

# Metallized Plastic Current Collectors

By

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with contributions from and collaborations with

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**Joe Turner and Gray Pieve/Coulometrics, Chattanooga, TN USA**

**Brian Morin & Carl Hu/SoteriaBIG, Greenville, SC USA**

**Advanced Automotive Battery Conference**

**San Diego, CA**

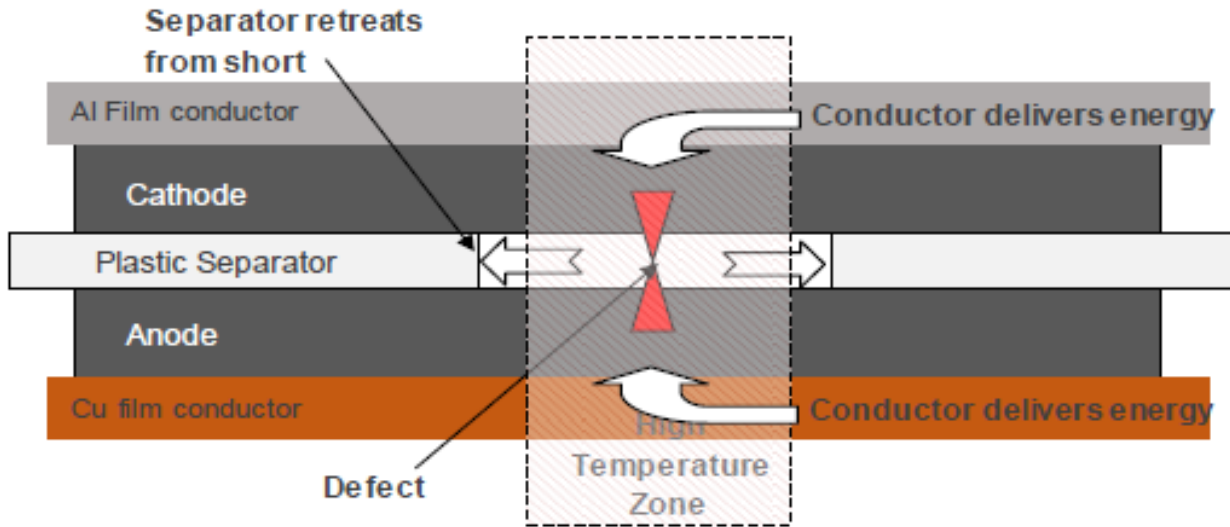
**24-27 June 2019**



# Outline

- Metallized plastic current collectors in prototype 18650 cells
  - Background: Why is NASA interested?
  - 1<sup>st</sup> 18650 cell build – polypropylene separator
  - Test plan
  - Test results at Coulometrics and at ESRF
  - CT images
  - X-ray Videography
  - Further testing at JSC
  - Preliminary findings
  - 2<sup>nd</sup> 18650 cell build – Dreamweaver separator
  - Preliminary test results at Coulometrics and at DLS
  - Preliminary findings
- Future work

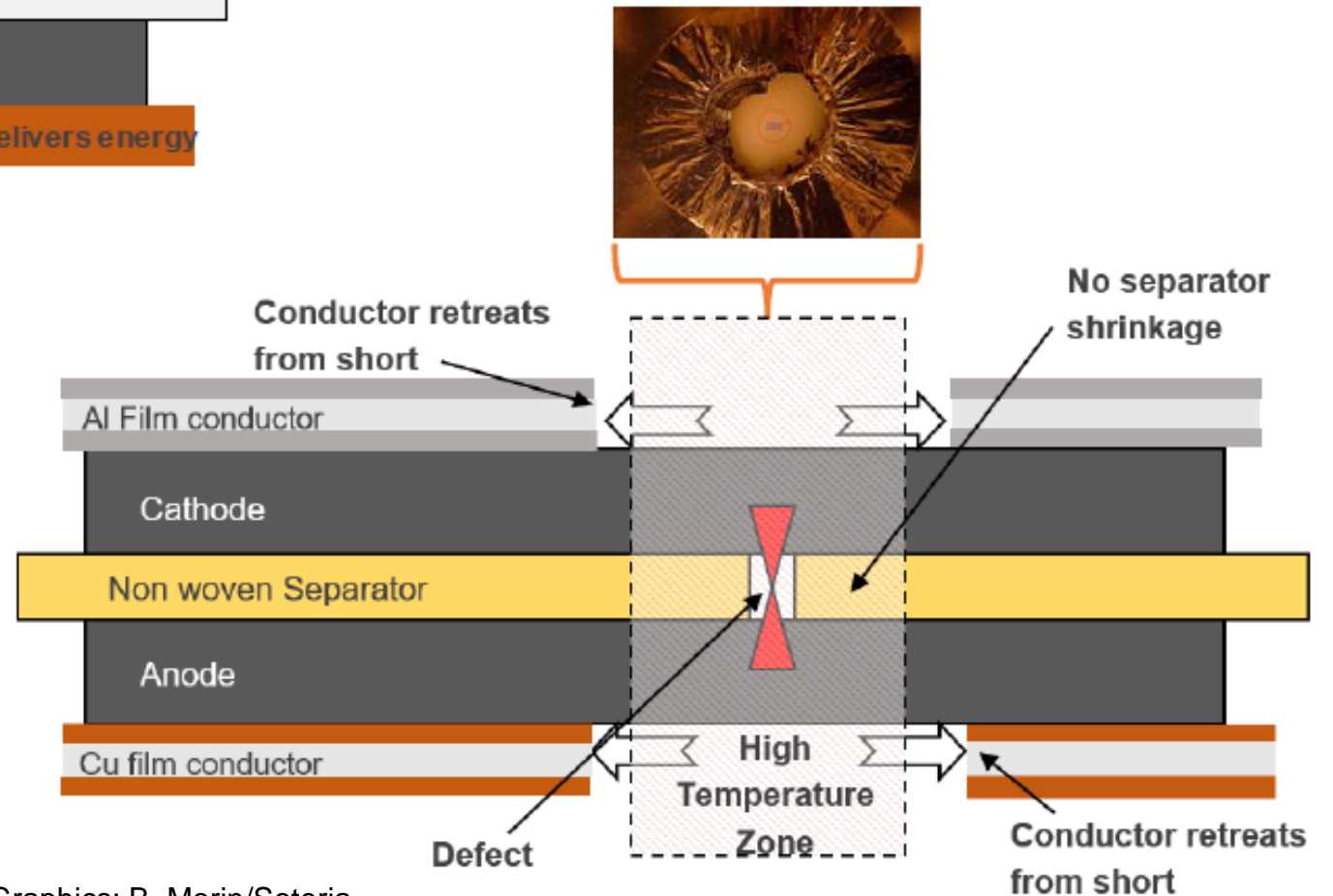
# Theory of Metallized Plastic Current Collectors



- Plastic substrate of current collector thermally breaks down and isolates the electrochemically active materials from the defect within milliseconds

- Internal short defect is fed rapidly through solid metal (Al, Cu) film current collectors
- Polymer separator thermally breakdowns and shrinks away creating higher internal short risk between anode and cathode

Soteria Battery Innovation Group

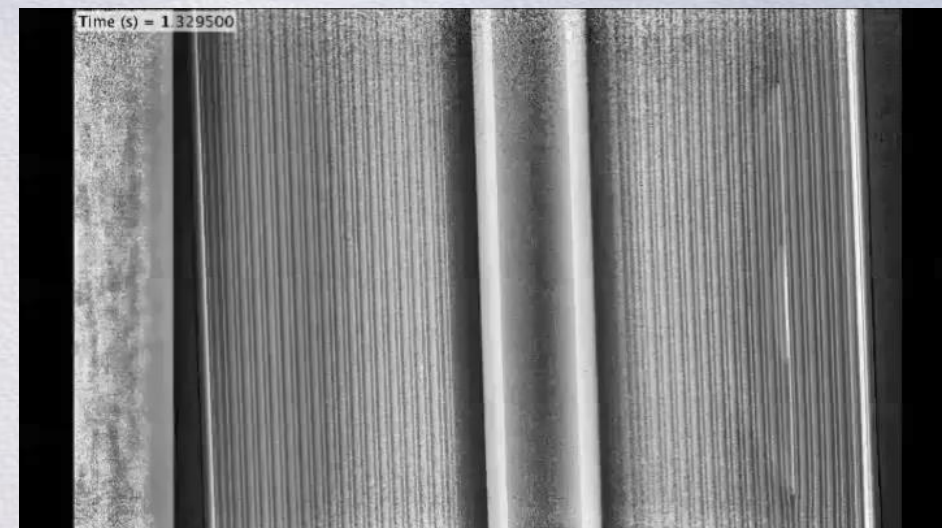
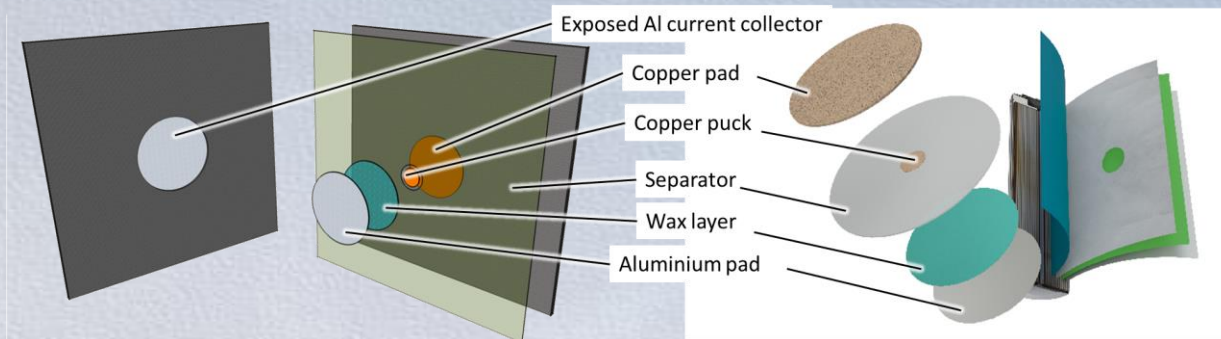


Graphics: B. Morin/Soteria



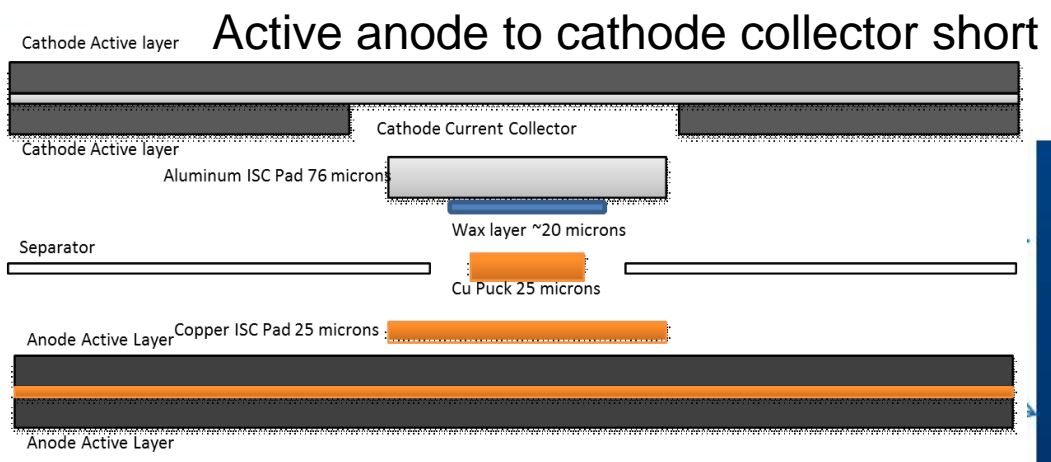
# Why Not Just Let Industry Mature This Technology?

- NASA/NREL is uniquely positioned to help Soteria quickly mature their innovation
  - Internal short tolerance
    - Our patented internal short circuit device verifying tolerance against
      - Short circuit type and location
      - More relevant field failure than nail penetration
  - Understanding how and why it works
    - Our SAA with UCL gives us access to European Synchrotrons with ultra high speed X-ray videography capable of giving us unprecedented insight into mechanism of the innovation
- NASA needs much higher performing batteries that are safe
  - Reference the Webinar we gave with UCL and NREL on 30 Jan 2019
  - <https://www.soteriabig.com/medianews.html>

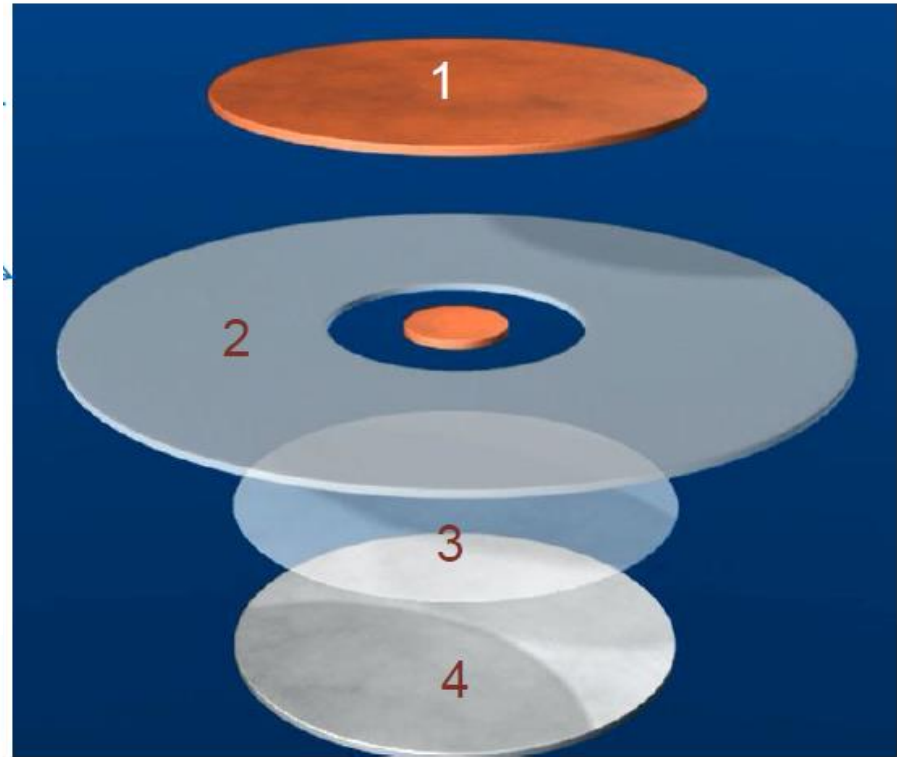




# NREL/NASA Cell Internal Short Circuit Device

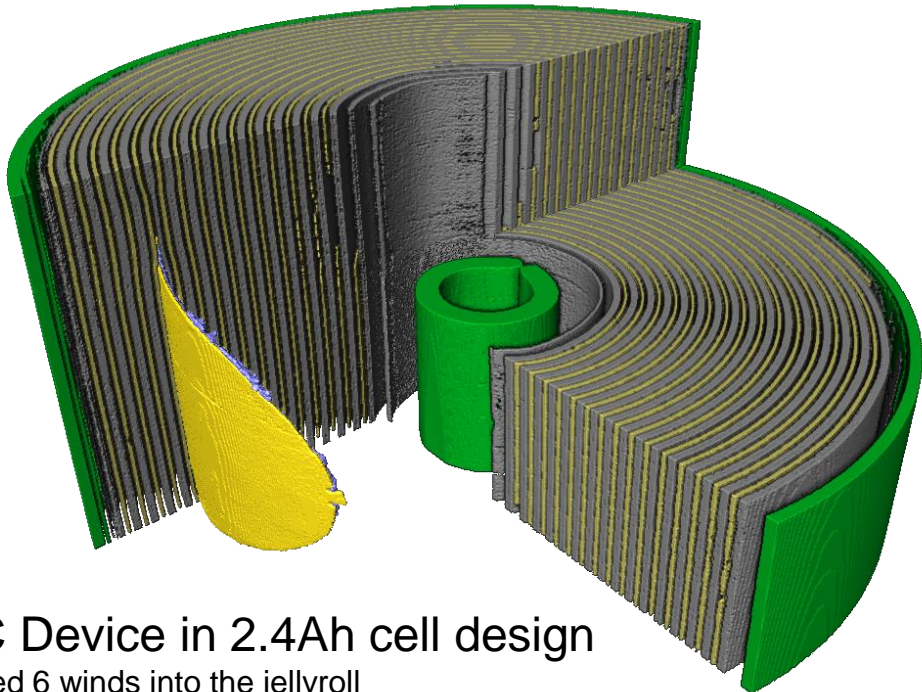


Exclusive Licensee, March 2018



Graphic credits: NREL

- Top to Bottom:
1. Copper Pad
  2. Battery Separator with Copper Puck
  3. Wax – Phase Change Material
  4. Aluminum Pad



ISC Device in 2.4Ah cell design  
Placed 6 winds into the jellyroll

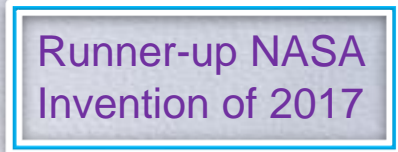
5 mm Tomography credits: University College of London

- 2010 Inventors:
- Matthew Keyser, Dirk Long, and Ahmad Pesaran at NREL
  - Eric Darcy at NASA

US Patent # 9,142,829 issued in 2015

Thin (10-20  $\mu\text{m}$ ) wax layer is spin coated on Al foil pad

Wax formulation used melts  $\sim 57^\circ\text{C}$

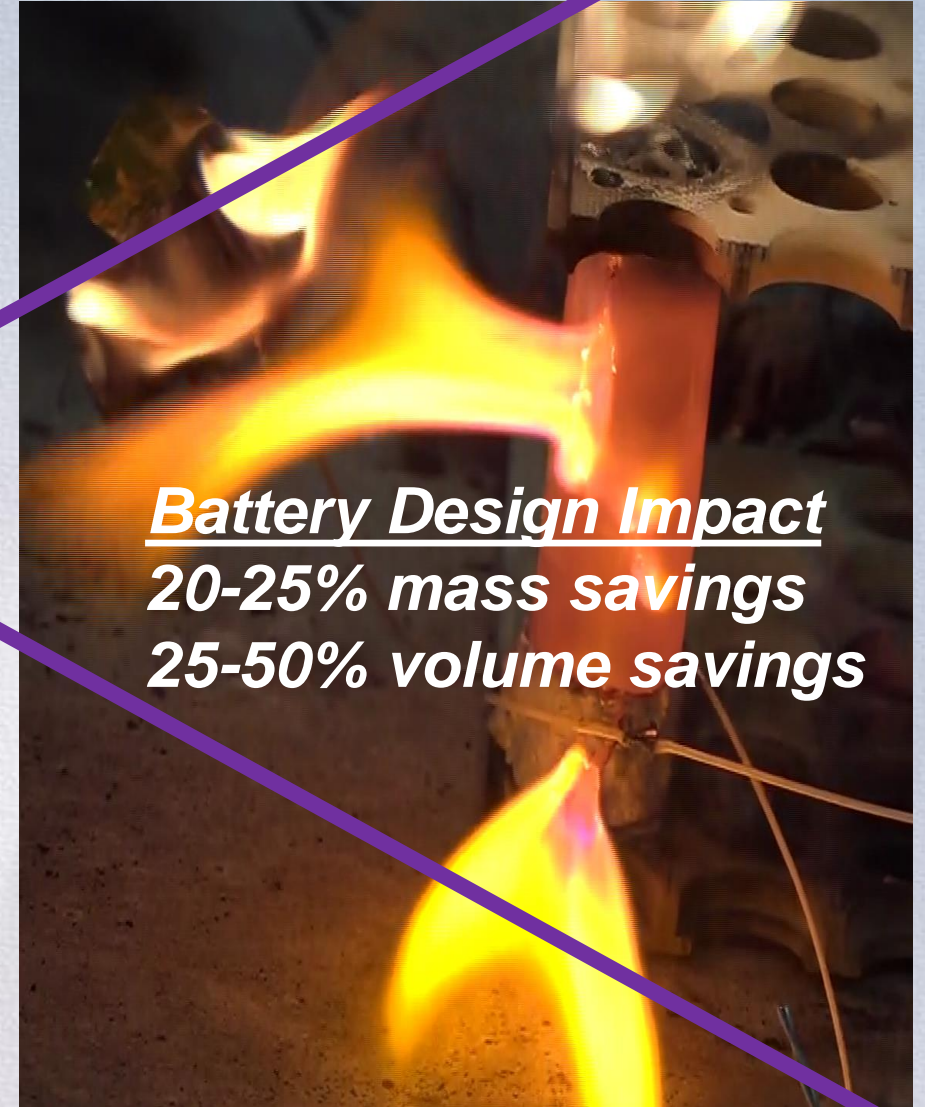


2016 Award Winner



# 5 Battery Design Guidelines for Reducing Hazard Severity from a Single Cell TR

- **Reduce risk of cell can side wall breaches**
  - Without structural support most high energy density (>660 Wh/L) designs are very likely to experience side wall breaching during TR
  - Battery should minimize constrictions on cell TR pressure relief
- **Provide adequate cell spacing and heat rejection**
  - Direct contact between cells nearly assures propagation
  - Spacing required is inversely proportional to effectiveness of heat dissipation path
- **Individually fuse parallel cells**
  - TR cell becomes an external short to adjacent parallel cells and heats them up
- **Protect the adjacent cells from the hot TR cell ejecta (solids, liquids, and gases)**
  - TR ejecta is electrically conductive and can cause circulating currents
- **Prevent flames and sparks from exiting the battery enclosure**
  - Provide tortuous path for the TR ejecta before hitting battery vent ports equipped flame arresting screens





# Plastic Collector Evaluation Plan

- Coulometrics (Chattanooga, TN) made 8 groups of prototype 18650 cells using a 2.0Ah Gr/NMC cell design with polypropylene separator
  - Group N01 with Al coated Soteria collector (qty 12)
  - Group N02 with Al coated Soteria collector and ISC device (qty 24)
  - Group N03 with Cu coated Soteria collector (qty 12)
  - Group N04 with Cu coated Soteria collector and ISC device (qty 24)
  - Group N05 with Al and Cu coated Soteria collectors (qty 12)
  - Group N06 with Al and Cu coated Soteria collectors and ISC device (qty 24)
  - Group N07 standard design to be used as control cells (qty 12)
  - Group N08 standard design with ISC device to be used as control cells (qty 12)
- Test Plan
  - Nail penetration and oven testing of 1 cell per group at Coulometrics
  - TR Calorimetry with nail trigger of cells without ISC device combined with X-ray videography at ESRF

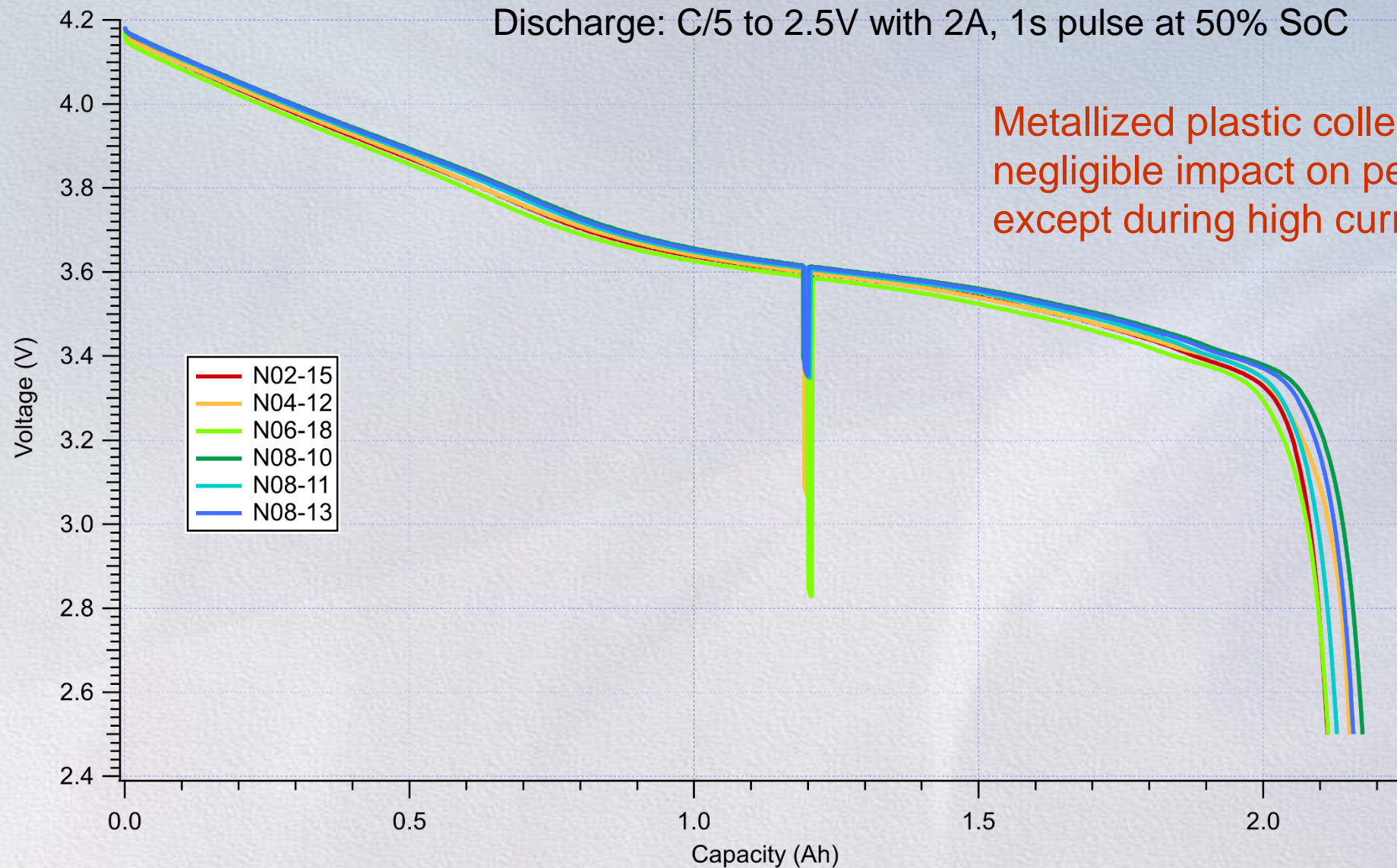




# Coulometric Cell Design Discharge Curve

Charge: C/5 to 4.2V to C/100

Discharge: C/5 to 2.5V with 2A, 1s pulse at 50% SoC





# Preliminary Results on Soteria Collector 18650 Trials

- At Coulometrics

- Nail penetration – All cells (no ISCD) driven into TR
  - Nail driven completely through cell
- Oven testing of cells with ISCD
  - Cell with Al only – no TR, no OCV change
  - Cell with Al & Cu – no TR, temp dip in OCV, no TR
  - Cell with Cu only – TR
  - Standard Cell - TR

- At ESRF

- Nail calorimetry – Mix results (12 cells tested)
  - 5 of 6 cells (without ISCD) with Soteria Al collector tolerated nail pen without TR response and with good OCV retention!
  - All 3 standard and 3 Cu Soteria CC cells driven into TR
  - Nail driven only half way through cell





# Summary of Nail Fractional TR Calorimetry

Run	Cell Design	S/N	Pre-test mass (g)	Post mass (g)	Result	Nail Temp °C
64	Standard collectors	N07-08	41.0541	27.25	TR	384.1
66	Standard collectors	N07-09	41.2351	10.38	TR	846.5
68	Standard collectors	N07-10	41.2962	29.44	TR	Open TC
71	Soteria Al CC only	N01-06	40.5470	29.45	TR	754.7
72	Soteria Al CC only	N01-07	40.5526	40.50	No TR	61.4
73	Soteria Al CC only	N01-08	40.5509	40.61	No TR	40.4
75	Soteria Cu CC only	N03-07	39.3374	21.88	TR	705.7
76	Soteria Cu CC only	N03-09	39.3144	26.44	TR	616.3
77	Soteria Cu CC only	N03-10	39.0459	23.31	TR	707.3 (before opening)
79	Soteria Cu & Al CC	N05-06	39.0257	39.15	No TR	35.3
80	Soteria Cu & Al CC	N05-07	39.1585	38.78	No TR	65.7
81	Soteria Cu & Al CC	N05-09	38.9251	38.68	No TR	66.7

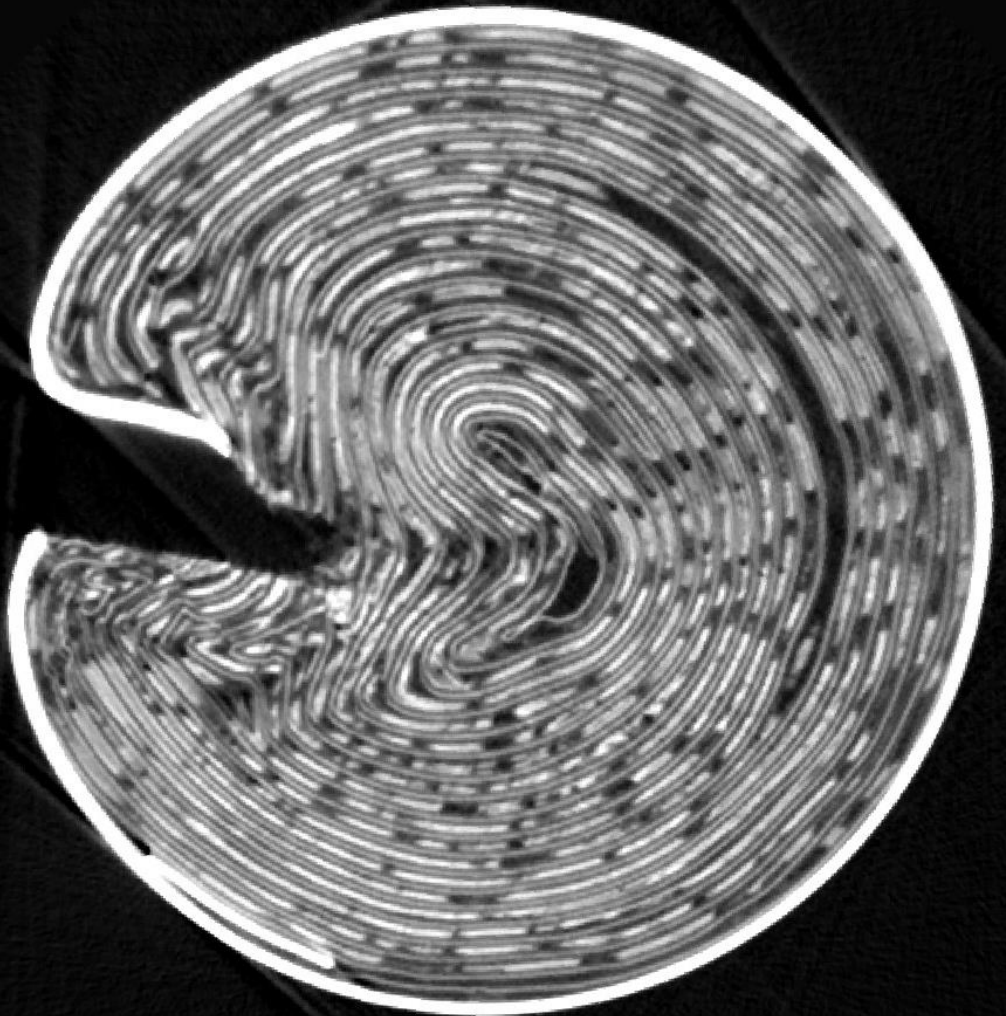
Run 73 – N01-08





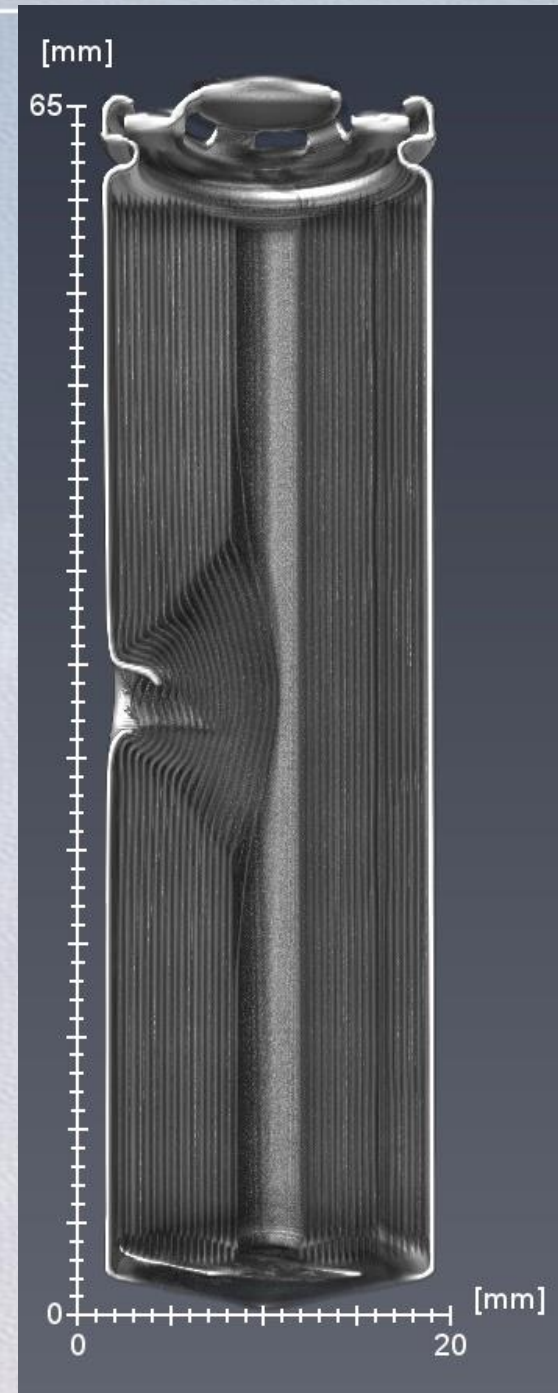
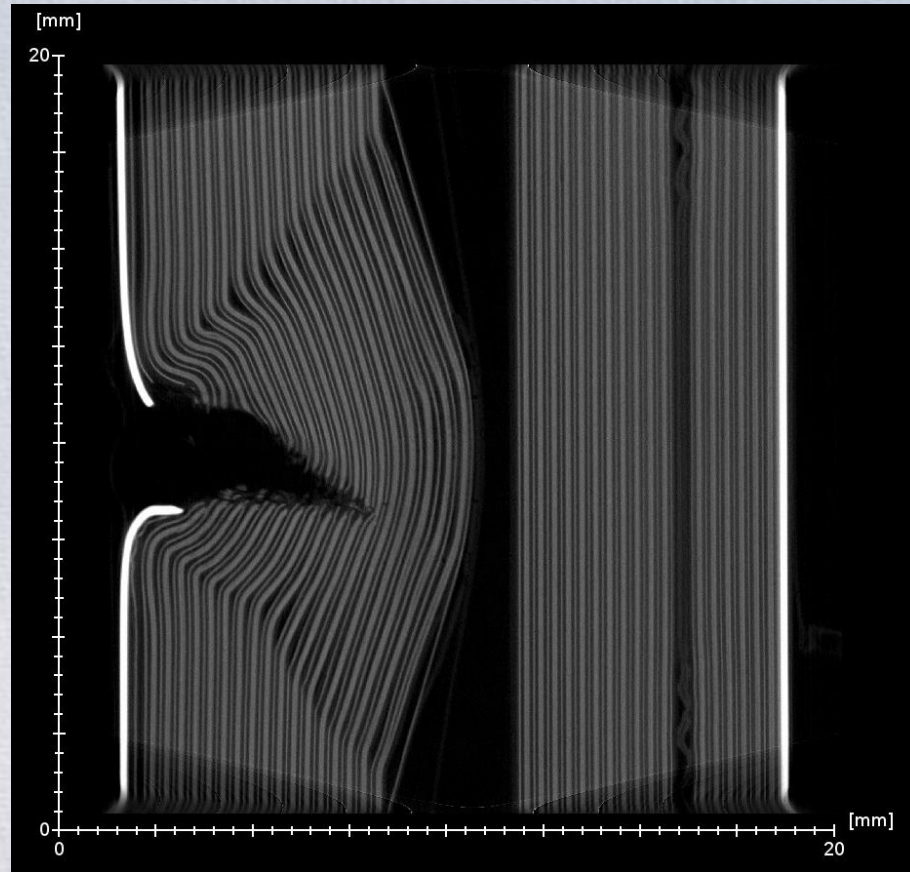
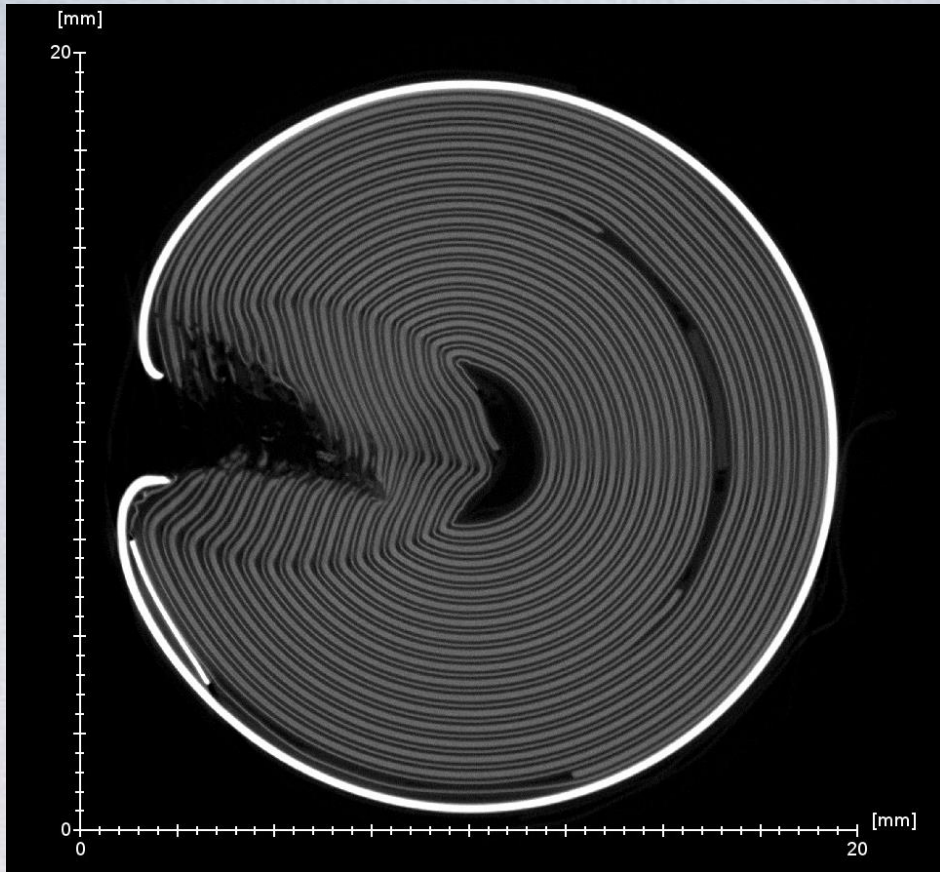
# Run 71 – Soteria AI CC N01-06

Post TR



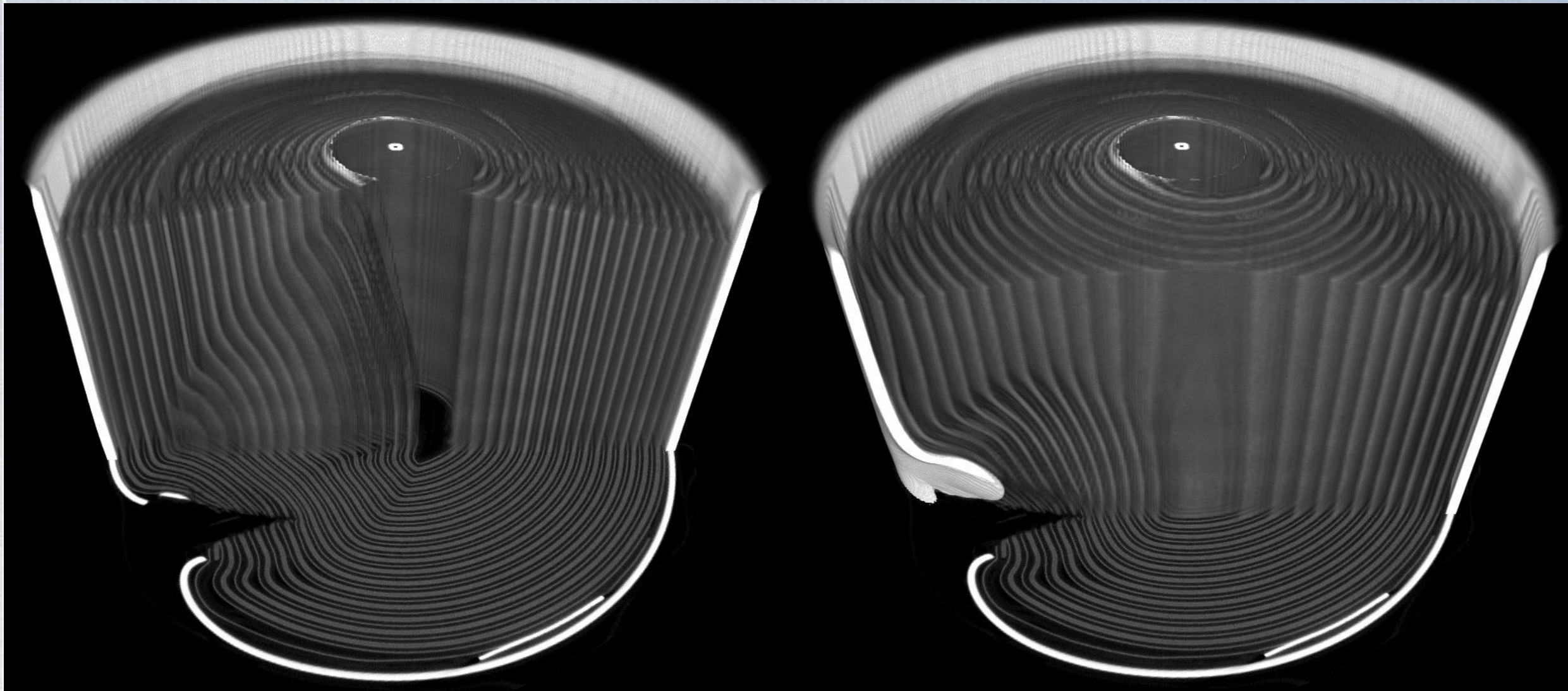


# Run 72 – Soteria Al CC after Nail FTRC N01-07, 4.00V



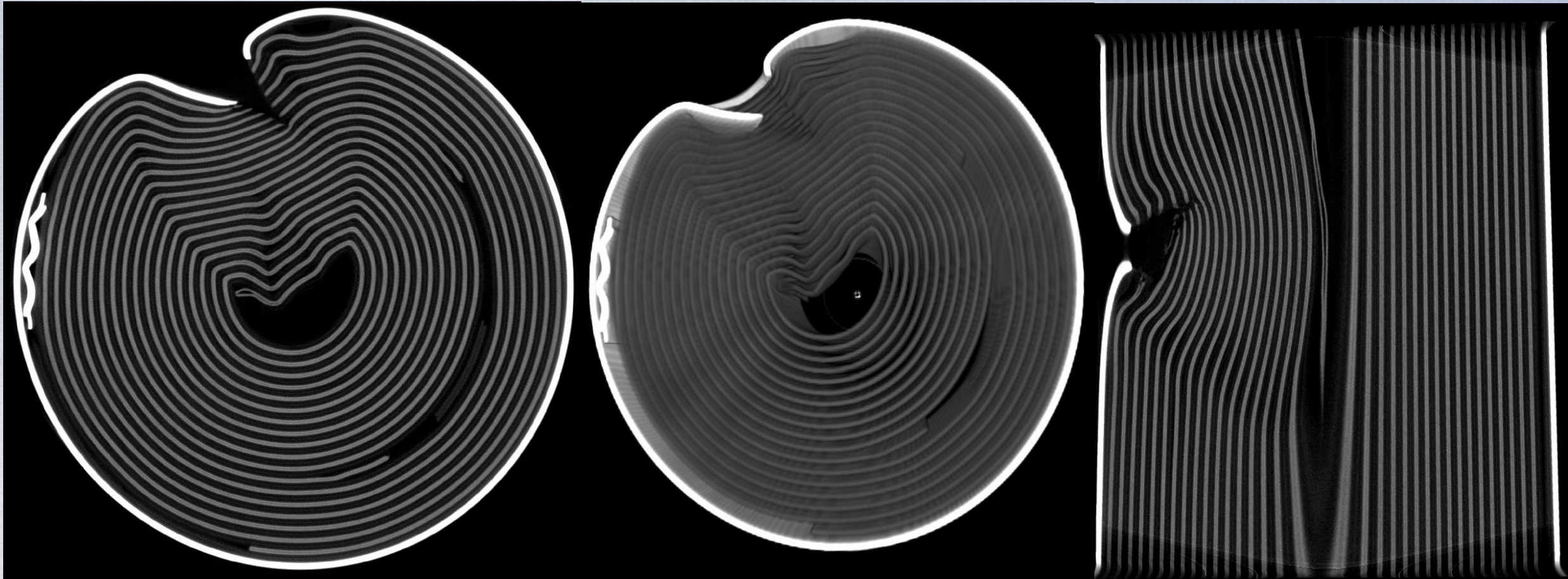


# Run 73 – Soteria AI CC N01-08, 4.07V



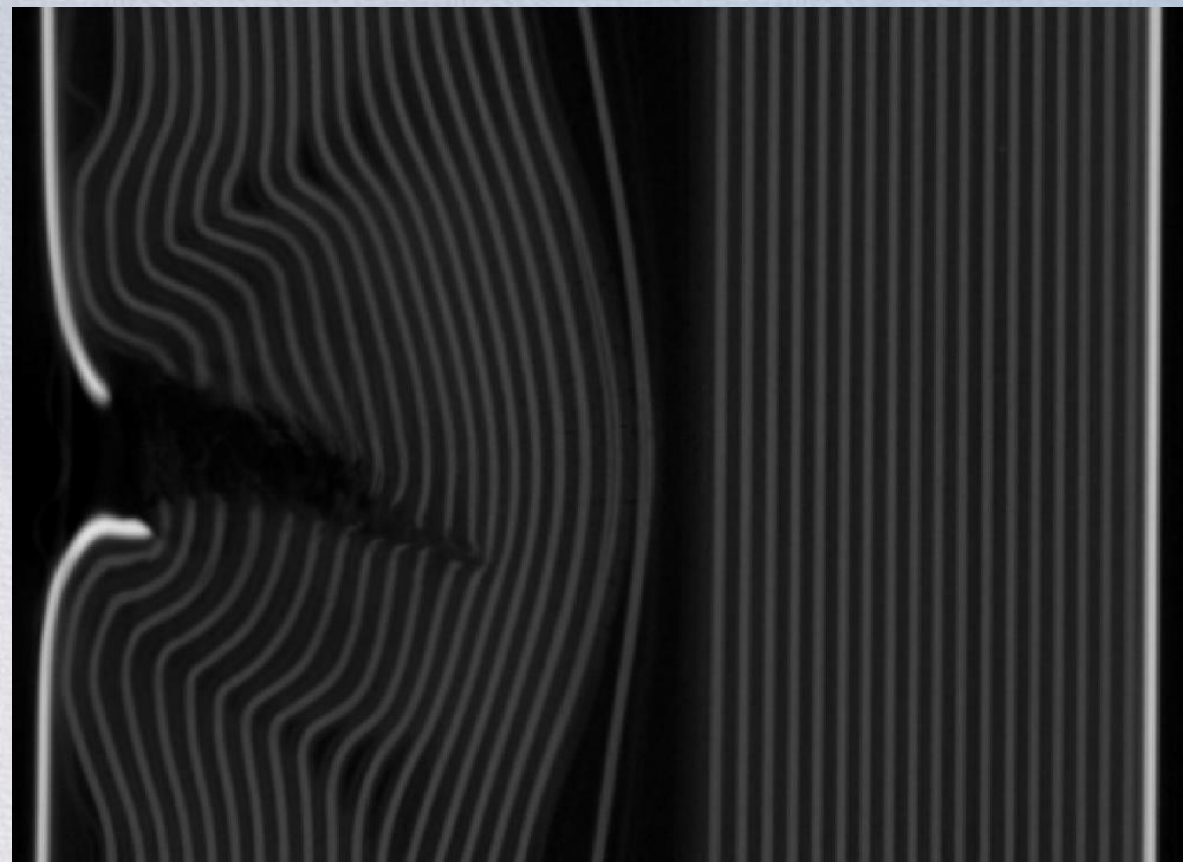
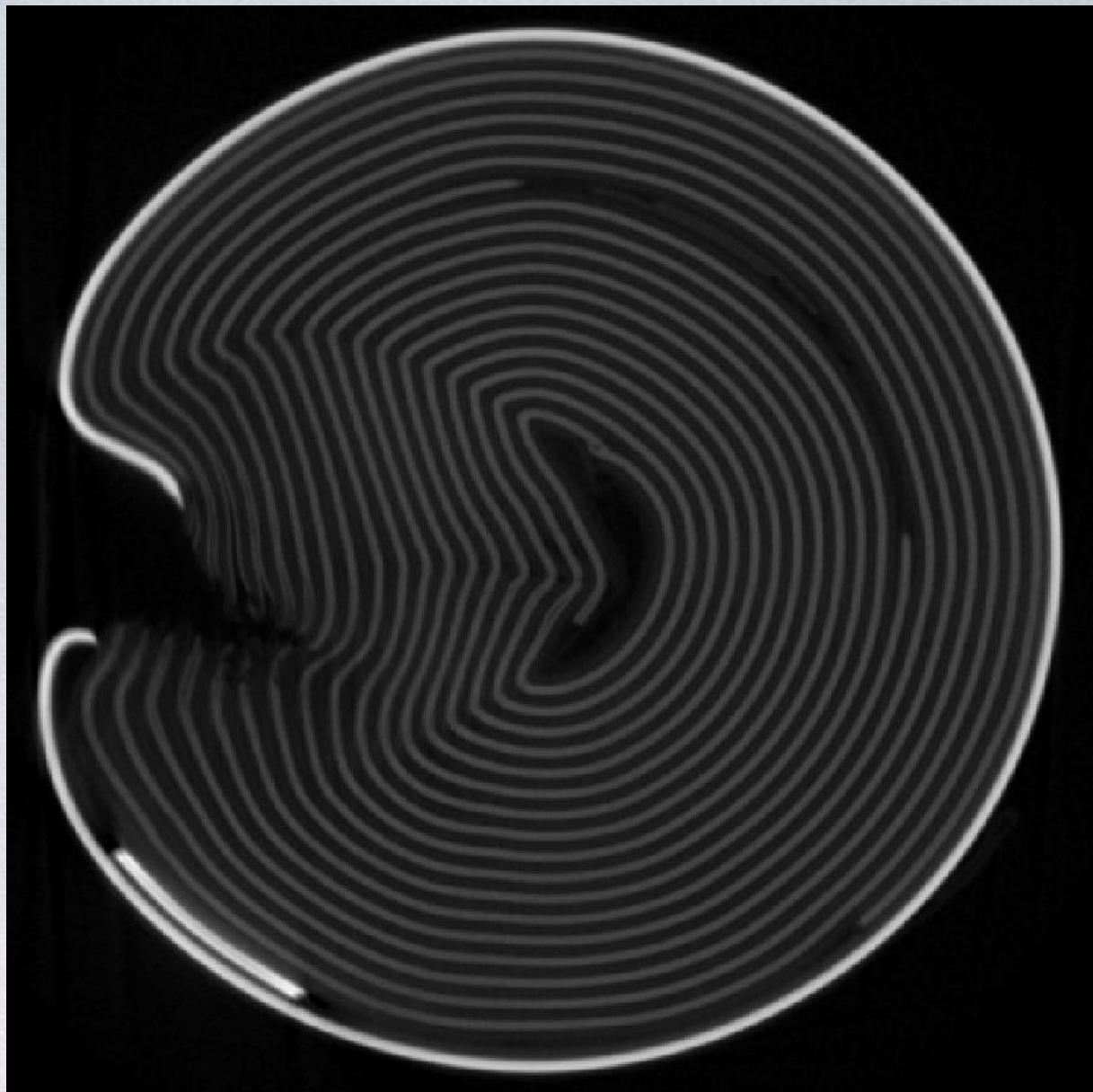


# Run 79 – Soteria Al+Cu CC N05-06, 4.04V



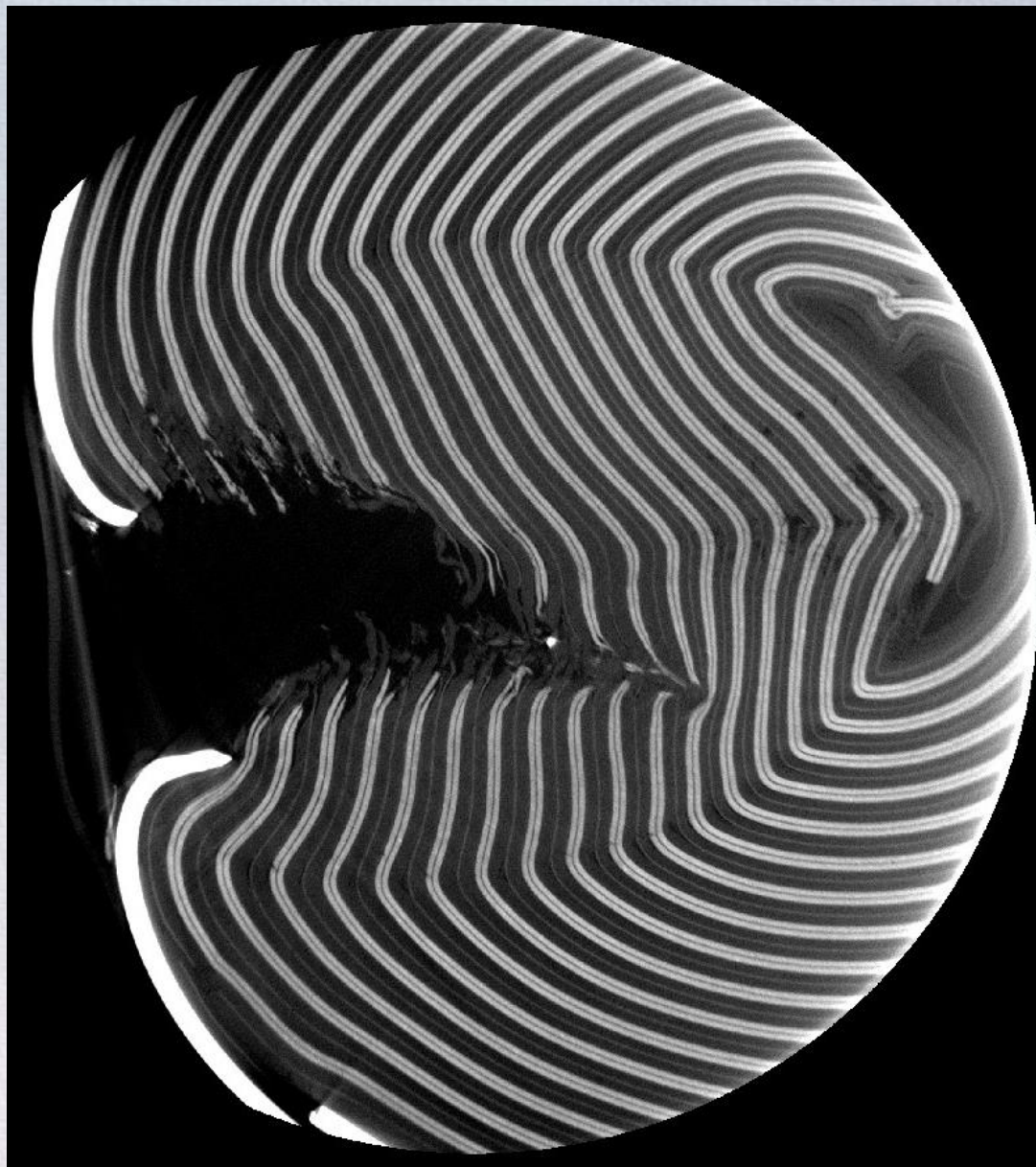


# Run 80 – N05-07 Soteria Al & Cu Collectors





# Run 80 – N05-07 Soteria Al & Cu Collectors (cont.)



- Fine focused CT image with 5.5 micron resolution
  - Both plastic collectors are visible
    - Cathode is bright layer with thin dark line in middle
    - Anode is dark layer with thin brighter line in middle
  - Collector appears missing near nail impingement interface
    - Only active material left dangling
  - Nail impingement causes several additional creases in the JR



# Run 80 – Soteria 18650, Al+Cu CC



Top of the nail

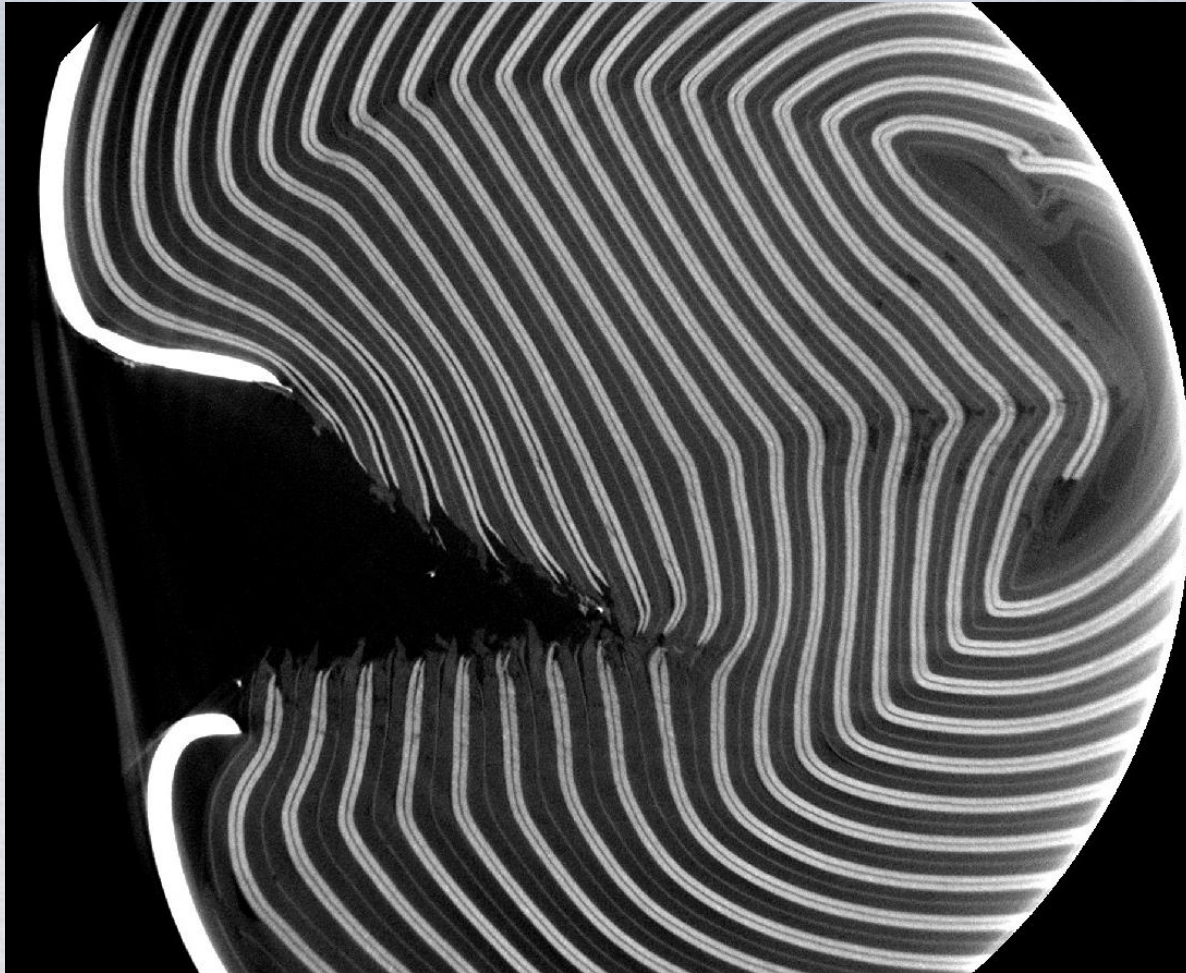


Bottom of the nail

Please note the absence of the current collector between the cathode and anode layers



# Run 80 – Soteria 18650, Al+Cu CC (cont.)



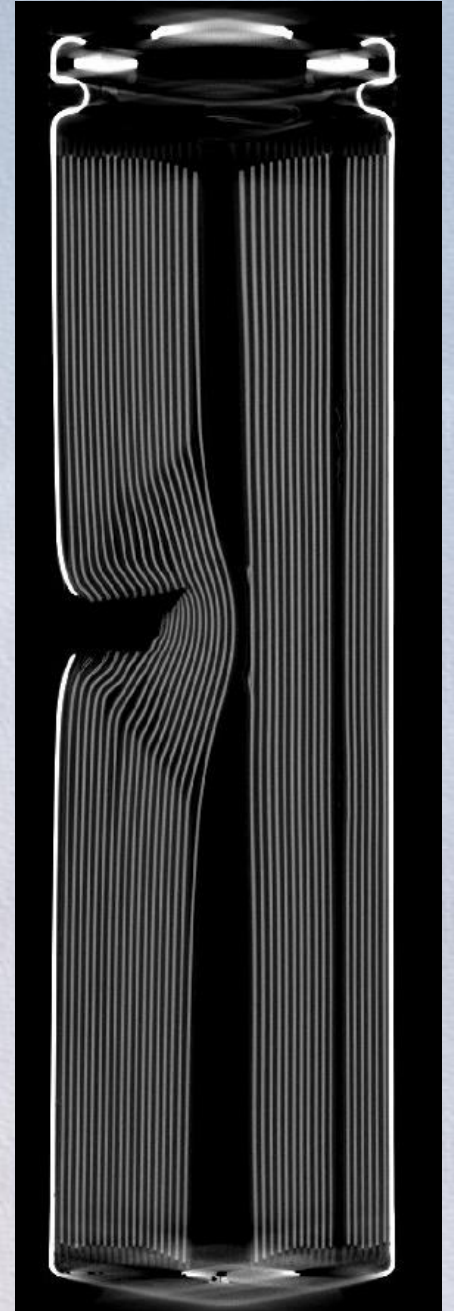
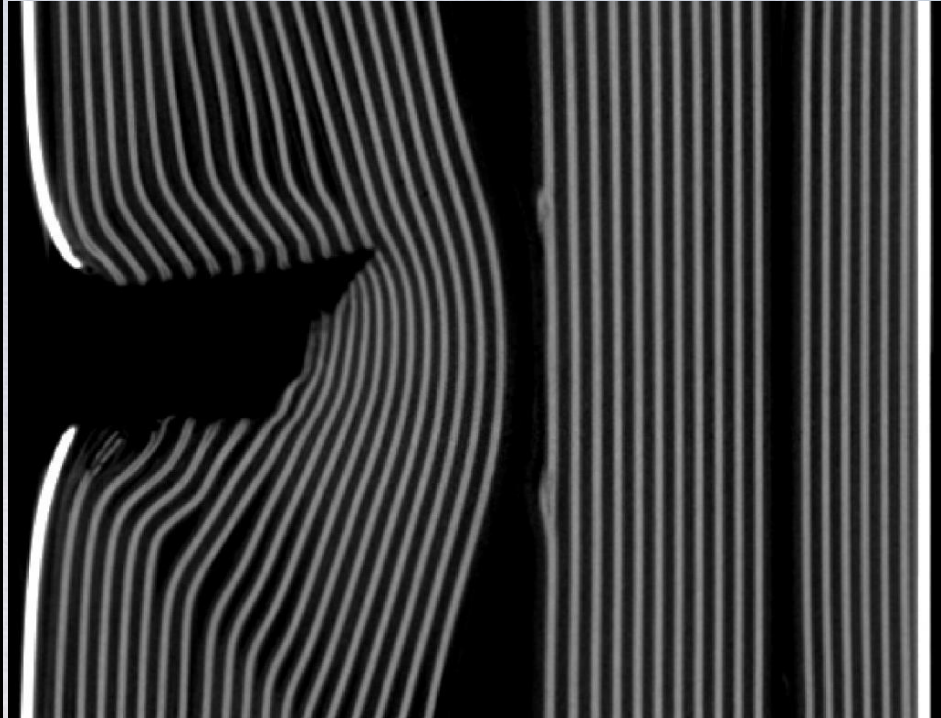
Nail penetration shape



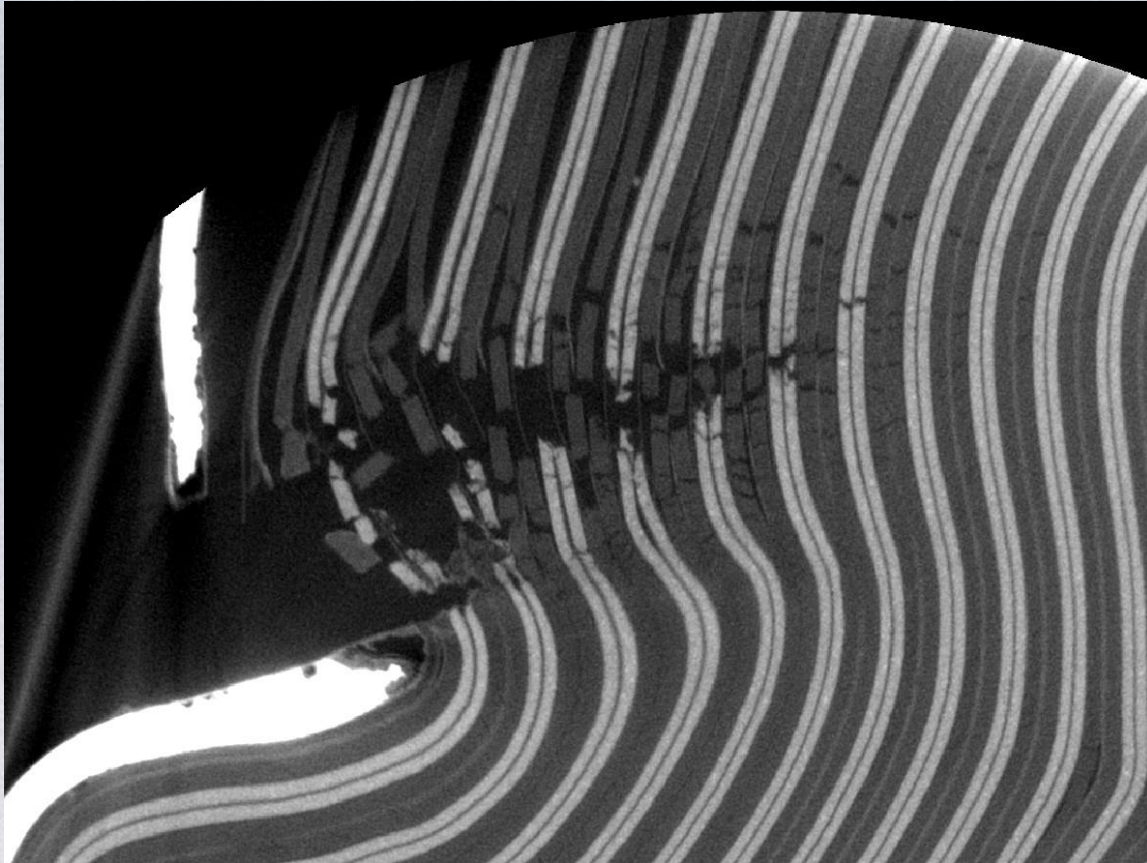
Max penetration depth



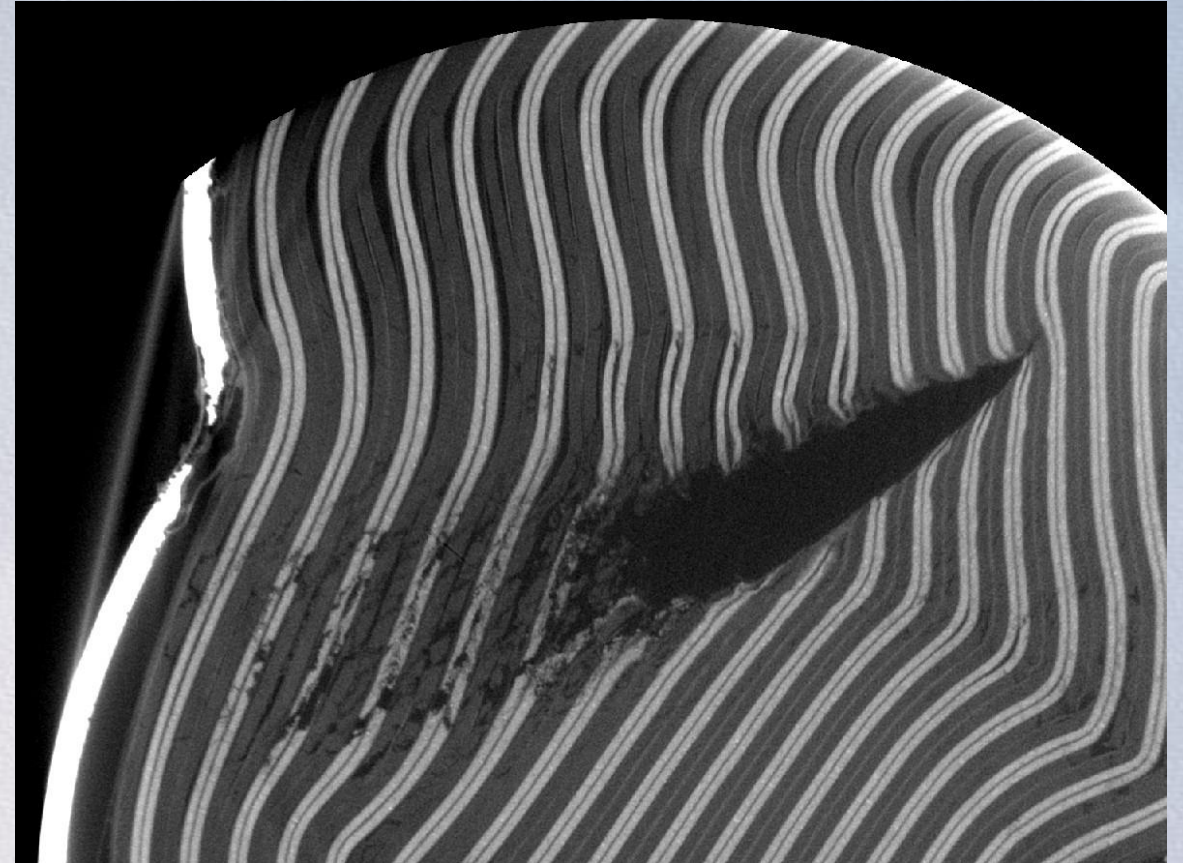
Run 81 – Soteria 18650, Al  
+ Cu CC N05-09







Top of the nail

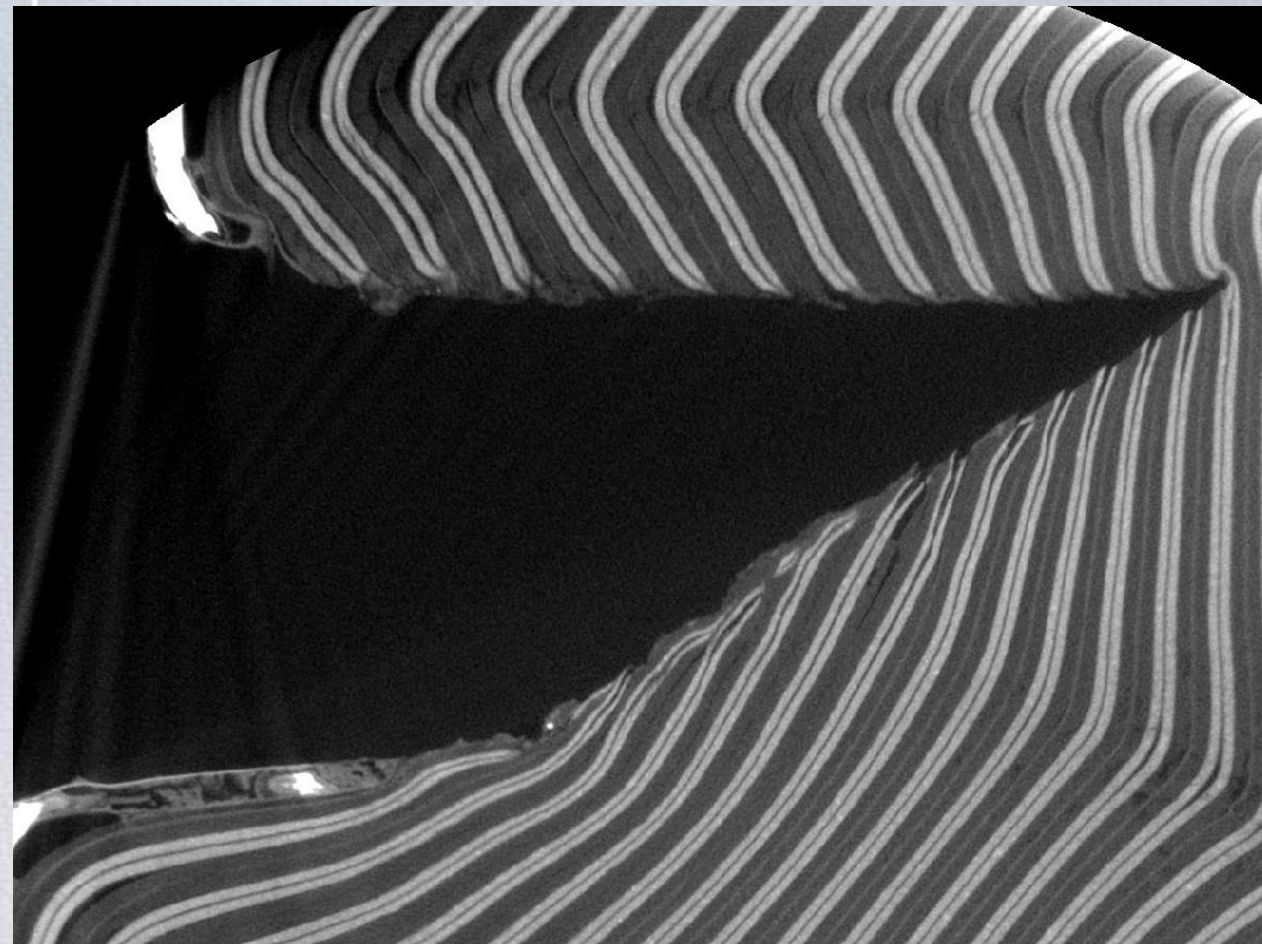


Bottom of the nail

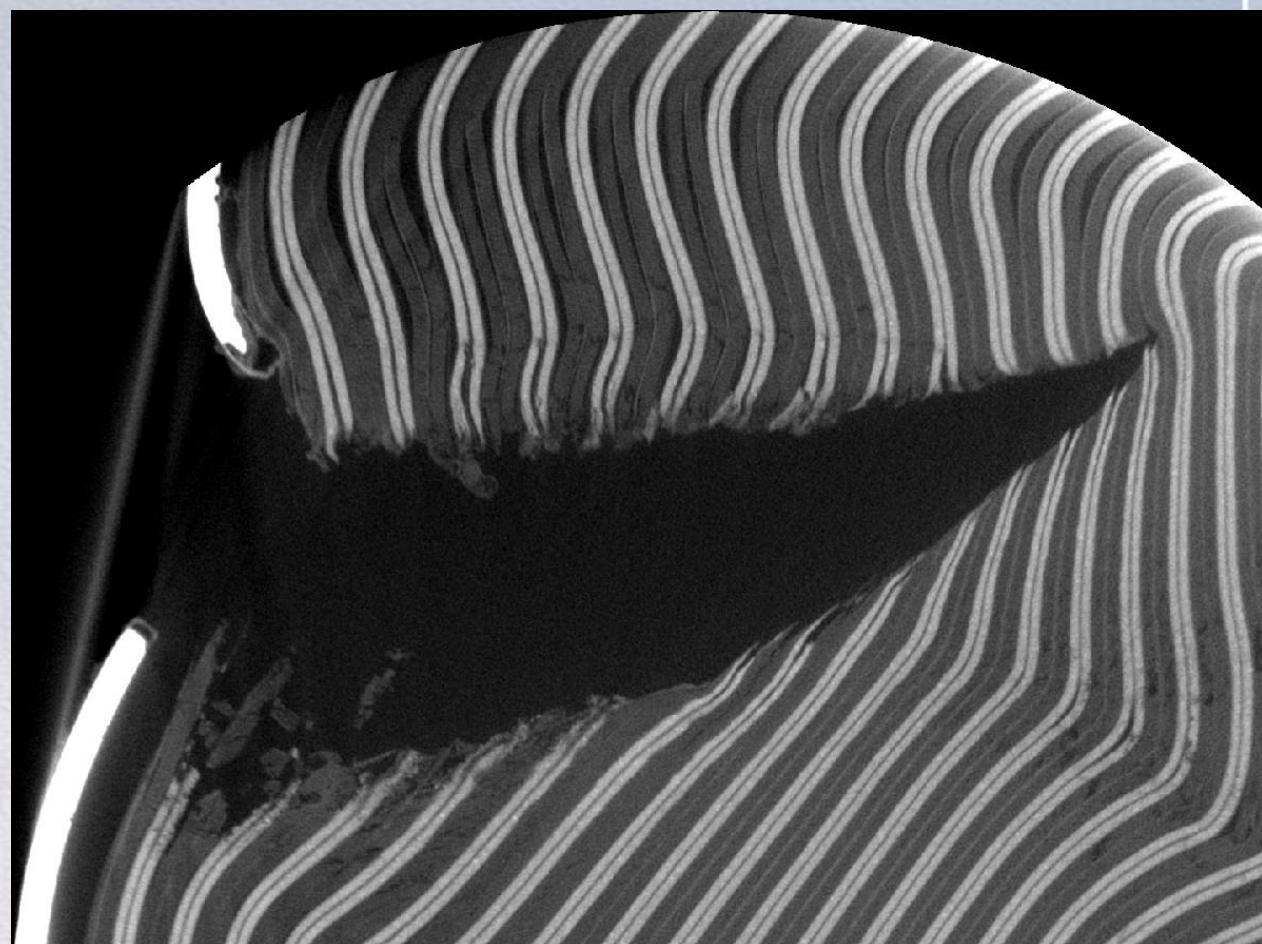
Please note the absence of the current collector between the cathode and anode layers



# Run 81 – Soteria 18650, Al+Cu CC, N05-09



Nail penetration shape



Max penetration depth



# The European Synchrotron (ESRF)





X-ray detector

Exhaust pipes

Calorimeter insulation case

Drill for nail penetration tests

X-ray beam

TC connection box



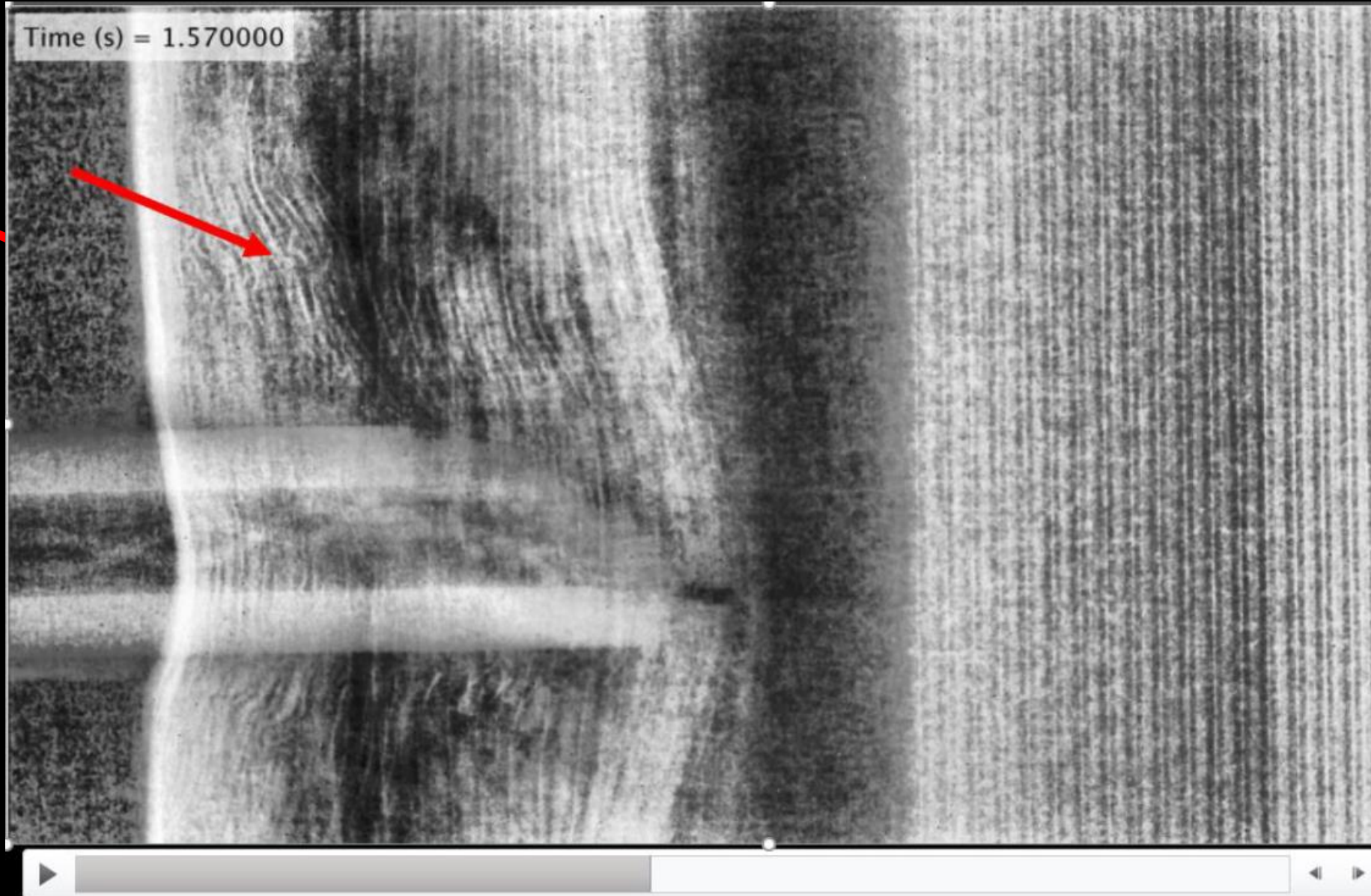


2.1 Ah Cell – 100 % SOC (4.2 V)  
Standard materials  
Without ISC device

# Do polymer collectors help protect against mechanically-induced thermal runaway?

Thermal runaway propagates almost immediately.

Notice the 'spring-back' as the metal CC's split around the nail.



Run 68

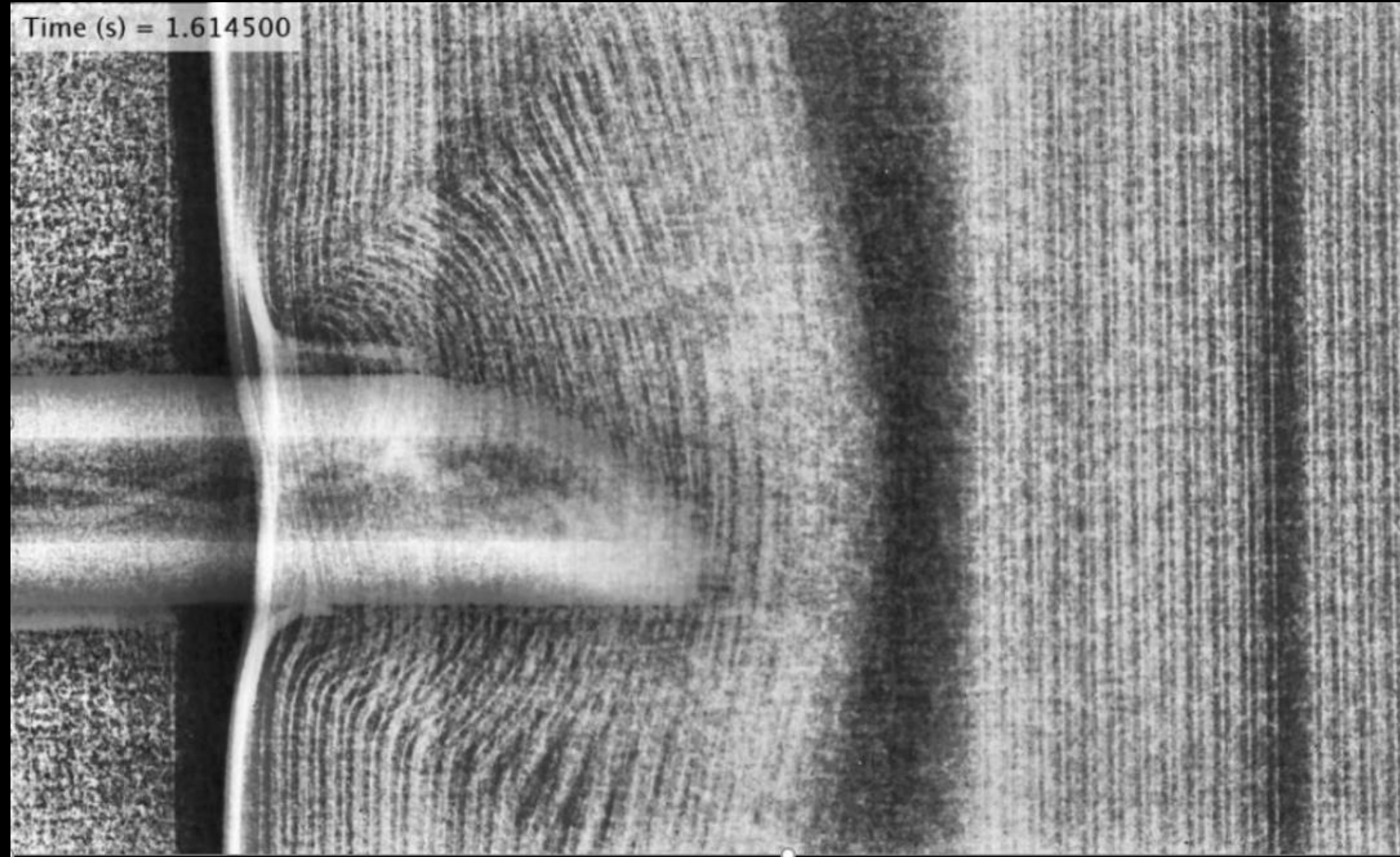


2.1 Ah Cell – 100 % SOC (4.2 V)  
Al coated polymer current collector  
Without ISC device

# Do polymer collectors help protect against mechanically-induced thermal runaway?

No thermal runaway propagation.

Notice that there is no 'spring-back' as the polymer CC travels with the nail.



Run 72



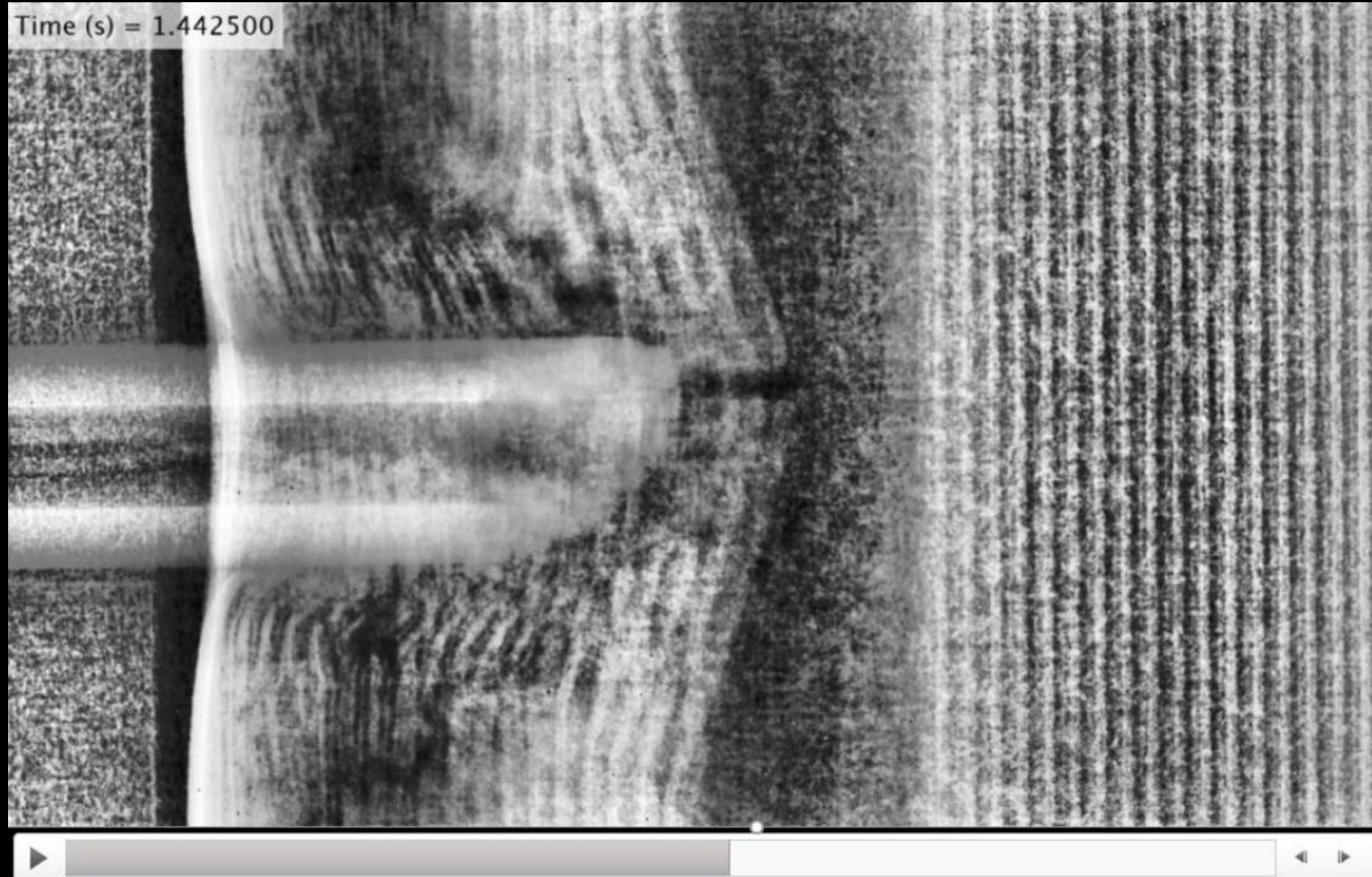
2.1 Ah Cell – 100 % SOC (4.2 V)  
Cu coated polymer current collector (-)  
Without ISC device

Do polymer collectors help protect against  
mechanically-induced thermal runaway?

With an electrically  
conducting nail,  
the negative  
electrode will  
always be  
connected via the  
casing.

Hence, if the (+) is  
not modified,  
shorts will occur.

Thermal runaway  
ensues, despite (-)  
polymer collector.



Run 76

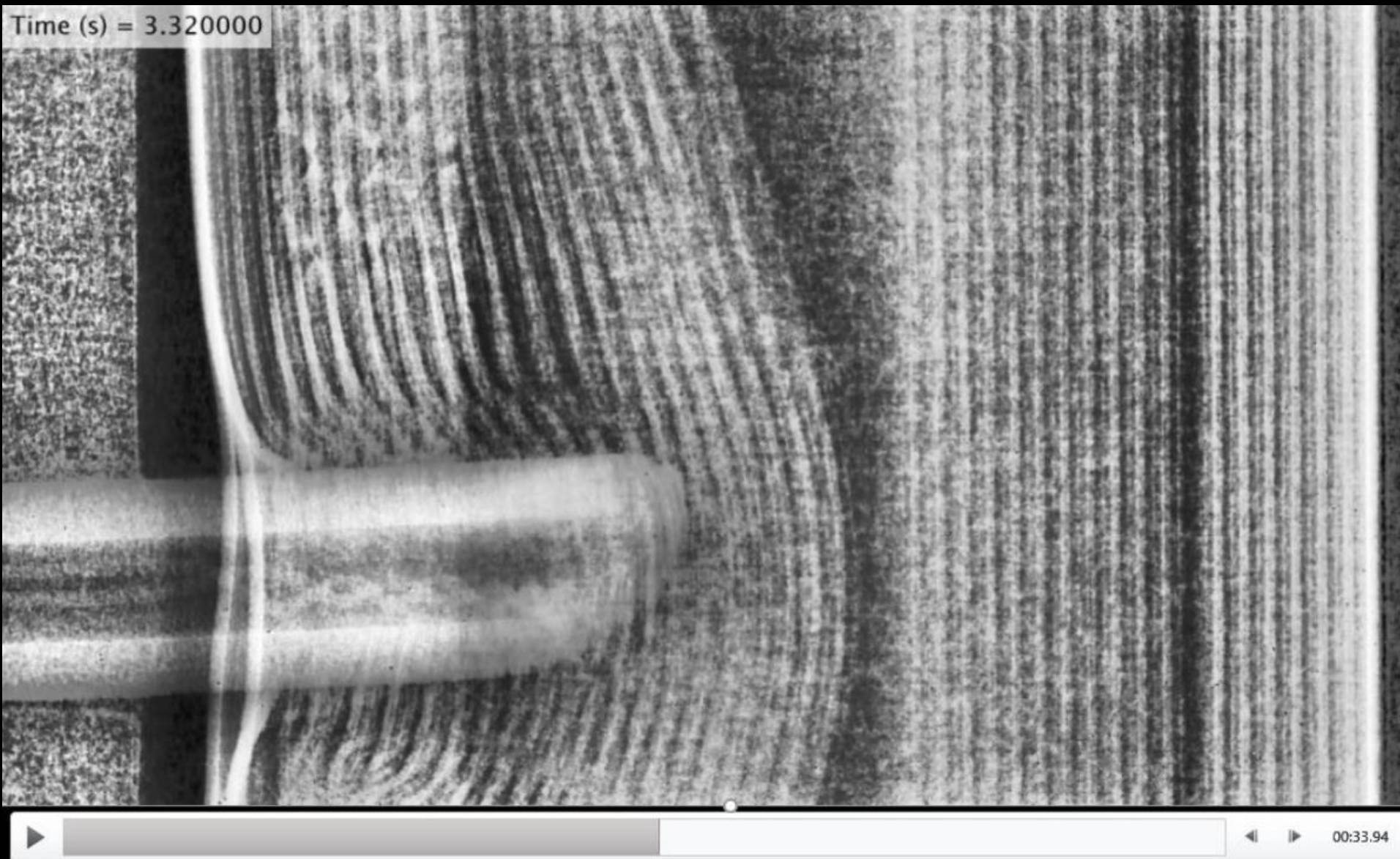


2.1 Ah Cell – 100 % SOC (4.2 V)

Al and Cu coated polymer current collectors (+ & -)

Without ISC device

Do polymer collectors help protect against mechanically-induced thermal runaway?



With Al (+)  
polymer collector,  
the (+) is protected  
and thermal  
runaway is  
prevented.

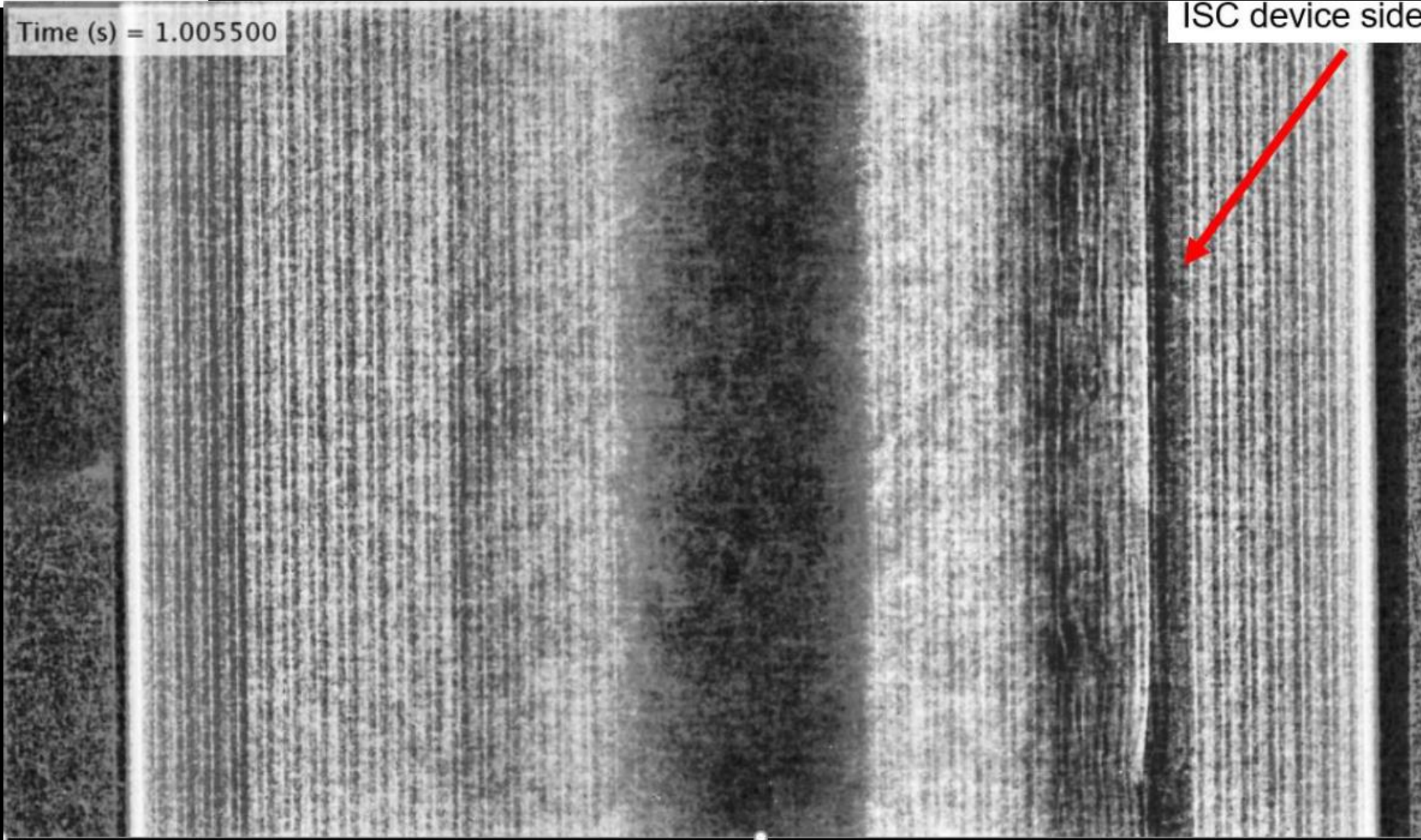
Run 81



2.1 Ah Cell – 100 % SOC (4.2 V)  
Standard materials  
With ISC device

Do polymer collectors help protect against internal  
short-circuit induced thermal runaway?

A short-circuit  
occurs and  
thermal runaway  
ensues.



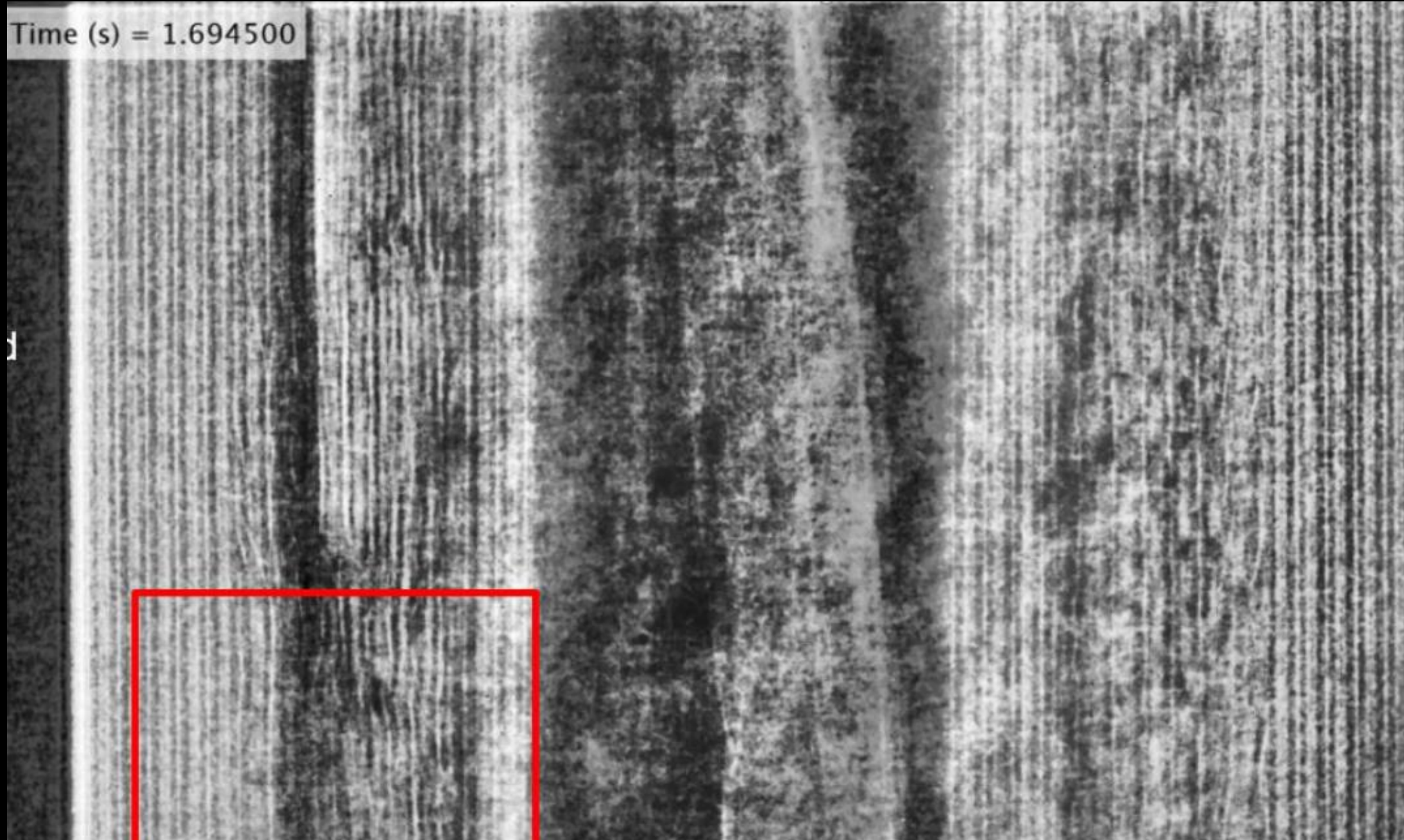
Run 25



2.1 Ah Cell – 100 % SOC (4.2 V)  
Al coated polymer collector (+)  
With ISC device

# Do polymer collectors help protect against internal short-circuit induced thermal runaway?

A short-circuit occurs and there is some delay, and activity, before thermal runaway ensues.

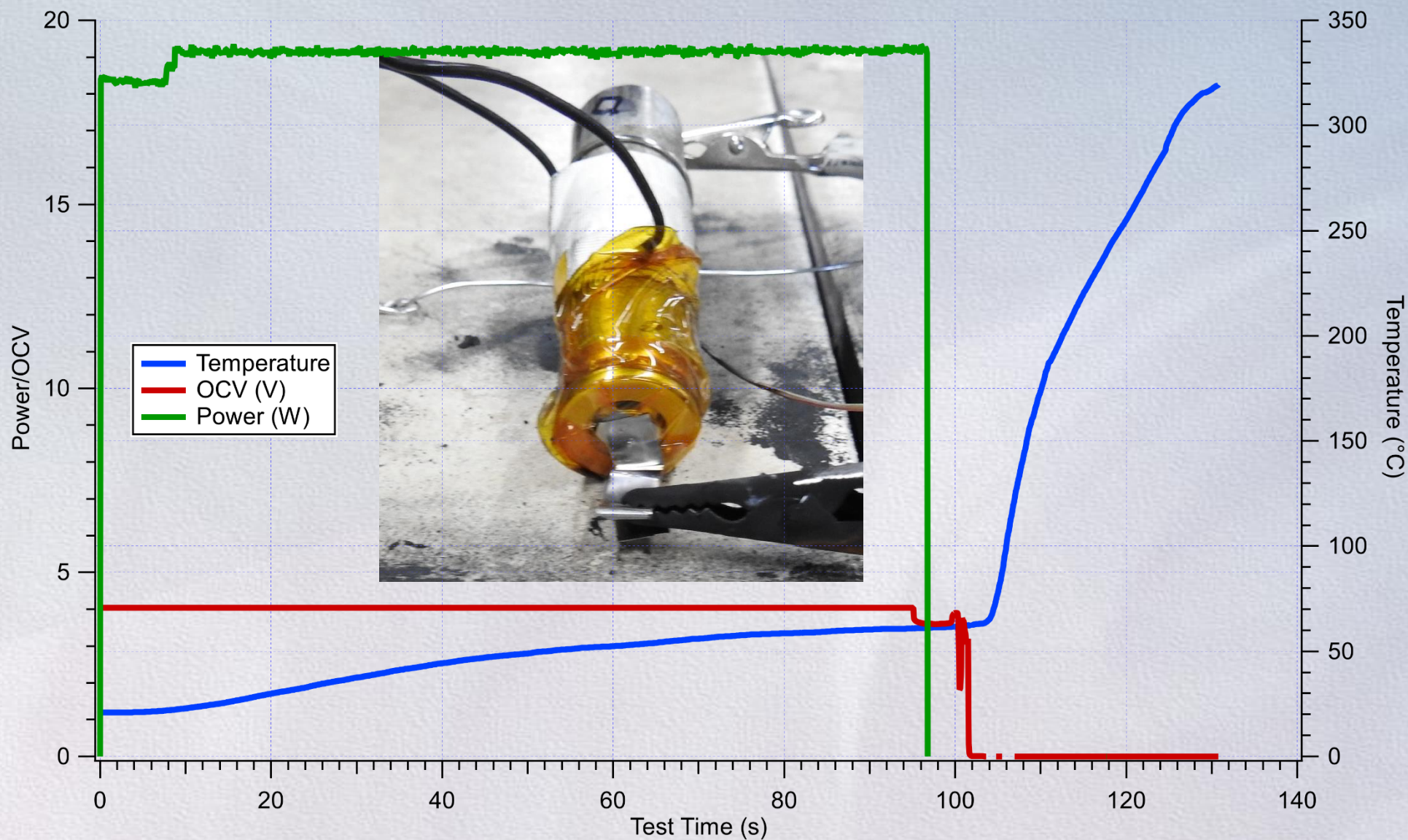


Run 26



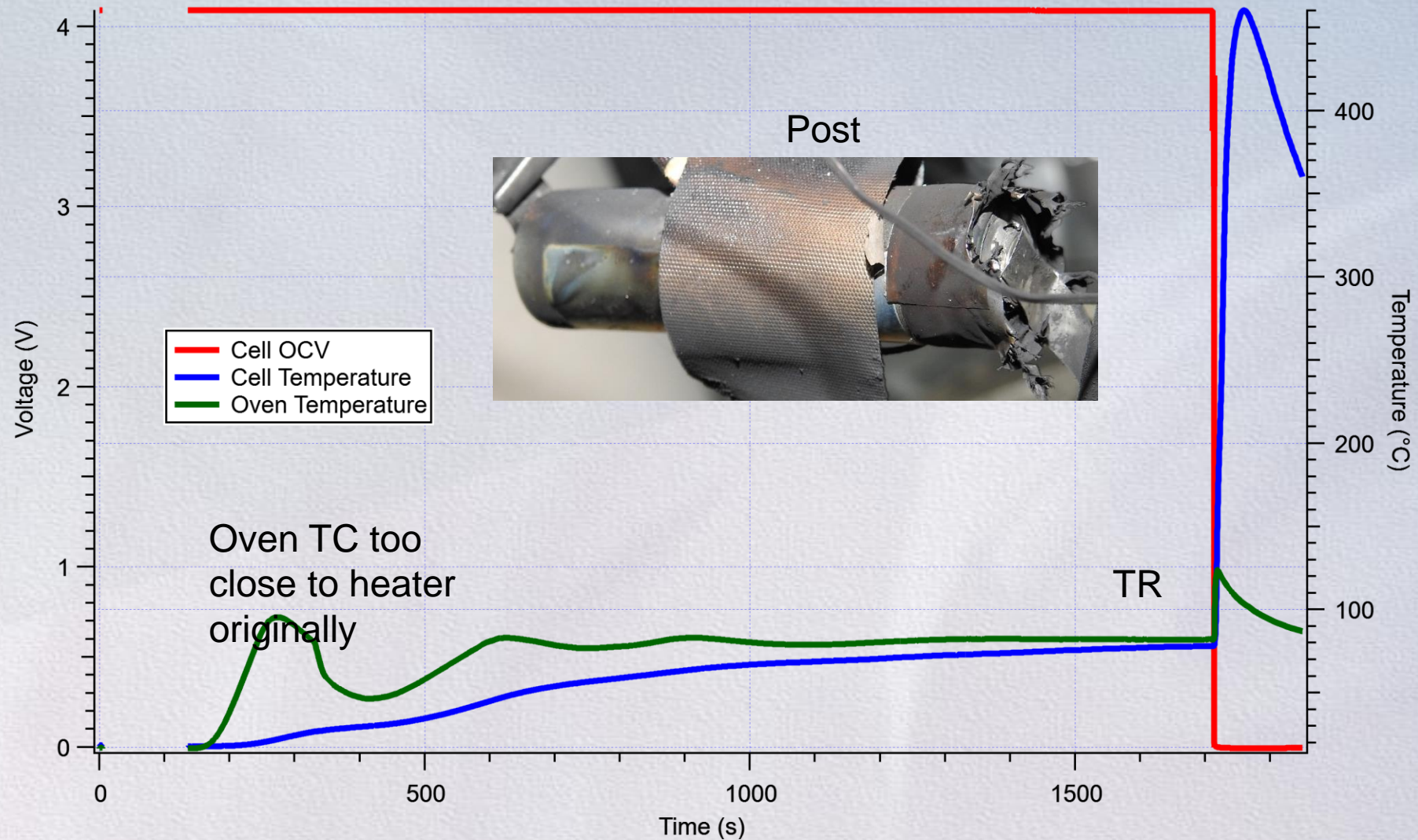
# Circumferential Heater Activation of ISCD at ESTA

N06 cell with both Al and Cu Soteria CCs





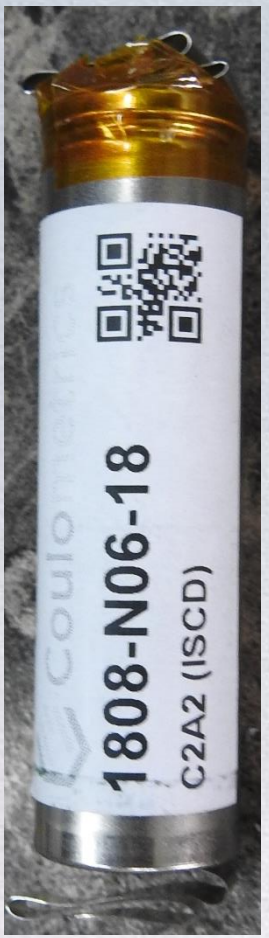
# 80°C Oven Test - N02-21 (Al Soteria)



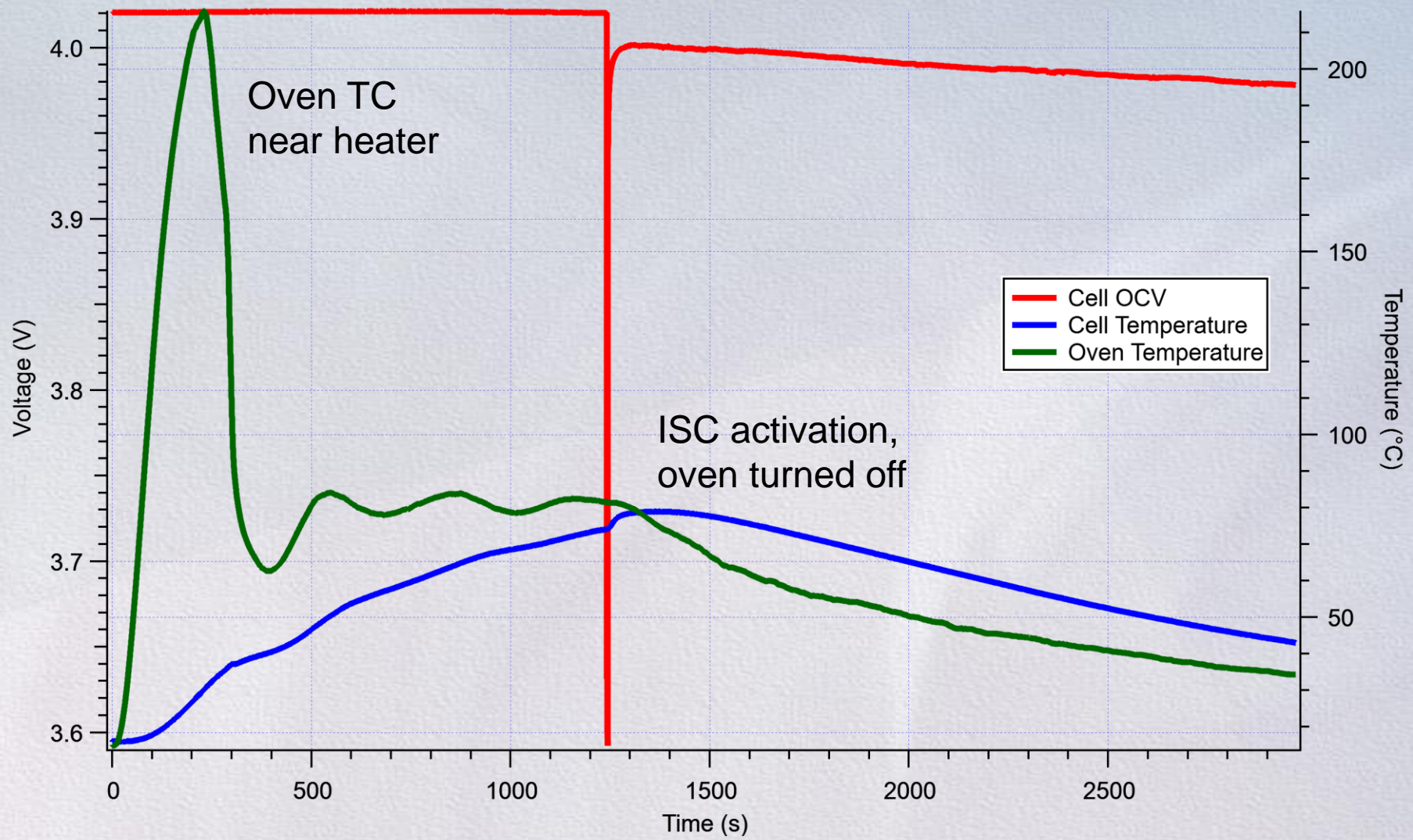


# 80°C Oven Test - N06-18 (Al & Cu Soteria)

ISCD activates, OCV dips & recovers - NO TR



Pre



Post



# Preliminary Findings & Future Work

- Preliminary Findings
  - Al coated plastic collector shows promise for preventing TR response to partial nail penetration
    - 5 of 6 fully charged cells partially penetrated followed by weeks of OCV retention!!!
    - Single anomaly might be due to nail shorting can to double Al tab
  - Cu coated plastic collector by itself is insufficient to prevent TR presumably due to
    - the greater electrical conductivity of the graphite active material and/or
    - nail bridging (-) can and (+) solid Al cathode collectors
  - Tolerance to the ISC device is mixed
    - Oven testing shows tolerance when both Al & Cu plastic are used (2 tests)
    - Oven testing is shows 1 out of 3 tolerance when only the Al plastic is used
    - Circumferential 18W heater triggers TR within seconds of ISCD activation (3 tests)
  - Ultra high speed X-ray videography linked to nail TR calorimetry
    - Nail interface with standard electrodes springs away violently leading to TR
    - Nail interface with electrodes is much less reactive with Al Soteria CC and much more localized and limited to the interface area
  - Ultra high speed X-ray to see phenomena near ISC device at activation
    - TR process takes generally more time to develop with Soteria Al CC
  - Need OCV sensing in our calorimetry to know when to stop heaters





# Next Round of 18650 Cells

- Combine Soteria plastic collectors with Dreamweaver cellulose separator (thermally stable to 300°C) and ISC device
  - Remove risk of possible shrinkage of the PP separator for inducing variability in the results
  - Device implanted with an offset of 180° from (+) tab
  - Coulometrics marked cell can with orientation of the device
  - Added OCV sensing for input heater control to our calorimetric tests
- All cell groups wound with Dreamweaver Gold cellulose separator
  - Group N11 - with Al coated Soteria collector (qty 20)
  - Group N12 - with Al coated Soteria collector and ISC device (qty 20 )
  - Group N15 - with Al and Cu coated Soteria collectors (qty 20)
  - Group N16 - with Al and Cu coated Soteria collectors and ISC device (qty 20)
  - Group N17 - Control cells (qty 20)
  - Group N18 – Control cells with ISC device (qty 20)
- Soteria films reduce mass by ~7% vs metal foils

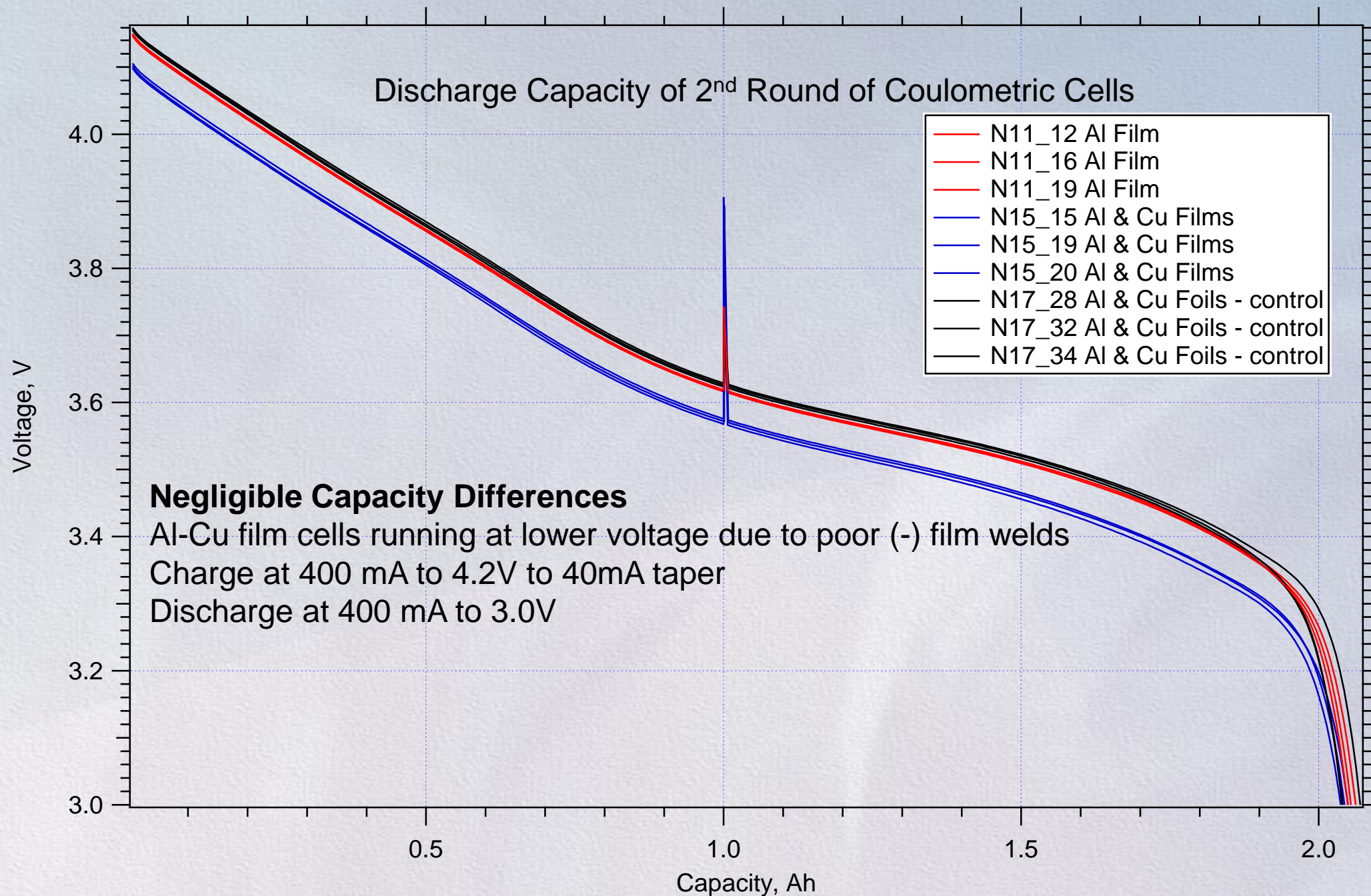
## Polypropylene Separator

Model	Description	Mass (g)
N01	Al film	40.5167
N02	Al film-ISC	40.3268
N03	Cu film	39.2326
N04	Cu film - ISC	39.8222
N05	Al&Cu film	39.00858
N06	Al&Cu film - ISC	38.906
N07	Control	41.18878
N08	Control - ISC	40.94635

## Cellulose (Dreamweaver) Separator

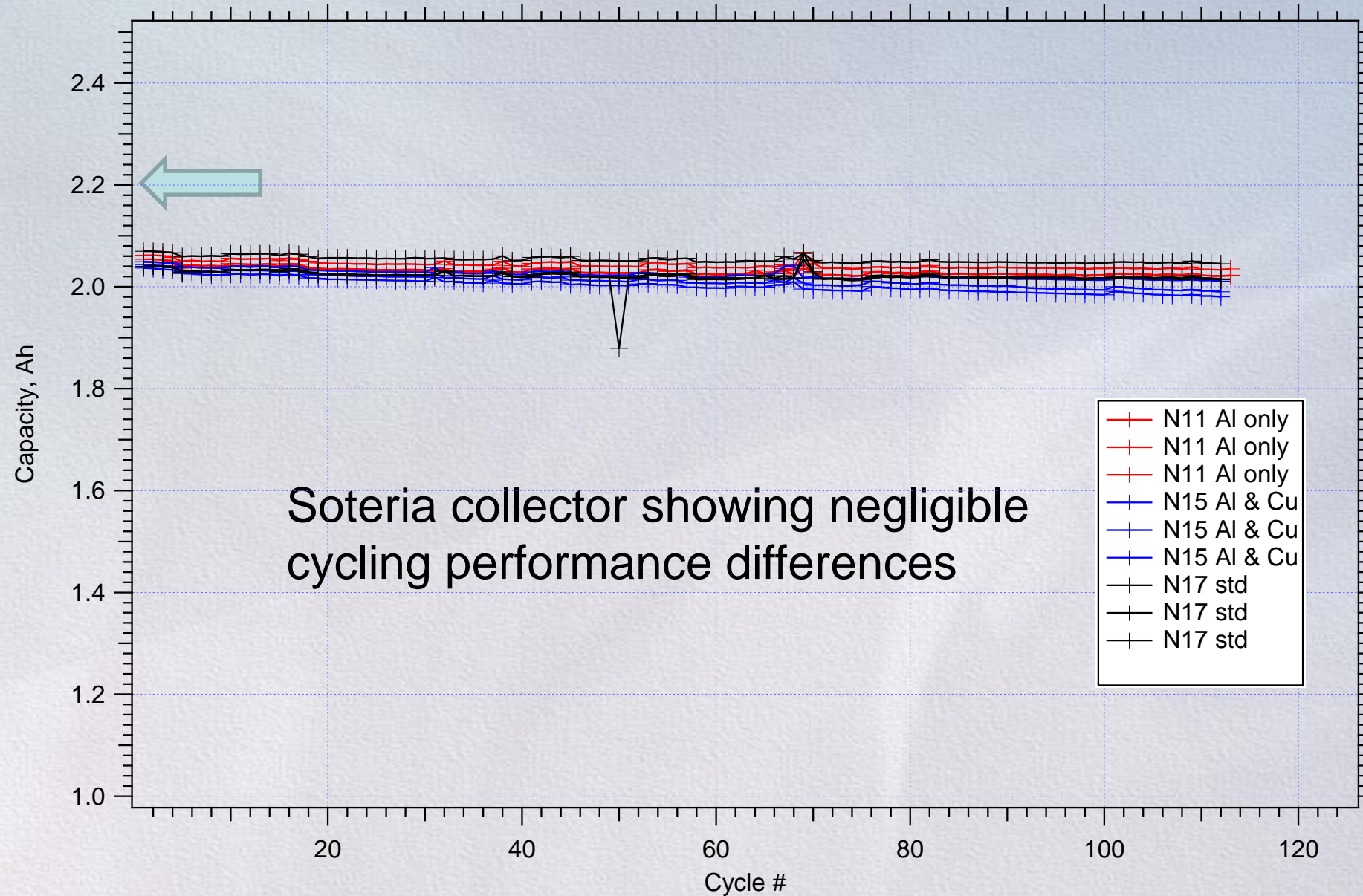
Model	Description	Mass (g)
N11	Al film	40.5322
N12	Al film-ISC	40.9239
N15	Al&Cu film	38.1988
N16	Al&Cu film - ISC	38.2153
N17	Control	41.0690
N18	Control - ISC	41.2829





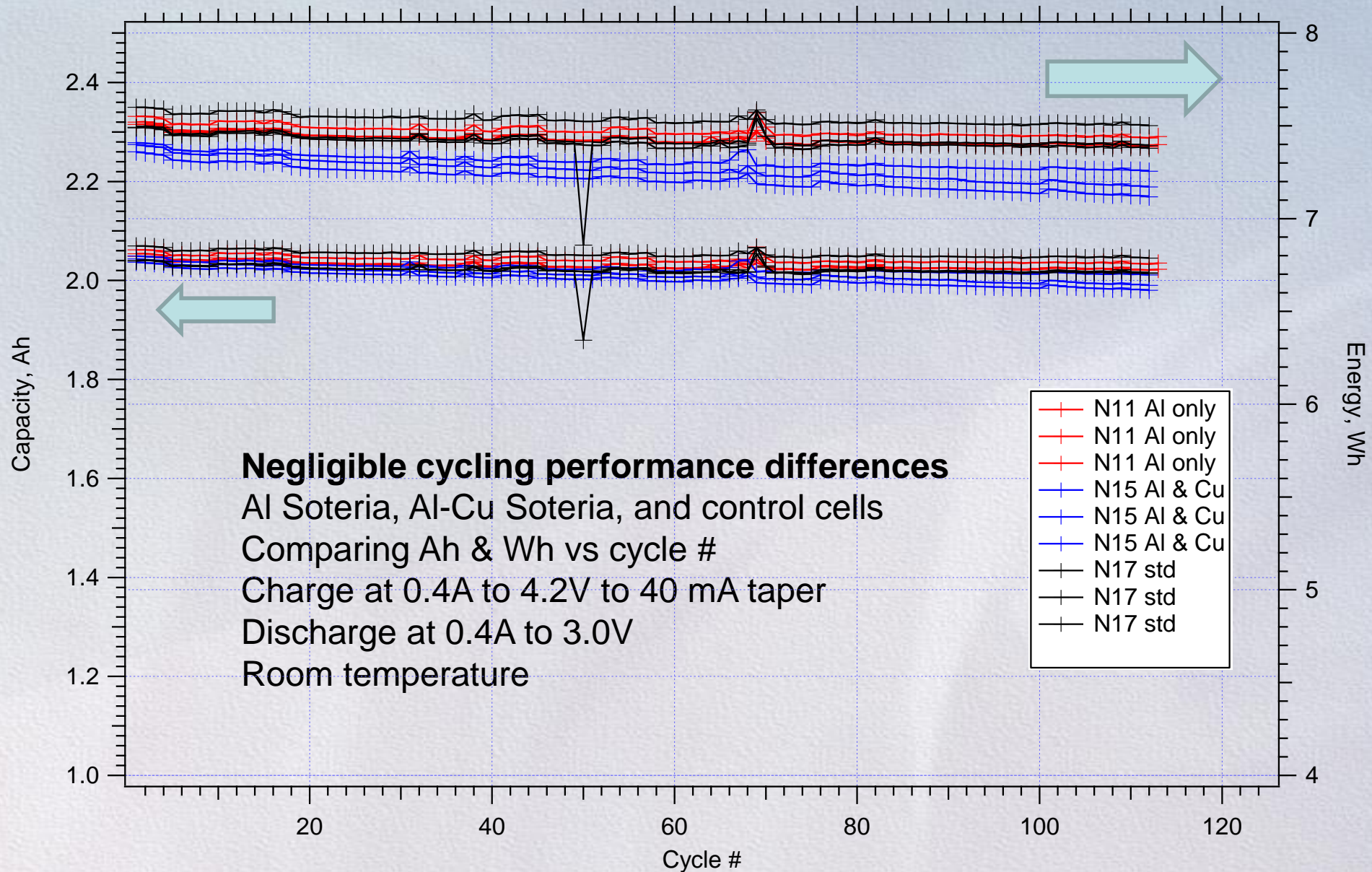


# Cycle Life Testing To Date with Dreamweaver Sep





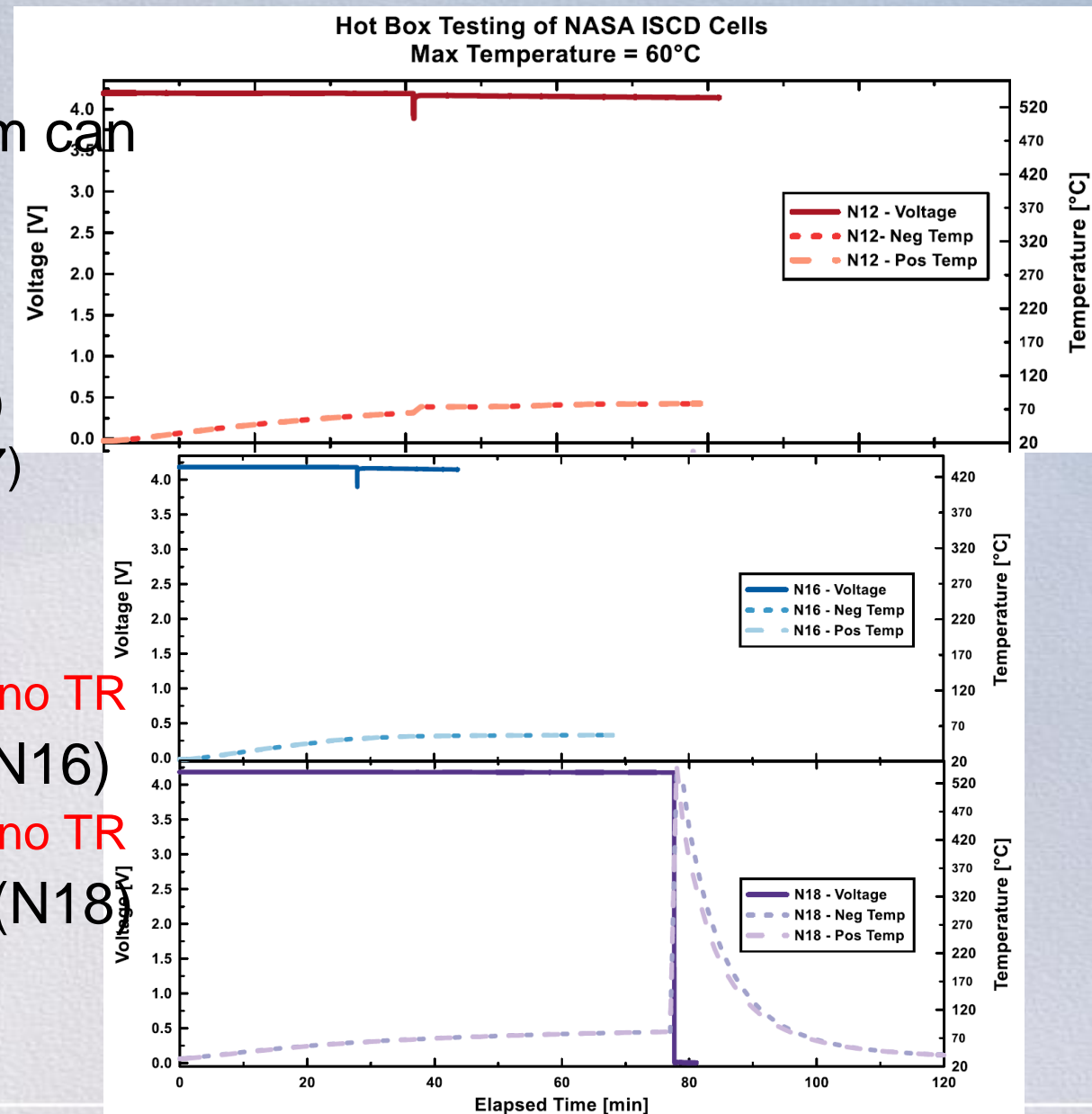
# Cycle Life Testing To Date with Dreamweaver Sep





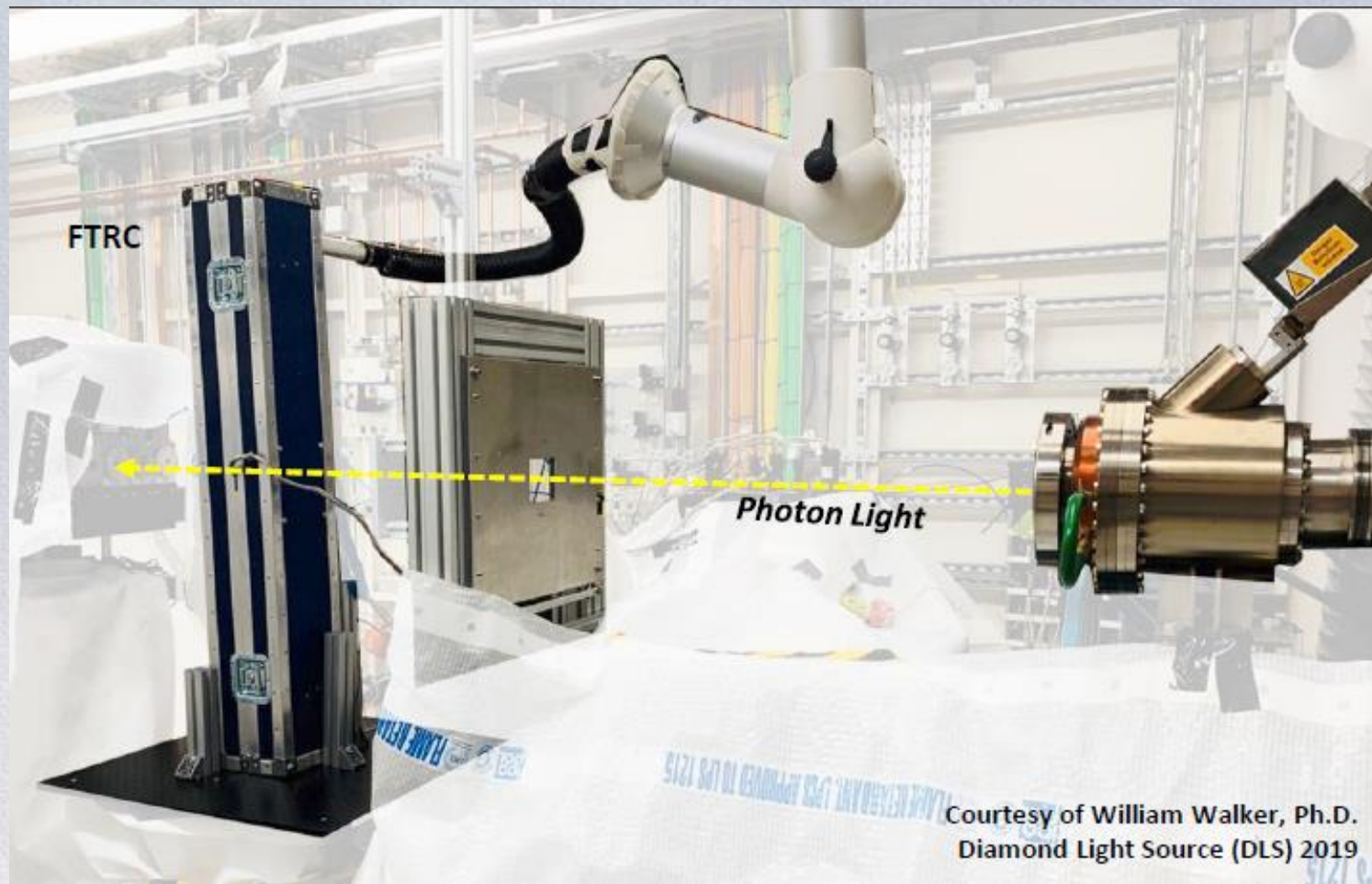
# Abuse Testing at Coulometrics

- Nail penetration
  - Nail driven completely through cell from can wall to can wall
  - All cell designs were driven to TR
    - Soteria Al & Dreamweaver sep (N11)
    - Soteria Al & Cu & Dreamweaver sep (N15)
    - Std Al & Cu foils & Dreamweaver sep (N17)
- Oven test (70°C) with ISCD
  - Soteria Al & Dreamweaver sep (N12)
    - Small, momentary dip in OCV,  $\Delta T = 10^\circ\text{C}$ , **no TR**
  - Soteria Al & Cu & Dreamweaver sep (N16)
    - Small, momentary dip in OCV,  $\Delta T = 10^\circ\text{C}$ , **no TR**
  - Std Al & Cu foils & Dreamweaver sep (N18)
    - OCV collapses, cell TR occurs





# Diamond Light Source (DLS) Synchrotron



The synchrotron accelerates electrons to near light speeds so that they give off light 10 billion times brighter than the sun. These bright beams are then directed off into laboratories known as 'beamlines'.

Enables high resolution X-ray videography at up 4000 frames/sec

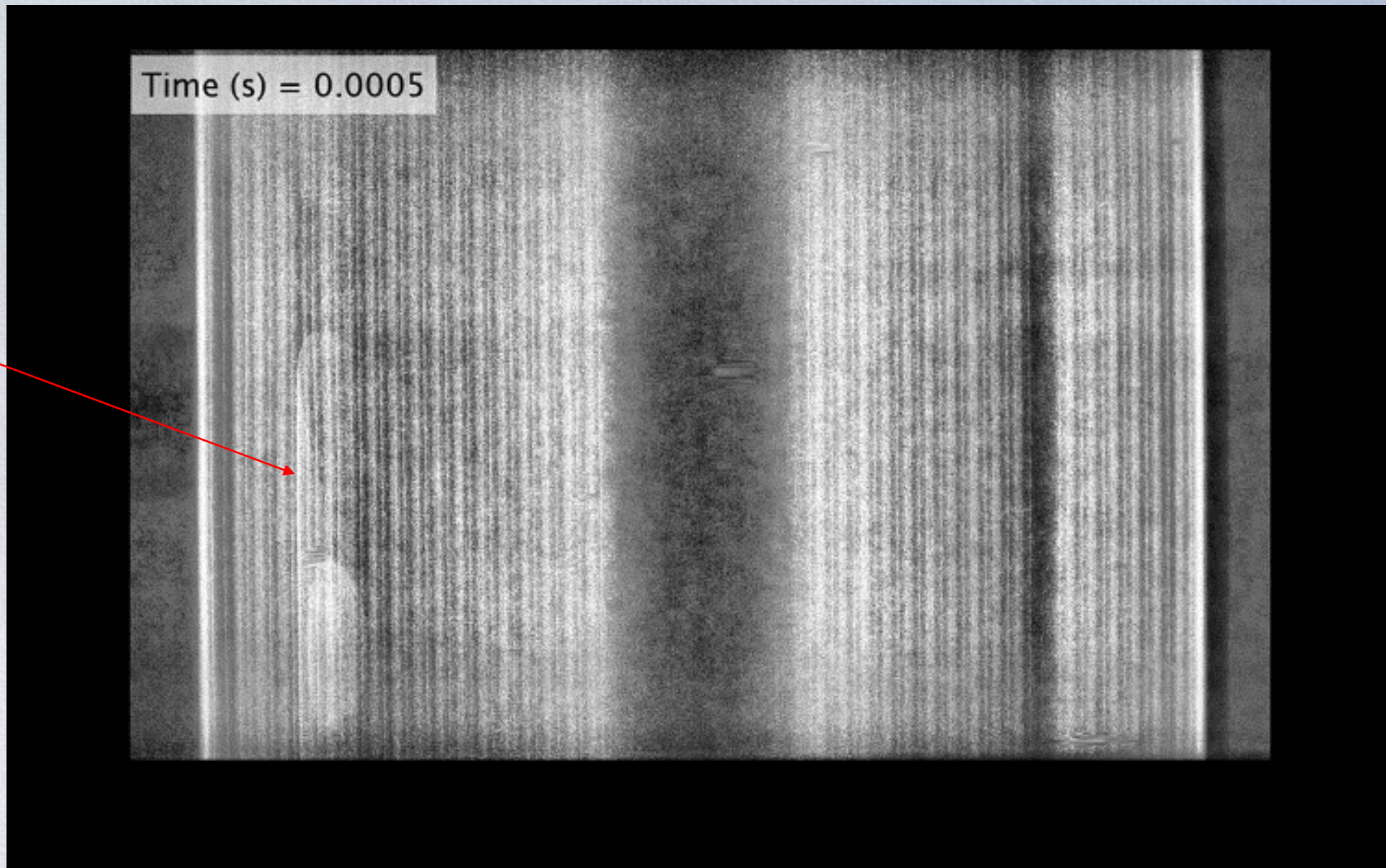


# DLS Calorimetric Test Matrix (42 runs)

- Thermally triggered runs with OCV sensing
  - Polymer separator groups – 12 runs
    - Al plastic only (w/ and w/o ISCD) – 4 runs
    - Cu plastic only with ISCD – 2 runs
    - Al & Cu plastic (w/ and w/o ISCD) – 3 runs
    - Controls (w/ and w/o ISCD) – 3 runs
  - Cellulose separator groups – 21 runs
    - Al plastic only (w/ and w/o ISCD) – 8 runs
    - Al & Cu plastic (w/ and w/o ISCD) – 6 runs
    - Controls (w/ and w/o ISCD) – 7 runs
- Nail penetration runs with cellulose separator groups – 9 runs
  - Al plastic only – 3 runs
  - Al & Cu plastic – 3 runs
  - Controls – 3 runs



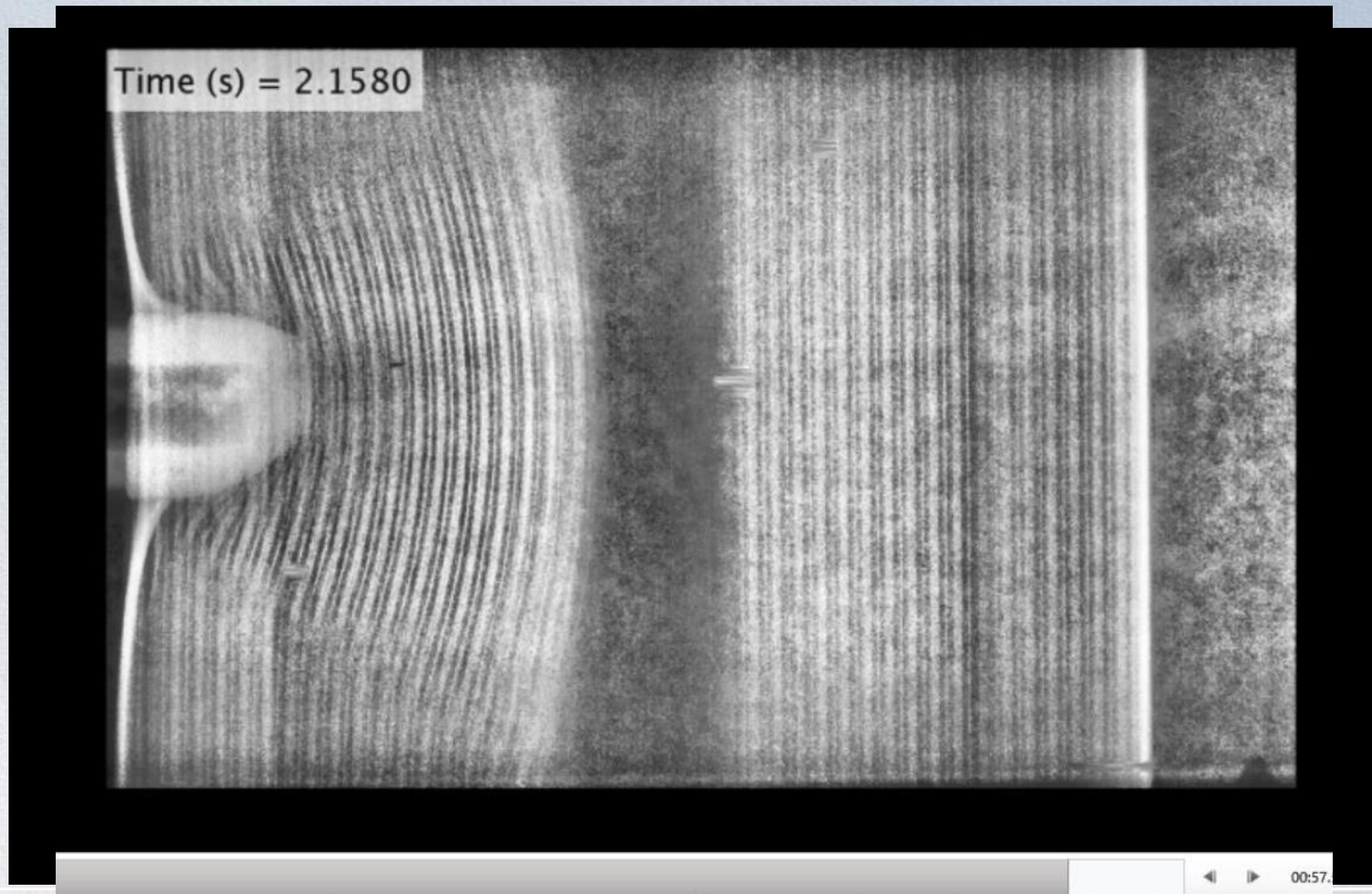
# Run 19 – Al Film, Cellulose Separator, and ISCD



Very boring video  
showing tolerance to  
the ISCD



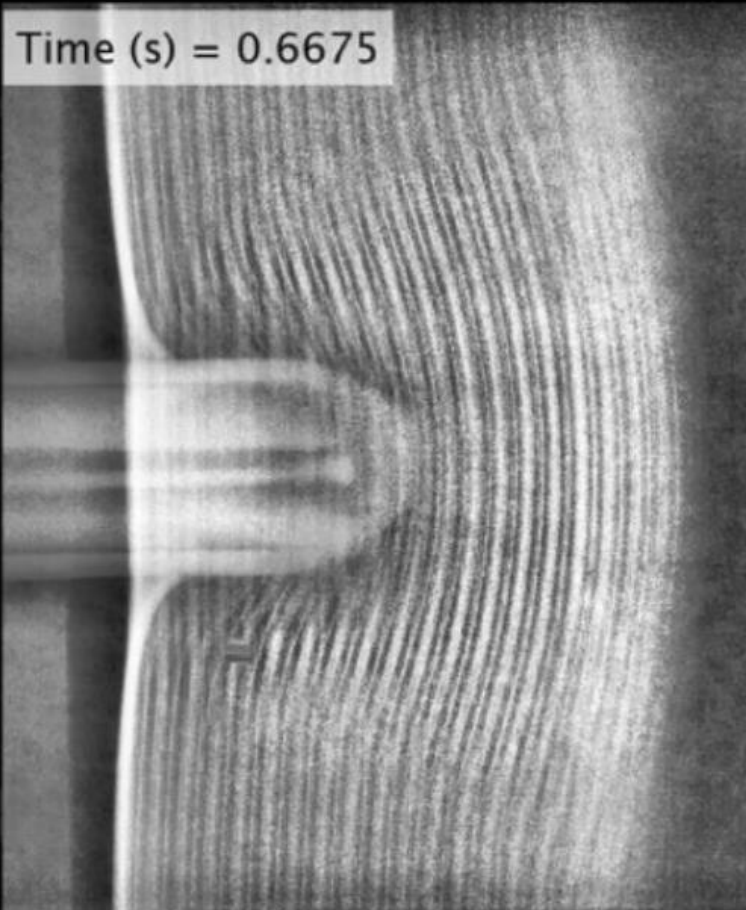
# Run 37 – Al Film & Cellulose with Nail Pen



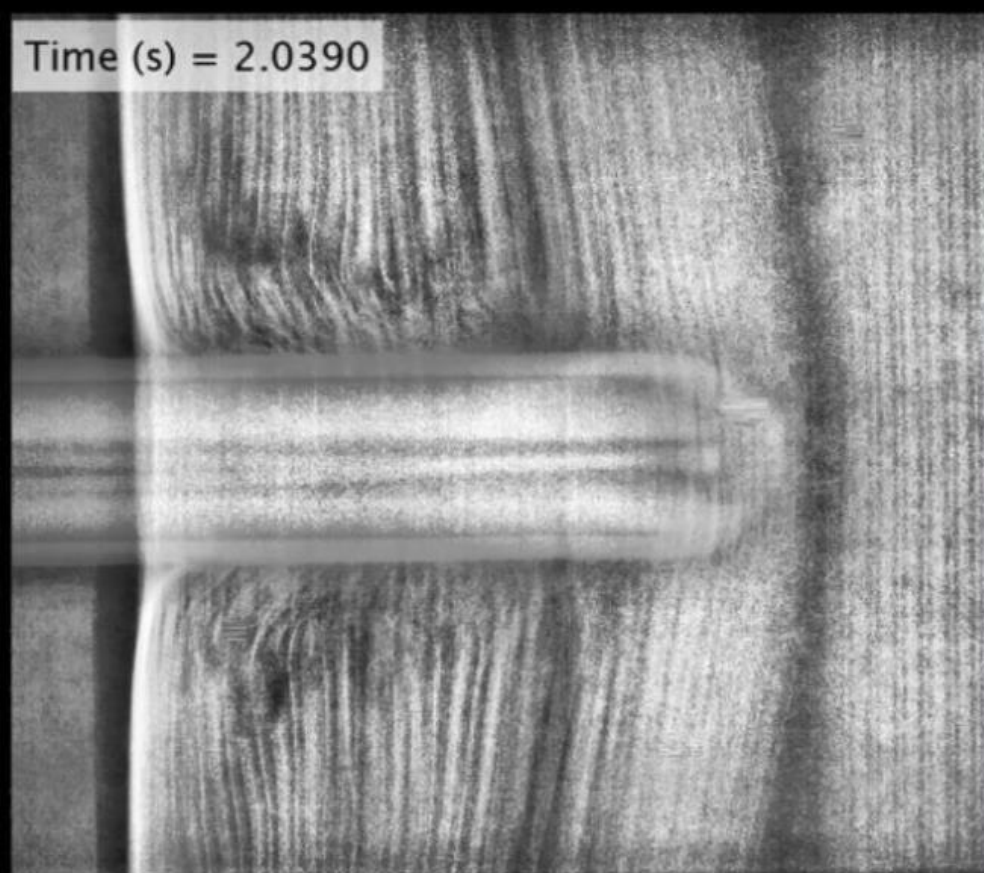


# Run 38 – Al Film & Cellulose with Nail Pen

Time (s) = 0.6675



Time (s) = 2.0390

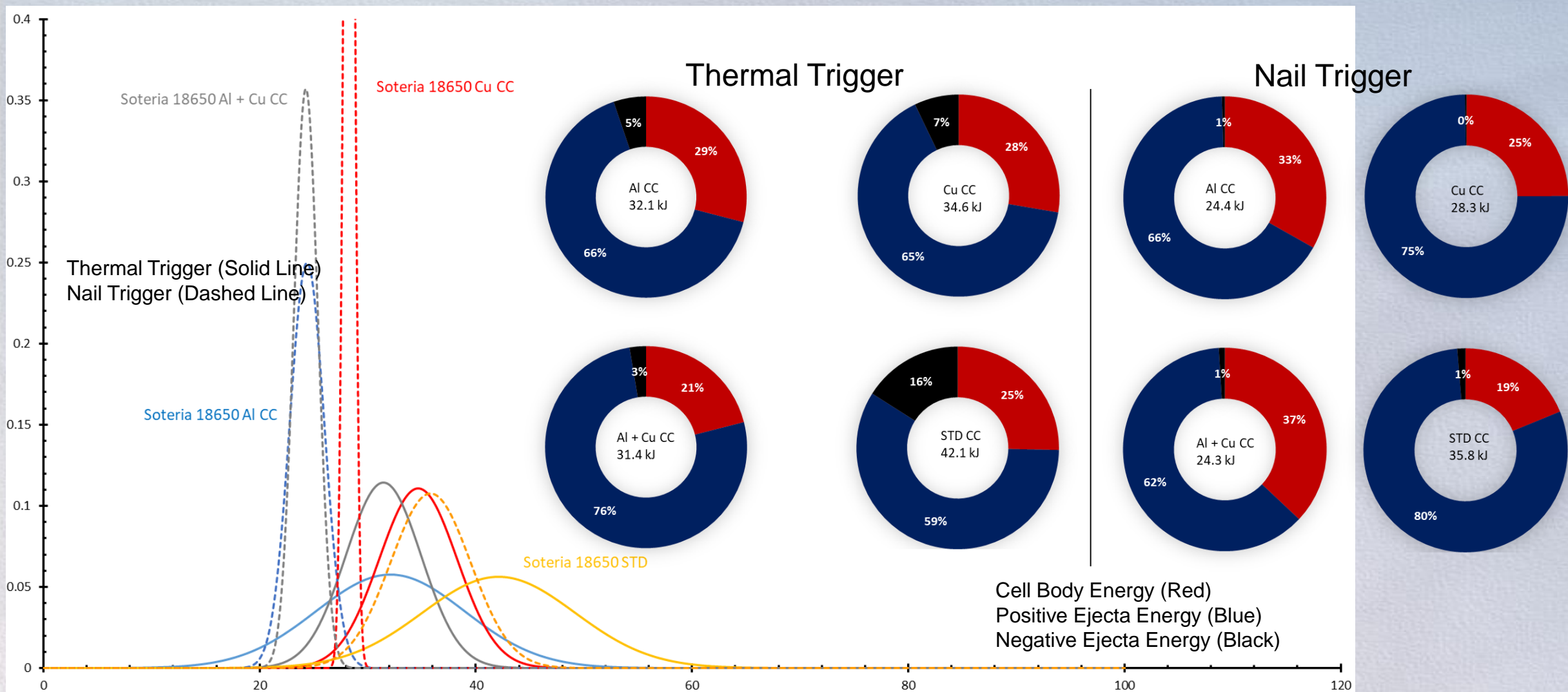


Tolerates initial nail penetration into ~10 layers, rests ~0.5 sec then is driven into TR upon deeper penetration



# Thermal Runaway Calorimetry Results

Credit: W. Walker/NASA



**Soteria polymer collectors reduce the thermal output (and violence) of TR vs standard cells**

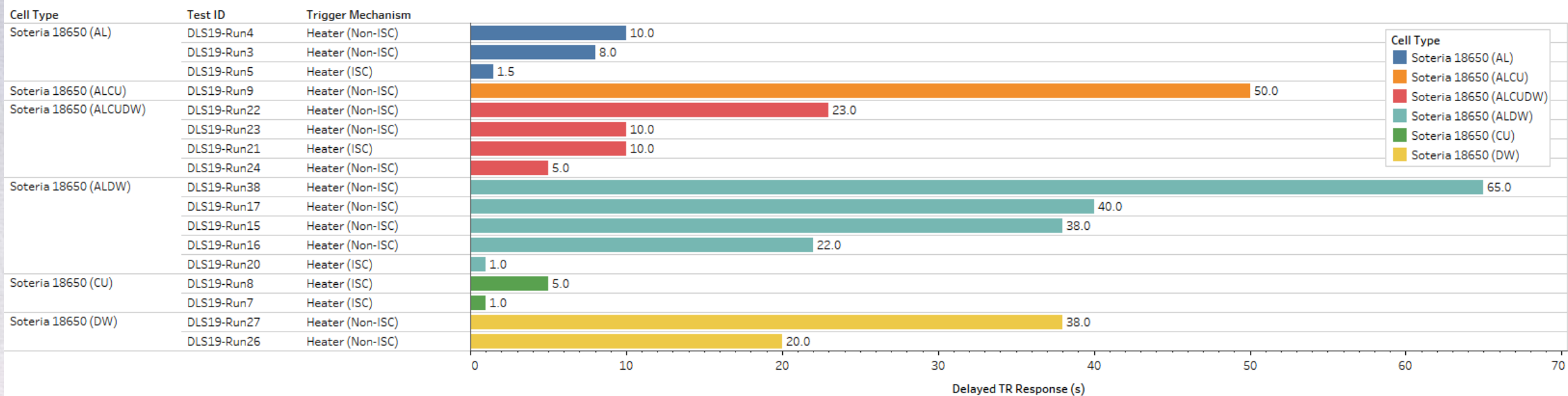
Cell Body Energy (Red)  
 Positive Ejecta Energy (Blue)  
 Negative Ejecta Energy (Black)



## PRE-TR OCV RESPONSE

- In recent synchrotron FTRC experiments, monitored OCV response during thermal trigger testing for combinations of 18650 cells using the Soteria current collectors and(or) the Dreamweaver separator:
  - Heated cells until OCV drop was observed and then cut-off power (as opposed to heat to trigger)
  - 5 cells resisted the internal short and did not go into thermal runaway (example on next slide)
  - For the cells that did fail, various delays were observed between initial OCV drop and thermal runaway (figure below)

Delayed TR Response from Initial OCV Drop

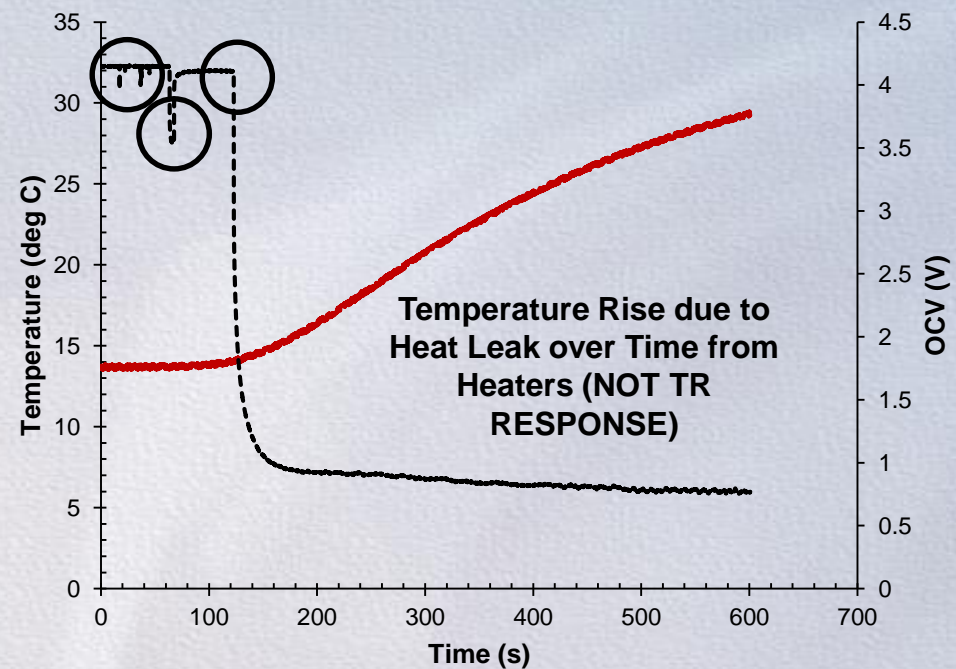
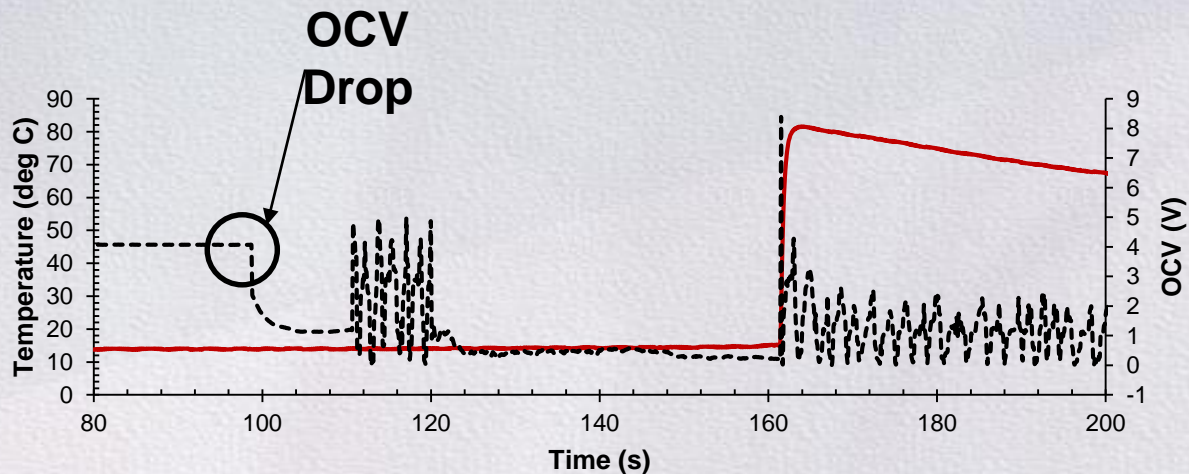
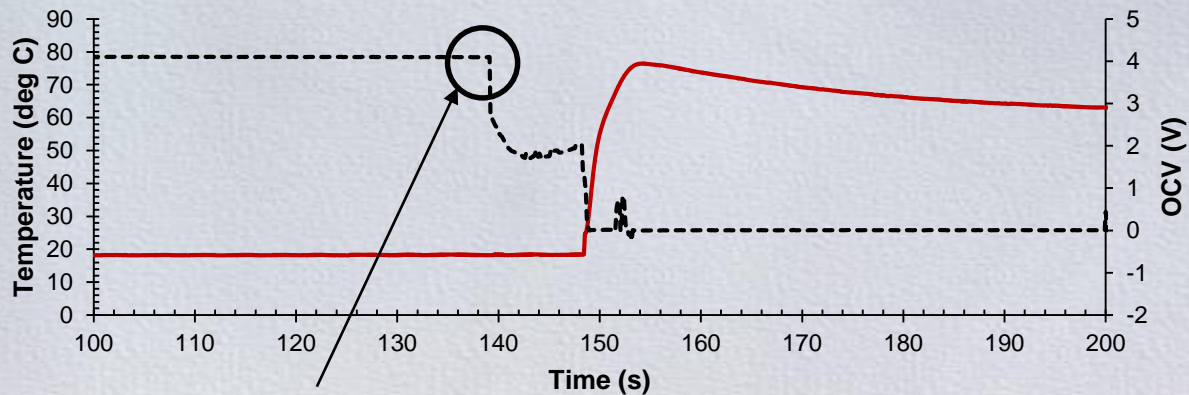


Sum of Delay for each Trigger Mechanism broken down by Cell Type and Test ID. Color shows details about Cell Type. The marks are labeled by sum of Delay.



## PRE-TR OCV RESPONSE

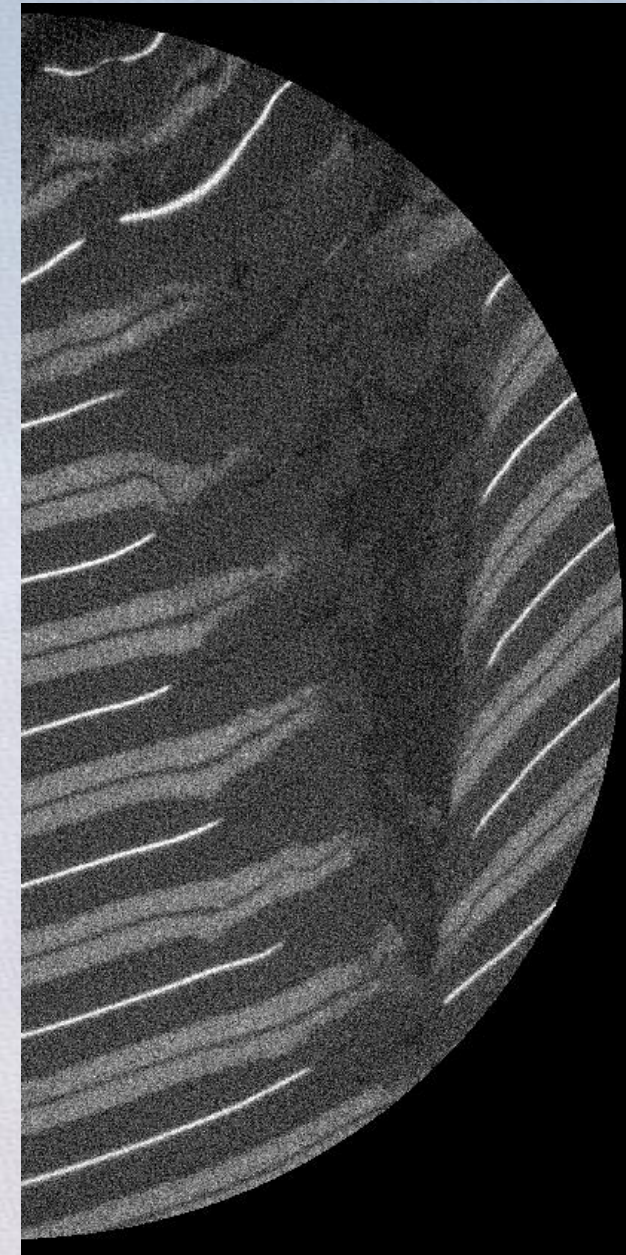
- Even when TR occurs, the cells with the Soteria current collector materials appear to put up a fight





# Preliminary Findings from Dreamweaver Cell Build

- Cell manufacturer (Coulometrics) testing results very consistent with polymer build
  - Can wall to can wall nail penetration caused immediate TR in all cells
  - Soteria collectors prevent TR response to ISC device hard short
- Heat triggered calorimetry results are mixed
  - TR prevented in some Soteria cells
  - TR triggered after multiple shorts (OCV dips) in some Soteria cells
  - TR triggered immediately in a few Soteria cells
  - TR triggered immediately in all control cells as expected
- Mixed tolerance to the ISC device and nail
- Post test CT imaging again shows the plastic collector vaporizing and isolating the active material from the shorting defect
- Overall, of the cells driven into TR, plastic collector films lower the calorimetric output vs metal foil cells
  - Plastic collector cells are harder to drive into TR than metal foil cells
  - TR is less violent than with metal foil cells
- Films and cellulose show no cycle life impact to date (75 cycles)
- More data reduction to come
  - Calorimetric output and OCV trending
  - Post test mass and cell carcass analyses
  - X-ray videography to date has insufficient resolution for insights into phenomena, future runs will focus entire FOV on ISCD





# Future Test Plans

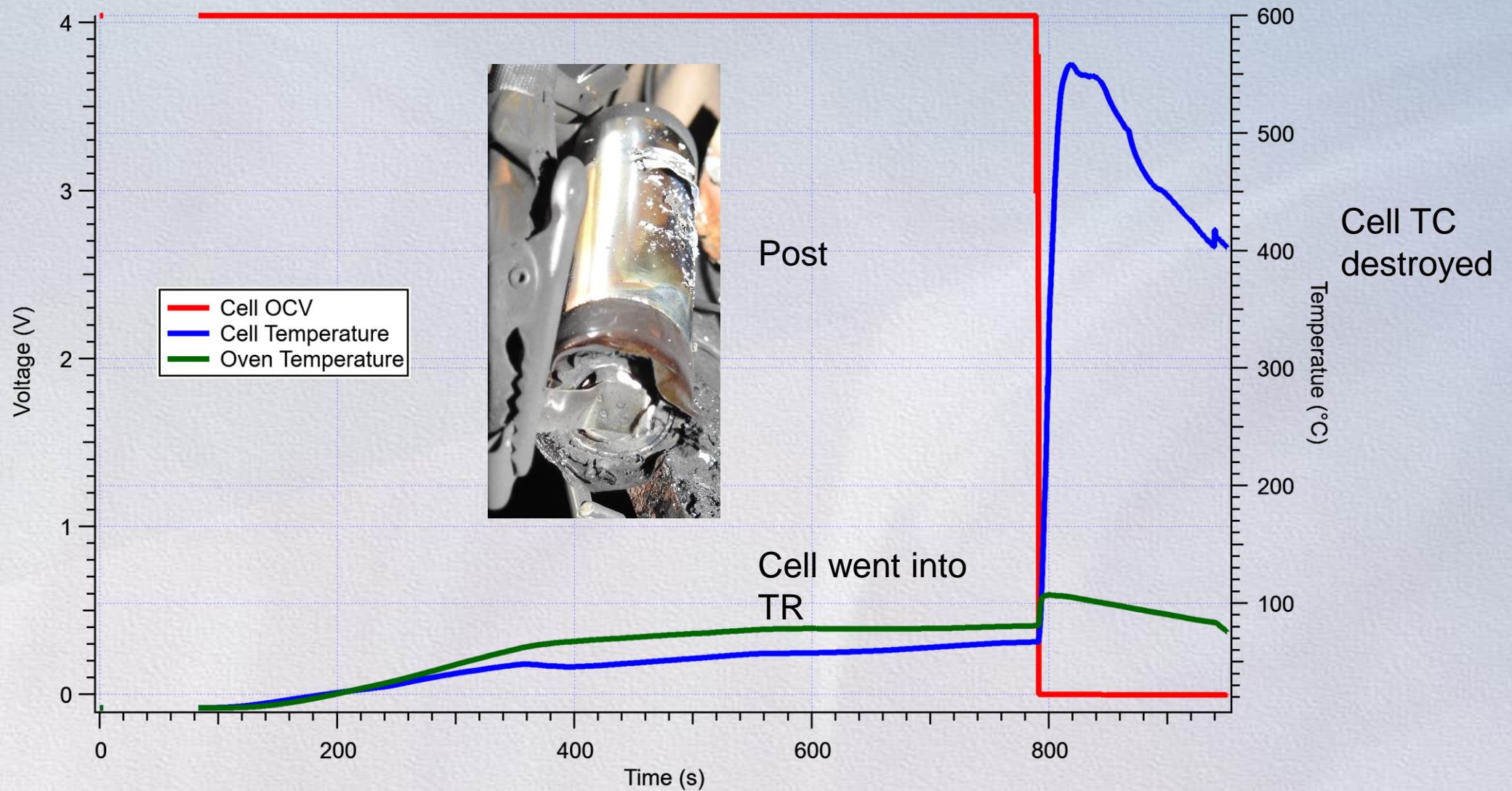
- Oven and calorimetric tests with ISCD cells
  - More runs to get more statistically significant data
- X-ray videography will focus field of view on ISCD for insights into the plastic film isolation phenomena
- Nail Penetration with non ISCD cells
  - Need to improve the consistency of the nail system
    - Speed
    - Depth of penetration
    - Angle of penetration
    - Sharpness
    - Location in cell
- We've made much progress but challenges remain
  - Understanding the variability in safety tolerance with the 18650 format
  - Achieving low resistance tab to collector connection



# Back Up Slides



# 80°C Oven Test - N02-17 (Al Soteria)

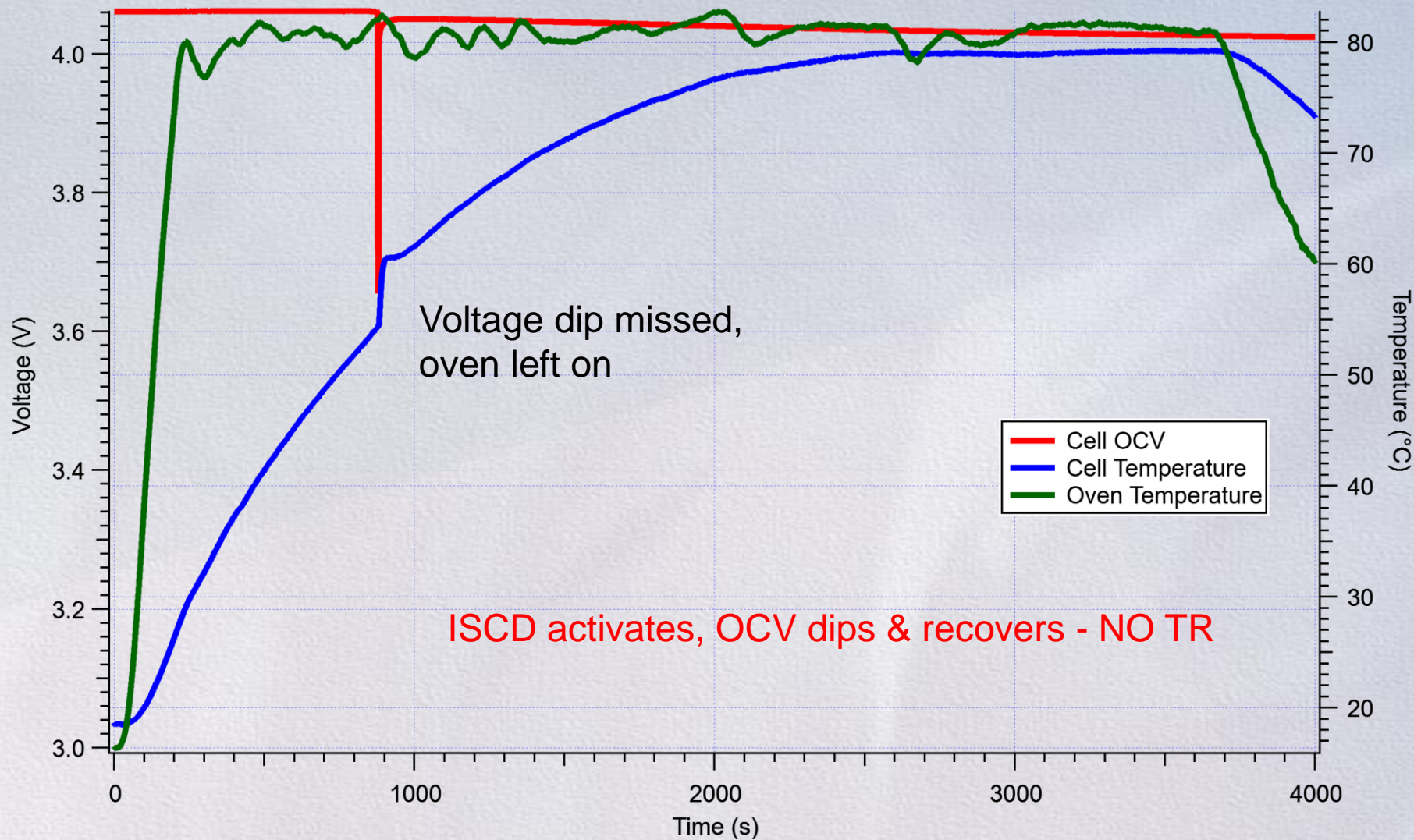




# 80°C Oven Test - N06-12 (Al & Cu Soteria)



Pre





# DLS Calorimetric Test Matrix (Cont.)

- Thermally triggered runs with OCV sensing
  - Polymer separator groups – 12 runs
    - Al plastic only (w/ and w/o ISCD)
      - Run 3 – OCV crashed, immediate TR
      - Run 4 - Turned heaters off as soon as OCV dropped. **TR initiated 3 s later**. X-ray data captured early
      - Run 5 ISCD – Cell went into TR upon ISCD activation
      - Run 6 ISCD - Turned heaters off when OCV dropped immediately from 4.2 to 3.5 V. Recorded x-ray. OCV bumped up back to 4.2 and then trickled down to 0.6 before the run was concluded. **No TR**
    - Cu plastic only with ISCD – 2 runs
      - Run 7 – near immediate TR
      - Run 8 - Turned off power **about 20s** before TR
    - Al & Cu plastic (w/ and w/o ISCD) – 3 runs
      - Run 9 ISCD - Cell shorted. Power cut. Battery underwent **TR about 50s later**. X-ray recorded the initial short.
      - Run 10 ISCD - Tolerated ISC **without TR**. It survived 4 shorts. Power was cut after the first short. The 4<sup>th</sup> OCV short was a collapse. Calorimetry captured
      - Run 11 – TR occurred, OCV sensing lost
    - Controls (w/ and w/o ISCD) – 3 runs
      - Run 12 – Immediate TR
      - Run 13 ISCD – Immediate TR
      - Run 14 ISCD – Immediate TR
  - OCV sensing helped: No TR in 2 of 9 cells and 3 more with no immediate TR
  - Uncertain why results are mixed with thermal triggering w/ or w/o ISCD



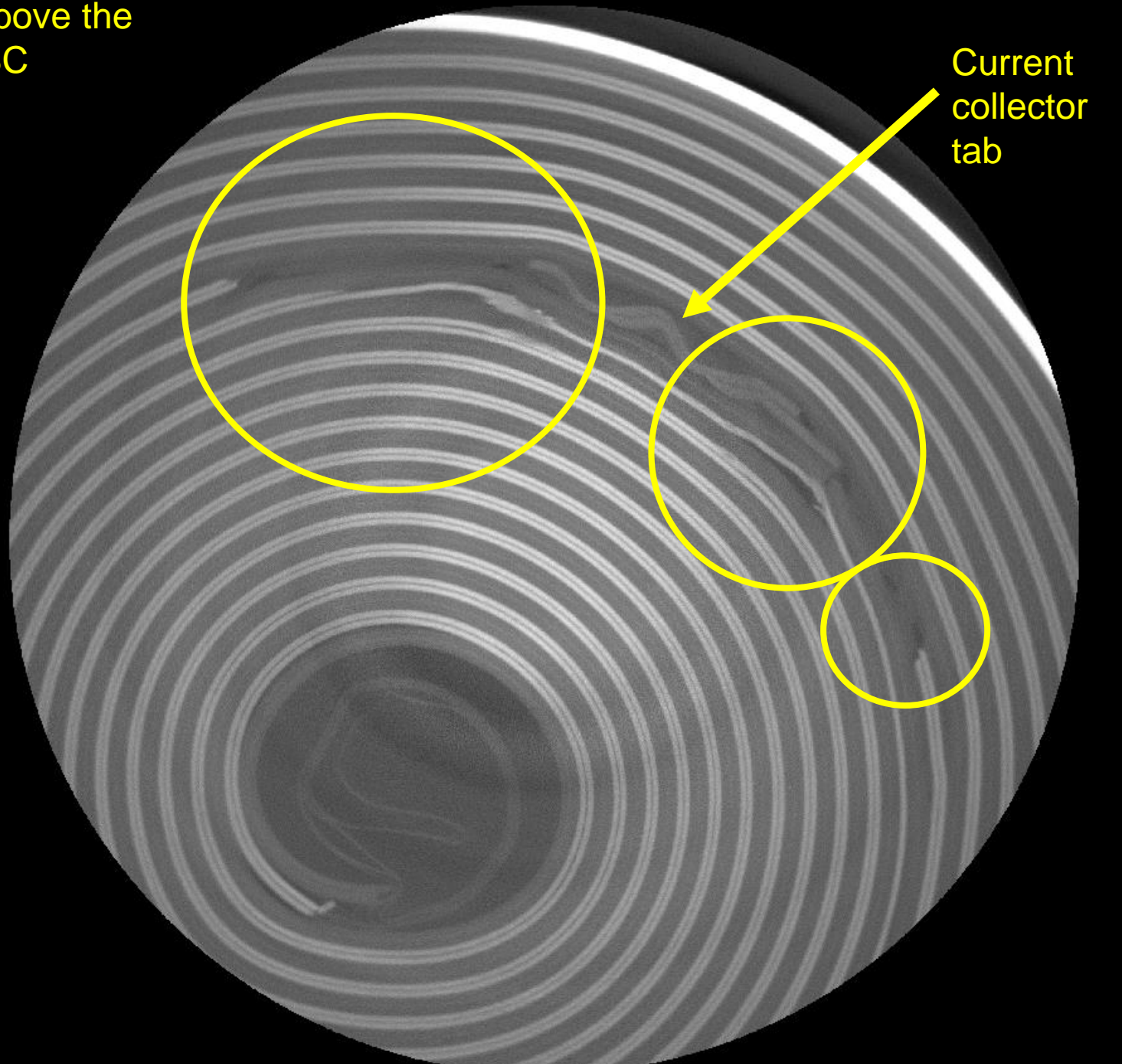
Run 10

N06-09 – Al & Cu film,  
plastic separator

- ISC Cell heated at 960 W until OCV dipped and heat removed
- **Cell did not go into TR**
- OCV returned after power was cut
- Second short captured with X-ray
- Cell survived second short with OCV retention

Collector vaporizes near perimeter of ISC device

Above the  
ISC





# DLS Calorimetric Test Matrix (Cont.)

- Thermally triggered runs with OCV sensing
  - Cellulose separator groups – 21 runs
    - Al plastic only (w/ and w/o ISCD) – 6 runs
      - Runs 15-17 N11 – Average 33s delay between OCV dip and TR
      - Runs 18-20 N12
        - » 18 & 19 no TR
        - » 20 had 1s delay followed by TR
    - Al & Cu plastic (w/ and w/o ISCD) – 8 runs
      - Runs 22-24 N15 – Average 13s delay between OCV dip and TR
      - Runs 21, 25-28 N16 – Average 33s delay between OCV dip and TR
    - Controls (w/ and w/o ISCD) – 7 runs
      - Runs 29-31 N17 – immediate TR
      - Runs 32-35 N18 – immediate TR
  - OCV sensing helped: No TR in 2 of 14 cells and **all others but one** putting up a fight prior to TR
  - All control cells (with Dreamweaver separator) went into immediate TR



# DLS Calorimetric Test Matrix (cont.)

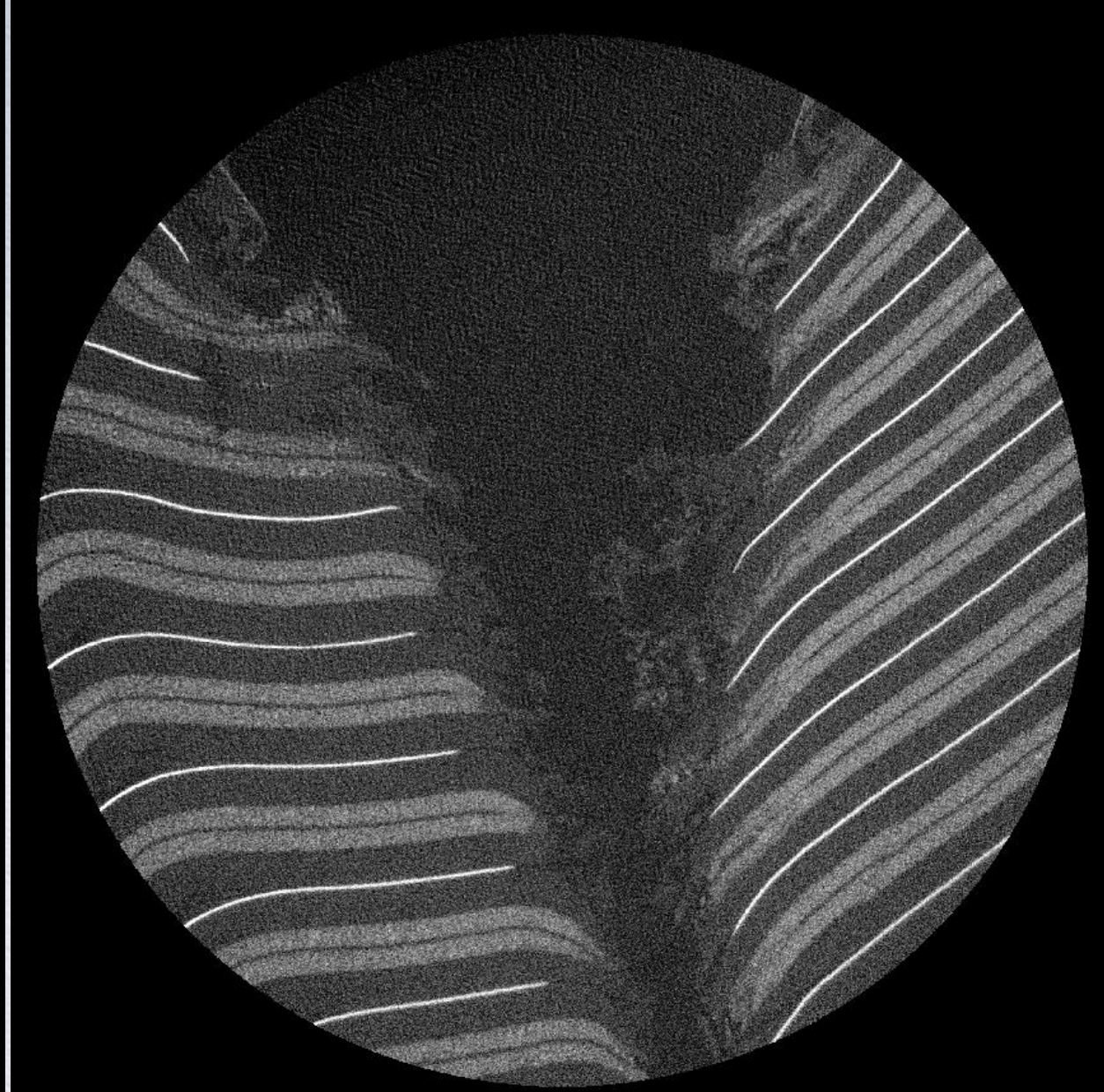
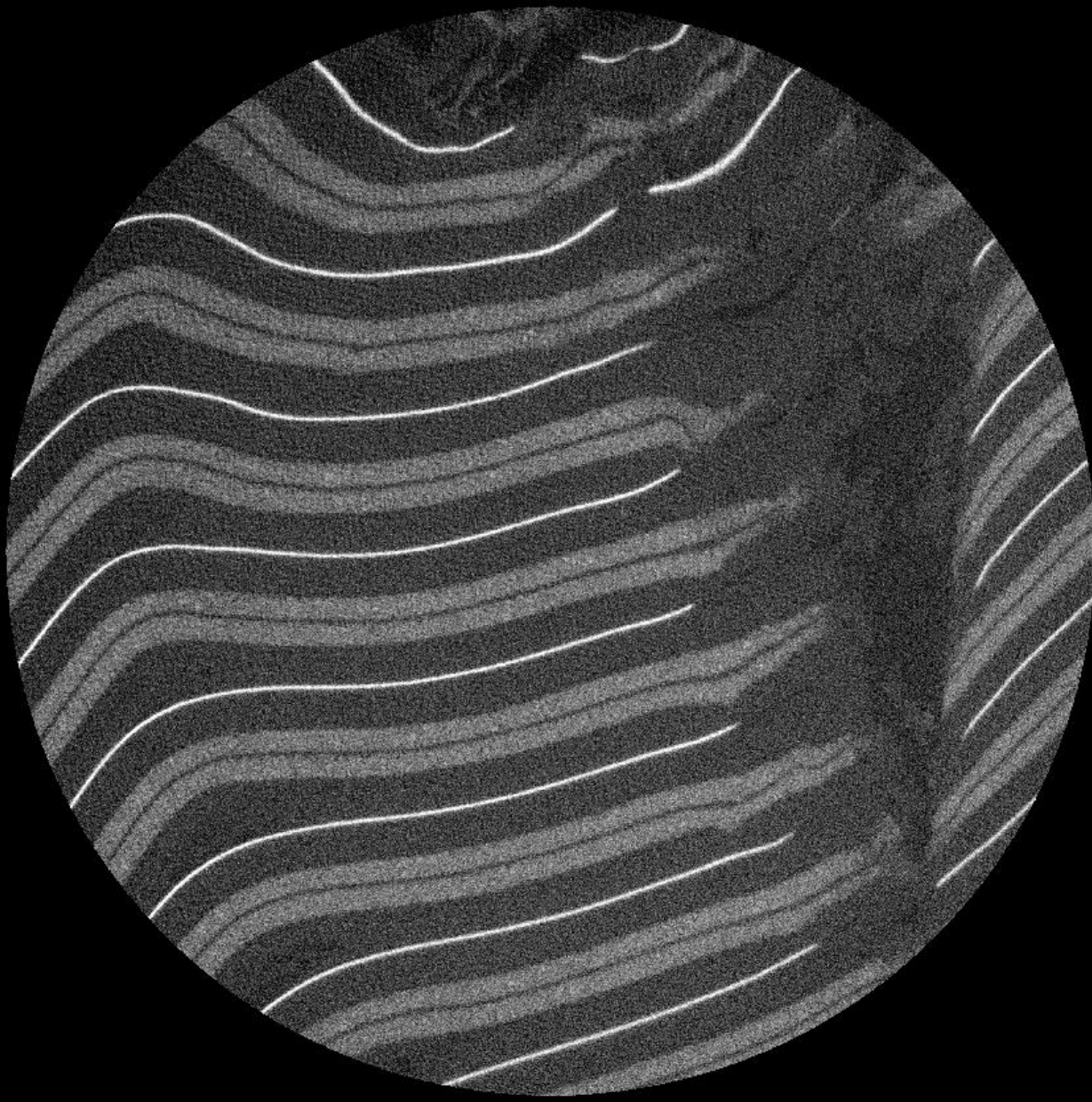
- Nail penetration runs with cellulose separator groups – 9 runs
  - Al plastic only – 3 runs
    - Run 36 – no TR
    - Run 37 – no TR
    - Run 38 - Nail penetrated partially with tolerance, then TR ensued when nail breached into the core, but not before
  - Al & Cu plastic – 3 runs
    - Run 39 - Nail penetrated partially with tolerance, then TR ensued when nail breached into the core, but not before
    - Run 40 – TR
    - Run 41 – TR
  - Controls – 3 runs
    - Run 42-44 – all went immediately into TR

Run 36





Run 36 – Soteria Al film with cellulose separator



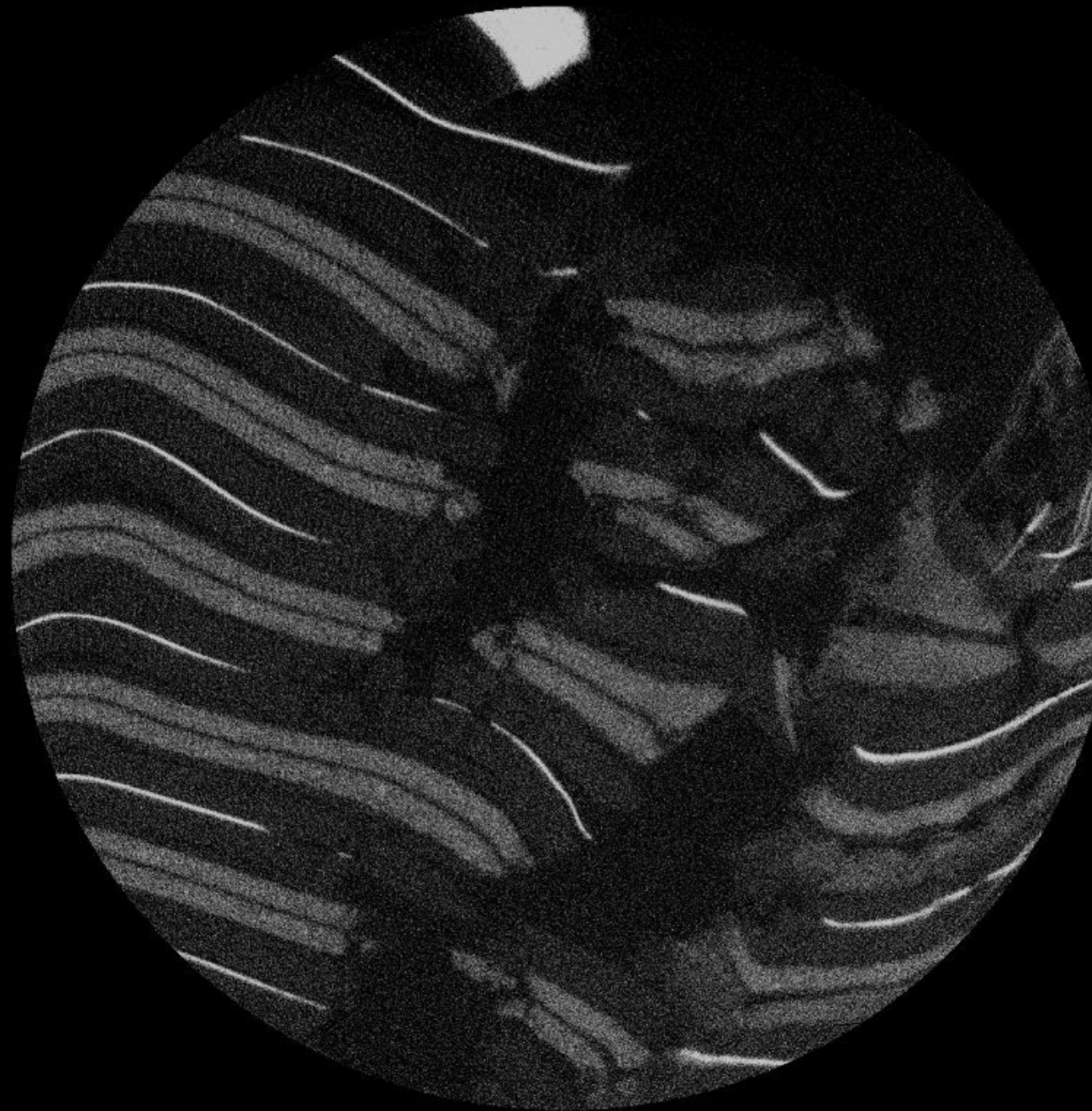


## Run 37 – Al film CC, Cell N11-05



- Nail penetration depth – 0.9 mm
- Cell did not go into TR, cell survived with OCV retention
- Solid copper current collector has different behaviour to So-CC, due to spring back, it remains in position near the nail interface





**Run 37 – Al film  
CC, Cell N11-05**