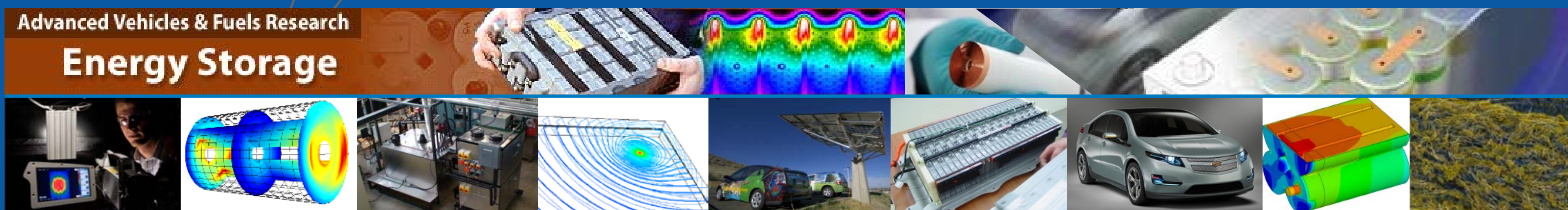
NREL/NASA Internal Short-Circuit Instigator in Lithium Ion Cells



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Eric Darcy – NASA JSC
Mark Shoesmith – E-One Moli
Ben McCarthy – Dow Kokam

NREL/PR-5400-66958

Presentation Outline

- Background
- Motivation
- Objectives
- NREL/NASA ISC Approach
- ISC Studies
  - Pouch Cell – Flammable vs. Non-flammable Electrolyte
  - 18650 Cylindrical Cell – Shutdown Separator Study
  - NASA Propagation Studies
- Conclusions and Summary
- Acknowledgements

Background: Li-Ion Cell Internal Short, a Major Concern

- Li-ion cells provide the highest specific energy (>280 Wh/kg) and energy density (>600 Wh/L) rechargeable battery building block to date with the longest life.
- Electrode/electrolyte thermal instability and flammability of the electrolyte of Li-ion cells make them prone to catastrophic thermal runaway under some rare internal short circuit conditions.
- Despite extensive QC/QA, standardized industry safety testing, and over 18 years of manufacturing experience, major recalls have taken place and incidents still occur.
- Many safety incidents that take place in the field originate due to an internal short that was not detectable or predictable at the point of manufacture.
- These internal short incidents are estimated at 1 to 10 ppm probability (well beyond 6 σ) in consumer applications using cells from experienced and reputable manufacturers[1].
- Estimated at 1 in 235 million with commercial cells screened for spacecraft applications[2].
- What about custom-made large cells?
  - Not enough data exists to build statistically useful probabilities.

Aftermath of an external short incident

Aftermath of a suspected internal short incident

1. Barnett, B., TIAX, NASA Aerospace Battery Workshop, Nov 2008
2. Spurrett, R., ABSL, NASA Aerospace Battery Workshop, Nov 2008

Motivation

Lithium Ion Battery Field Failures - Mechanisms

- Latent defect (i.e., built into the cell during manufacturing) gradually moves into position to create an internal short while the battery is in use.
  - Sony[3] concluded that metallic defects were the cause of its recall of 1.8-million batteries in 2006
- Inadequate design and/or off-limits operation (cycling) causes Li surface plating on anode, eventually stressing the separator

Both mechanisms are rare enough that catching one in the act or even inducing a cell with a benign short into a hard short is inefficient.

Current abuse test methods may not be relevant to field failures

- Mechanical (crush, nail penetration, etc.)
  - Cell can or pouch is breached; pressure, temperature dynamics are different
- Thermal (heat to vent, thermal cycling, etc.)
  - Cell exposed to general overheating rather than point-specific overheating
  - Not a valid verification of “shutdown” separators
- Electrical (overcharge, off-limits cycling, etc.)
  - Not relevant to the latent-defect–induced field failure

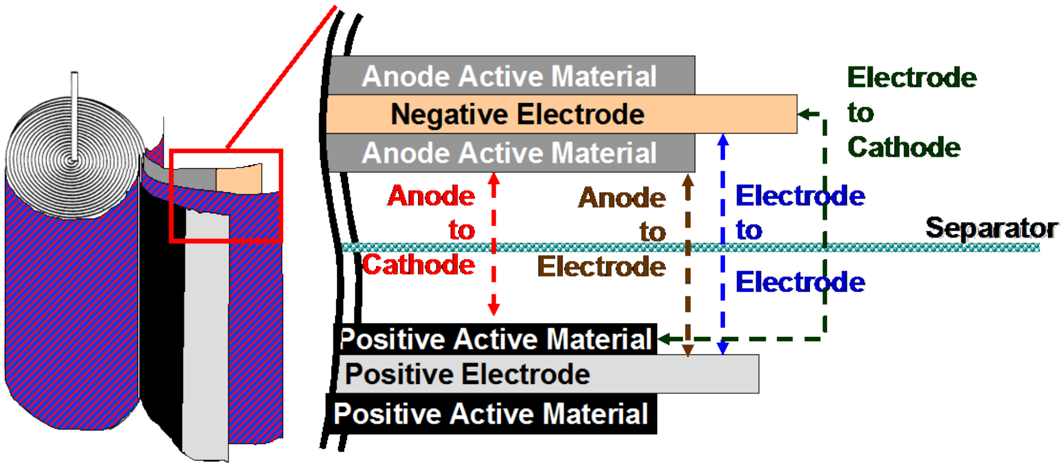
To date, no reliable and practical method exists to create on-demand internal shorts in Li-ion cells that produce a response that is <u>relevant</u> to the ones produced by field failures.

3. Nikkei Electronics, Nov. 6, 2006

NREL/NASA Objectives

Establish an improved ISC cell-level test method that:

- Simulates an emergent internal short circuit.
  - Capable of triggering the **four** types of cell internal shorts



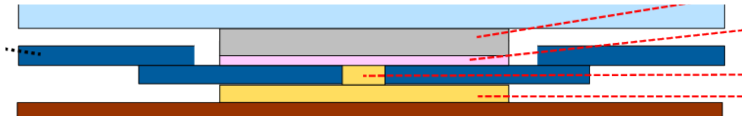
Spiral wound battery shown – can also be applied to prismatic batteries.

- Produces consistent and reproducible results
- Cell behaves normally until the short is activated – age cell before activation.
- We can establish the test conditions for the cell – SOC, temperature, power, etc…
- Provides relevant data to validate ISC models

NREL/NASA Cell Internal Short Circuit Development

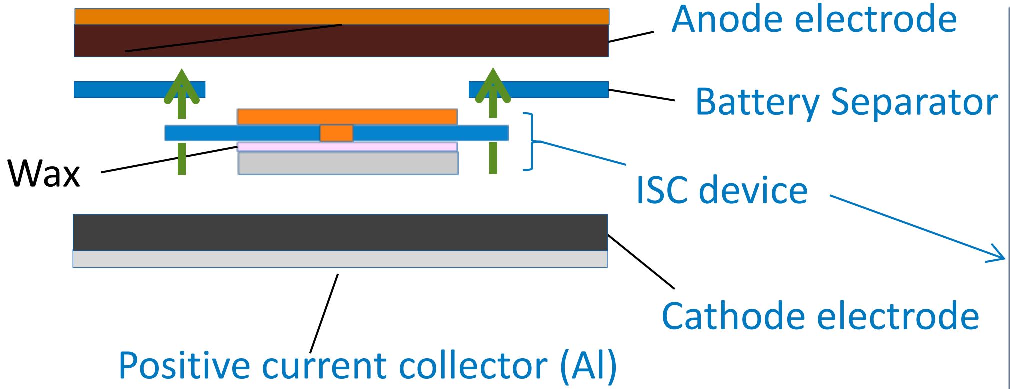
Internal short circuit device design

- Small, low-profile and implantable into Li-ion cells, preferably during assembly
- Key component is an electrolyte-compatible phase change material (PCM)
- Triggered by heating the cell above PCM melting temperature (presently 40°C – 60°C)
  - NREL has developed an ISC that triggers at 47°C and 57°C.
- In laboratory testing, the activated device can handle currents in excess of 300 A to simulate hard shorts (< 2 mohms).
- Phase change from non-conducting to conducting has been 100% successful during trigger tests.

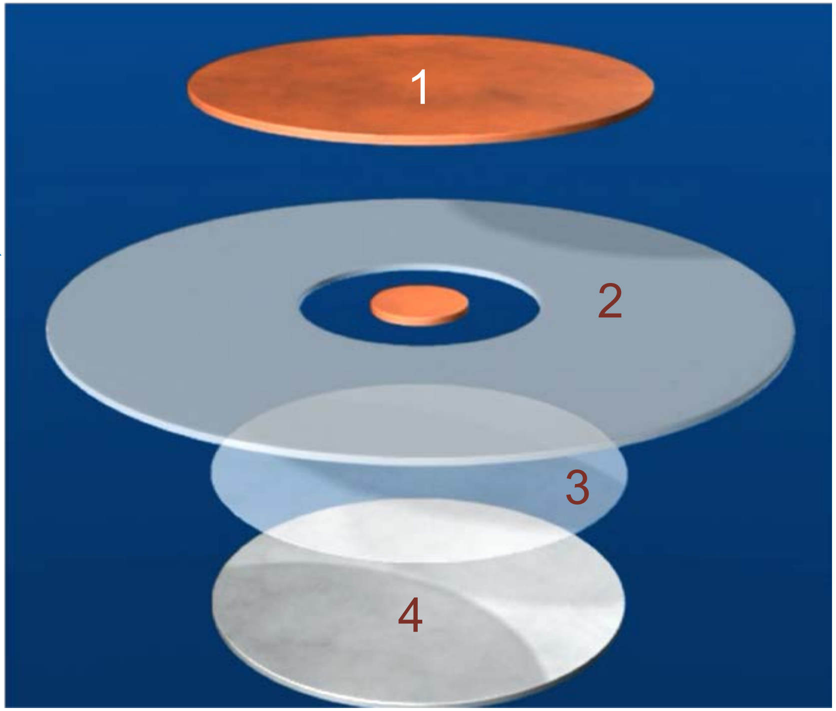


Patent application filed for the ISC Device

NREL/NASA Internal Short Design



Graphics are not to scale and for illustration only



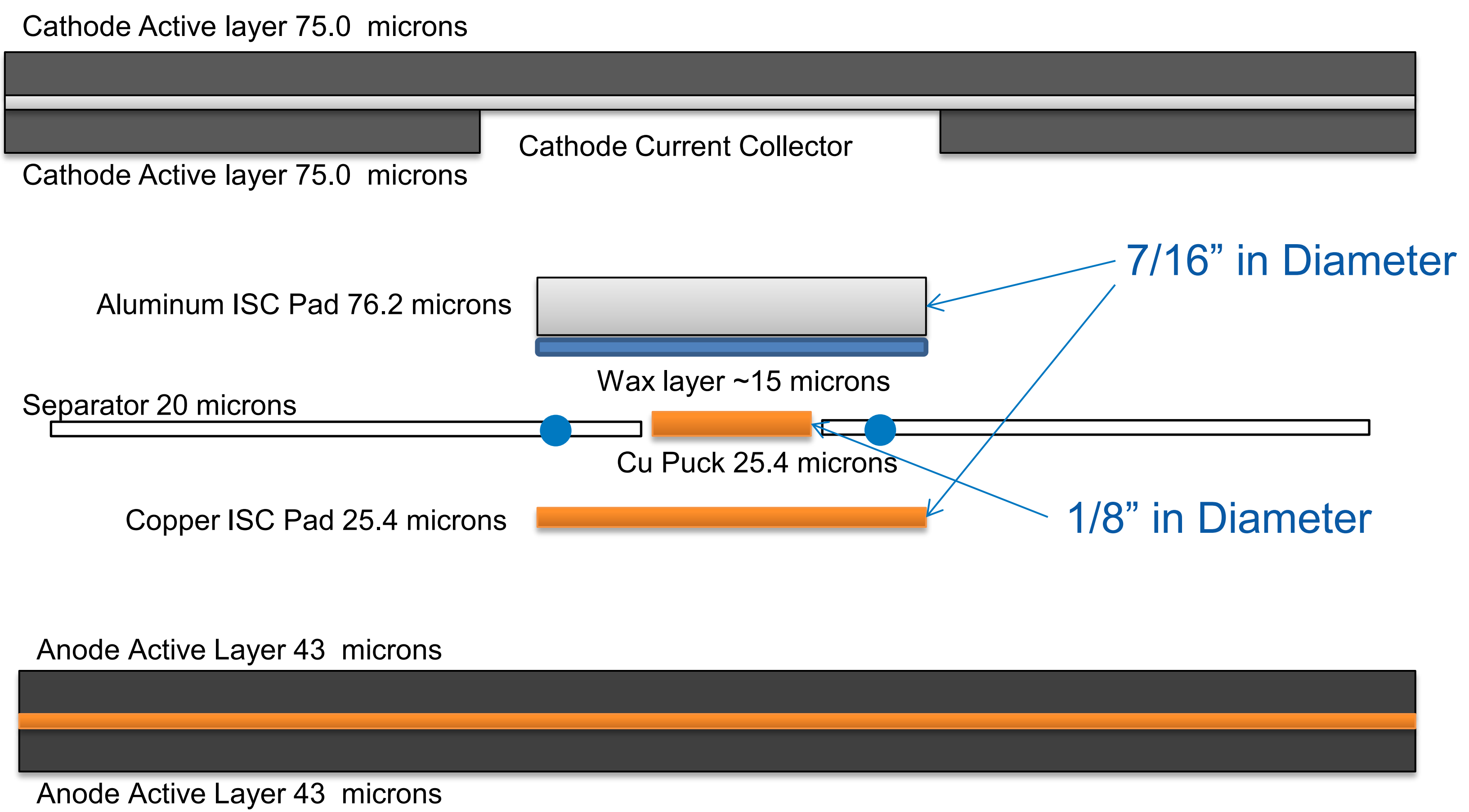
Top to Bottom:
1. Copper Pad
2. Battery Separator with Copper Puck
3. Wax – Phase Change Material
4. Aluminum Pad

Four Types of ISC

Type	ISC Device Description
1	Cathode – Anode
2	Collector – Anode
3	Cathode – Collector
4	Collector – Collector

ISC Device Example for a Type 2 Short

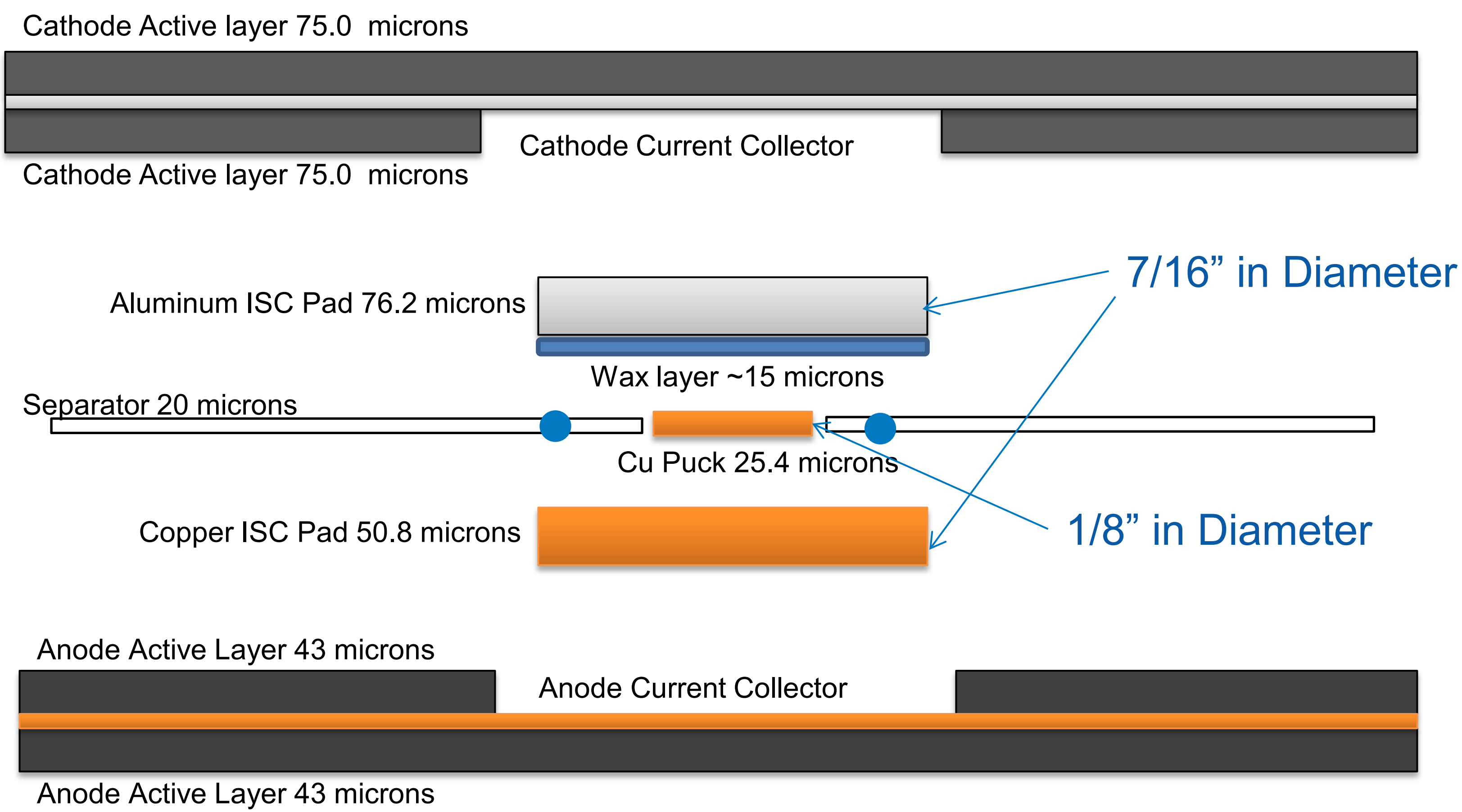
Cathode current collector to Anode active material



● Superglue used to hold ISC together.

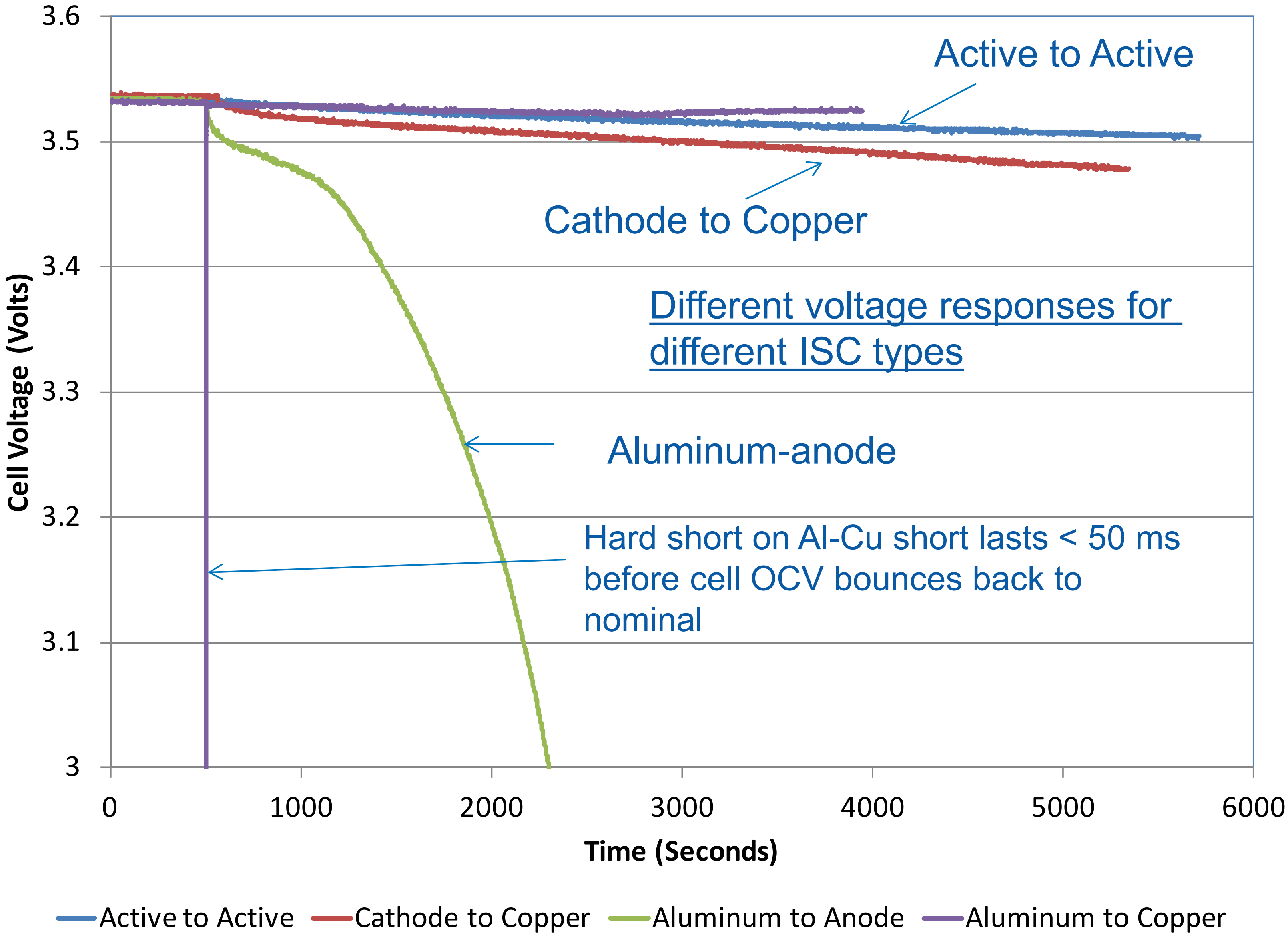
ISC Device Example for a Type 4 Short

Cathode current collector to Anode current collector

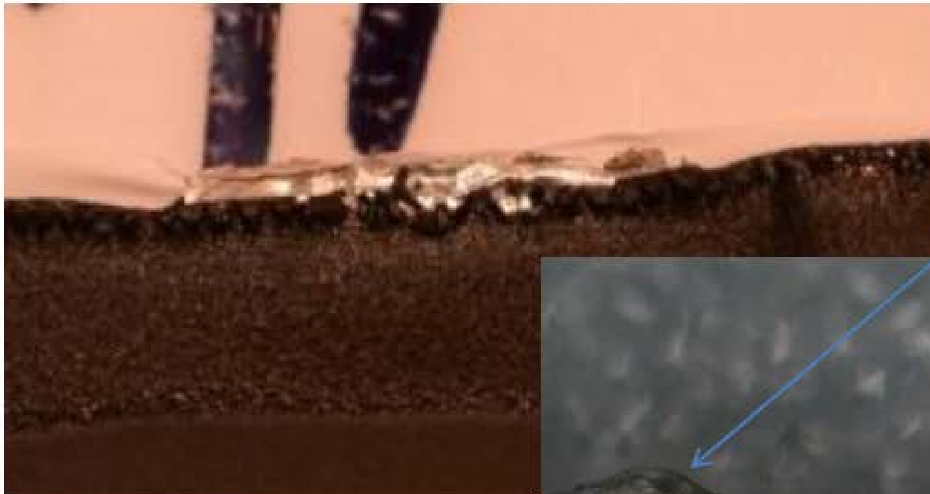


- Superglue used to hold ISC together.

Dow Kokam 8 Ah Cell Activation at 10% SOC



Macro Image of Cathode DK Cell Tab – Al to Cu ISC



Molten Al is evident several places

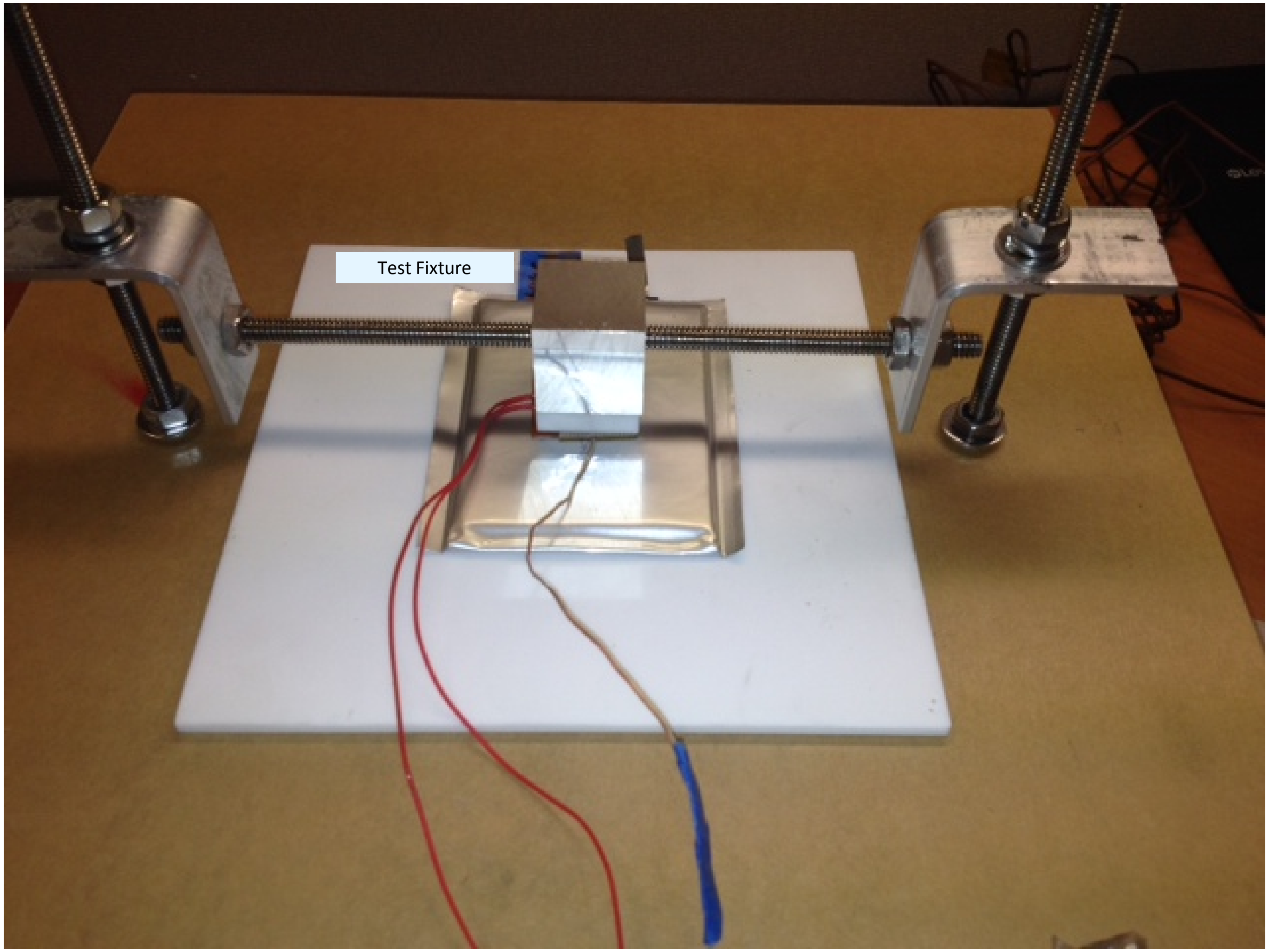
Tab was thermally overstressed, fused open during the hard short incident

Photo Credits: Eric Darcy, NASA

ISC Device Implantation and Test Results

- **Pouch Cell – Non-flammable (NF) electrolyte**
- 18650 Cylindrical Cell – Shutdown Separator Study
- NASA Propagation Studies with ISC Trigger

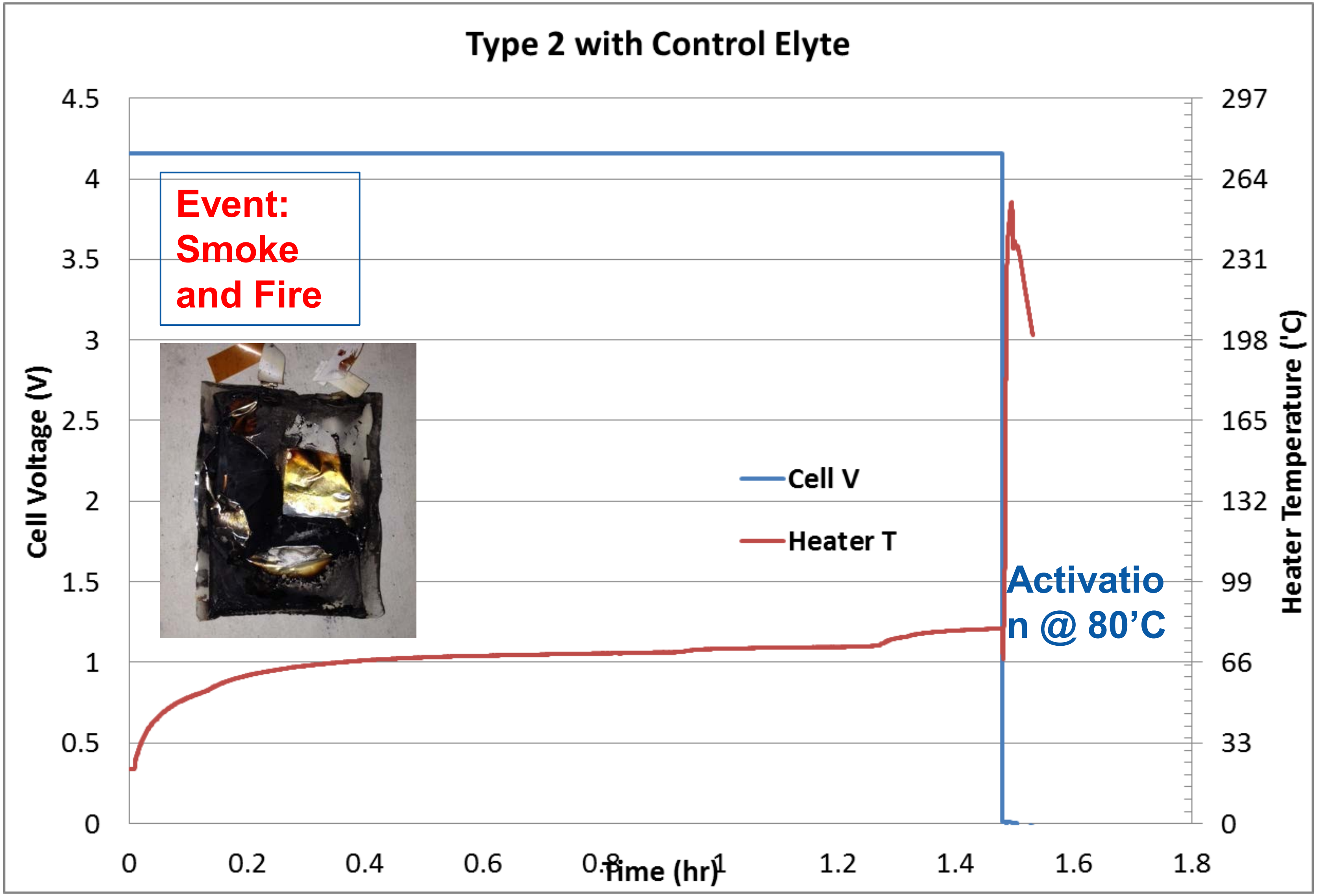
Test Fixture



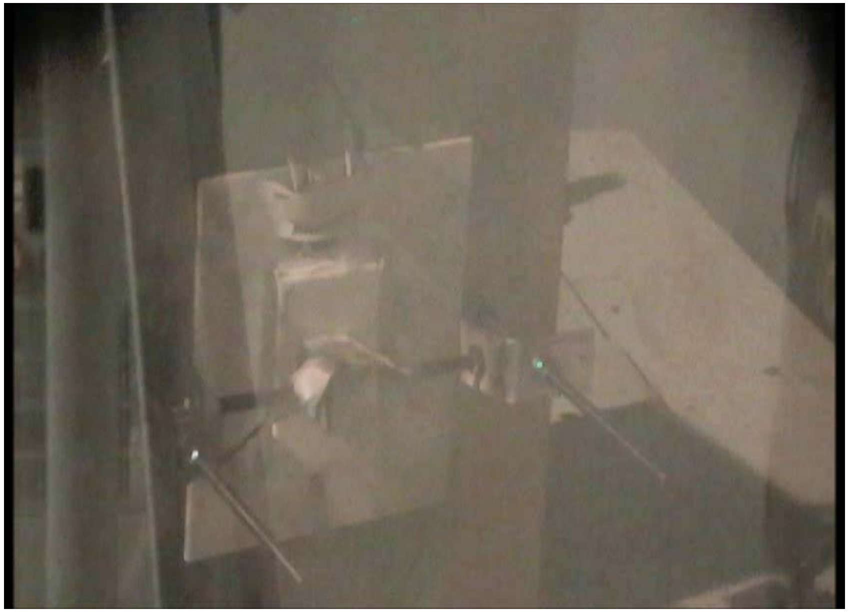
~20 Ah cells were testing with two types electrolytes and with a type 2 and type 4 ISC.

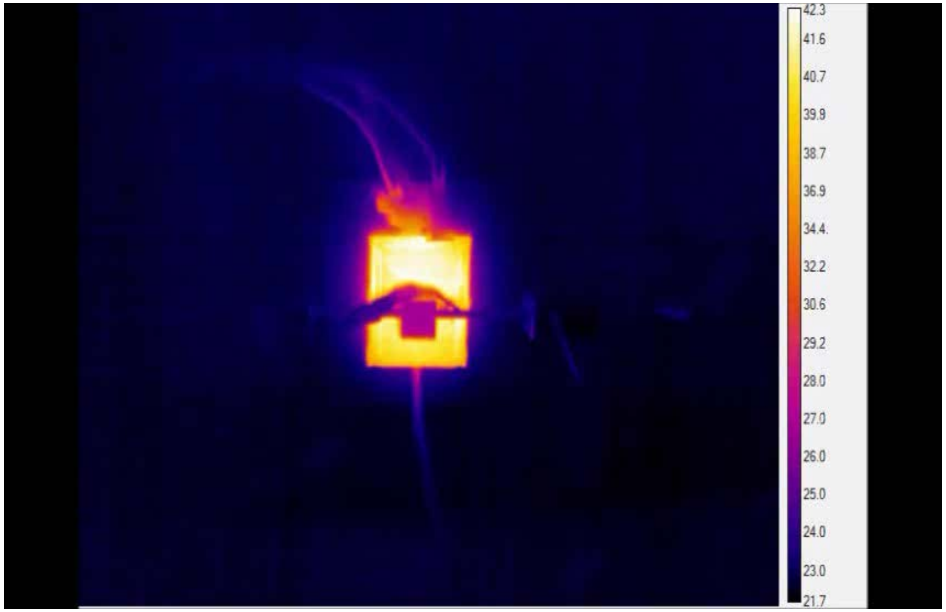
Type 2 Short

Type 2, Control Electrolyte

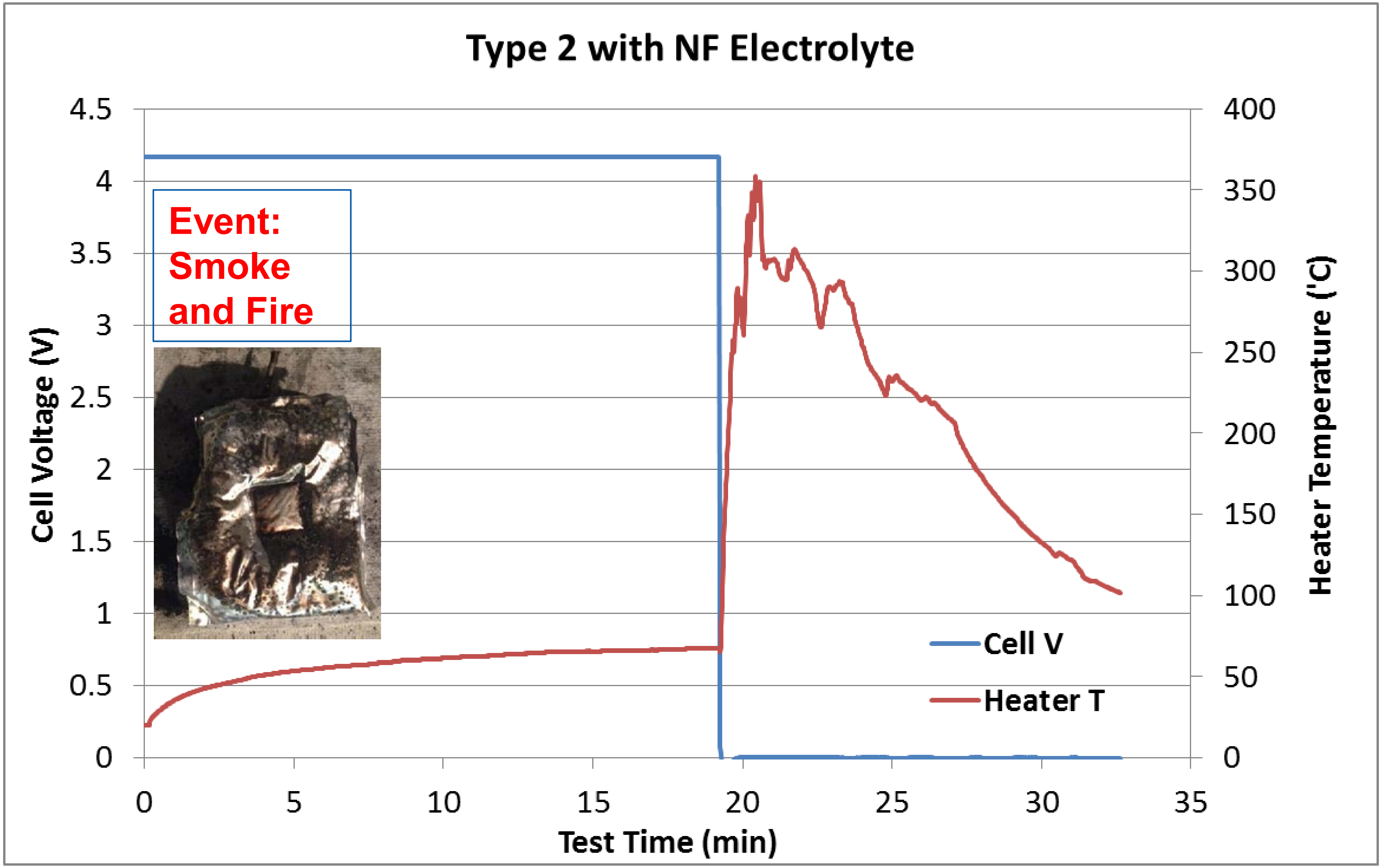


Type 2, Control Electrolyte

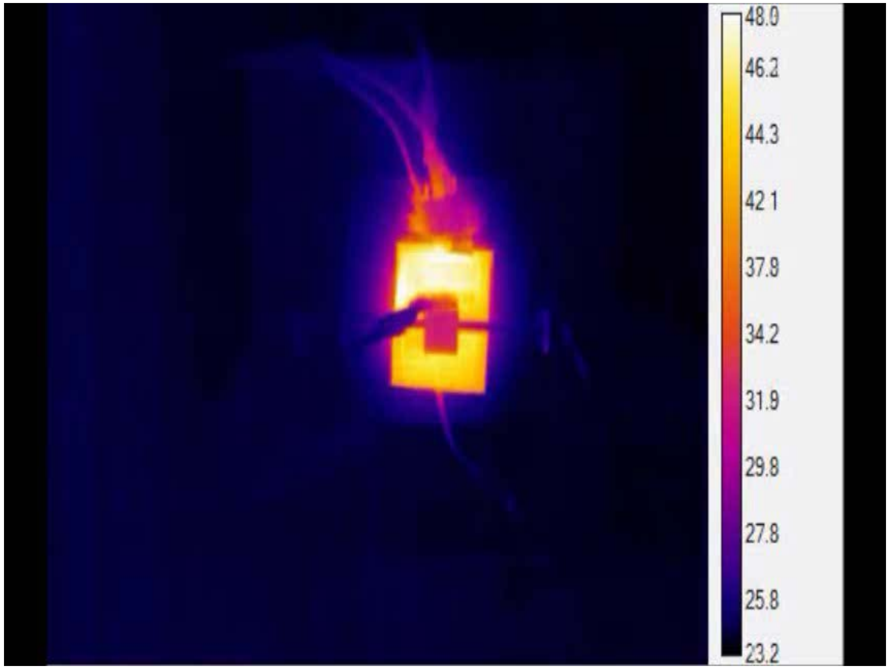




Type 2, Non-flammable (NF) Electrolyte



Type 2, NF Electrolyte



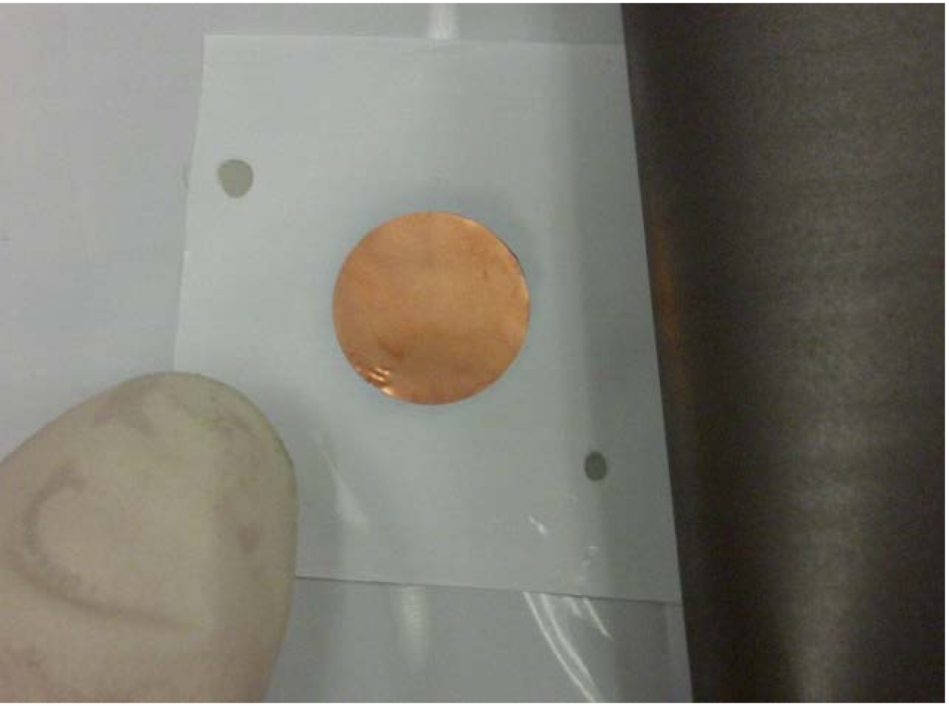
Non-flammable Electrolyte Study

- Both the control and the NF electrolyte caught fire and the cell temperature exceeded 300^{o}C.
- The NF electrolyte showed no improvement over the control electrolyte.
- A type 4 (electrode to electrode) ISC was also tested (not shown) with similar results.
- The manufacturer believes the NF electrolyte would have done better with a cathode material that does not evolve oxygen at higher temperatures such as $LiFePO_4$.

ISC Device Implantation and Test Results

- **Pouch Cell – Non-flammable (NF) electrolyte**
- 18650 Cylindrical Cell – Shutdown Separator Study
- NASA Propagation Studies with ISC Trigger

ISC Implantation – Active to Active



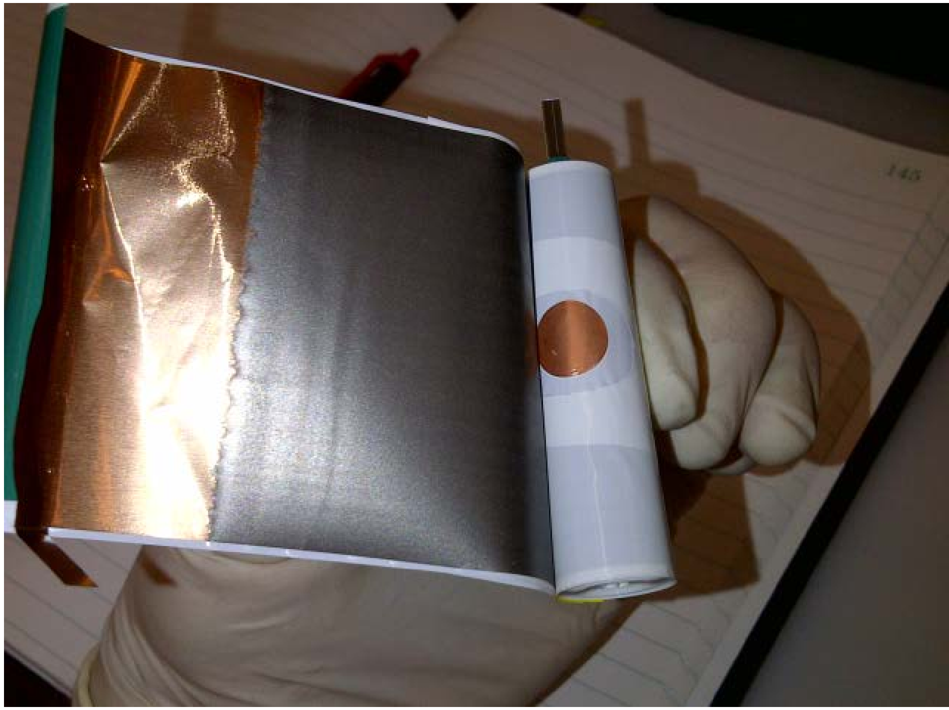


Photo Credits: Mark Shoesmith, E-One Moli

CT Scan of ISC in E-One Moli Cell

Click on Image to see video – approximately 10 seconds into video the ISC will appear in the lower left hand corner of the cell.

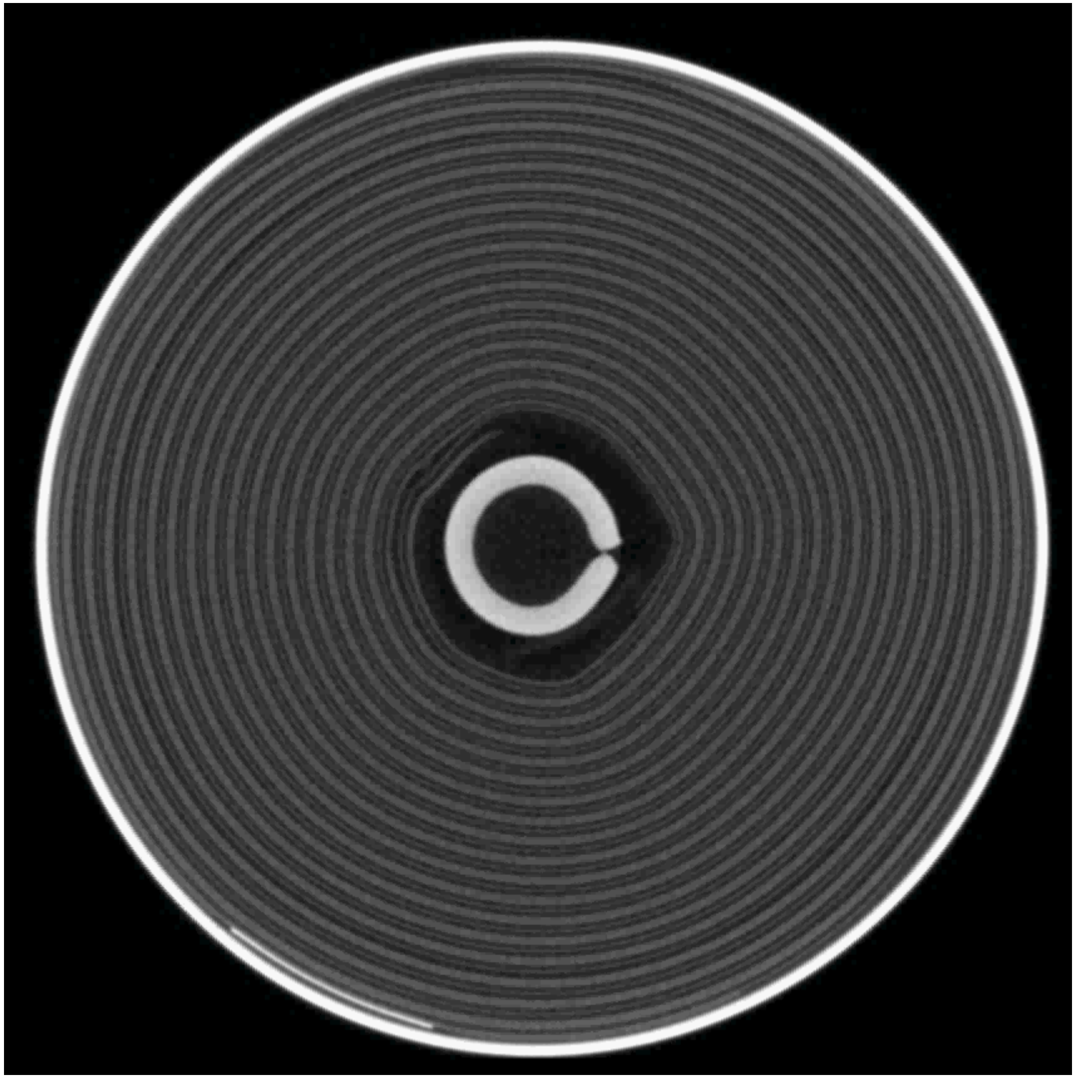


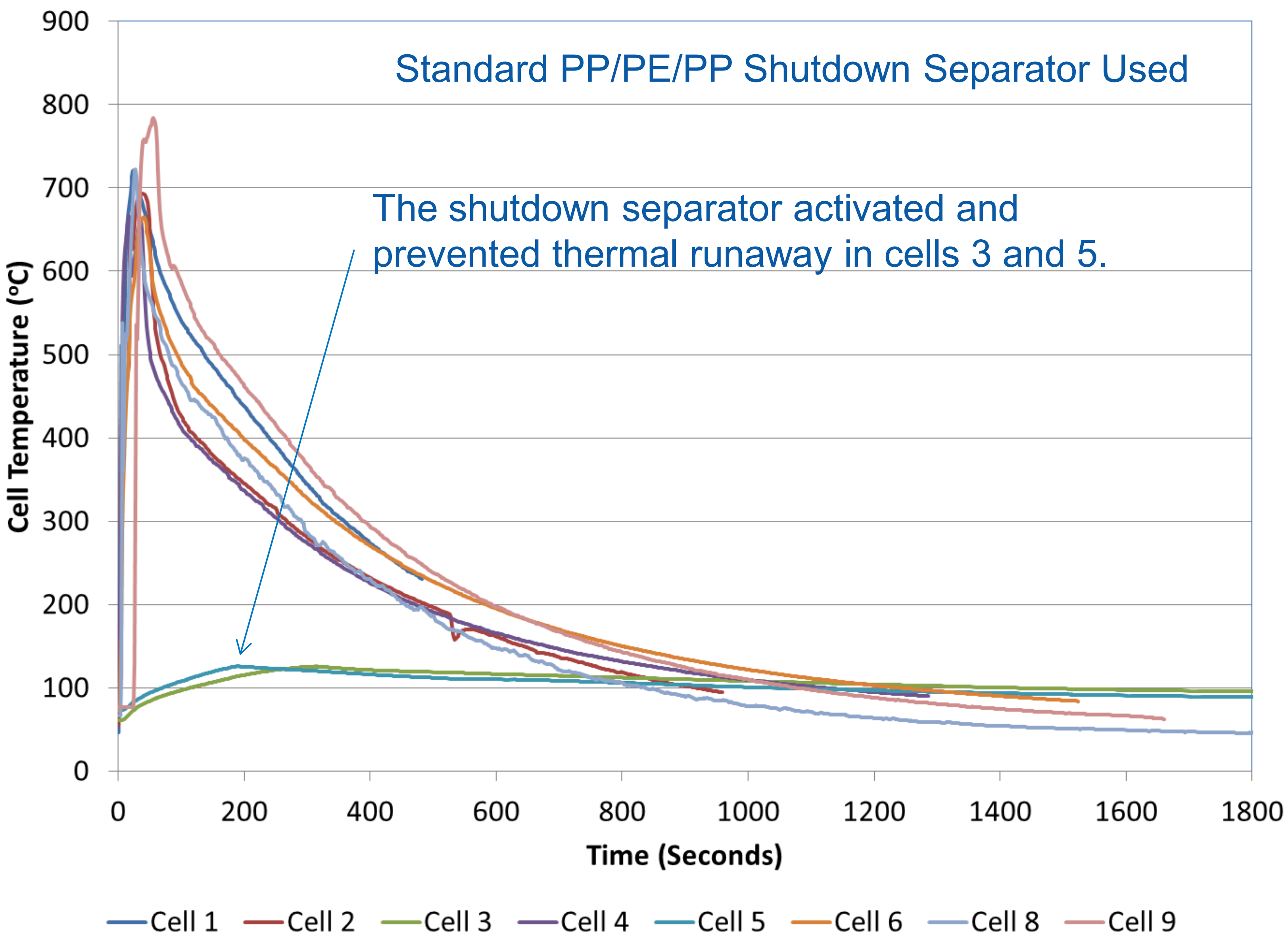
Photo Credits: Mark Shoesmith, E-One Moli

Type 2 ISC – Shutdown Separator Study

Cell	Successful Formation	Successful Activation?	Thermal Runaway?
1	Yes	Yes	Yes
2	Yes	Yes	Yes
3	Yes	Yes	No
4	Yes	Yes	Yes
5	Yes	Yes	No
6	Yes	Yes	Yes
7	Yes	No	-
8	Yes	Yes	Yes
9	Yes	Yes	Yes
10	Yes	No	-

Type 2 ISC – Aluminum Collector to Anode
8 out of 10 ISCs Activated

Type 2 ISC – Successful Activation



Aluminum to Anode ISC Activation – 18650 Cell Activation – 100% SOC

Photo Credit: Mark Shoesmith, E-One Moli

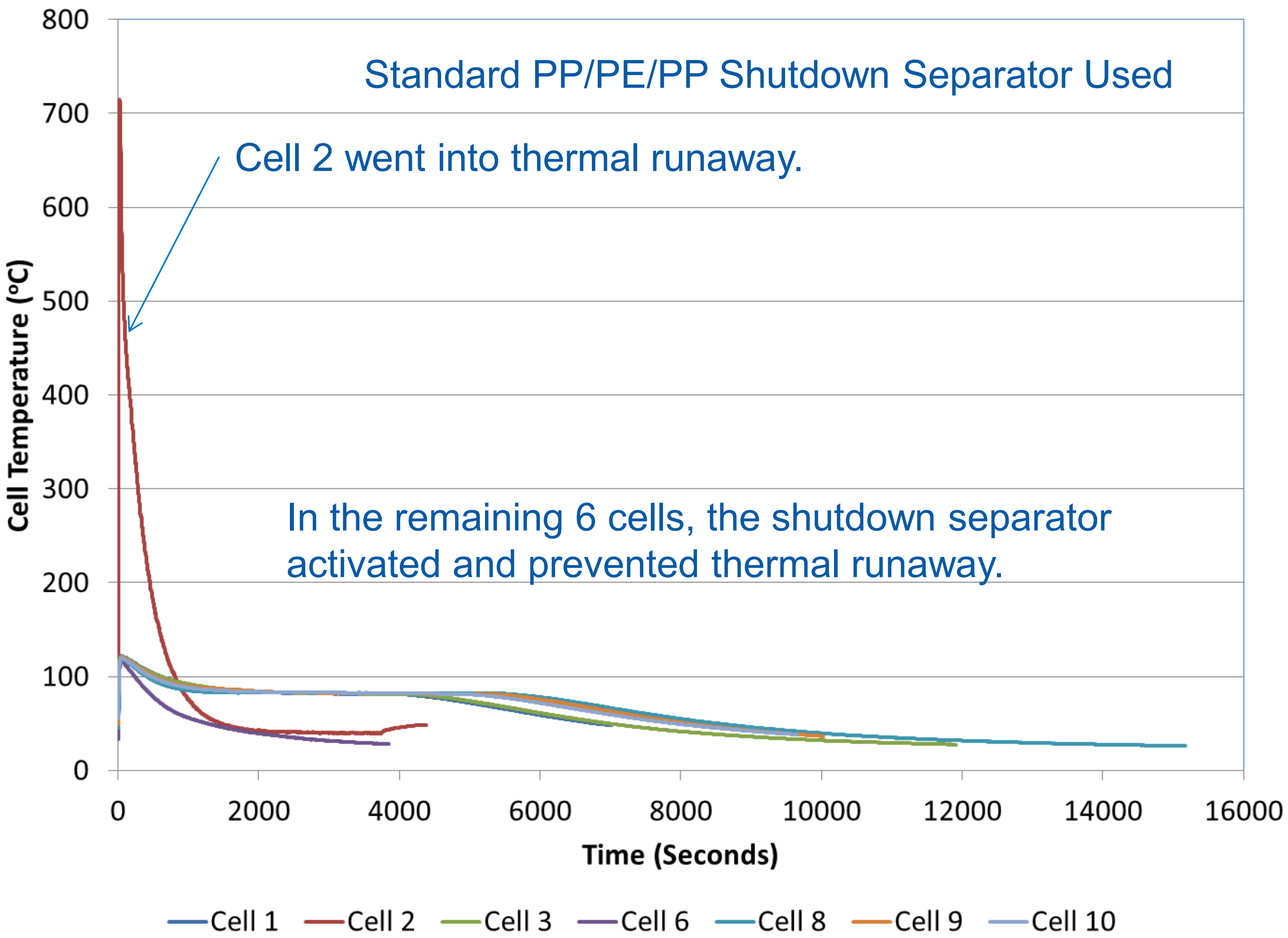
PP Separator Used - Non-Standard Separator

Type 4 ICS Shutdown Separator Study

Cell	Successful Formation	Successful Activation?	Thermal Runaway?
1	Yes	Yes	No
2	Yes	Yes	Yes
3	Yes	Yes	No
4	Yes	No	-
5	Yes	No	-
6	Yes	Yes	No
7	Yes	No	-
8	Yes	Yes	No
9	Yes	Yes	No
10	Yes	Yes	No

Type 4 ISC – Collector to Collector
7 out of 10 ISCs Activated

Type 4 ISC – Successful Activation



Why are Type 2 Shorts More Severe?

Type 4 = Cu Collector to Al Collector

Type 2 = Anode active material to Al Collector

1. Sony[1] recall in 2006 was attributed to type 2 shorts
2. Battery Association of Japan[2] replicates type 2 short and establishes test method
3. Celgard[3] cell experiments were first to compare the 4 types of shorts and indicate the more catastrophic nature of Type 2 shorts
4. TIAX[4] uses Type 2 short to demonstrate latency of defect during acceptance testing

Why? One possible theory;

- Involving carbon anode material provides the right impedance to maximize the power/energy delivered into the short
  - Type 4 shorts are lower impedance, end more quickly, and deliver less energy to the short

1. Nikkei Electronics, Nov. 6, 2006
2. Battery Association of Japan, Nov 11, 2008 presentation on web
3. S. Santhanagopalan, et. al., J. of Power Sources, 194 (2009) 550-557
4. Barnett et. al, Power Sources Conference, Las Vegas, NV, 2012

ISC Shutdown Separator Study

- Type 2 and Type 4 Short with shutdown separator
  - Type 4 (collector to collector) ISC
    - 7 out of 10 ISCs activated.
    - 1/7 cells went into thermal runaway.
    - 6/7 cells - the shutdown separator prevented the cell for going into thermal runaway.
  - Type 2 (aluminum collector to anode) ISC
    - 8 out of 10 ISCs activated.
    - 6/8 cells went into thermal runaway.
    - 2/8 cells – the shutdown separator prevented the cell for going into thermal runaway.
  - Initial test results for this cell indicates that the aluminum to anode ISC is more severe than the collector to collector ISC.

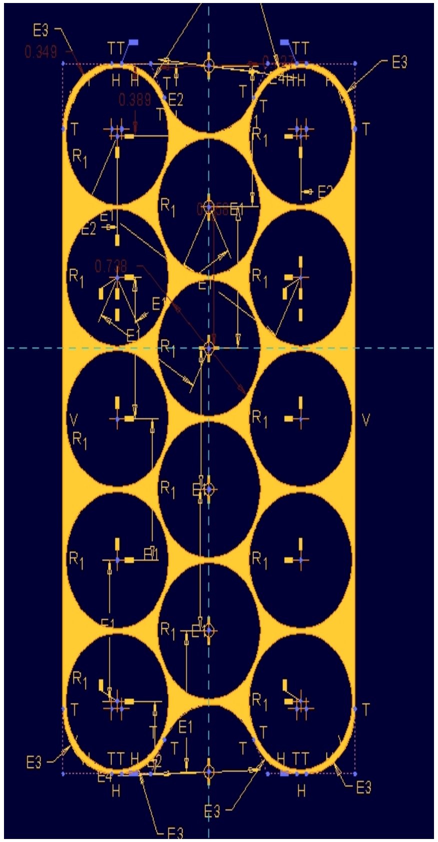
- Testing indicates that the ISC can be used to assess what type of internal short circuit the manufacturer should protect against.

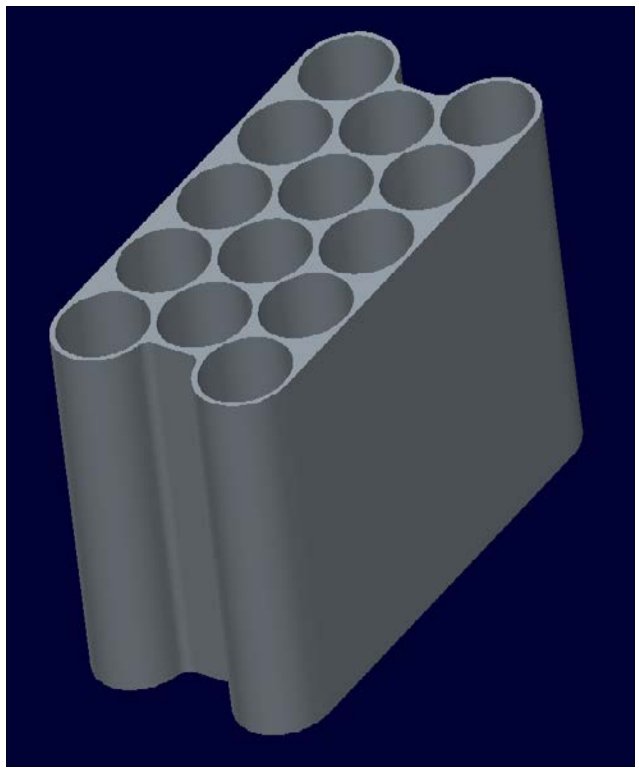
ISC Device Implantation and Test Results

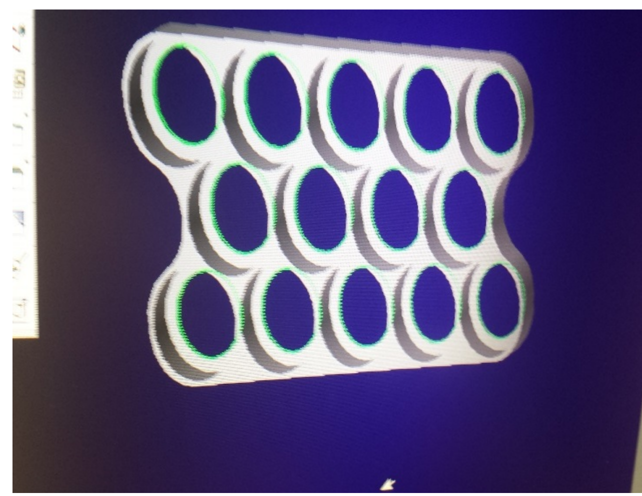
- **Pouch Cell – Non-flammable (NF) electrolyte**
- 18650 Cylindrical Cell – Shutdown Separator Study
- NASA Propagation Studies with ISC Trigger

Conductive Interstitial Material Design

- 14 nested cells with 1mm and 0.5 mm cell spacing
- Matching G10/FR4 capture plates for the cell ends
- Initial tests done with Al 6061T6
- Cells inserted into bores with their original shrink sleeve and 100 μm mica paper sleeve





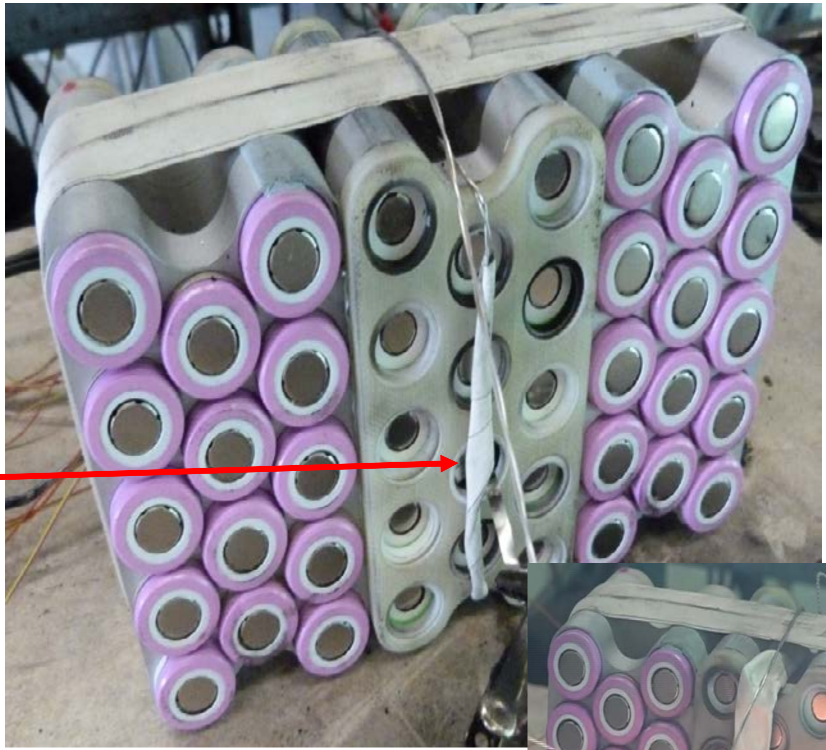


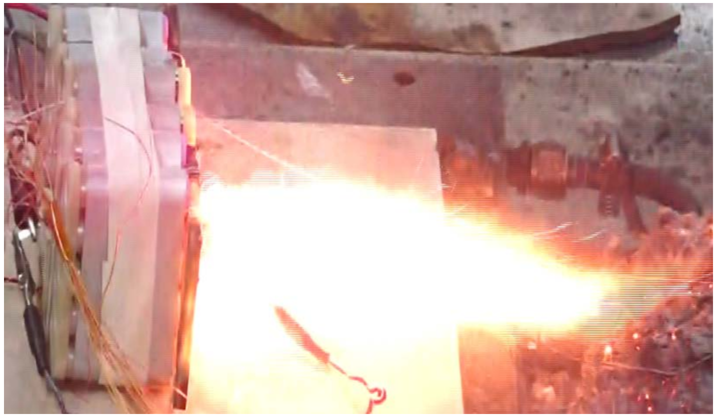
E-One Moli 2.4 Ah Implantation ISC Summary

- 60 cells Assembled with ISC Devices
- 59 cells: Successful formation
  - 1 cell short during formation leading to thermal runaway
- 58 cells successfully completed C/10 cycle
  - 1 cell short during C/10 cycling leading to thermal runaway
- 9/10 cells completed successful activation testing
  - All cells short ~60'C all cells go into thermal runaway
- 50 cells in storage for shipping
  - All cells holding voltage indicating no premature activation.
- 3 cells activated at 0% SOC to satisfy DOT regulations with shipping cells from Vancouver to NASA JSC.
  - All ISCs activated at 0% SOC and the temperature rise was typically less than 10^{o}C

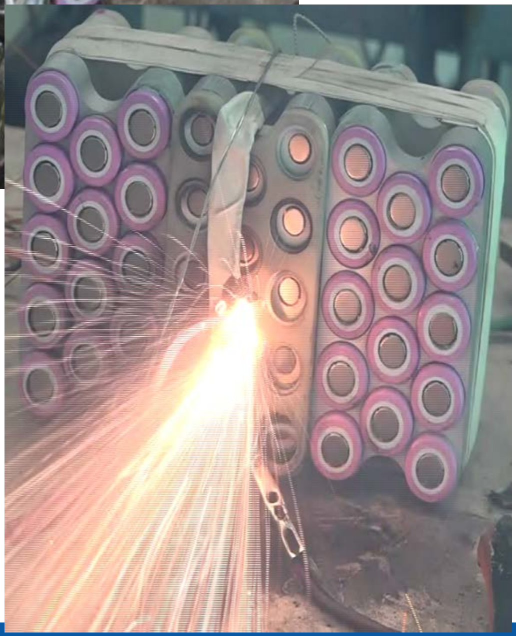
Used Moli Cell with ISC Device as Trigger Cell

- Fully populated heat sinks with fully charged Panasonic cells in middle heat sink
- Moli cell with ISC device in interior trigger position
- Used bottom heater to drive Moli cell to >60°C to activate ISC device

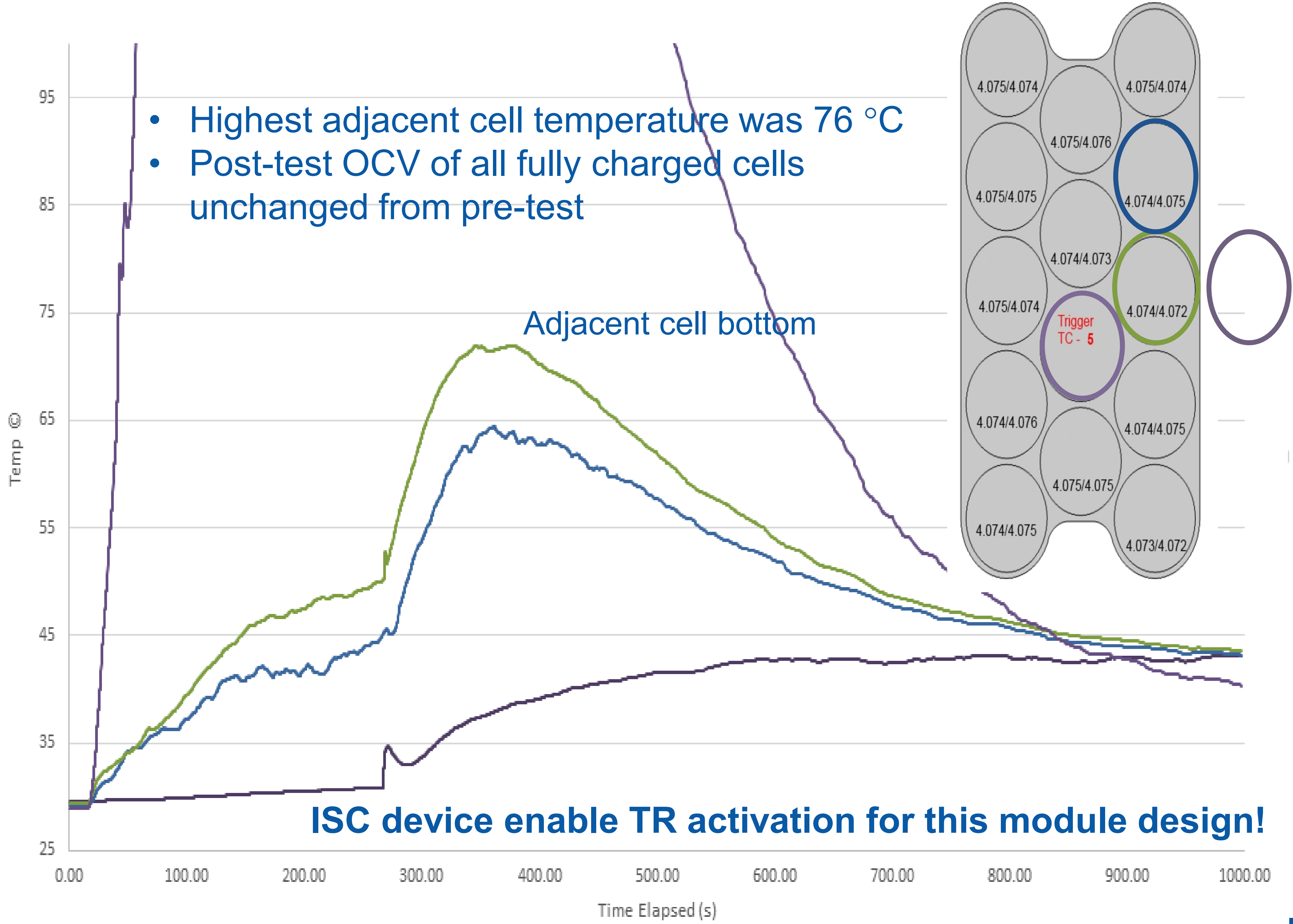




TR achieved in 3 mins in all 3 trials to date



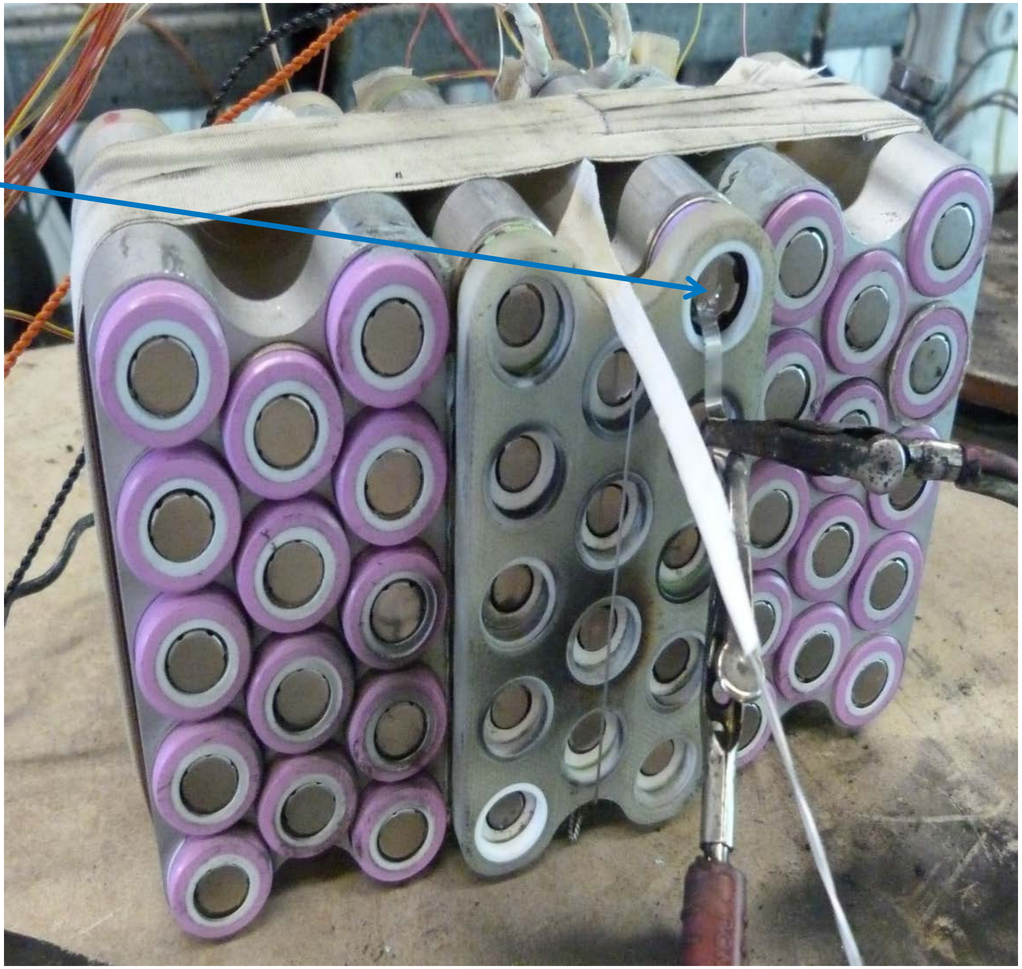
- Highest adjacent cell temperature was 76 °C
- Post-test OCV of all fully charged cells unchanged from pre-test

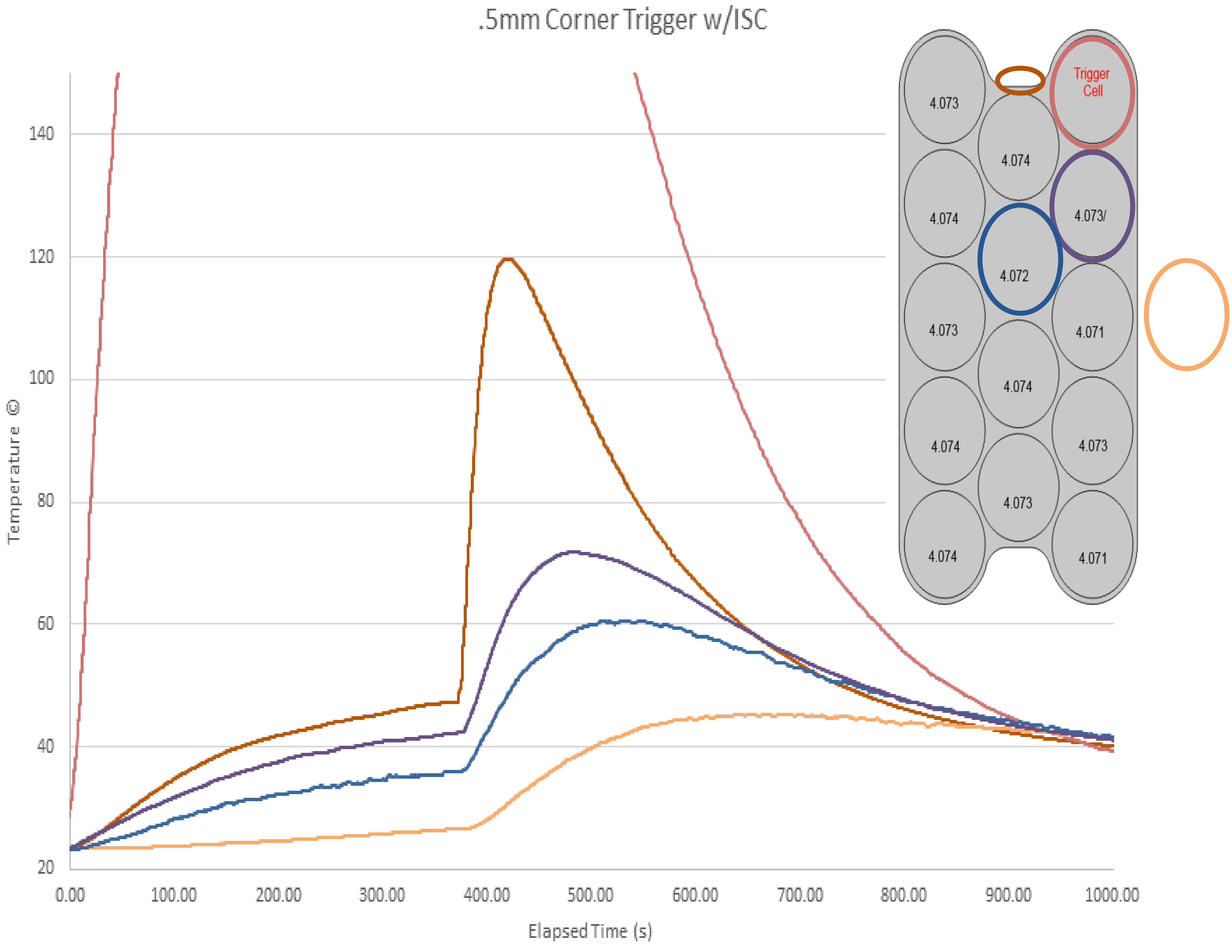


ISC device enable TR activation for this module design!

Propogation Test Using Moli ISC Cell In Corner Position

- Corner trigger cell position.
- No propagation, venting or adjacent cell damage.
- Highest adjacent cell temperature was 72 °C!
- Pre/post OCV yet again unchanged!





.5mm Corner Trigger w/ISC
Temperature ©
140
120
100
80
60
40
20
0.00
100.00
200.00
300.00
400.00
500.00
600.00
700.00
800.00
900.00
1000.00
Elapsed Time (s)
4.073
4.074
Trigger Cell
4.074
4.073/
4.072
4.073
4.071
4.074
4.074
4.073
4.073
4.074
4.071

5 Design Driving Factors for Reducing Hazard Severity of Single Cell TR

Reduce risk of cell can side wall ruptures

- Without structural support most high energy density (>600 Wh/L) designs are very likely to experience side wall ruptures during TR

Provide adequate cell spacing

- Direct contact between cells without alternate heat dissipation paths nearly assures propagation

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

- Tortuous path for the ejecta before hitting battery vent ports equipped flame arresting screens works well

Summary and Conclusions

- US Patent # 9,142,829
  - NREL – Matt Keyser, Dirk Long, and Ahmad Pesaran
  - NASA – Eric Darcy
- Used to Study
  - Type of Separators
  - Non-flammable electrolytes
  - Electrolyte Additives
  - Fusible Tabs
  - Propagation Studies
  - Gas generation within a cell
  - Much more…
- Being used to make batteries safer.

Acknowledgments

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    - Dave Howell
    - Brian Cunningham
- Acknowledgements
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        - Jacob Darst, Kyle Karinshak, and Stephanie Scharf, NASA summer/fall interns
        - Dereck Lenoir, Thomas Viviano, Tony Parish, Henry Bravo/NASA test
        - Gary Bayles, consultant, SAIC

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