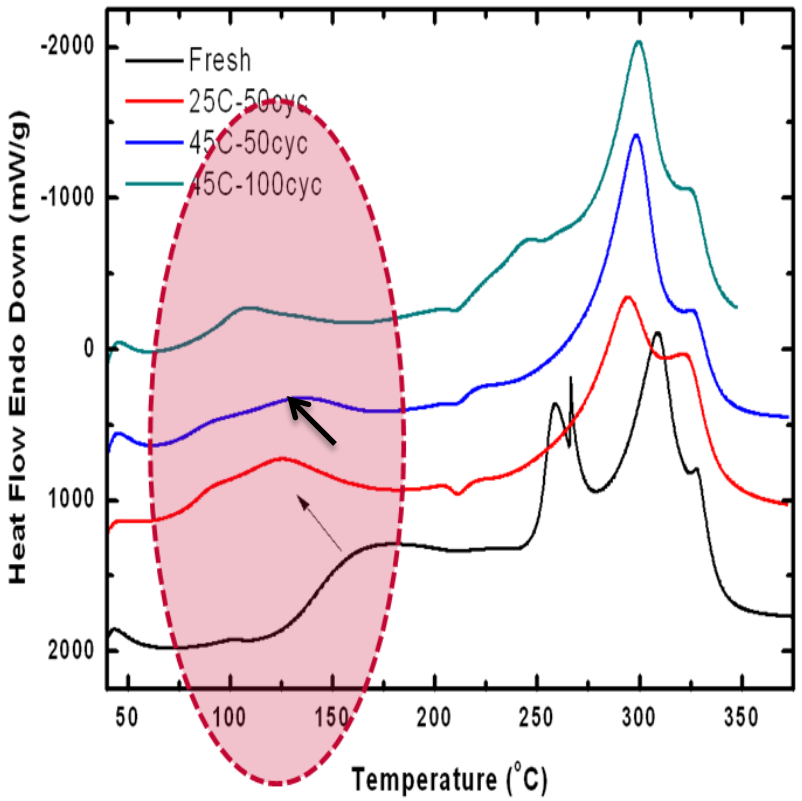
Cathode Material

Anode Material

DSC Analysis



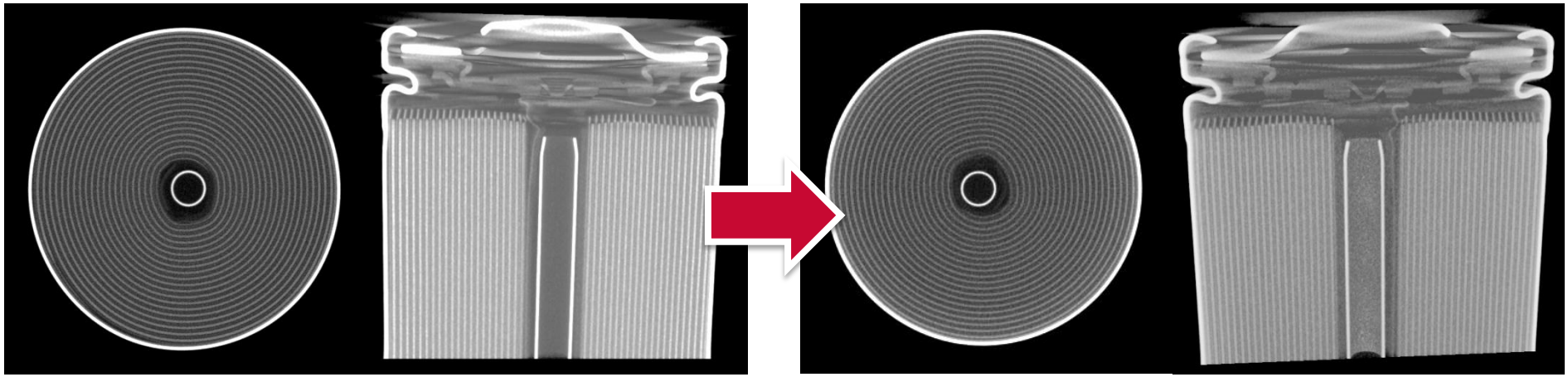
Cathode Material



Anode Material

VIBRATION TEST & CONSTRUCTION INTEGRITY

	Fresh Sample		100 Cycles, 25ºC		100 Cycles, 45ºC		200 Cycles, 45ºC	
	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 45ºC)

AGING EFFECT SUMMARY

	Hypothesis	UL's Investigation on 18650 Cell
Mechanical Integrity	Getting worse on aged battery	No different observed (from vibration test and CT images)
Activity of Material(s)/Component(s)	Aged battery become less active	Aged battery become less active (from IIISC test)
Dendrite Formation & Lithium Plating	Potential issue in aged battery	N/A (can not be observed directly, and no voltage drop observed from Vibration test)
Thermal Stability of Material(s)/Component(s)	Aged battery becomes worse	Aged battery become worse (from DSC data)
Polarization Effect	More apparent on aged battery	More apparent on aged battery (from EIS and overcharging test)
Risk of Electrolyte Leakage	More risk on aged battery	No different observed (from vibration test)
Tolerance to Thermal Abusive Conditions	Aged battery become less tolerant to thermal abuse	Aged battery become less tolerant to thermal abuse (from Hot Box test)

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

ACKNOWLEDGEMENT

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