Investigating Polymer Current Collectors for Isolating Internal Shorts in High Energy Li-ion Cells

8µm Aluminum Metalized Film Current Collector

China

Technical Features (Typical Properties)

PROPERTY	SPECIFICATION
Metal	Al
Substrate	PET
Substrate Thickness (µm)	6 µm
Total Thickness (µm)	8 µm
Metal Coating Thickness	1 µm/side
Surface Resistivity (mOhm/square)	22.86
Tensile (MPa)	27033

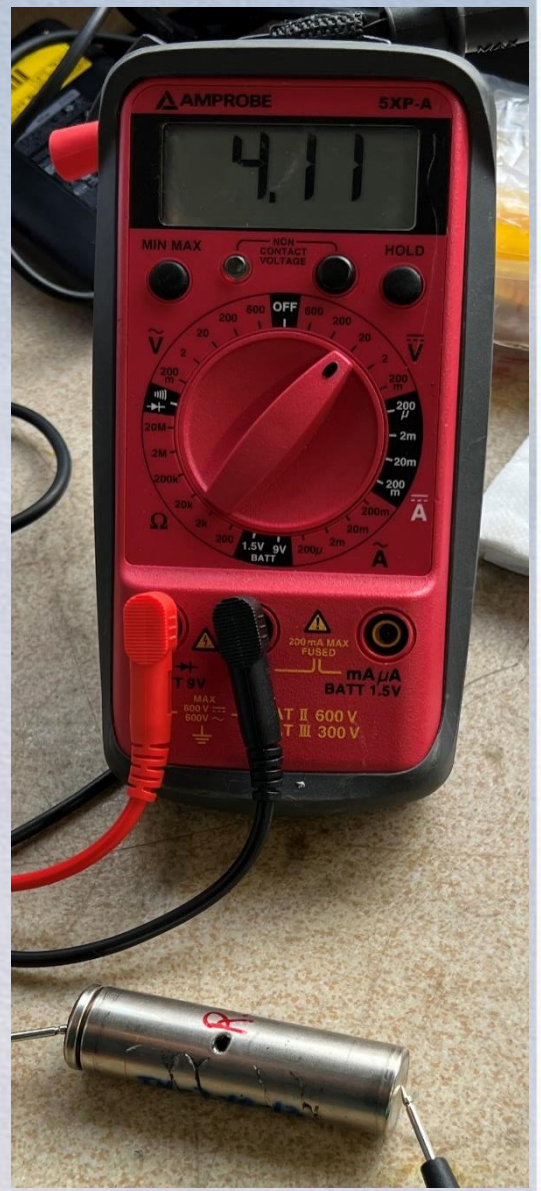
With the European Synchrotron Radiation Facility

Eric Darcy/NASA-JSC

International Battery Materials Association
Halifax, Nova Scotia, Canada
9-13 Sep 2024

Plastic Current Collector Investigation

- Motivation
  - What limits the effectiveness of Plastic Current Collectors (PCCs) in isolating shorts?
  - Obviate the design burden of achieving passive propagation resistance (PPR)
- Team Effort
- Cell Designs with Soteria Al PCC
  - BAK 4.5Ah 21700 and 2.75Ah 18650
  - *Nanotech Energy 3.3Ah 18650*
- Test and Examination Results
  - Fast nail penetration at ESRF
  - Post test CT imagery
- Investigating Cell Design Drivers for Success



Team Effort

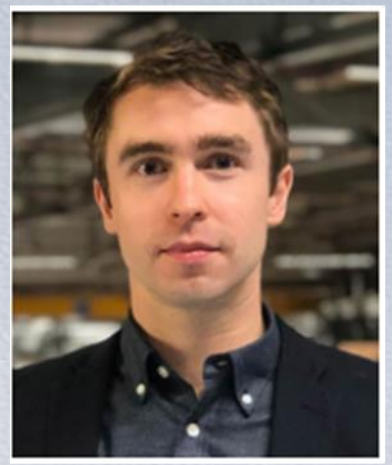

Dr. Eric Darcy


John Darst


David Petrushenko


Jesus Trillo

NASA-JSC


Dr. Donal Finegan

NREL


Dr. Paul Shearing

Oxford University


Alexander Rack

ESRF

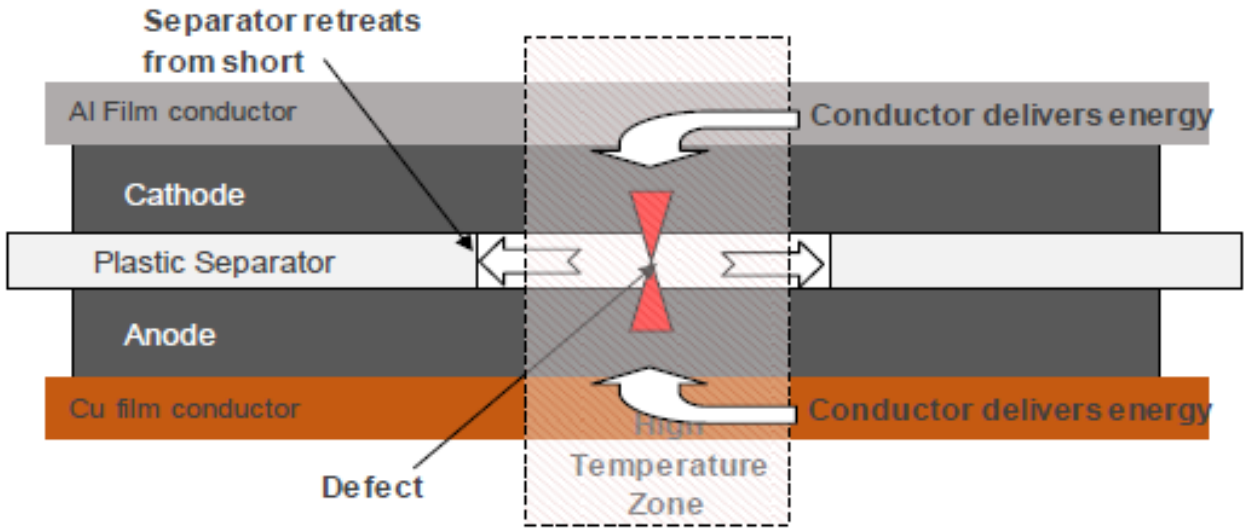
- Jacob Darst, David Petrushenko, Jesus Trillo, Brenda Esparza, Thuong Nguyen, Vince Glover, and Eric Darcy/NASA, Houston, TX, USA
- Donal Finegan/NREL, Golden, CO, USA
- Charlie Kirchner-Burles, Mark Buckwell, Hamish Reid, Matilda Fransson, and Rhodri Jervis/UCL, London, UK
- Inez Kesuma and Paul Shearing, Oxford University, Oxford, UK
- Ludovic Broche and Alexander Rack/ESRF, Grenoble, France
- Jesse Mutter, Josh Gaskin, and Ed Buiel/Coulometrics, Chattanooga, TN, USA
- Brian Morin and Joe Turner/SoteriaBIG, Greenville, SC, USA
- *Curtis Collar/Nanotech Energy, Chico, CA*

Acknowledgements

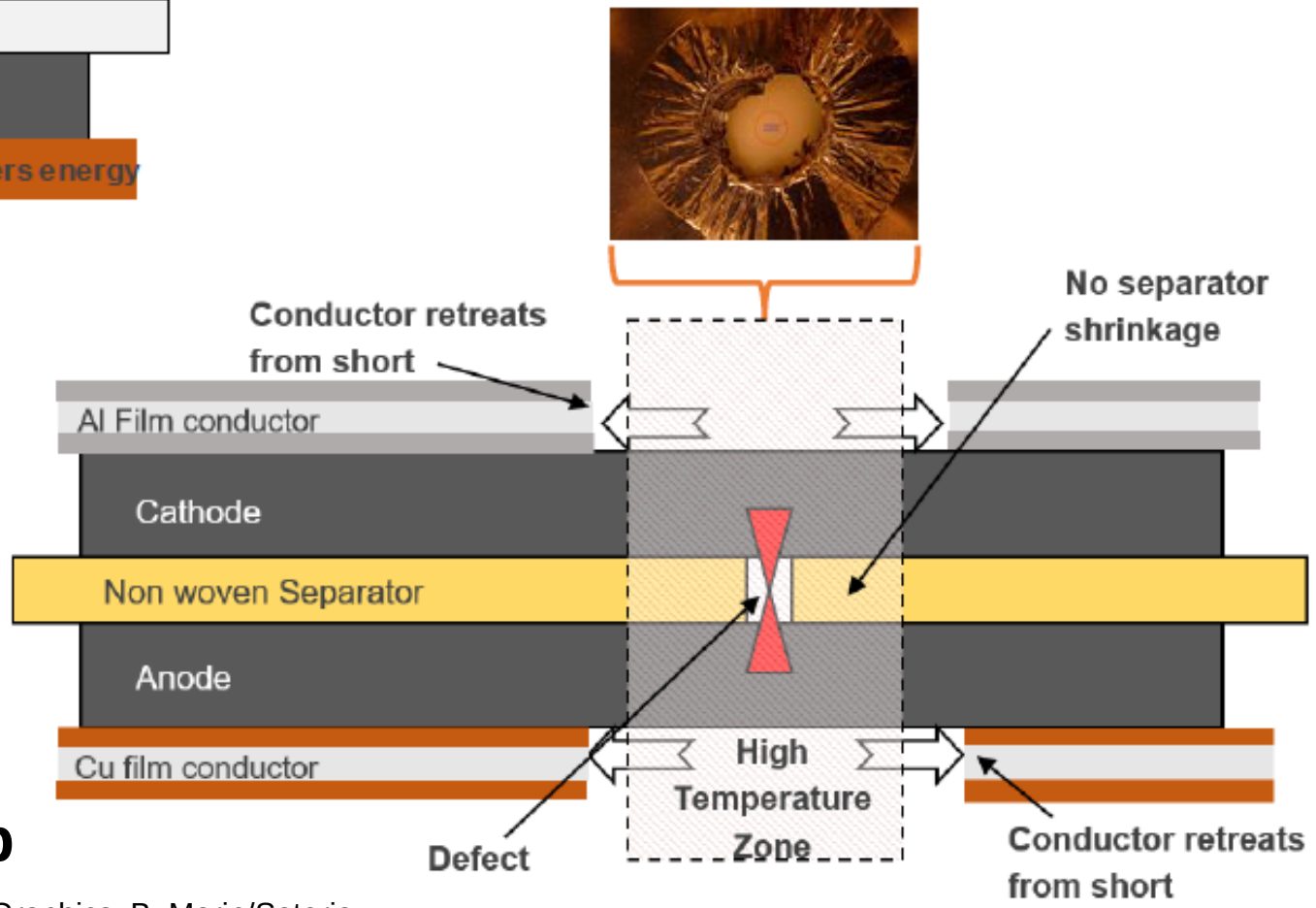
Thanks for the sponsors of our cell strategic reserve for funding this effort

- Orion, CCP, HLS, and NAVSEA

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

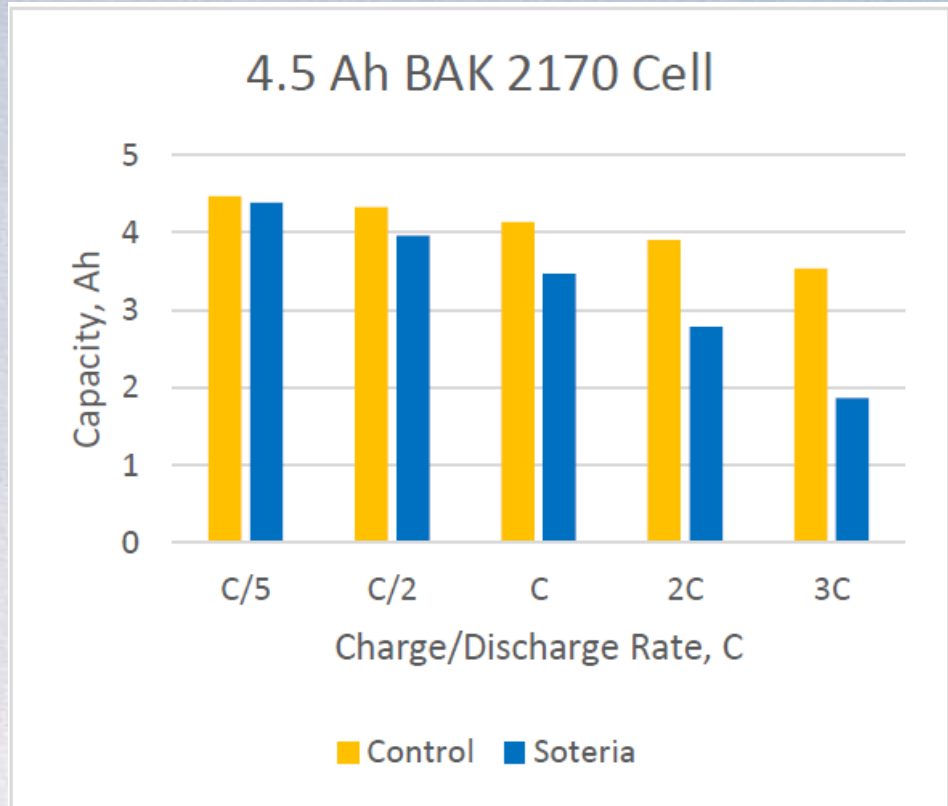
Soteria Battery Innovation Group

Graphics: B. Morin/Soteria

BAK 21700 Cell Designs

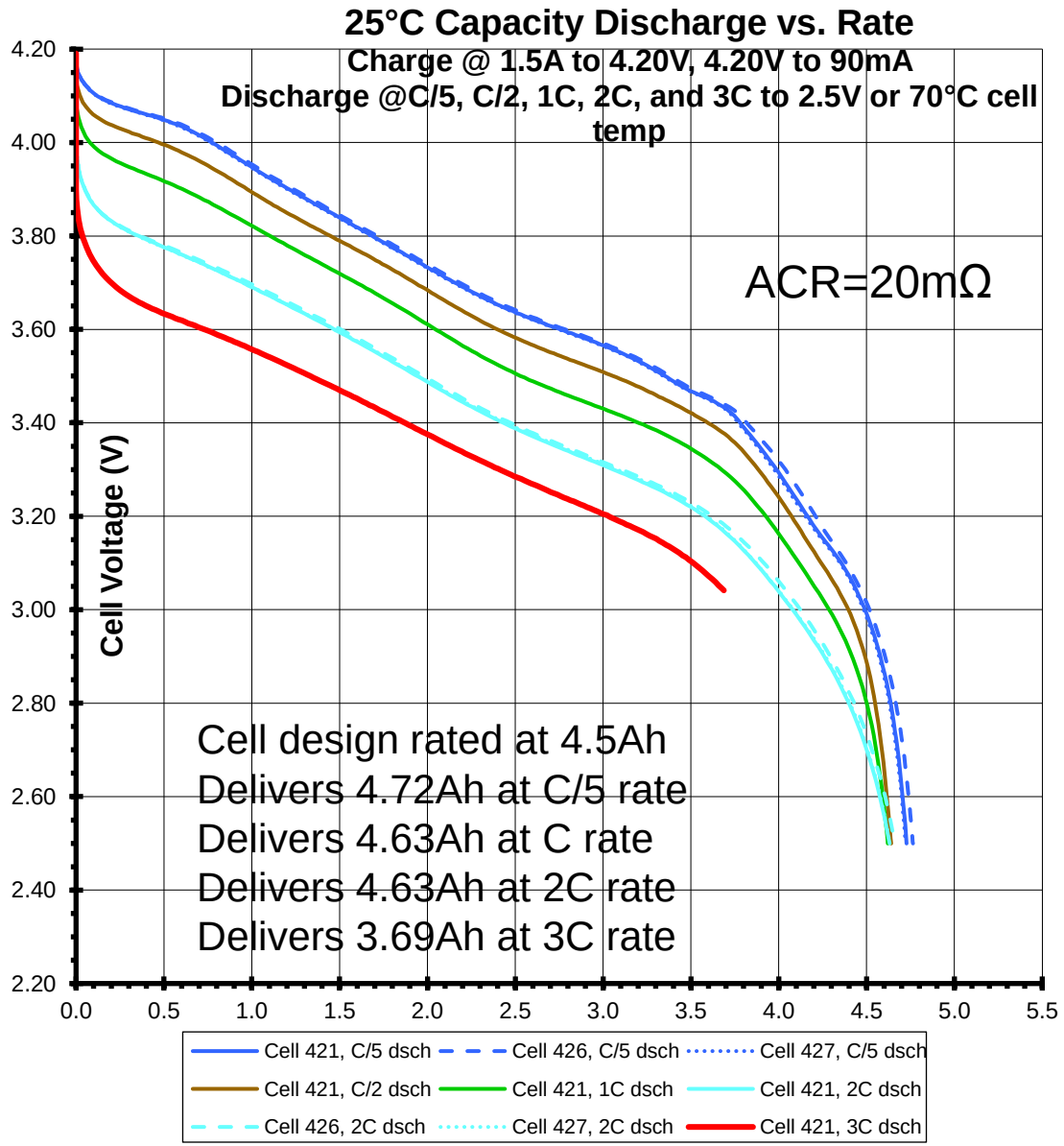
Soteria Cell Preliminary Specifications	
Manufacturer	BAK Power Battery
Separator	Polyolefin Film
Current Collector	Soteria Al, Standard Cu
Nominal Voltage	3.6V
Capacity	4.5Ah
AC impedance	42 mΩ
Weight	66 g
Energy Density	205 Wh/kg
Voltage Range	2.5V-4.2V

Control Cell Preliminary Specifications	
Manufacturer	BAK Power Battery
Separator	Polyolefin Film
Current Collector	Standard Foils
Nominal Voltage	3.6V
Capacity	4.5Ah
AC impedance	20 mΩ
Weight	67 g
Energy Density	227 Wh/kg
Voltage Range	2.5V-4.2V

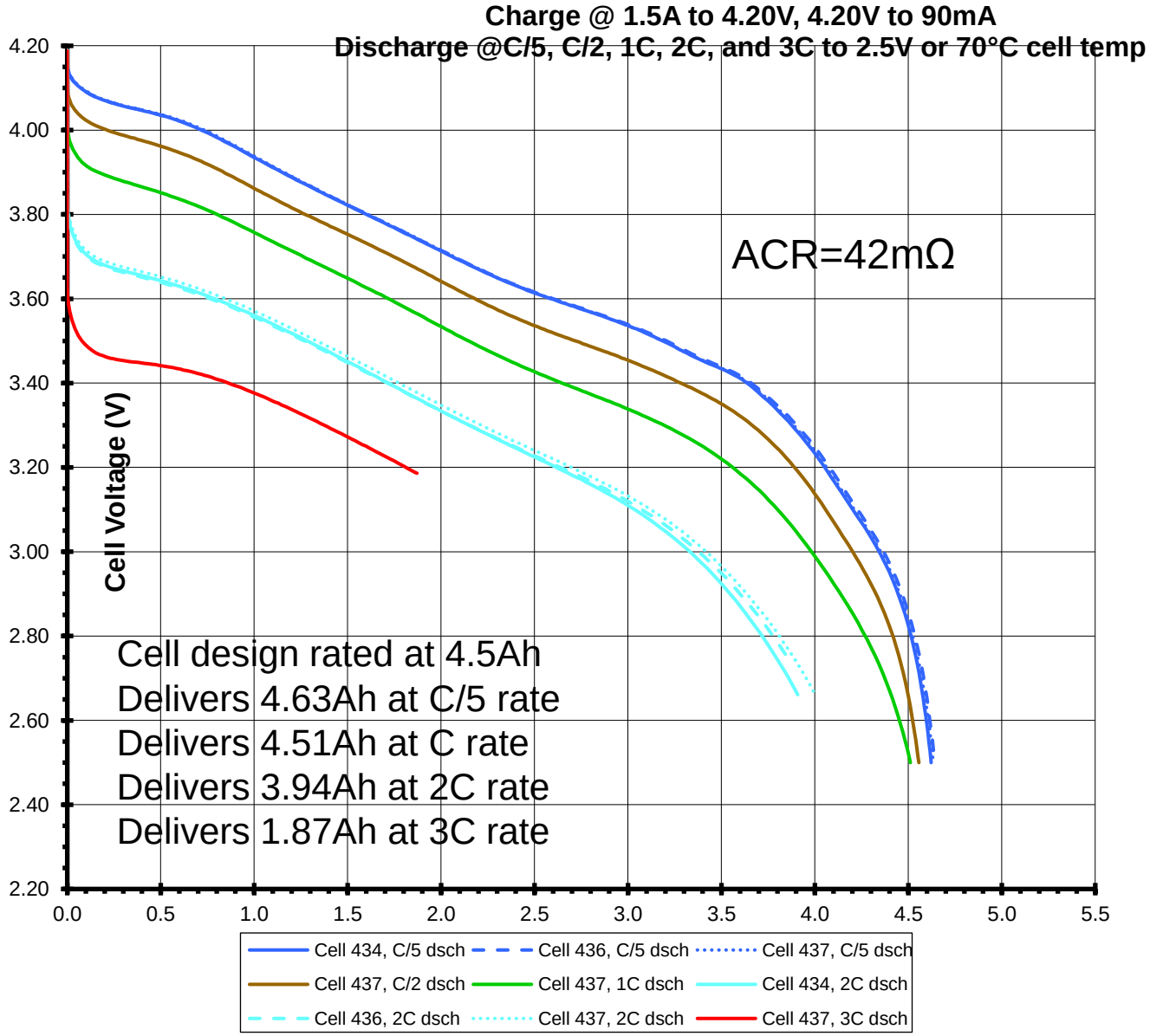


- Soteria polyester PCC only applied to cathode
  - 6 µm PET substrate metalized with 1 µm aluminum coating on both sides
- Polycrystalline NMC 811, ceramic coated separator
- Tab-to-PCC ultrasonically welded connection
- Measured 251 Wh/kg and 684 Wh/L on initial cycle with the Al PCC

BAK 21700 Li-ion Control Cells (no PCC)

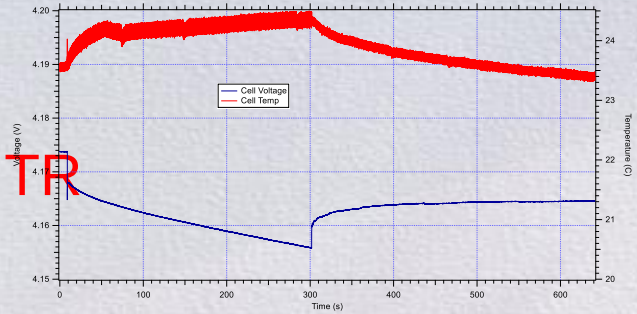


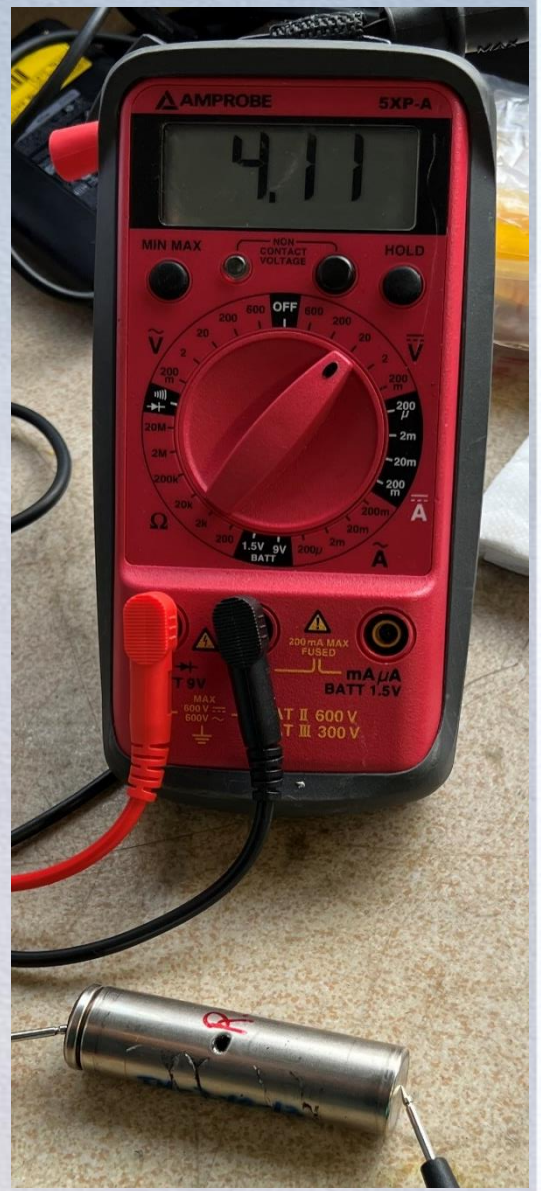
BAK 21700 Li-ion Plastic Current Collector (PCC)



BAK 21700 4.6Ah Test Matrix and Results (Nail)

- Soteria metalized polyester (15)
  - PCC only on cathode (cell achieves 251 Wh/kg)
  - Cu foil on anode like all other features in control version
  - 14 of 15 cells tolerated nail penetration at 100% SoC
    - No fire, sparks, venting, or TR in those 14
    - Muted TR in 1 cell, generating ~50% kJ of control average
- Control cells (8)
  - Al and Cu foil CCs
  - All 8 cells went into TR





$\Delta t_{max} < 1°C$
$\Delta vmax < 19mV$

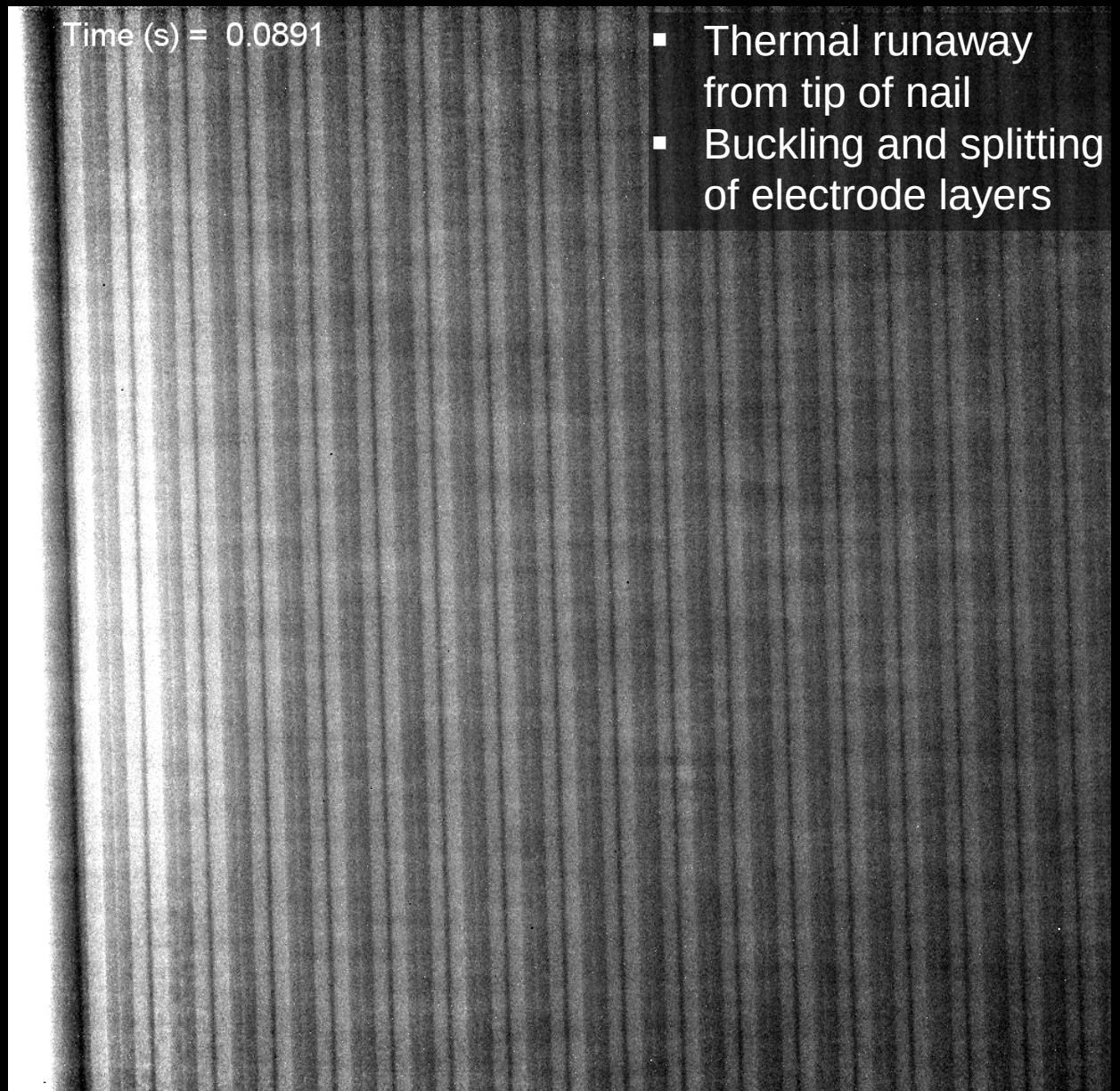
Tolerance demonstrated with near zero degradation of OCV!!!

Radiography at 3000 fps of 21700 cells

Dense material is dark (nail, can, NMC)

Control cell

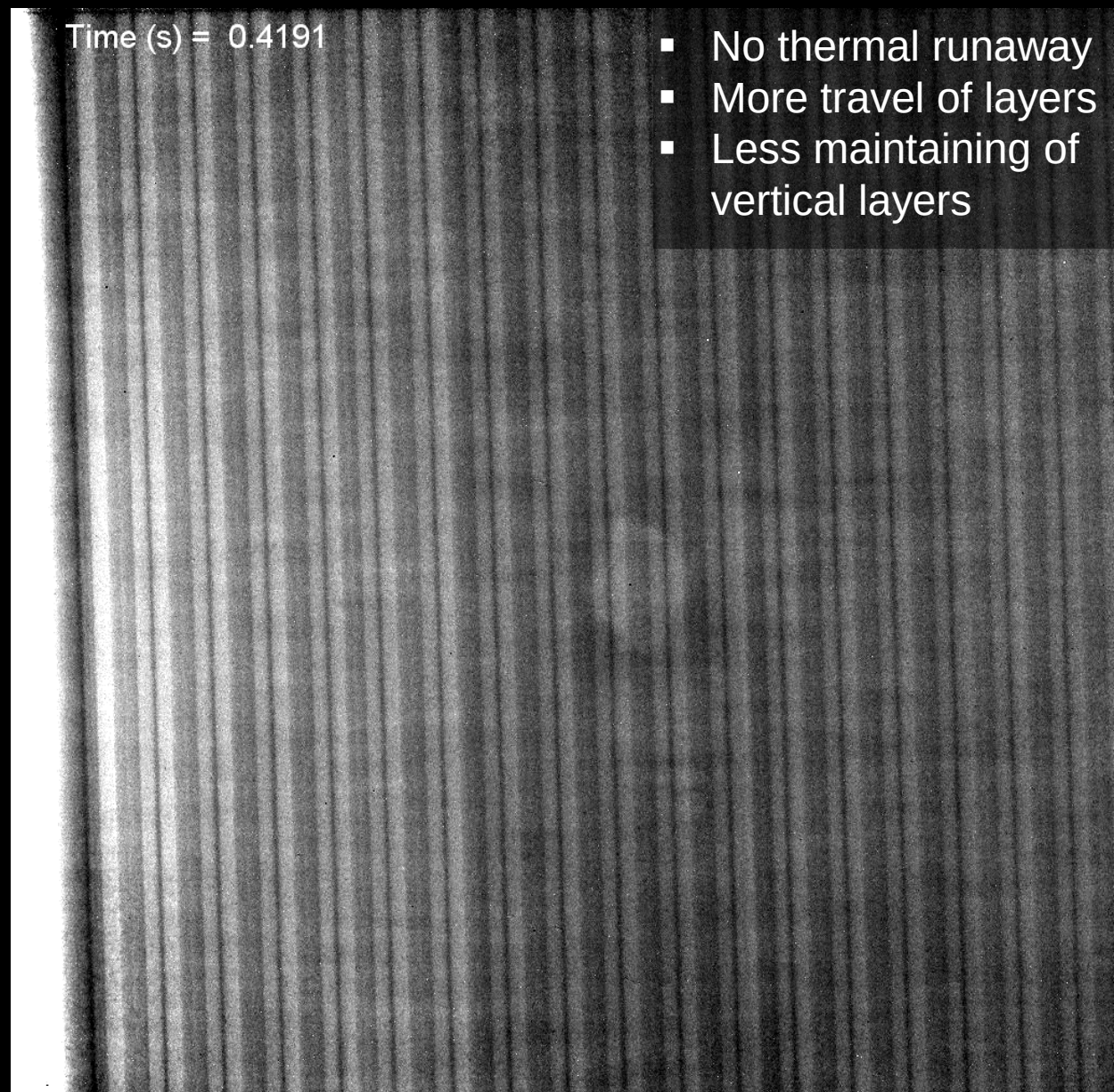
Run 025



- Thermal runaway from tip of nail
- Buckling and splitting of electrode layers

Cell with PCC

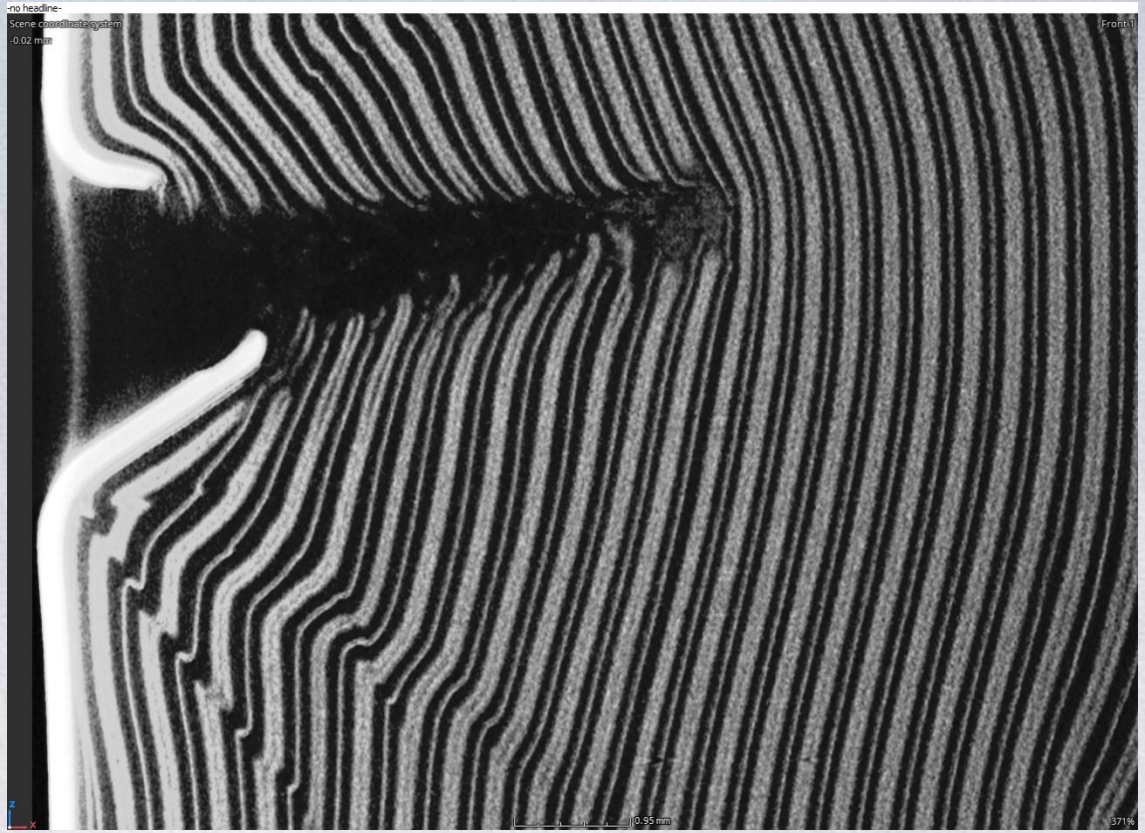
Run 020



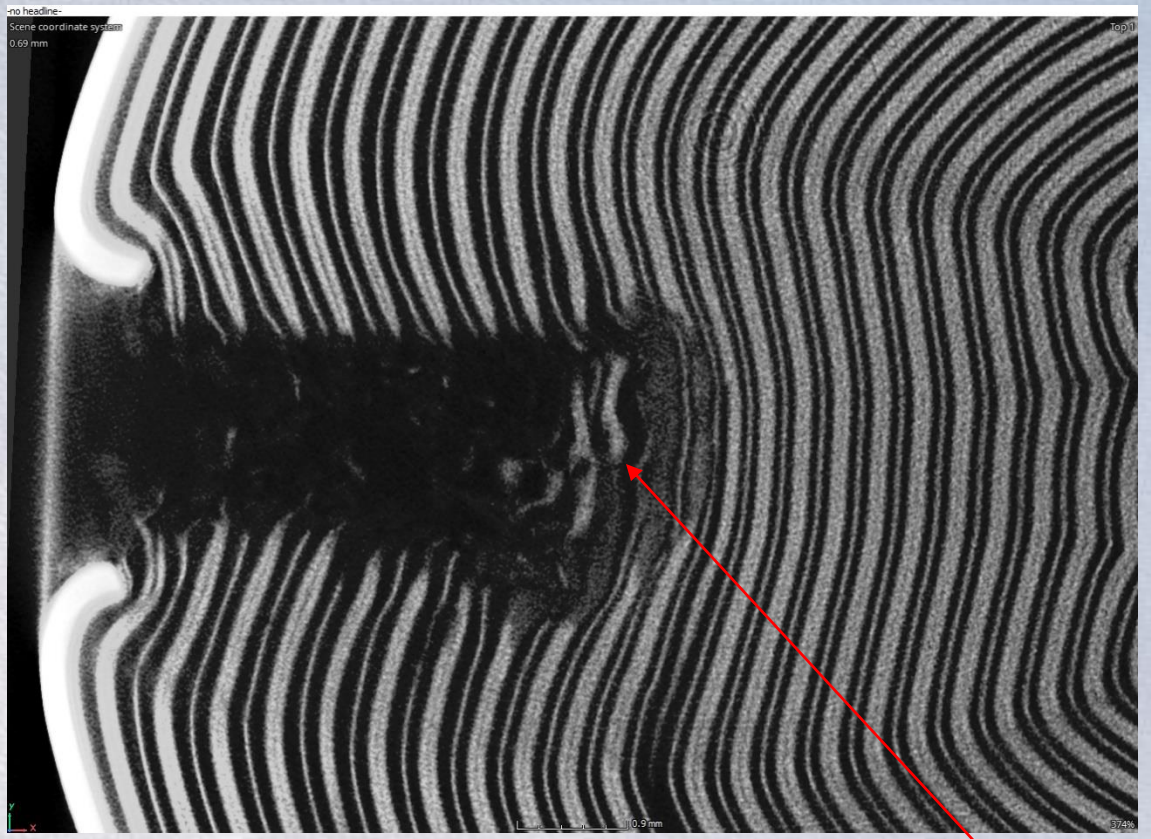
- No thermal runaway
- More travel of layers
- Less maintaining of vertical layers

CT Images of BAK 21700 with Cathode PCC

Axial view of nail penetration zone

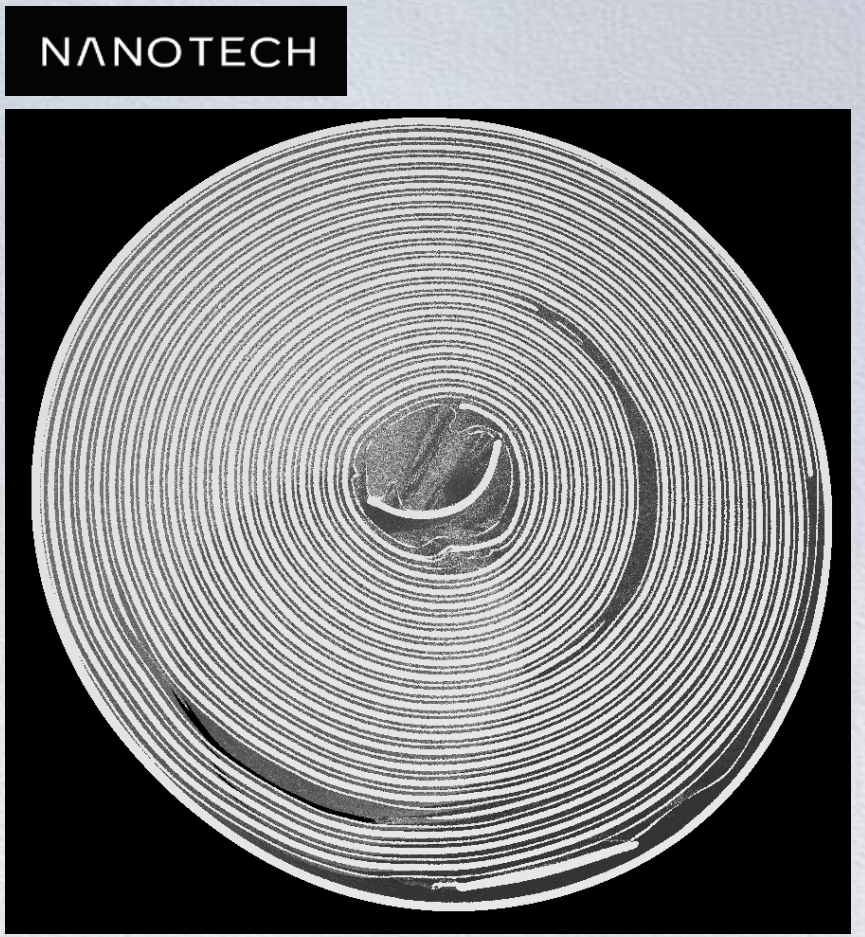


Radial view of nail penetration zone



Reversing the image brightness from the video: Bright is most dense material, cell can, NMC
Al coated PCC for cathode is thin gray layer between NMC active material coatings.
Axial view shows cathode PCC is clearly missing at nail interface (split ends).

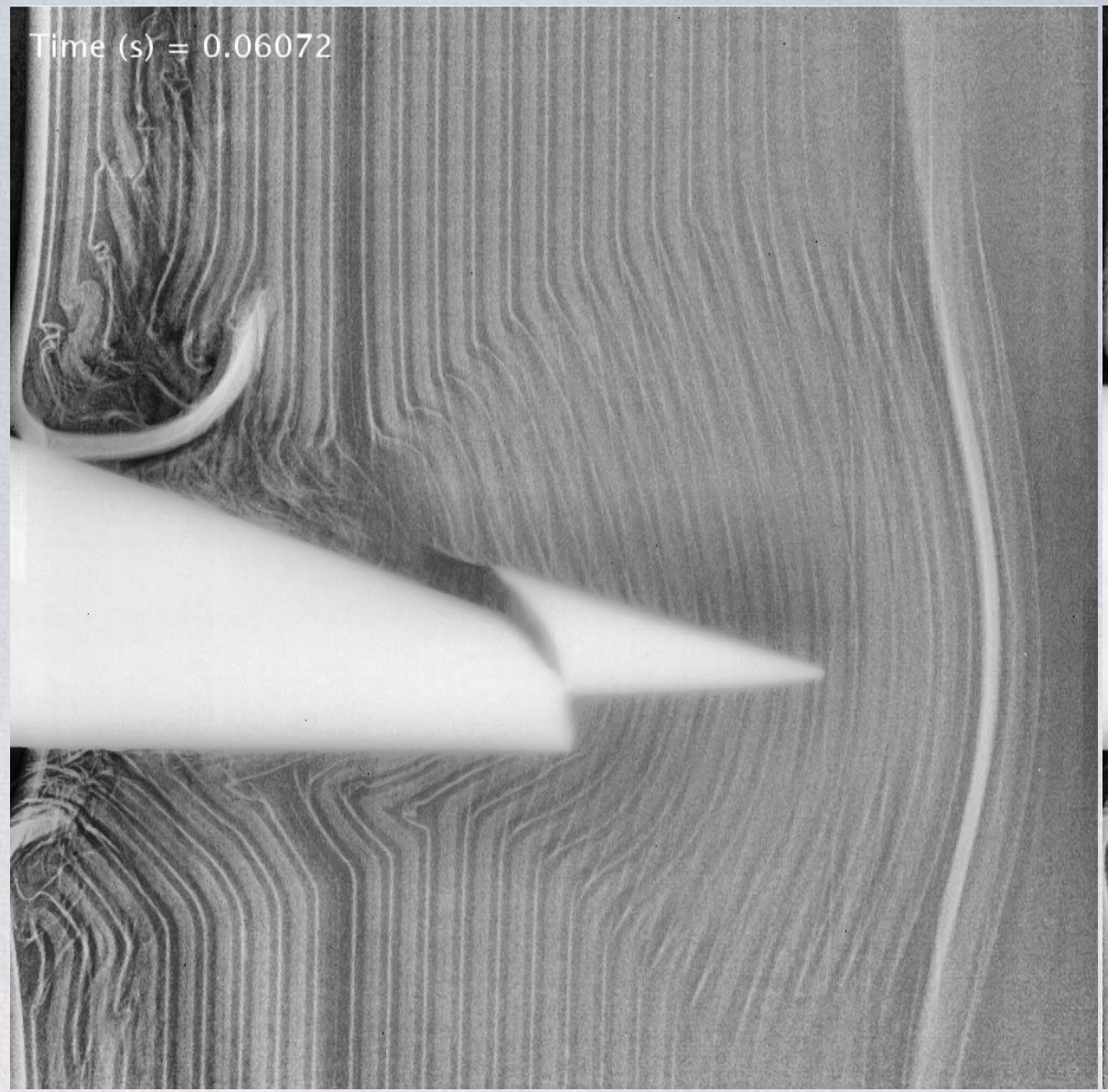
3.3Ah Nanotech Energy 18650

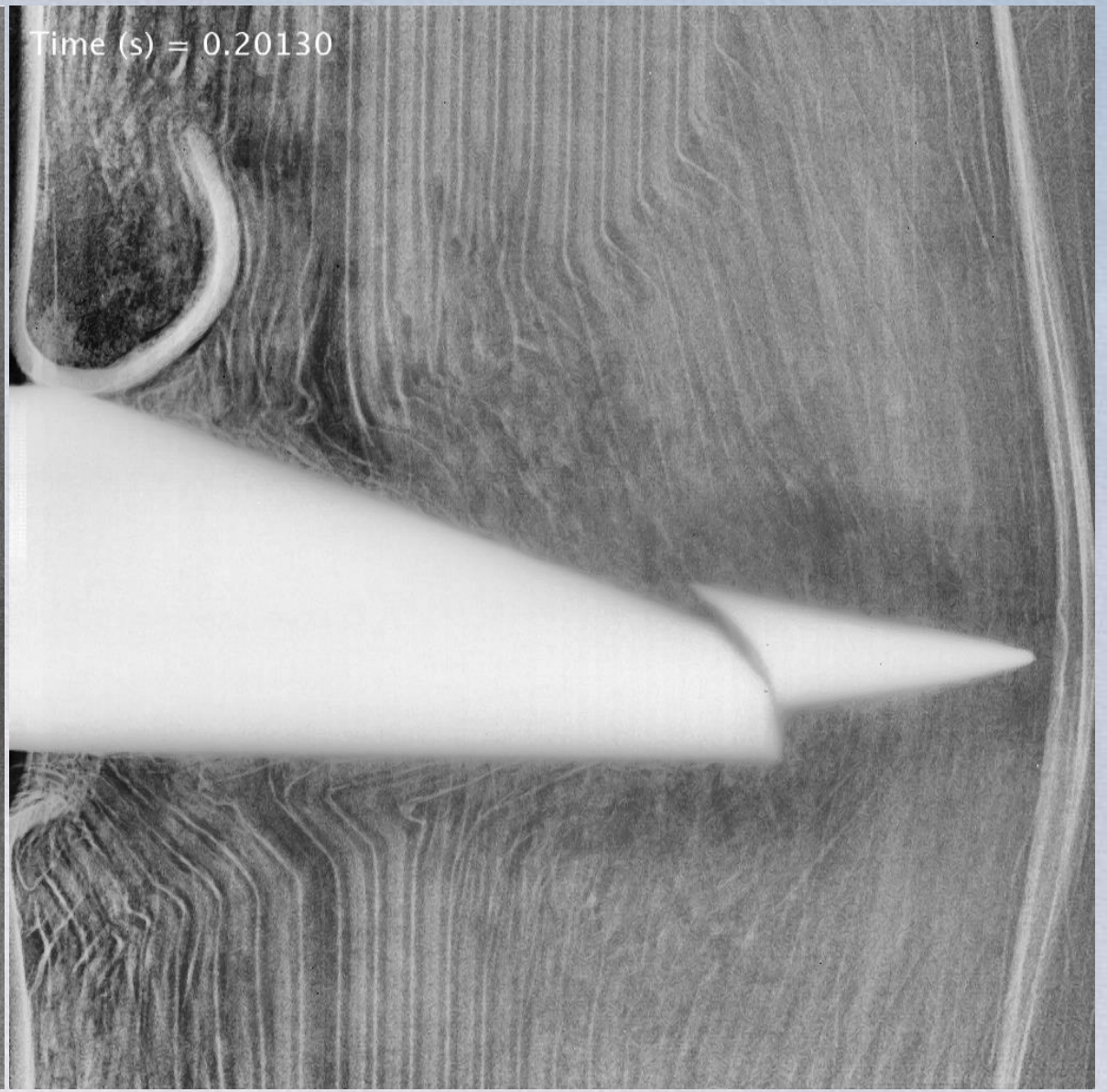


- Prototype cell design
  - Soteria Al PET PCC (1 + 6 + 1 µm)
    - Bobby pinned Al tab connections
  - Graphite with 10% Si doping
  - NMC 811 cathode
  - Ceramic coated separator (12 µm)
  - Two tabs on both electrodes for high-rate performance
  - Made in Chico, CA
- Nail penetration at ESRF
  - 6 cells with Al PCC for cathode
  - 6 control cells with metal foil CCs

44.674g w/ Al PCC	266 Wh/kg
45.472g w/ metal CCs	262 Wh/kg

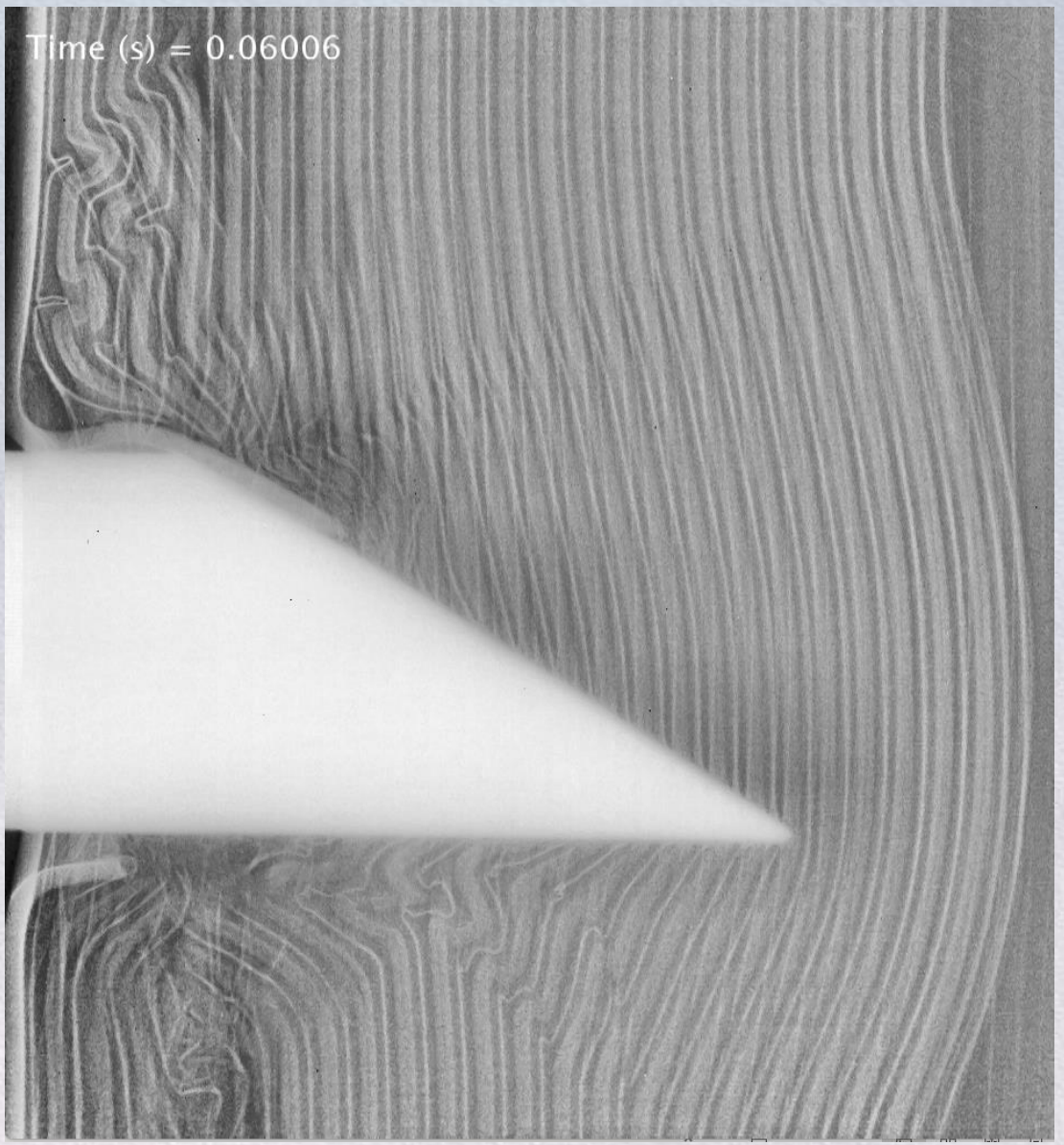
Nanotech Control Cell – Immediate TR

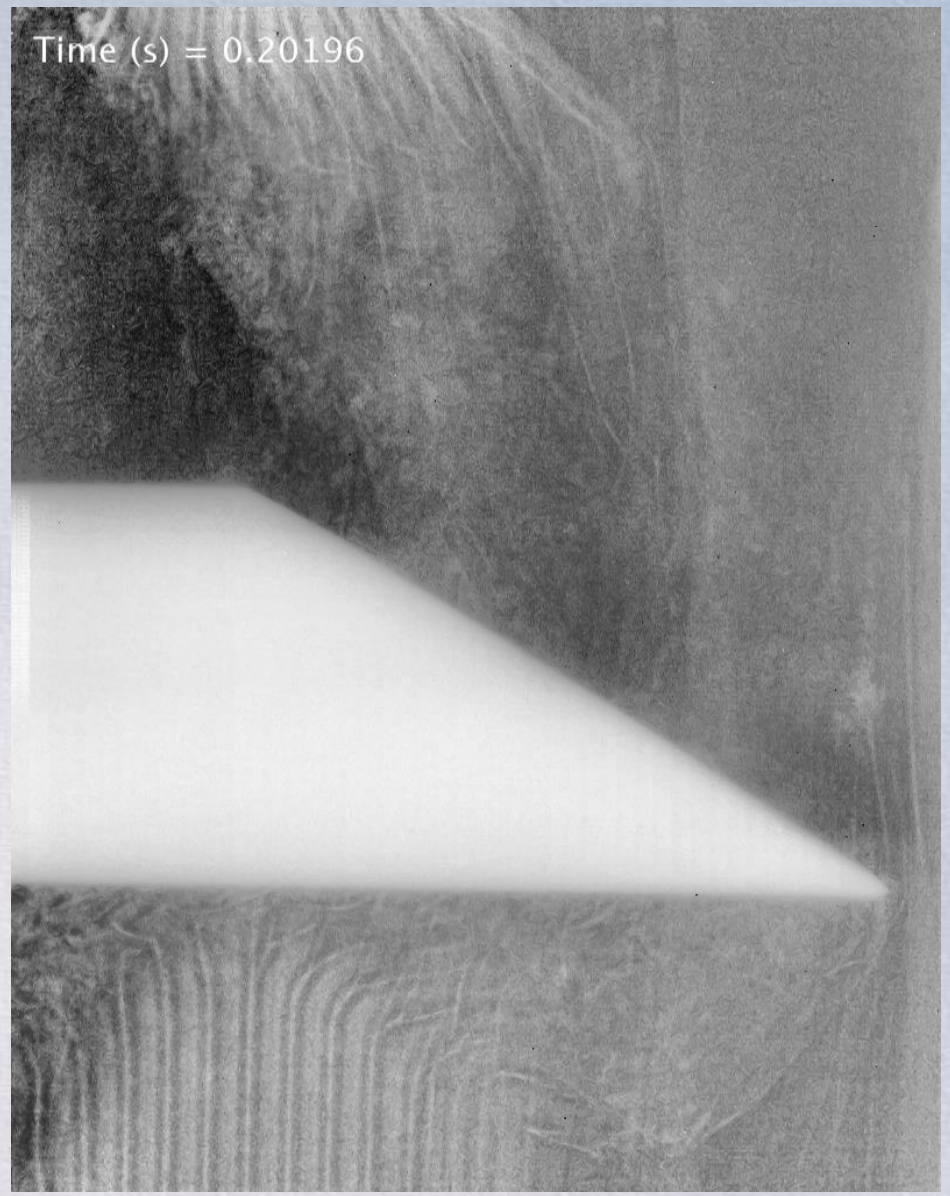




Run 25 – Burst of gas generation at 0.06s breaks nail with TR well underway at 0.2s

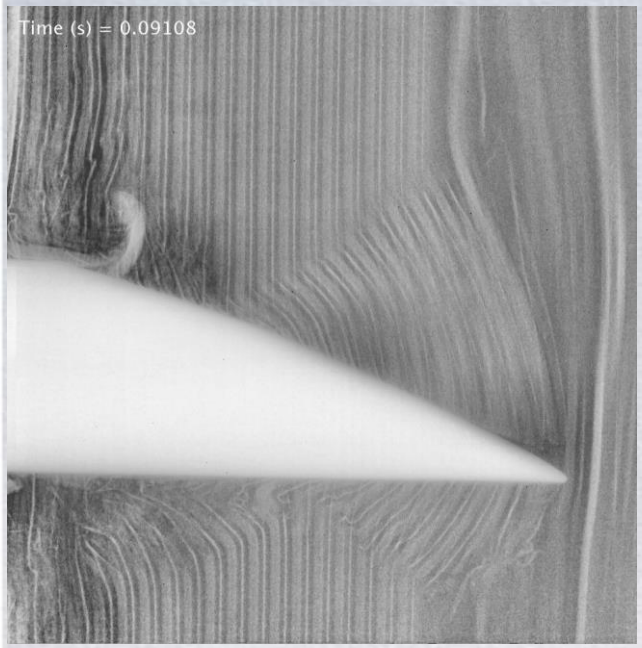
Nanotech Control Cell – Immediate TR

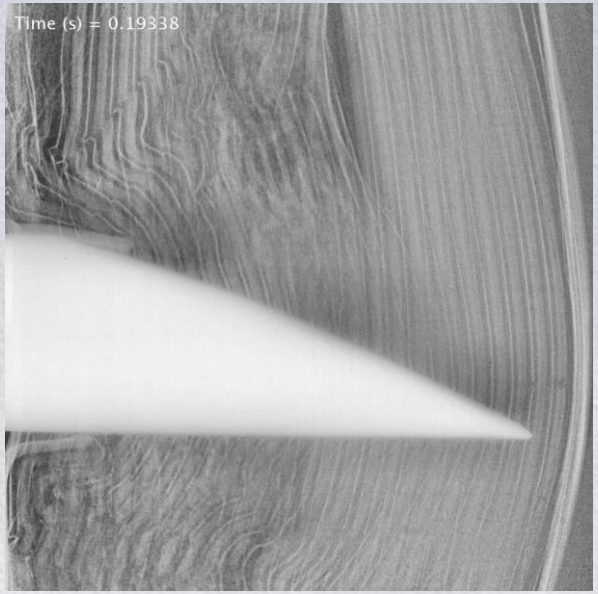


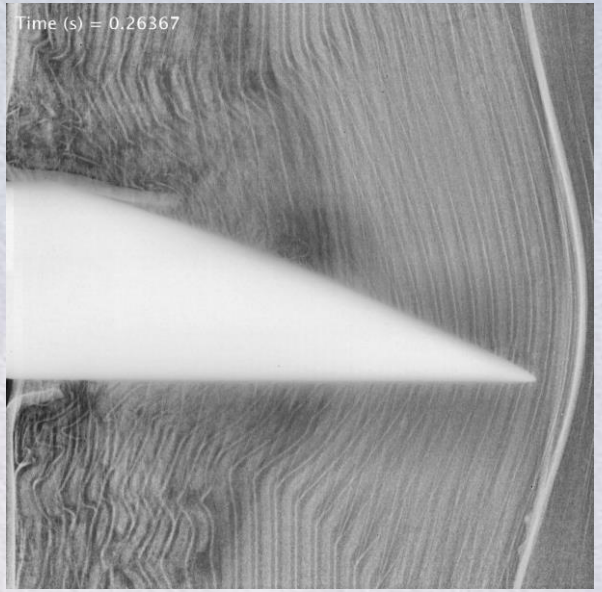


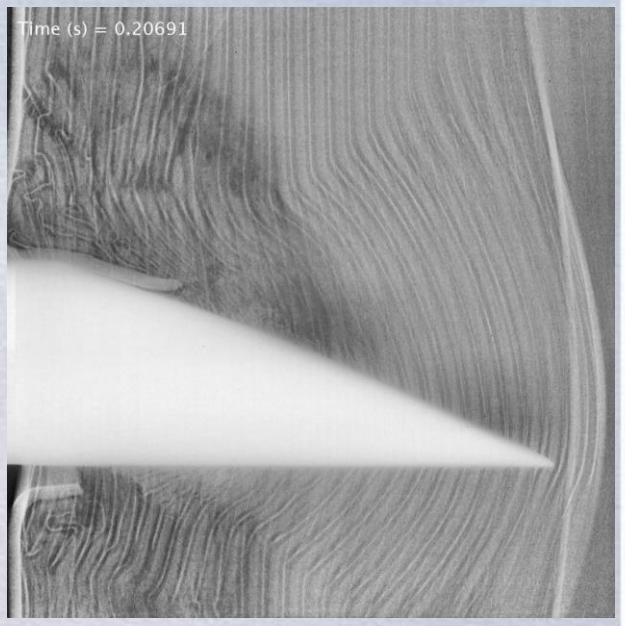
Run 26 – TR initiation visible at 0.06s and well underway at 0.2s

More Nanotech Control Cells – Immediate TR



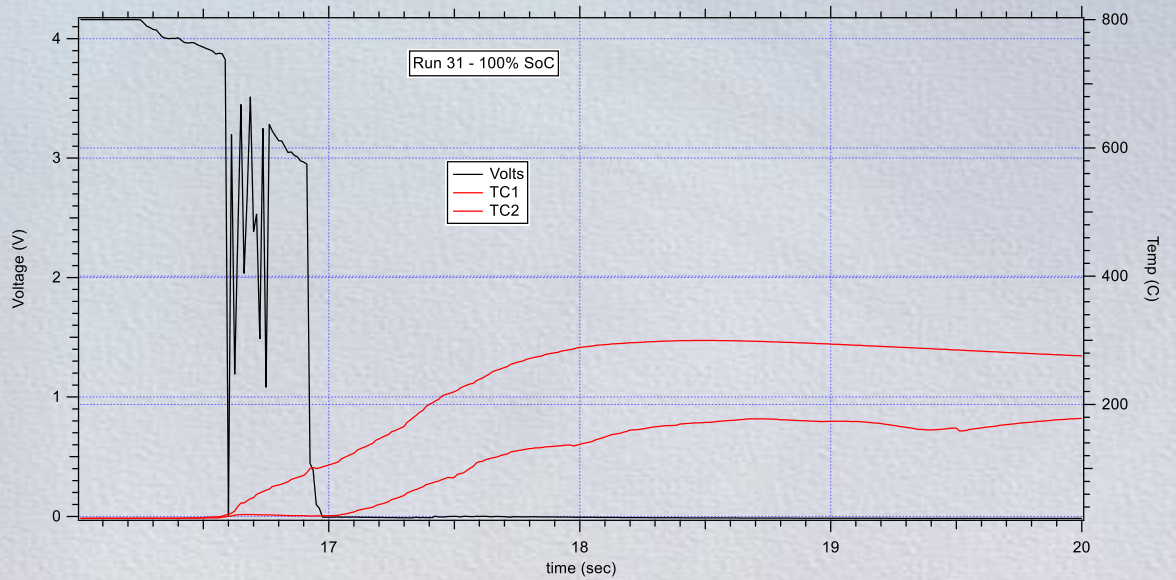


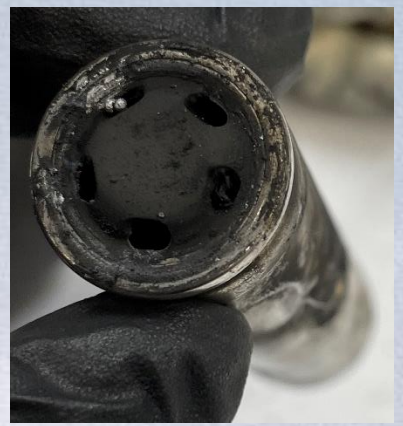




Runs 27-30, within 0.26s, TR initiation is apparent

Nanotech 3.3Ah with Soteria AI PCC - Not Immediate TR to Nail

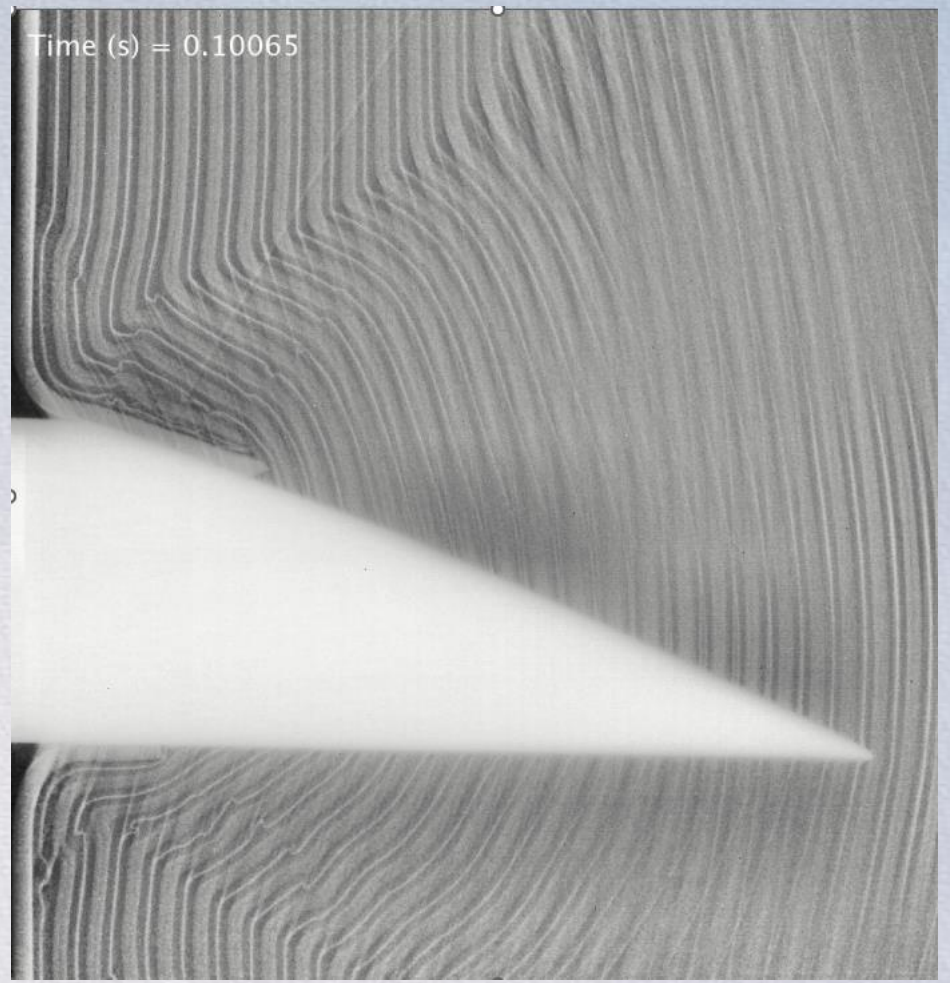




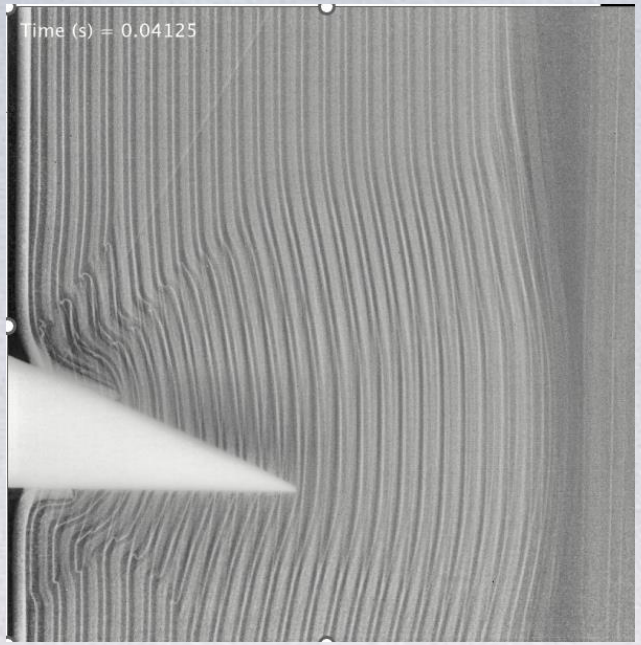
3.3Ah Nanotech 18650 – 100% SoC

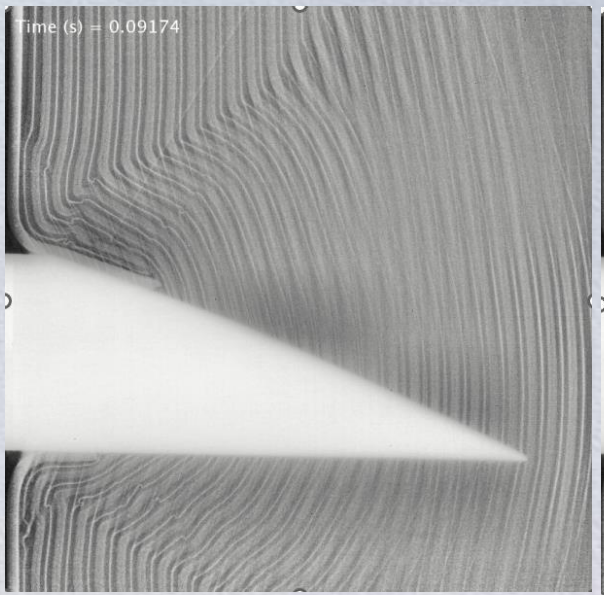
Run 31

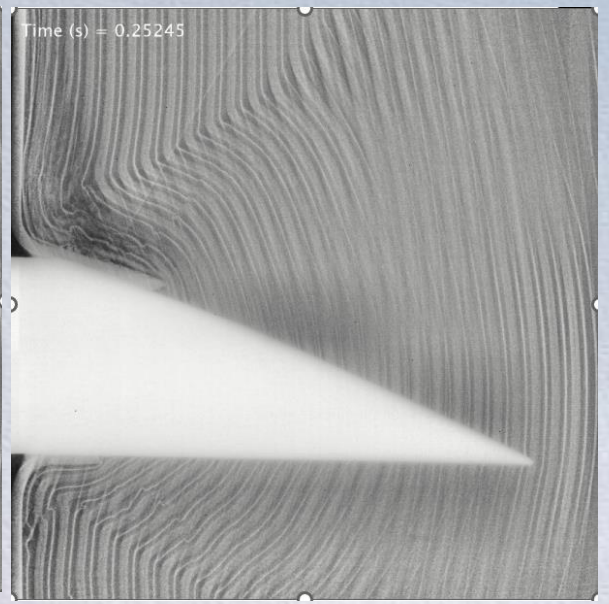
- **Nail slices through causing PCC in NMC to swell in winds head of nail**
- **Nail induces impact cone zone**
- **Nail penetration takes 100ms**
- **Electrode bending and shearing at nail impact cone zone, particularly above nail near can**
- **Onset of TR starts after full insertion above nail near can**
- **Full TR develops radially over next 900ms**

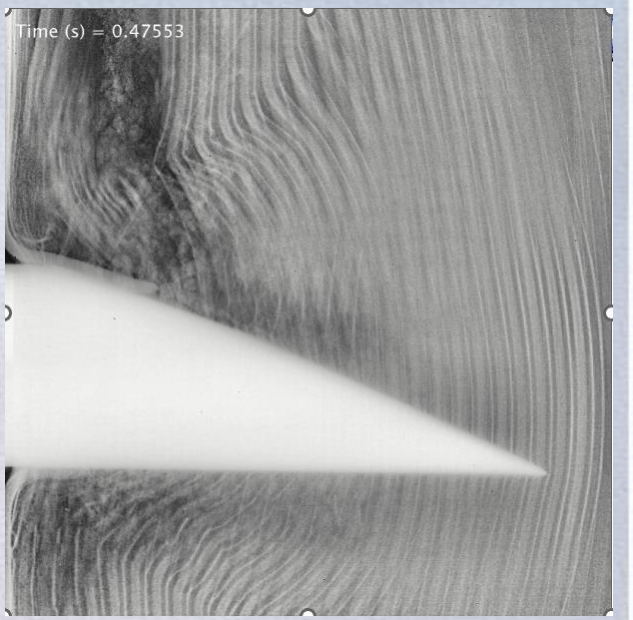


Run 31 – Nanotech 3.3Ah with Soteria Al PCC



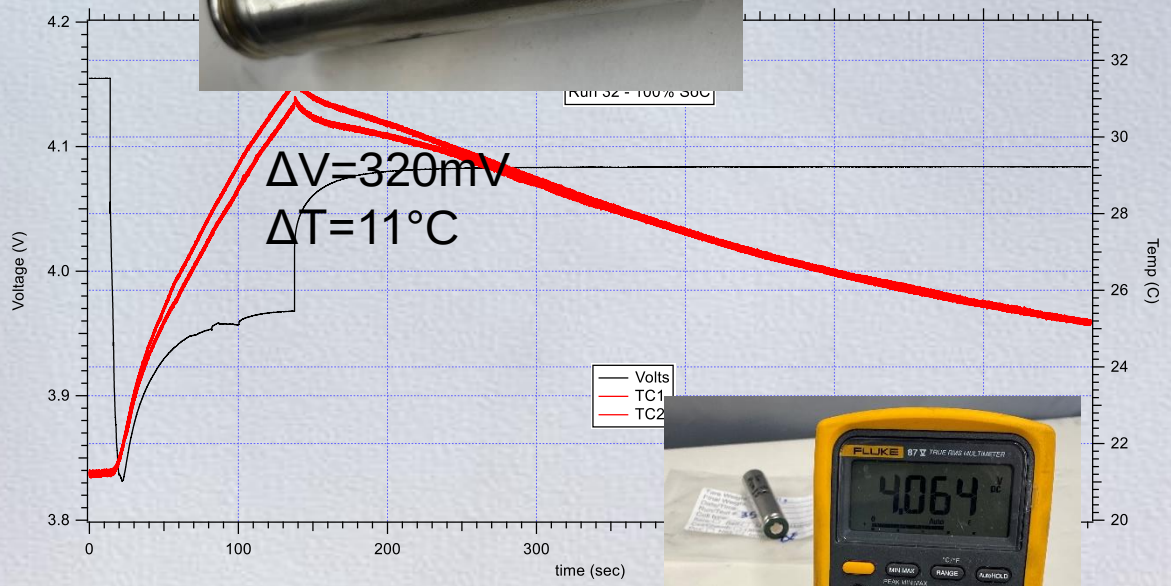


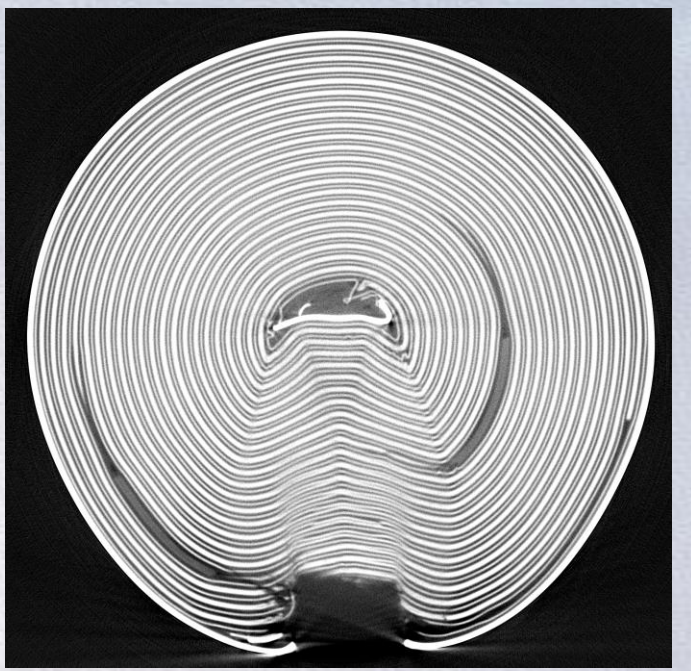




- Nail slices through causing PCC in NMC to swell in winds head of nail
- Nail induces impact cone zone
- Nail penetration takes 100ms
- Electrode bending and shearing at nail impact cone zone, particularly above nail near can
- Onset of TR starts after full insertion above nail near can
- Full TR develops radially over next 900ms

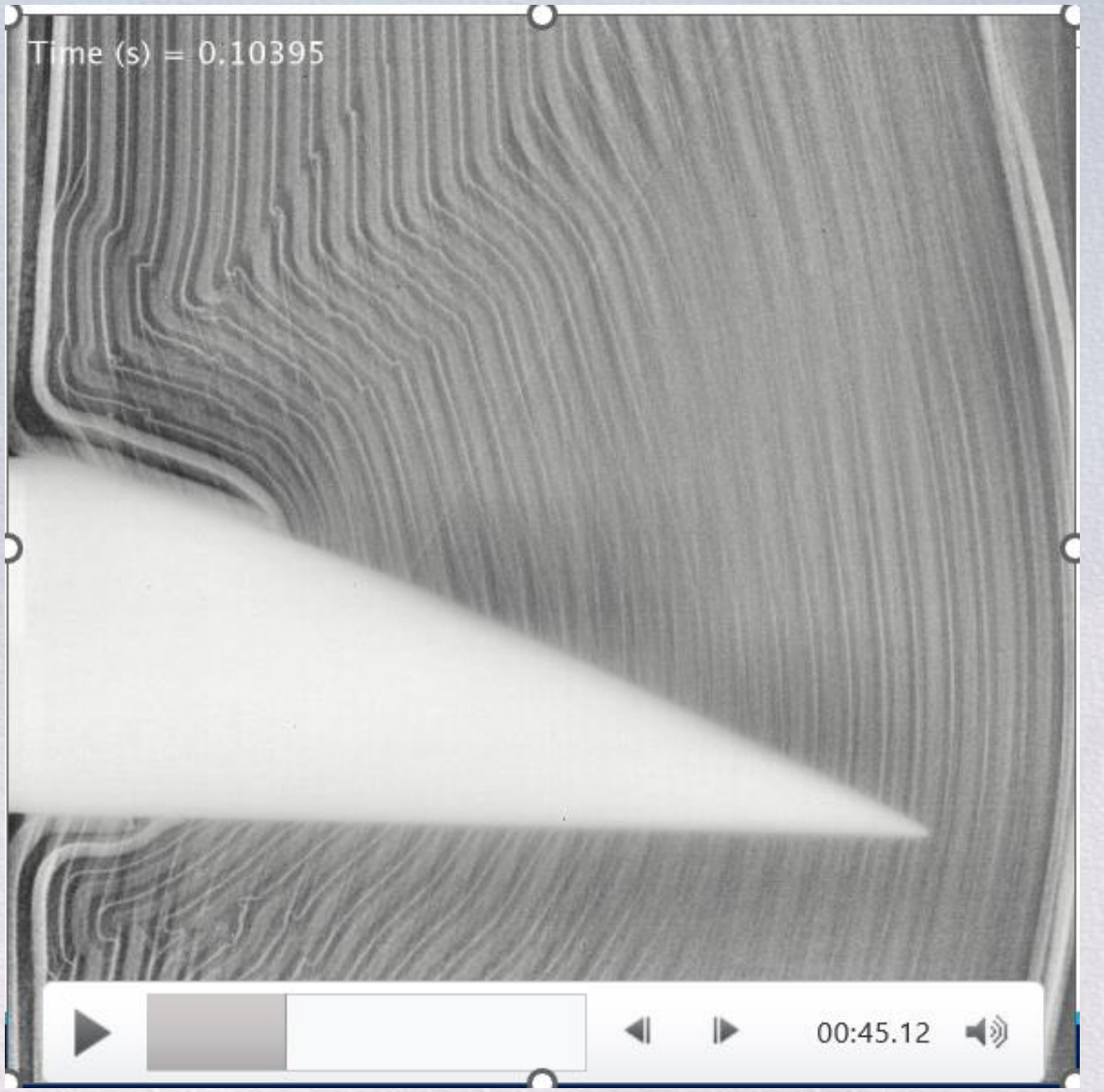
Tolerance to Nail – 100% SoC



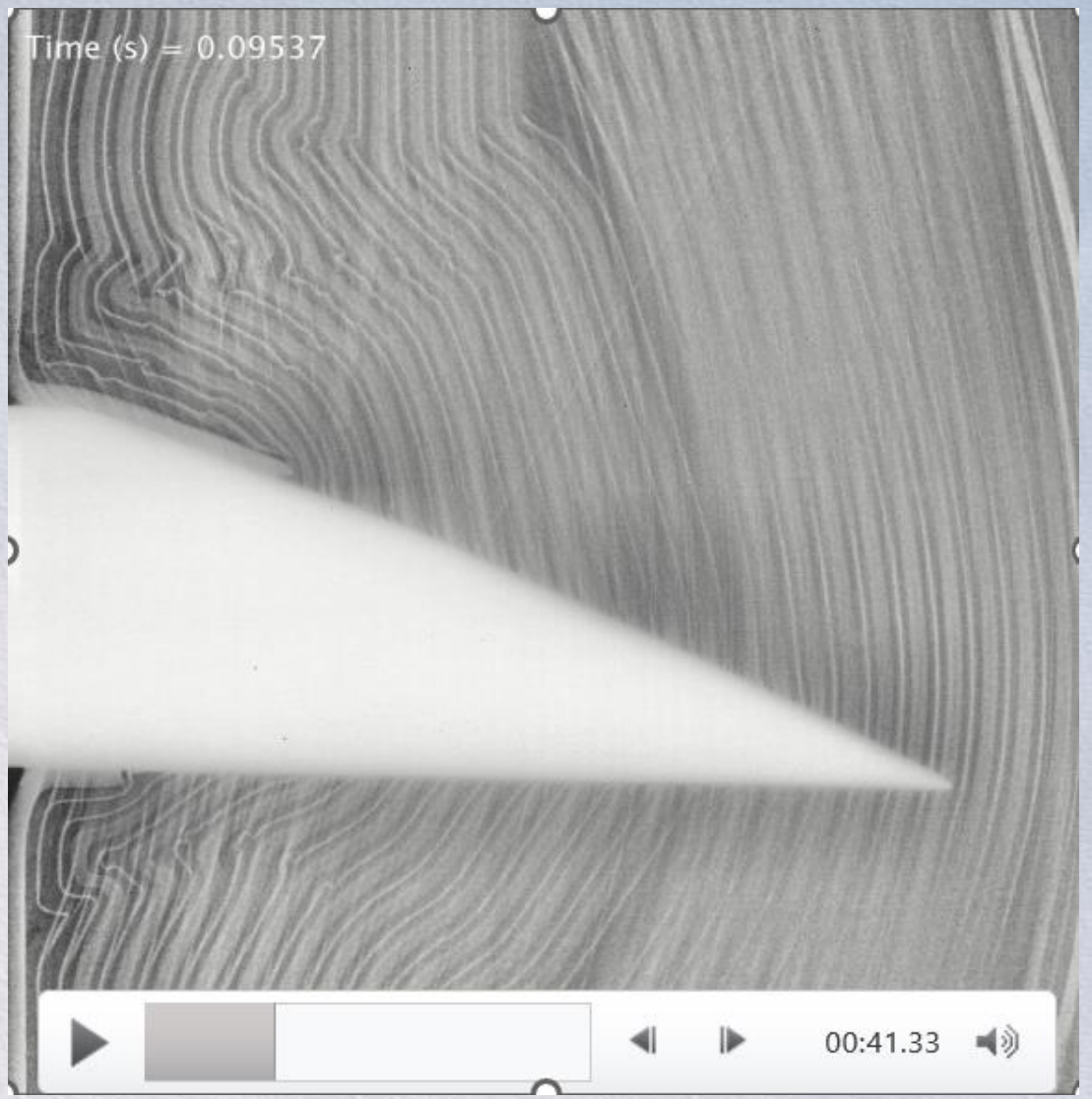


3.3Ah Nanotech 18650 – 100% SoC

Run 32

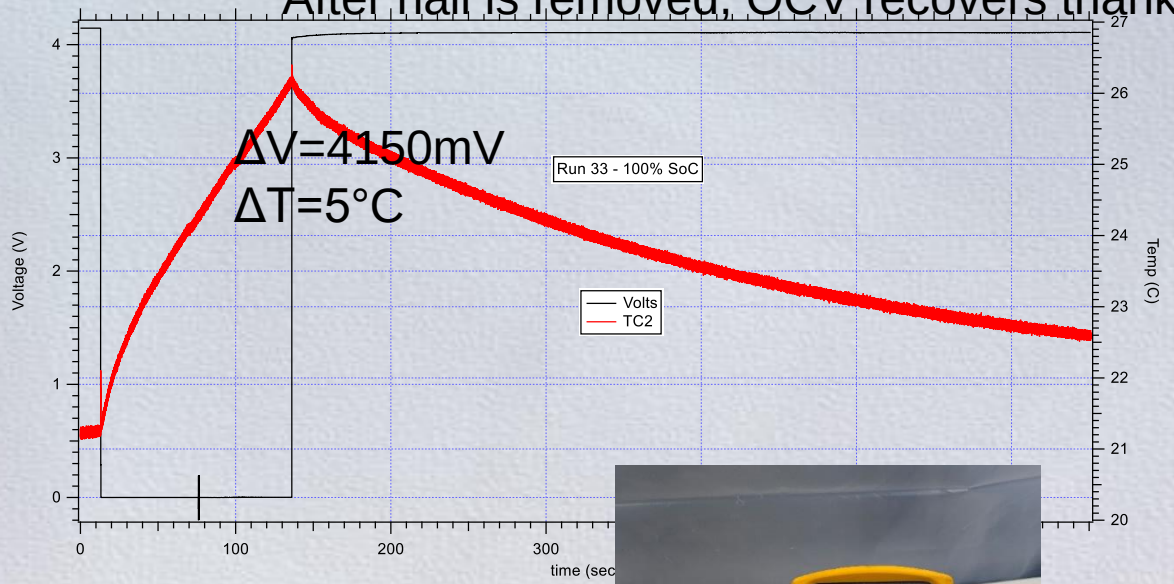


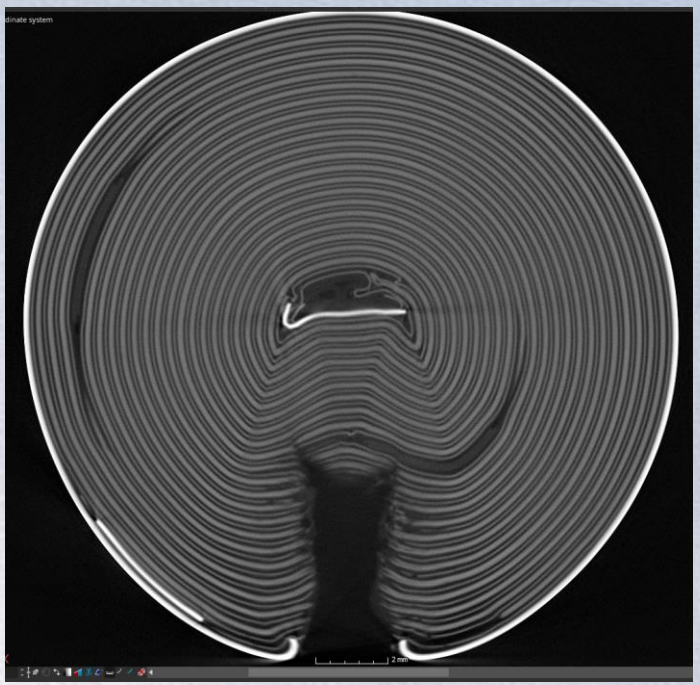
Run 33



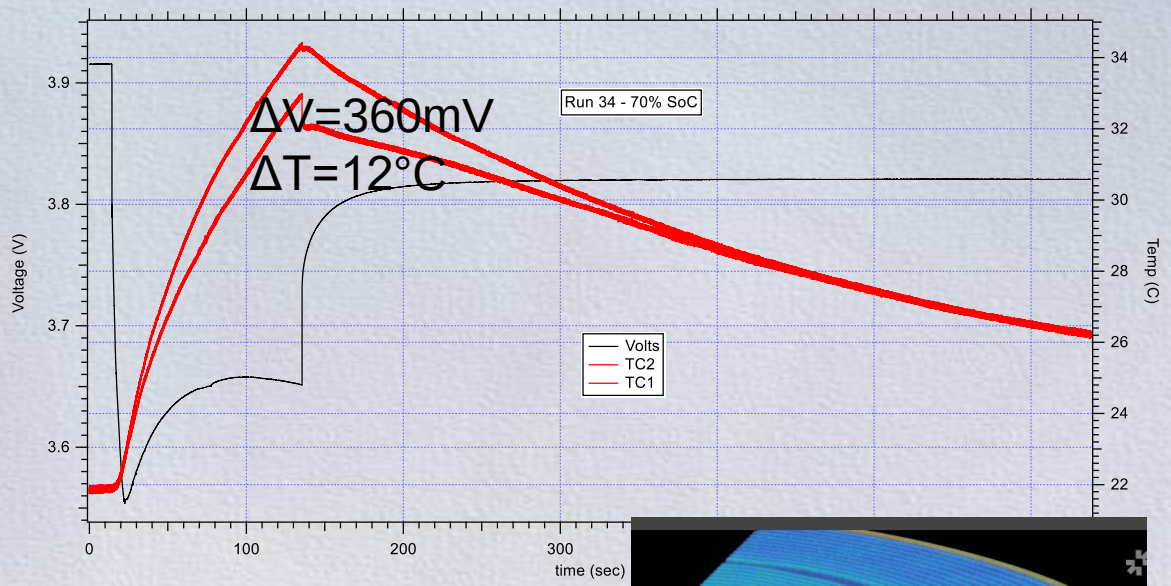
Tolerance to Nail – 100% SoC

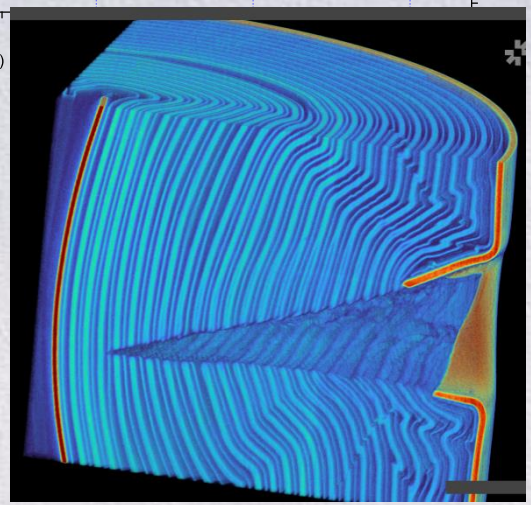
Nail shorts to one of the (+) tab which fuses from PCC causing zeroing of OCV
After nail is removed, OCV recovers thanks to 2nd (+) tab connection to PCC





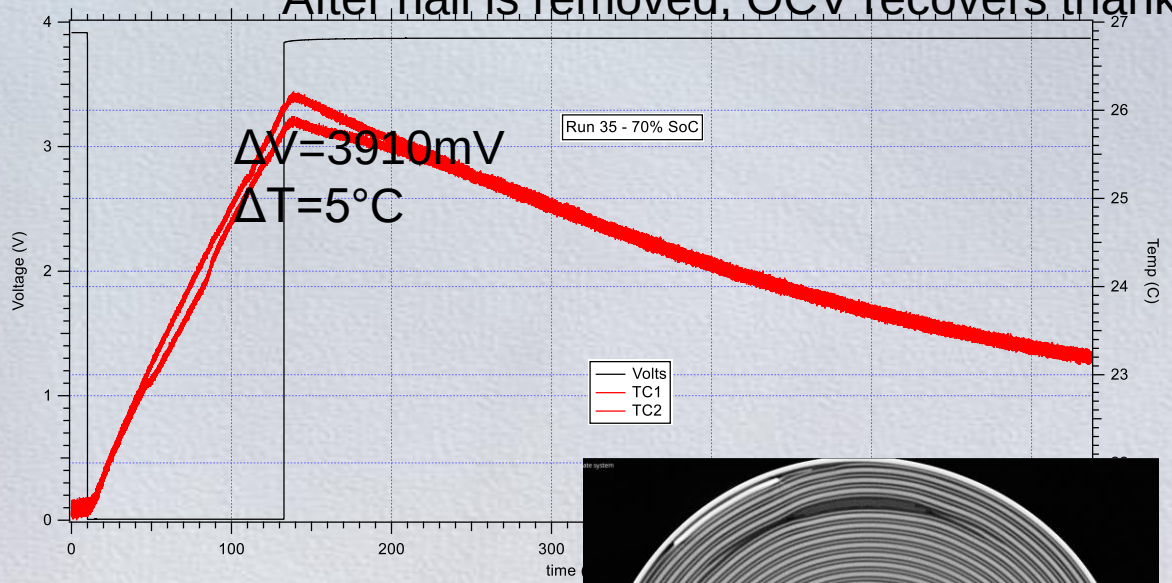
Tolerance to Nail – 70% SoC

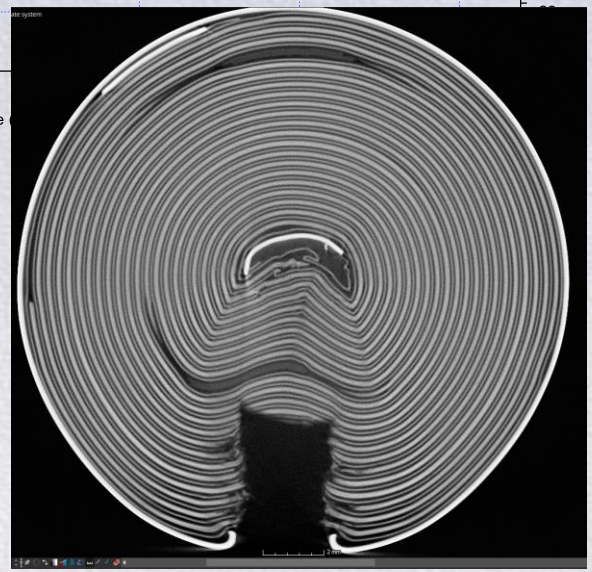




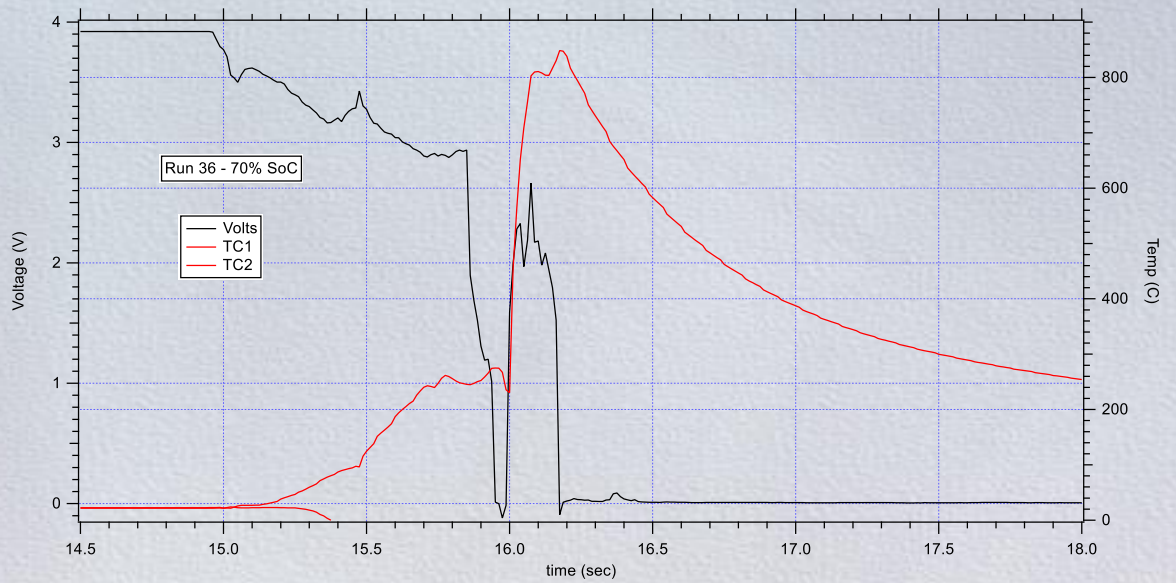
Tolerance to Nail – 70% SoC

Nail shorts to one of the (+) tab which fuses from PCC causing zeroing of OCV
After nail is removed, OCV recovers thanks to 2nd (+) tab connection to PCC

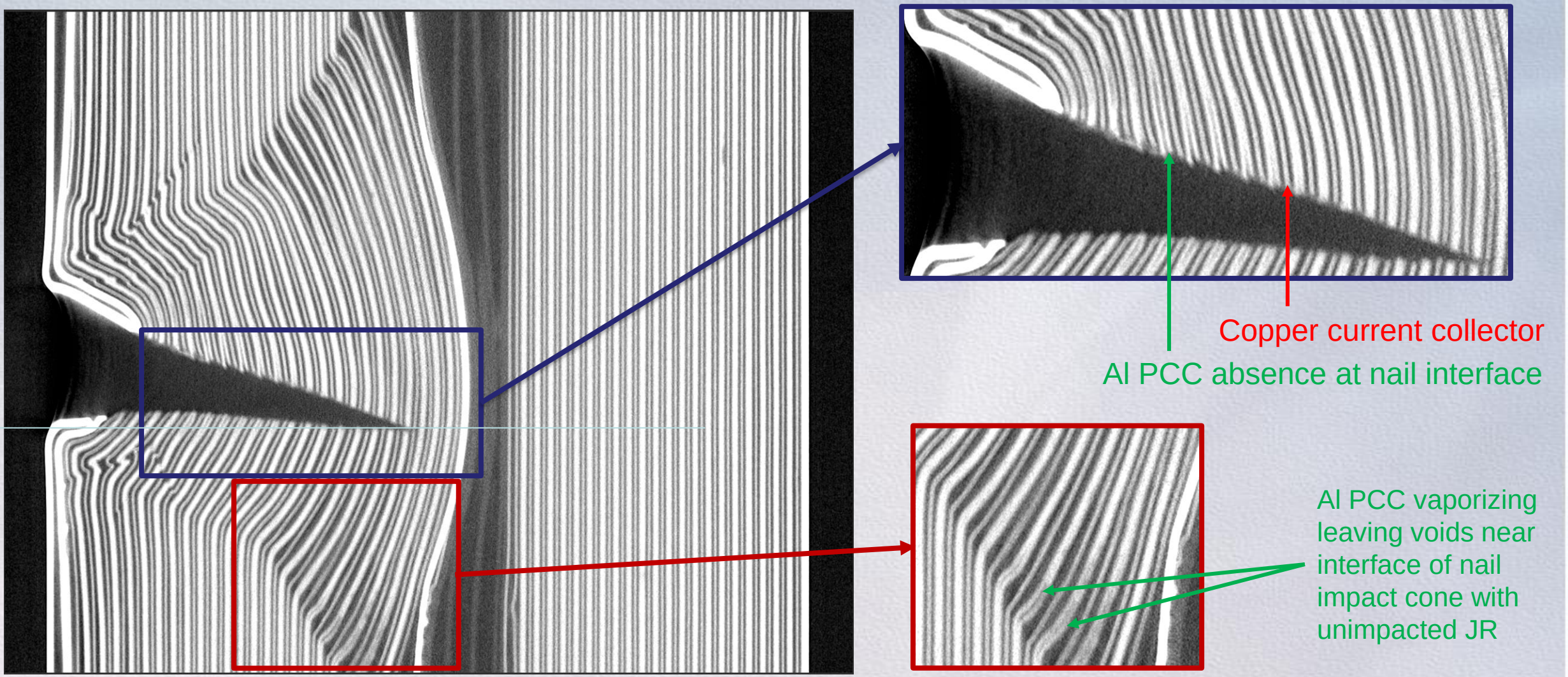




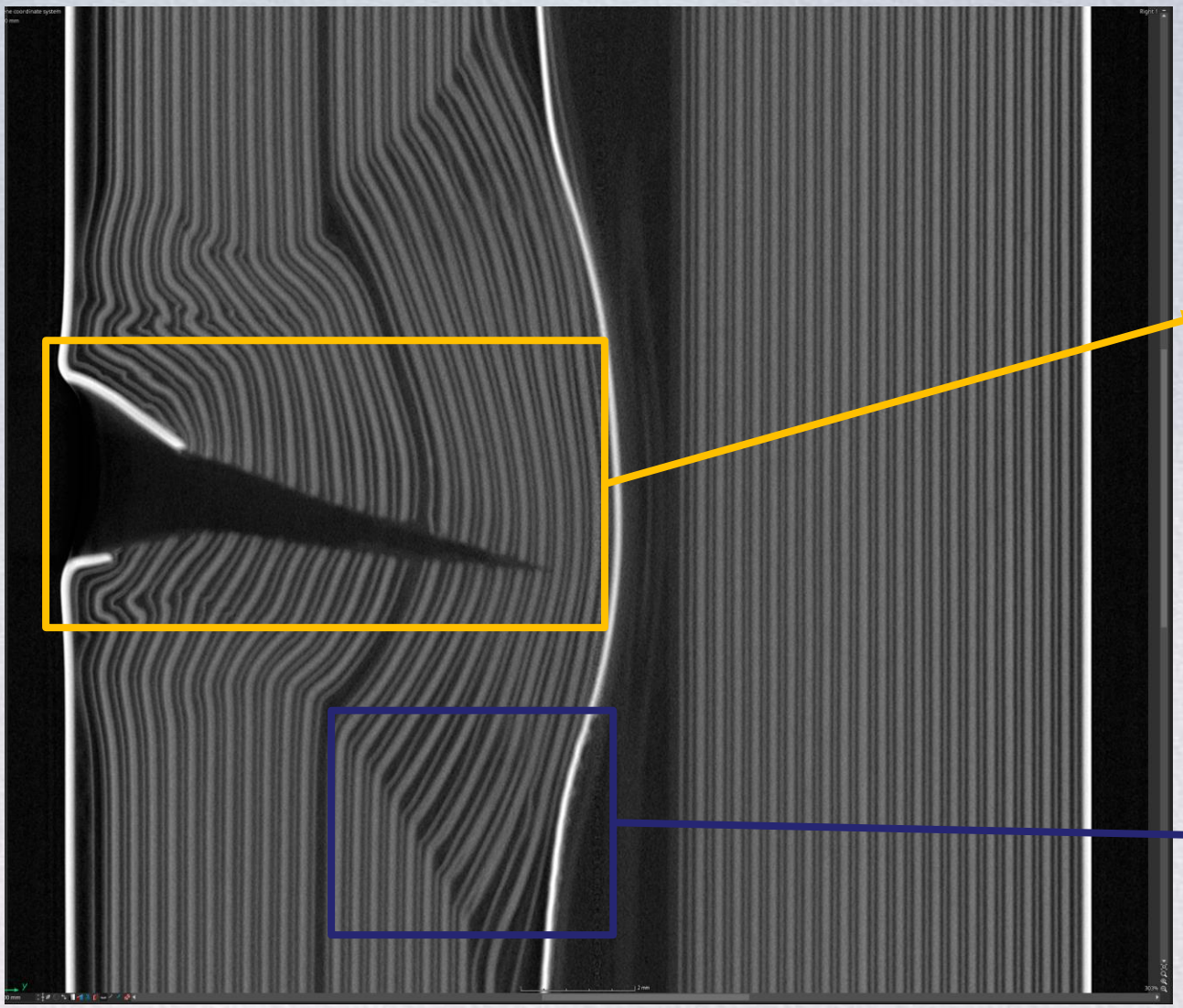
TR 1s after Nail Penetration – 70% SoC

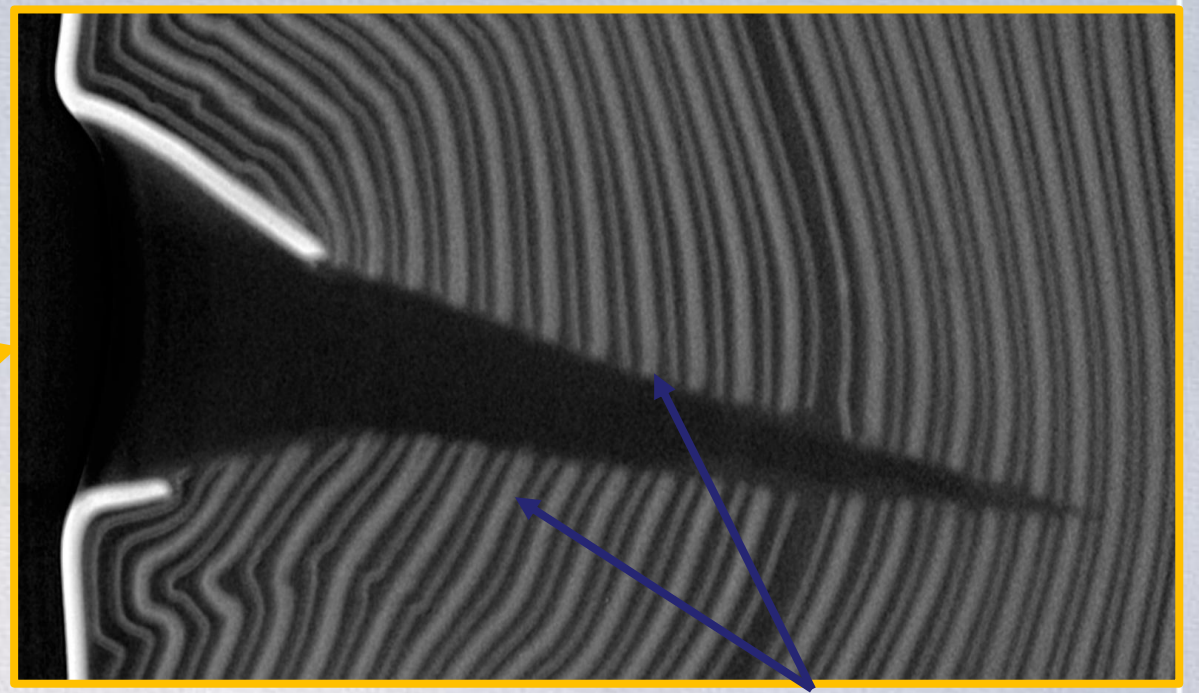


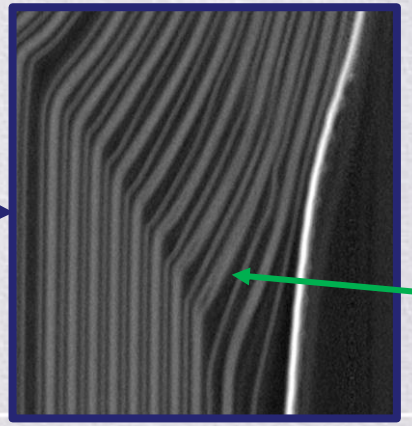
Nanotech 3.3Ah Run32 at 100% SoC



Nanotech 3.3Ah Run33 – 100% SoC







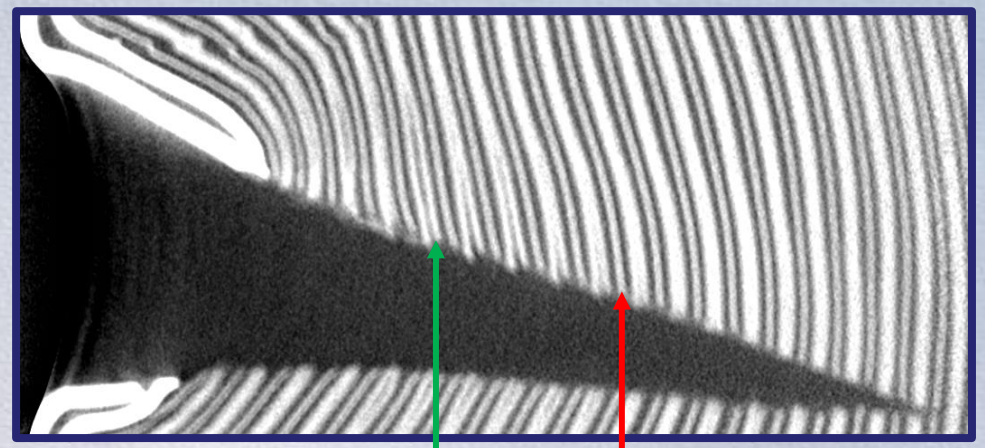
Delamination of NMC near nail interface (absence of PCC)

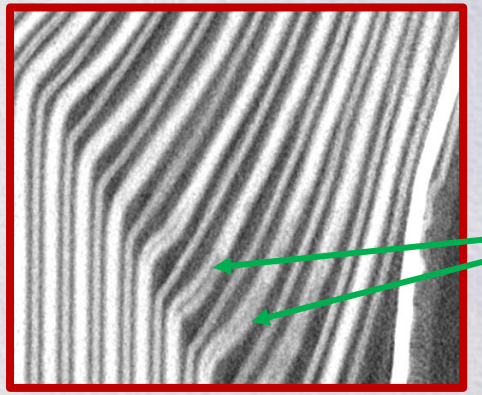
Al PCC vaporizing leaving voids near interface of nail impact cone with unimpacted JR

Observations

- Nanotech Energy cell design with PCC is on threshold of getting full benefit of Al PCC
  - 2 of 3 cells tolerate nail at 100% SoC
    - Even with nail contacting a (+) tab
  - 2 of 3 cell tolerate nail at 70% SoC
    - Even with nail contacting a (+) tab
- Specific energy or energy density isn't main driver since performance is independent of SOC
- CT images reveals absence of PCC near nail interface and at shear cone interface
- Maybe winding tension is too high
  - 2.9Ah BAK 18650 cell design is 9 of 9 in nail tolerance at 100% SoC

NANOTECH





Cylindrical Cell PCC Findings To Date

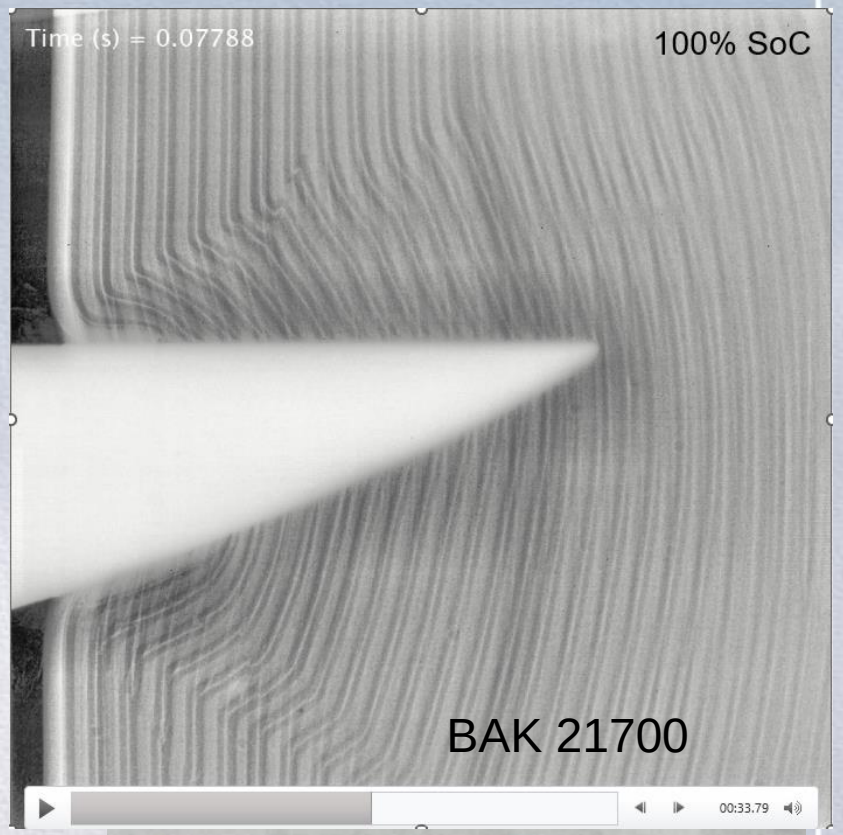
Nail Tolerance

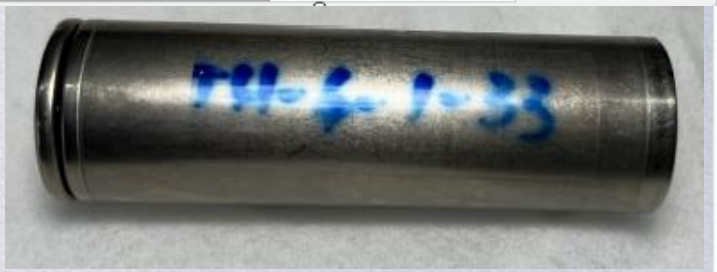
Soteria polyester PCC is reliable in tolerating nail penetration in 64 out of 65 Li-ion cells with designs <251 Wh/kg

- 2.1Ah Coulometric 18650s (33 for 33) up to 193 Wh/kg
- 2.9Ah BAK 18650s (9 for 9) achieving 233 Wh/kg
- 4.6Ah BAK 21700s (14 for 15) achieving 250 Wh/kg
- 10Ah SVolt Pouch Cells (9 for 9) achieving 243 Wh/kg

Higher energy (>260 Wh/kg) 21700 cell designs fail nail penetration nearly every time so far

- 5.165Ah Coulometrics (3 for 24, even at 70% SoC, 191 Wh/kg)
  - Adding cellulose (DW) separator doesn't help
  - Adding DW separator & Cu PCC doesn't help
  - Replicating poor cathode adhesion of BAK design & Al PCC doesn't help



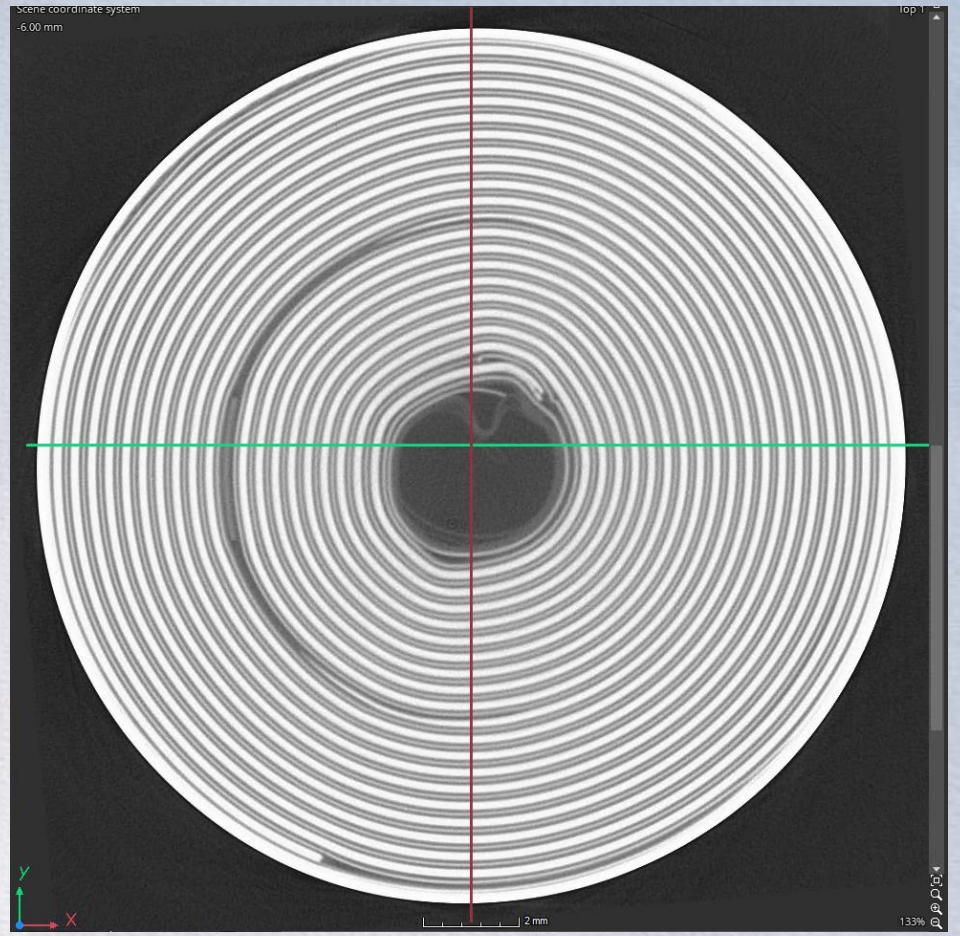


Our Cell Design Driving Factors Investigation Continues

- PCC renders electrode jellyrolls more flexible
  - Less electrode shearing occurs

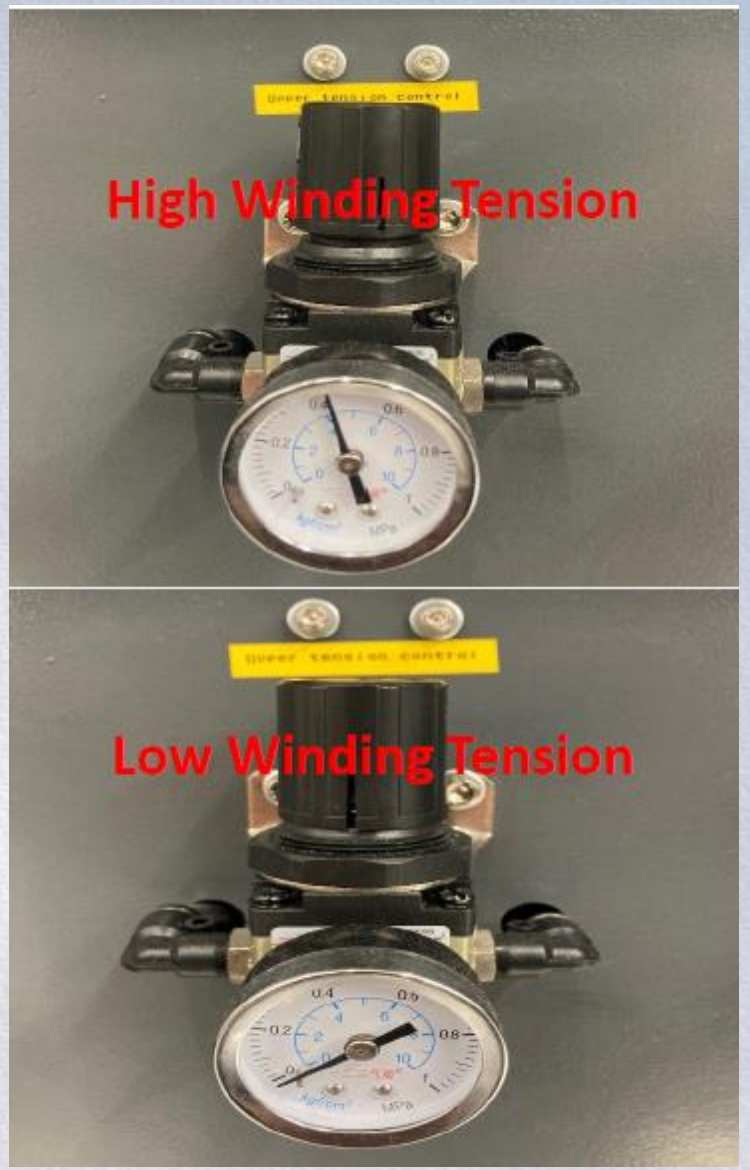
Planned new cells builds at Coulometrics with Forge Nano active materials

- Winding tension study
  - 4.9Ah in 21.6mm diameter can
    - Wound at similar **high** tension as previously
    - Soteria Al PCC and Cu foil (**group 1**)
    - Al and Cu foil CC (**group 2**)
  - 4.6Ah in 21.6mm diameter can
    - Shorter jellyroll wound at **lower** winding tension
    - Soteria Al PCC and Cu foil (**group 3**)
    - Al and Cu foil CC (**group 4**)
  - All cells with the following design
    - ALD treated polycrystalline NMC811
    - ALD treated graphite
    - Ceramic coated separator
    - Soteria 6µm PET with 1µm Al on both sides



Winding Tension Study

- 4.4Ah cell designs built with **high** winding tension
  - Jellyroll wound at 0.4 Mpascals (58psi)
  - Metal foils cell design yields 4.38±0.10Ah
    - DCR average 18.6 ± 1.1 mohms
    - 15 µm Al, 10 µm Cu foils
  - Al PCC cell design yields 4.38±0.10Ah
    - DCR average 42.9 ± 10.1 mohms
    - 8 µm Al PCC film, 10 µm Cu foil
- 4.1Ah cell designs built with **low** winding tension
  - Jellyroll wound at 0.0 Mpascals
  - Metal foils cell design yields 4.08±0.11Ah
    - DCR average 18.3 ± 1.6 mohms
    - 15 µm Al, 10 µm Cu foils
  - Al PCC cell design yields 4.10±0.10Ah
    - DCR average 42.9 ± 31.1 mohms
    - 8 µm Al PCC film, 10 µm Cu foil
- 4.1Ah cell designs built with **low**
  - Electrode lengths reduced to accommodate minimal winding tensions



All cells went into immediate TR

	Cell Set ID	Cap. (Ah)	16µm CC Sep.	NAIL TYPE: 3.3mm NASA									
				Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Cell 6	Cell 7	Cell 8	Cell 9	Cell 10
	2404-FN01	4.38	Y	●	●	●	●	●	●	●	●	●	●
Al PCC design	2404-FN02	4.38	Y	●	●	●	●	●	●	●	●	n/a	n/a
	2404-FN03	4.10	Y	●	●	●	●	●	●	●	●	n/a	n/a
Al PCC design	2404-FN04	4.10	Y	●	●	●	●	●	●	●	●	n/a	n/a

○ - No TR
⊙ - Delayed TR (after 1 minute or more)
● - Immediate TR

- All cell designs went into immediate TR
- Same nail as used in NASA's FTRC with ~6mm insertion depth
- Winding tension has no impact on PCC effectiveness

Cell DPAs

- 2.75Ah BAK 18650 with Al PCC
  - Loosest JR fit inside can
- Coulometrics cell DPAs
  - 4.9Ah with 21.6mm dia can with Al PCC
    - Very tight JR fit inside can
  - 4.4Ah with 21.3mm dia can with Al/Cu foils
    - Medium tightness of JR fit inside can
  - 4.4Ah with 21.3mm dia can with Al PCC
    - Tight JR fit inside can
  - 4.1Ah with 21.3mm dia can with Al/Cu foils
    - Medium tightness of JR fit inside can
  - 4.1Ah with 21.3mm dia can with Al PCC
    - Tight JR fit inside can

- Driving factor could be the tightness of the JR fit inside the cell can walls
  - Nanotech and Coulometrics will loosen the fit in future builds

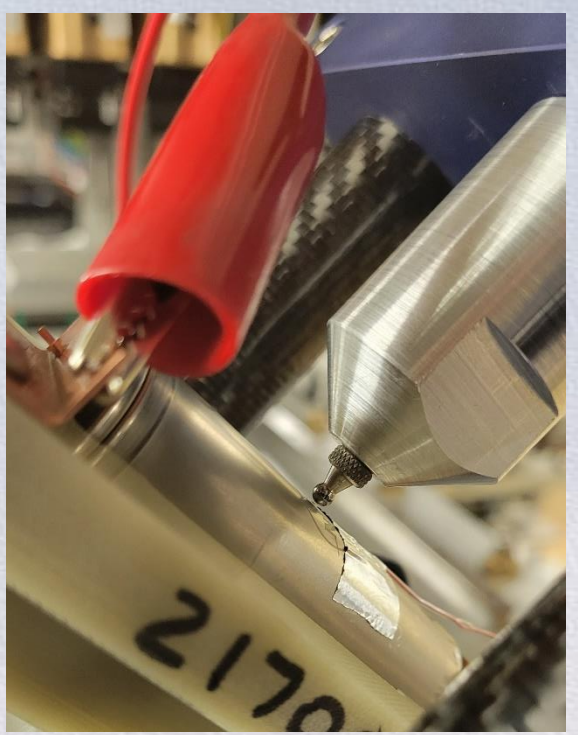
BACK UP

In-situ X-ray CT during indentation and nail penetration

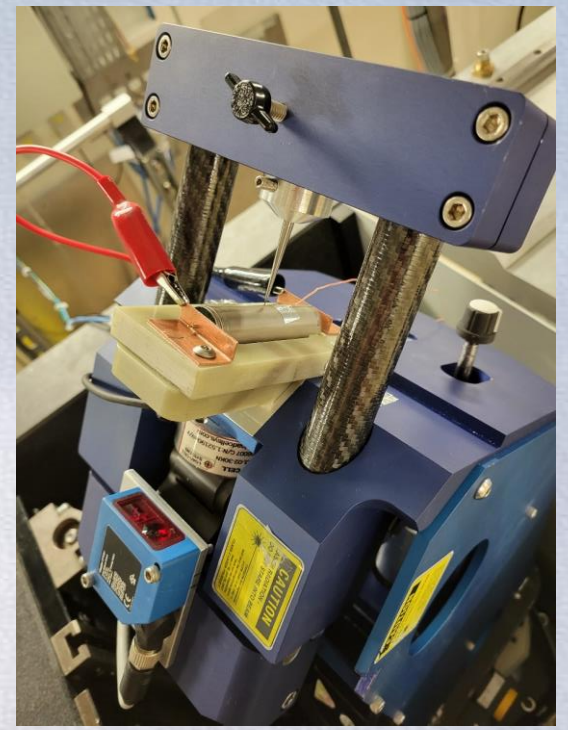
NREL in-situ CT stage:

- Circumferentially transparent to X-rays.
- Measures voltage, temperature, displacement, and force.
- Capable of > 10 kN force.
- Compact design.
- Facilitates continuous rotation during data recording.

Blunt indentation



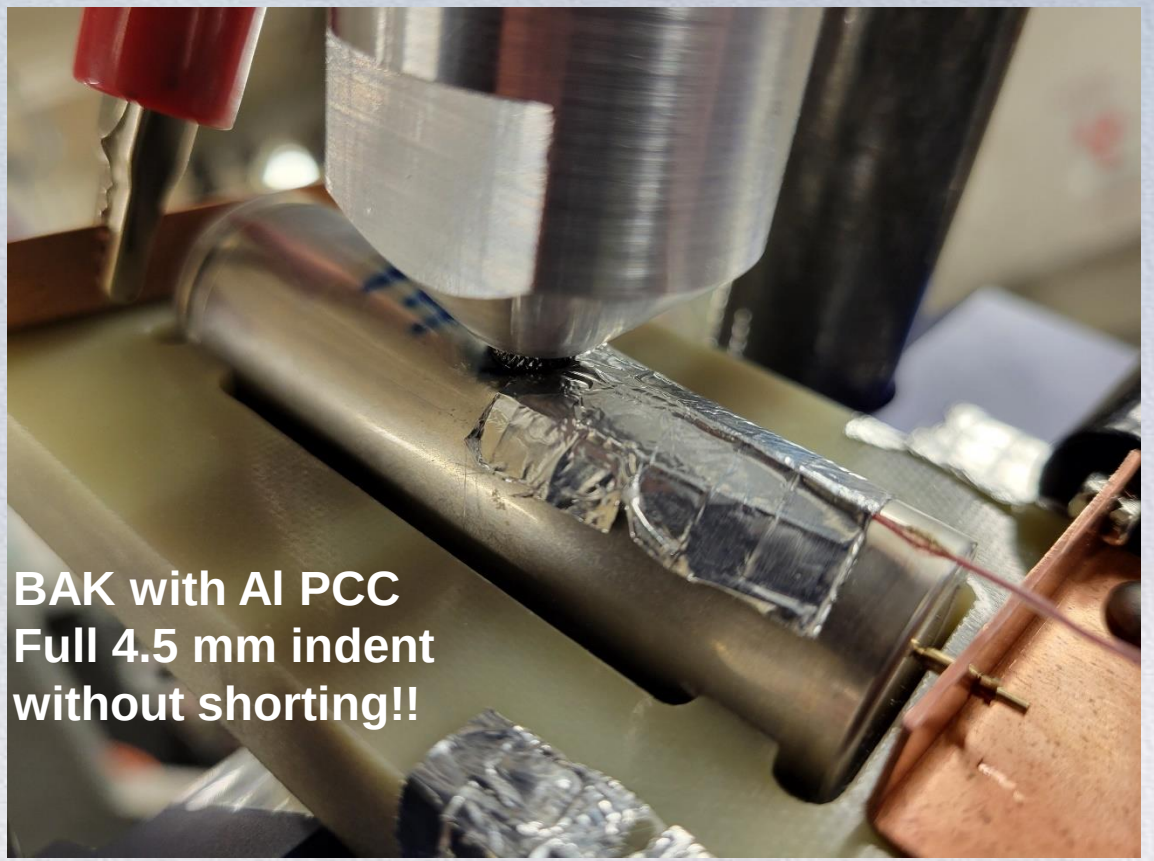
Nail penetration

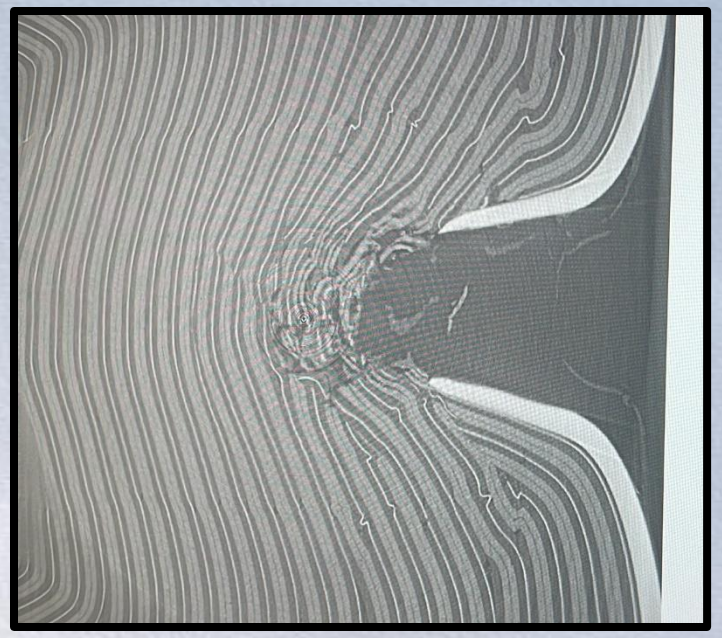


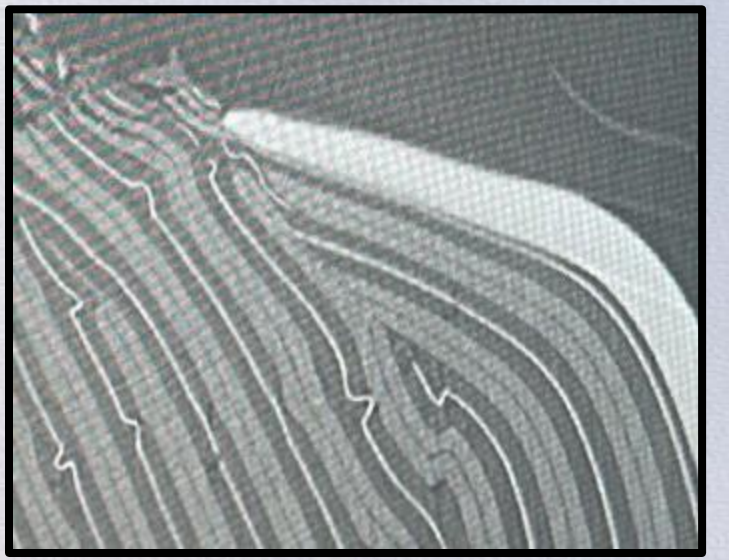
Compare Al coated PET cells to control cells

- 4.6Ah BAK 21700 w/ and w/o 6µm PET with 1µm Al coating (250 Wh/kg)
- 4.9Ah Coulometric 21700 w/ and w/o 6µm PET with 1µm Al coating (achieving > 270 Wh/kg)
- All while fully discharged (OCV ~2.9V)

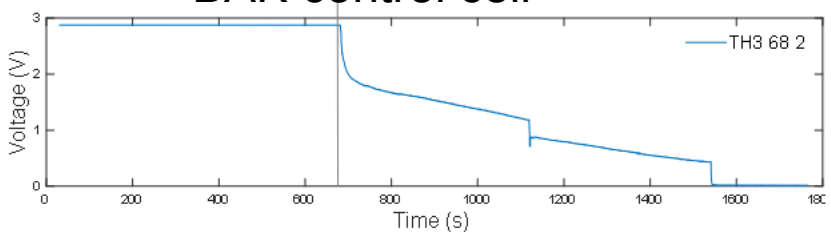
X-ray CT during blunt indentation



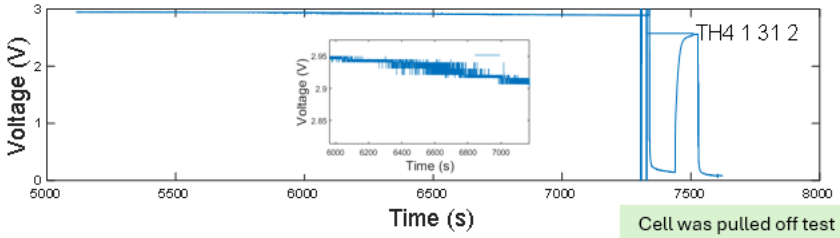




BAK control cell



BAK Al PCC cell

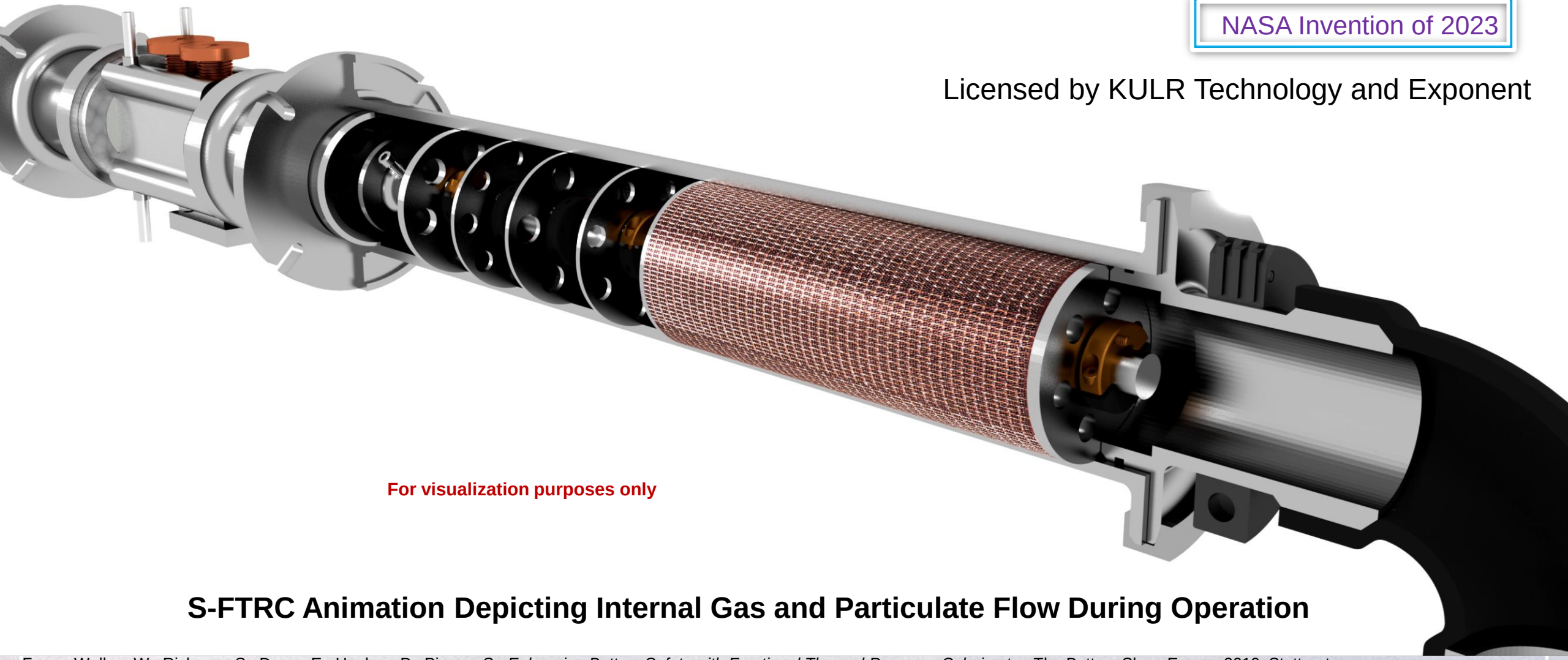


Cell was pulled off test here. It did not short.

Small Cell Fractional Thermal Runaway Calorimeter

NASA Invention of 2023

Licensed by KULR Technology and Exponent

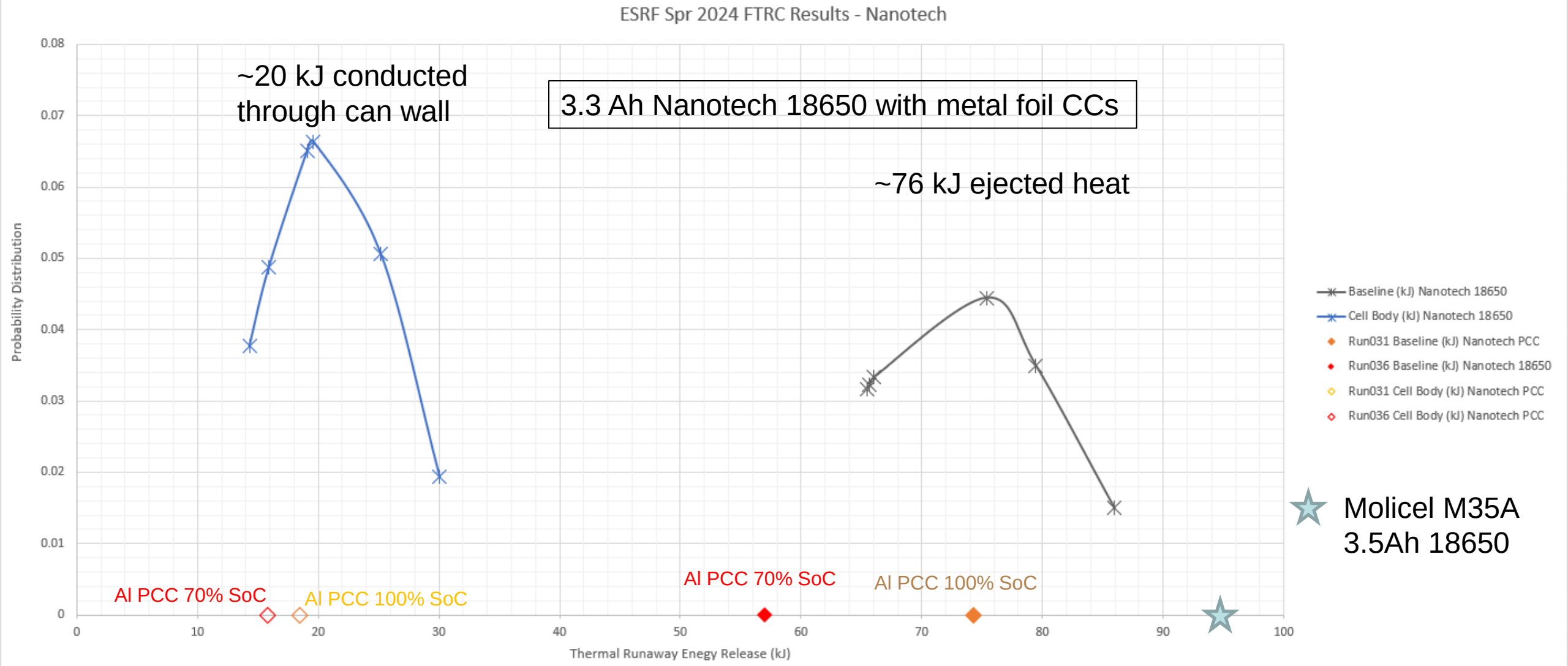


For visualization purposes only

S-FTRC Animation Depicting Internal Gas and Particulate Flow During Operation

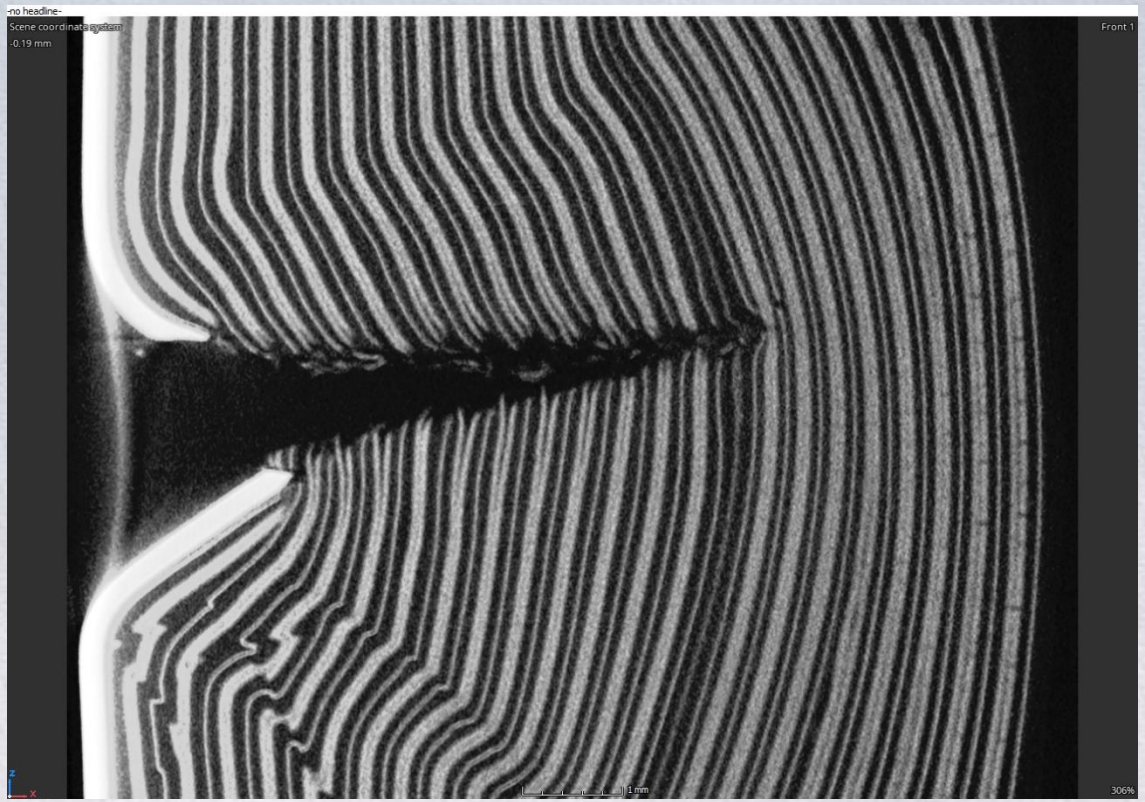
From: Walker, W., Rickman, S., Darcy, E., Hughes, P., Pizano, S., *Enhancing Battery Safety with Fractional Thermal Runaway Calorimetry*, The Battery Show Europe 2019, Stuttgart, Germany, May 2019.

Preliminary FTRC Energy Yields

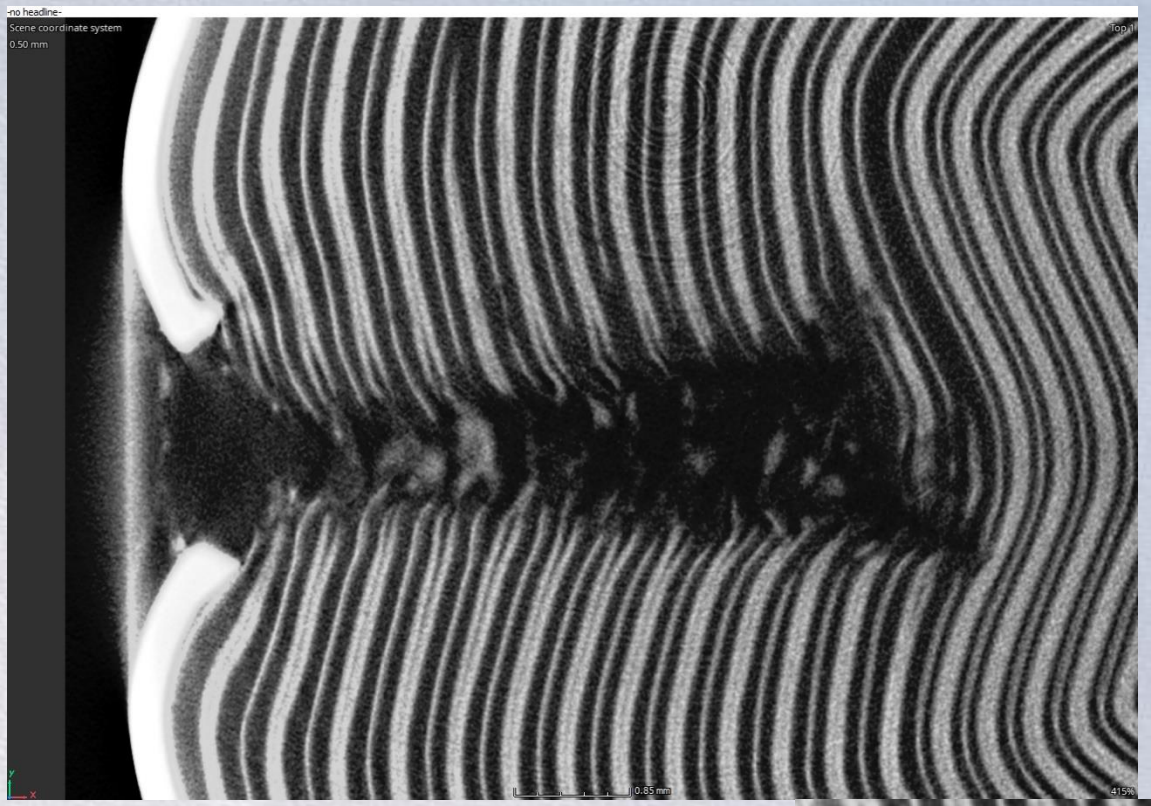


CT Images of BAK 18650 with Cathode PCC

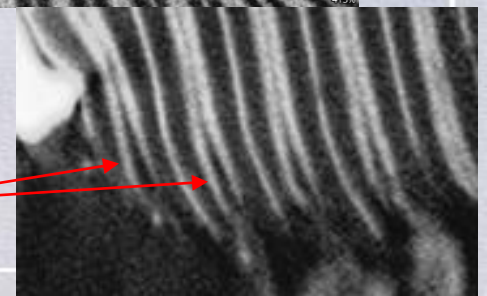
Axial view of nail penetration zone



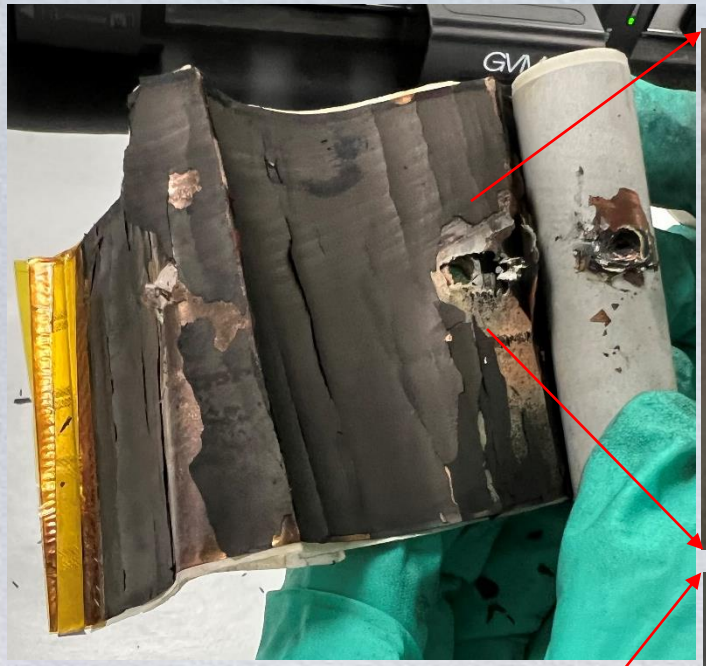
Radial view of nail penetration zone

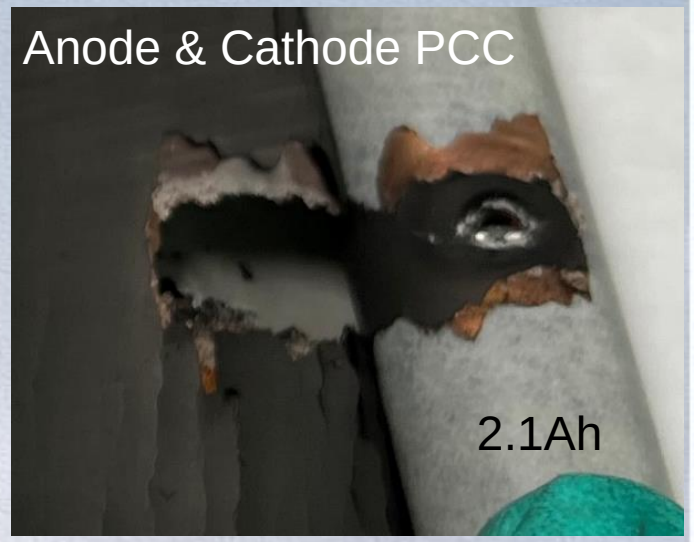


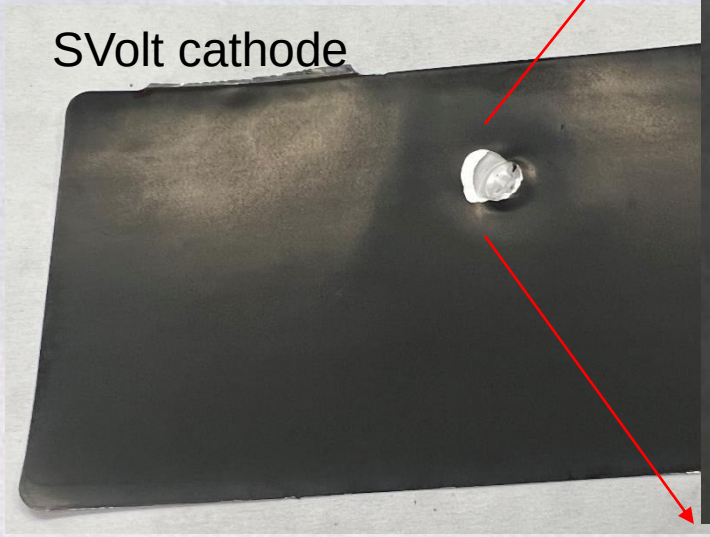
Reversing the image brightness from the video: Bright is most dense material, cell can, NMC.
Al coated PCC for cathode is thin gray layer between NMC active material coatings.
Axial and radial view show cathode PCC is clearly missing at nail interface (split ends).

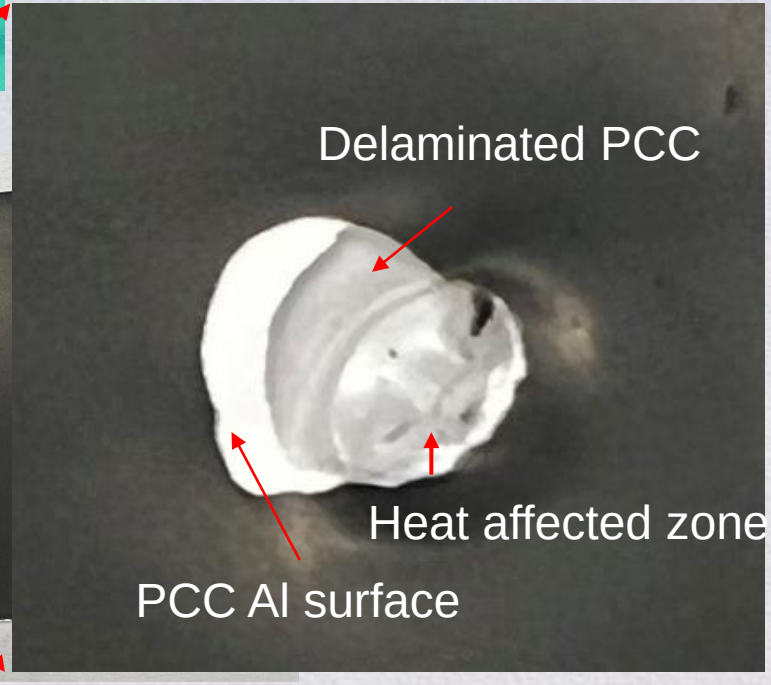


DPA Reveals Thermal Effect in PCC Response









- Difficult unwinding due to melting of polyester CC and polyolefin separator ending glued together at nail interface
- Nail hole reveals thermally stressed PCC