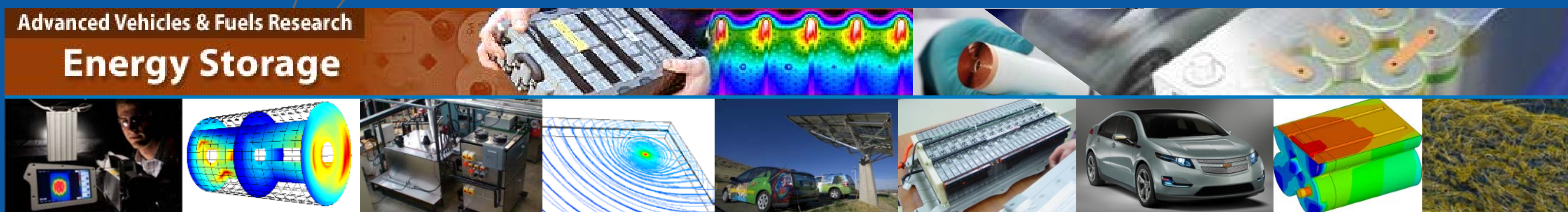
NREL/NASA Internal Short-Circuit Instigator in Lithium Ion Cells



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Ben McCarthy – Dow Kokam

Battery Safety Conference 2013 – San Diego

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NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Presentation Outline

- Background
- Motivation
- Objectives
- NREL/NASA ISC Approach
- ISC Cell Testing
  - Pouch Cell
  - 18650 Cylindrical Cell
- Conclusions and Summary
- Future Work

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

- Li-ion cells provide the highest specific energy (>180 Wh/kg) and energy density (>360 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

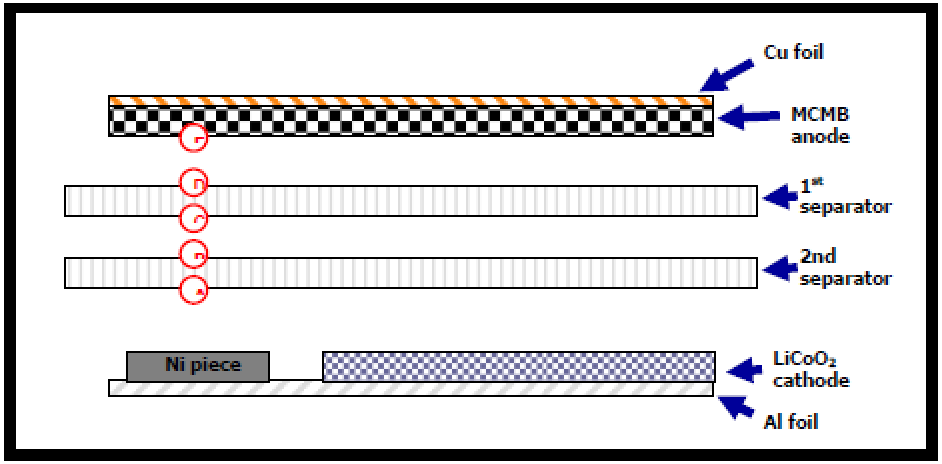
The Bigger Picture

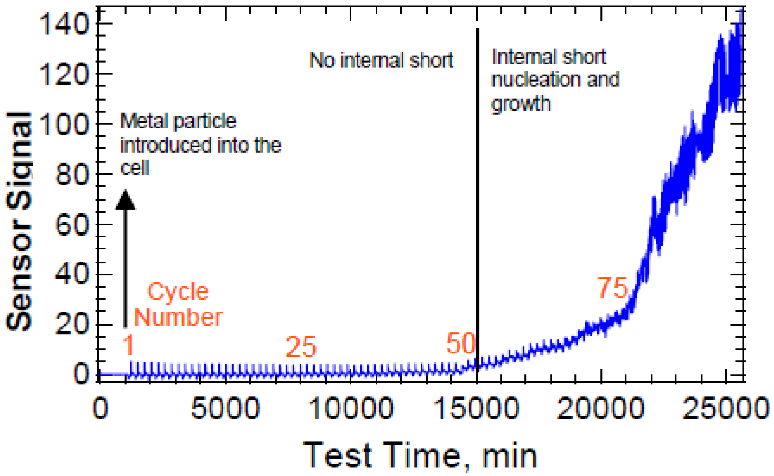
Cost Effective Contamination Mitigation

- Identifying Sources (native and foreign)
- Characterizing credible contamination properties
  - Electrical, magnetic, mechanical, electrochemical, and thermal
- Quantifying and understanding the effects
  - Implantable, on-demand internal short circuit testing to determine which types of particles, where placed, and under what conditions are most hazardous
  - Mapping the unsafe zone of internal short circuit conditions for a given cell design and thermal conditions with math models
- Cost Effective Prevention Measures
  - Manufacturing audits
    - What cleanliness and filtering measures have best cost/benefit ratio?
    - What particle sampling methods are most effective?
  - Non-Destructive Testing
    - What kind of CT scanning system is needed to detect hazardous defects in large, asymmetric cell designs?
    - How effective is acceptance testing to screen out internal shorts?
  - Destructive Testing
    - DPA of sample from lot to assess cell quality and absence of defects

Why is metallic Foreign Object Damage (FOD) mitigation critical?

- Latency potential of metallic FOD has been demonstrated*
  - Small Ni particle implanted in commercial cells in key location
  - Reassembled cell passes acceptance testing
  - Requires > 50 cycles for it to develop into thermal runaway hazard
- One can not screen out all potential latent defects by acceptance testing alone
  - Implementation of effective manufacturing FOD mitigation measures is key
  - Periodic line audits are a must
  - As are cell DPAs



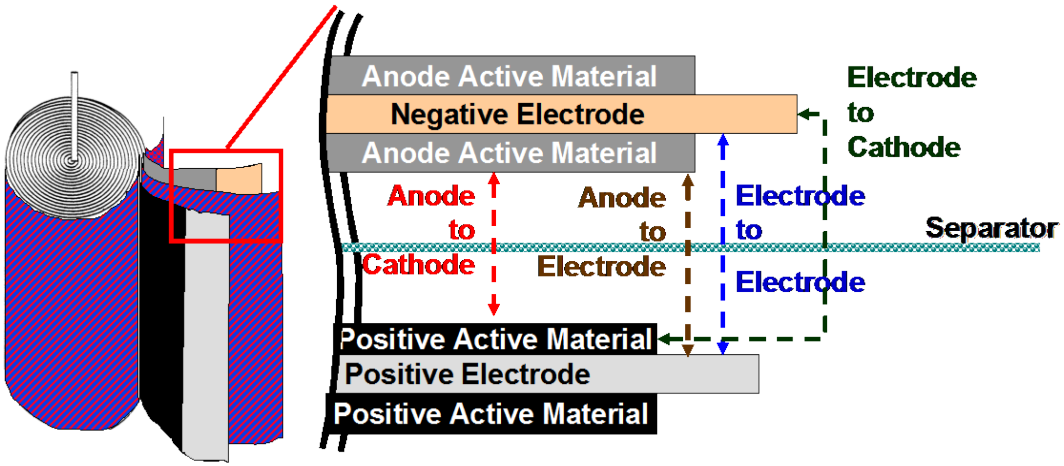


* Barnett et. al, Power Sources Conference, Las Vegas, NV, 2012

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



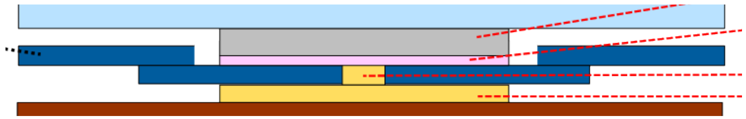
Spiral wound battery shown – can also be applied to prismatic batteries.

- 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

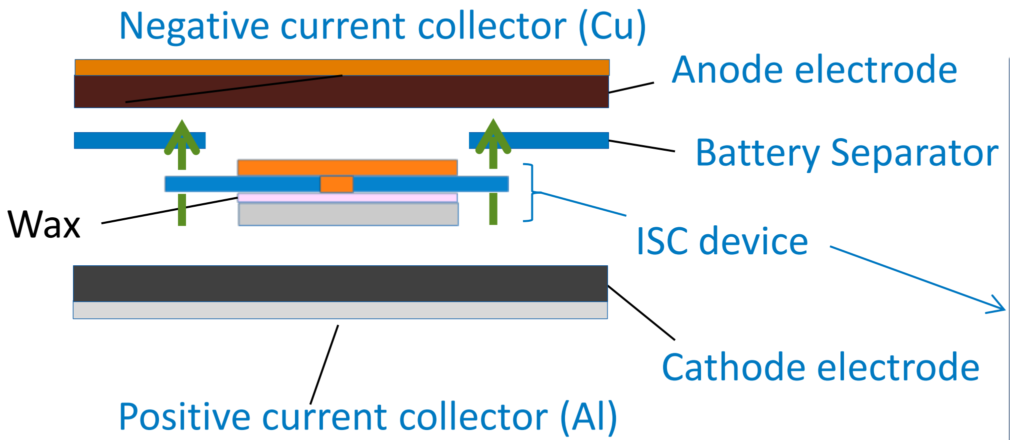
Internal short circuit device design

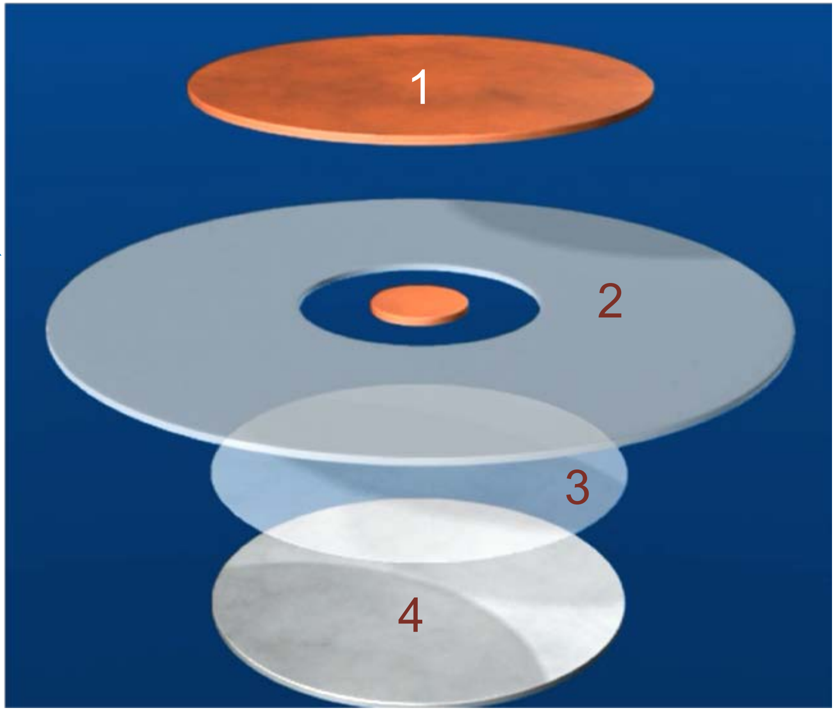
- Small, low-profile and implantable into Li-ion cells, preferably during assembly
- Key component is an electrolyte-compatible phase change material (PCM)
- Triggered by heating the cell above PCM melting temperature (presently 40°C – 60°C)
  - NREL has developed an ISC that triggers at 47°C and 57°C.
- 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

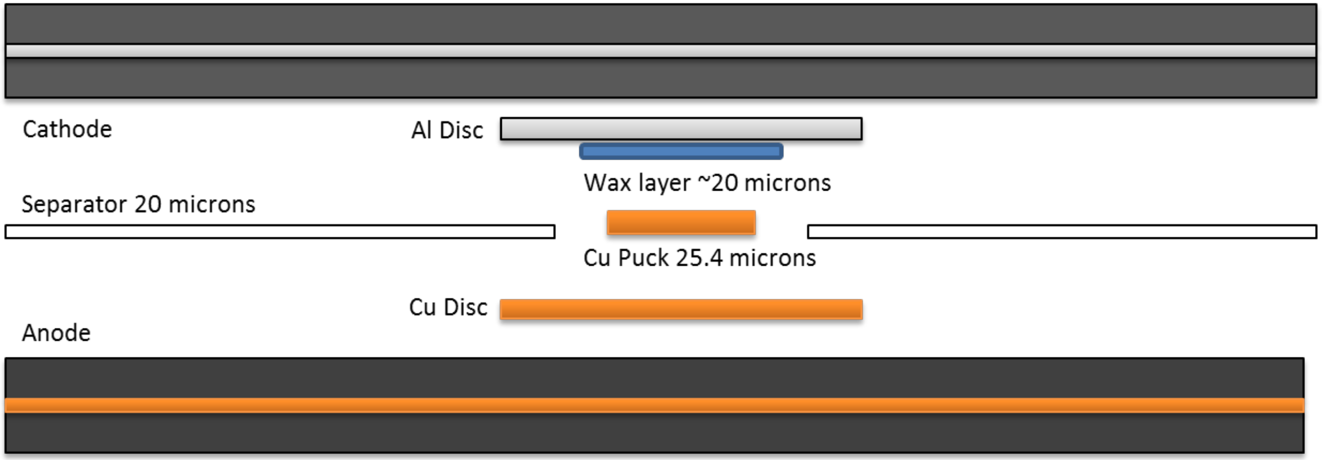
Top to Bottom:

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

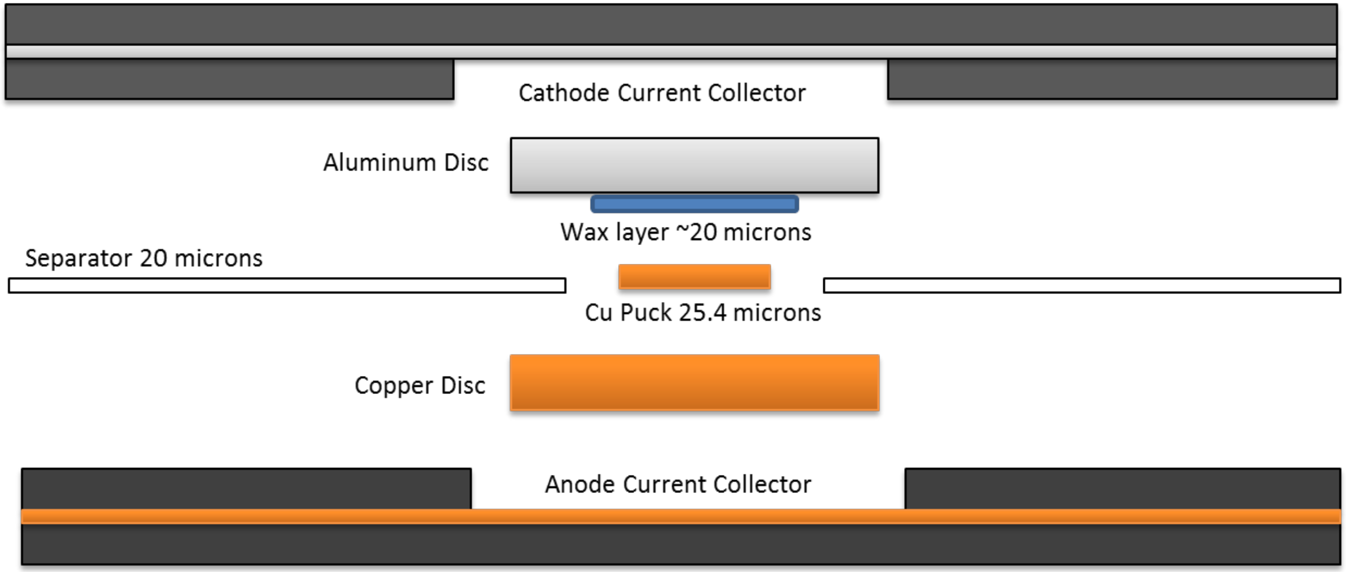
Four Types of ISC

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

Active to Active ISC and Collector to Collector ISC



Active to Active ISC
Type 1



Collector to Collector ISC
Type 4

Notes on NREL/NASA ISC Design Types

- Design thicknesses have not been optimized.
- When active material is removed, the ISC components can be chosen in order to minimize the effect on cell thickness. In other words, the ISC can have a limited affect on the cathode/anode pair thickness when inserted into cell.
- Presently, the copper puck is 4 mm in diameter. Future testing will assess the potential for reducing the size of the copper puck (future tests would be ~1-2 mm in Diameter) and aluminum and copper pad diameters.

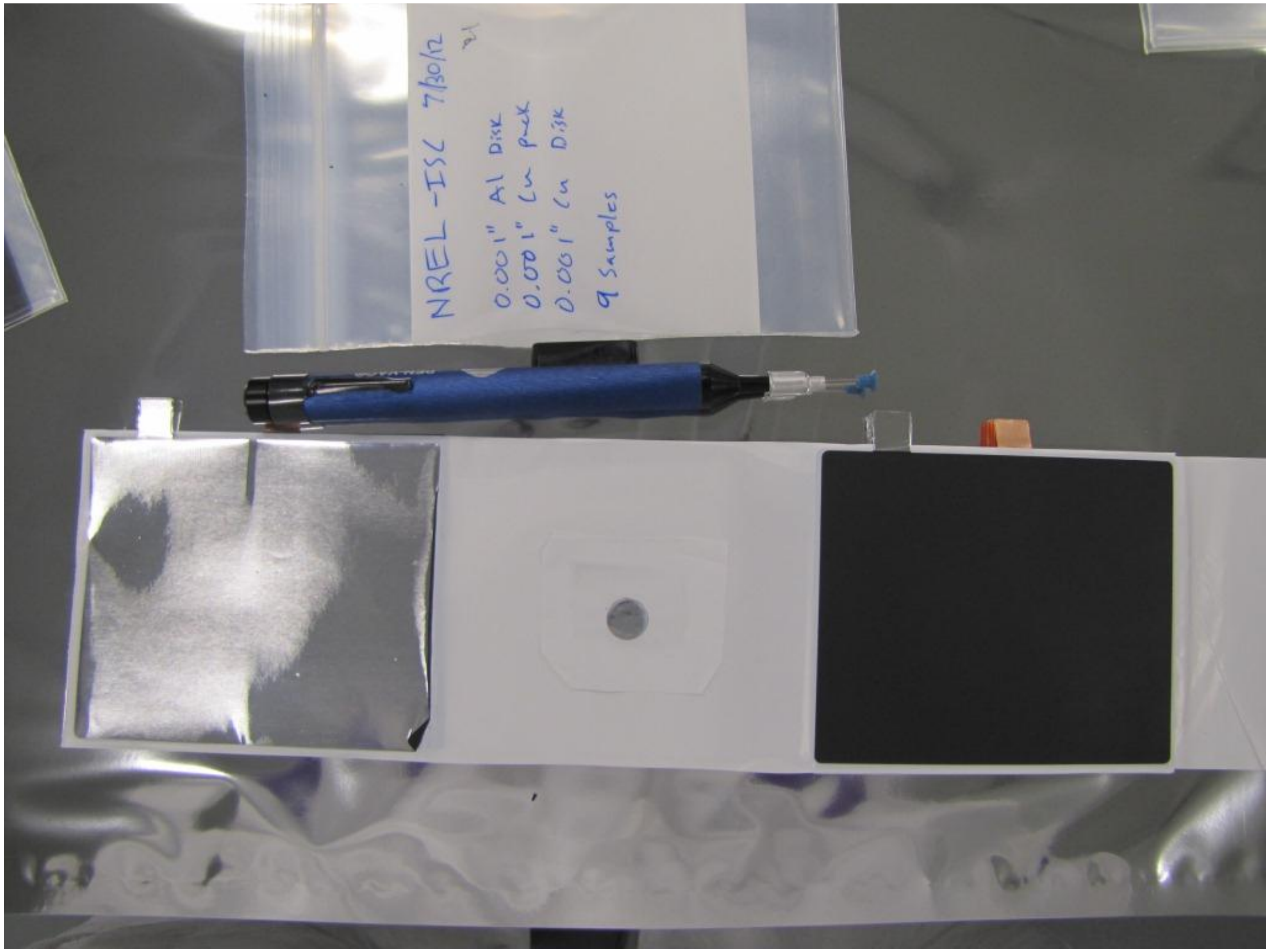
ISC Device Implantation and Test Results

- 8 Ah Pouch Cell
- 18650 Cylindrical Cell – 2.4 Ah

ISC Device Implantation and Test Results

- **8 Ah Pouch Cell**
- 18650 Cylindrical Cell – 2.4 Ah

Type 1 ISC
Active to Active



Prismatic electrode stack design with multiple electrodes connected in parallel
Photo Credit: Ben McCarthy, Dow Kokam

Dow Kokam Cells - Activation

- After formation and five C-rate cycles at Dow Kokam, the cells were shipped to outside test facility for ISC activation.
- Cells were shipped (Missouri to Alabama) at 0% SOC and kept cool with ice packs in an insulated container.
- Four cells (one for each type of ISC) were chosen for ISC device activation.
- The cells were charged to 10% SOC and then brought to $80^{o}C$ for ISC device activation.

Test Fixture for DK Pouch Cell

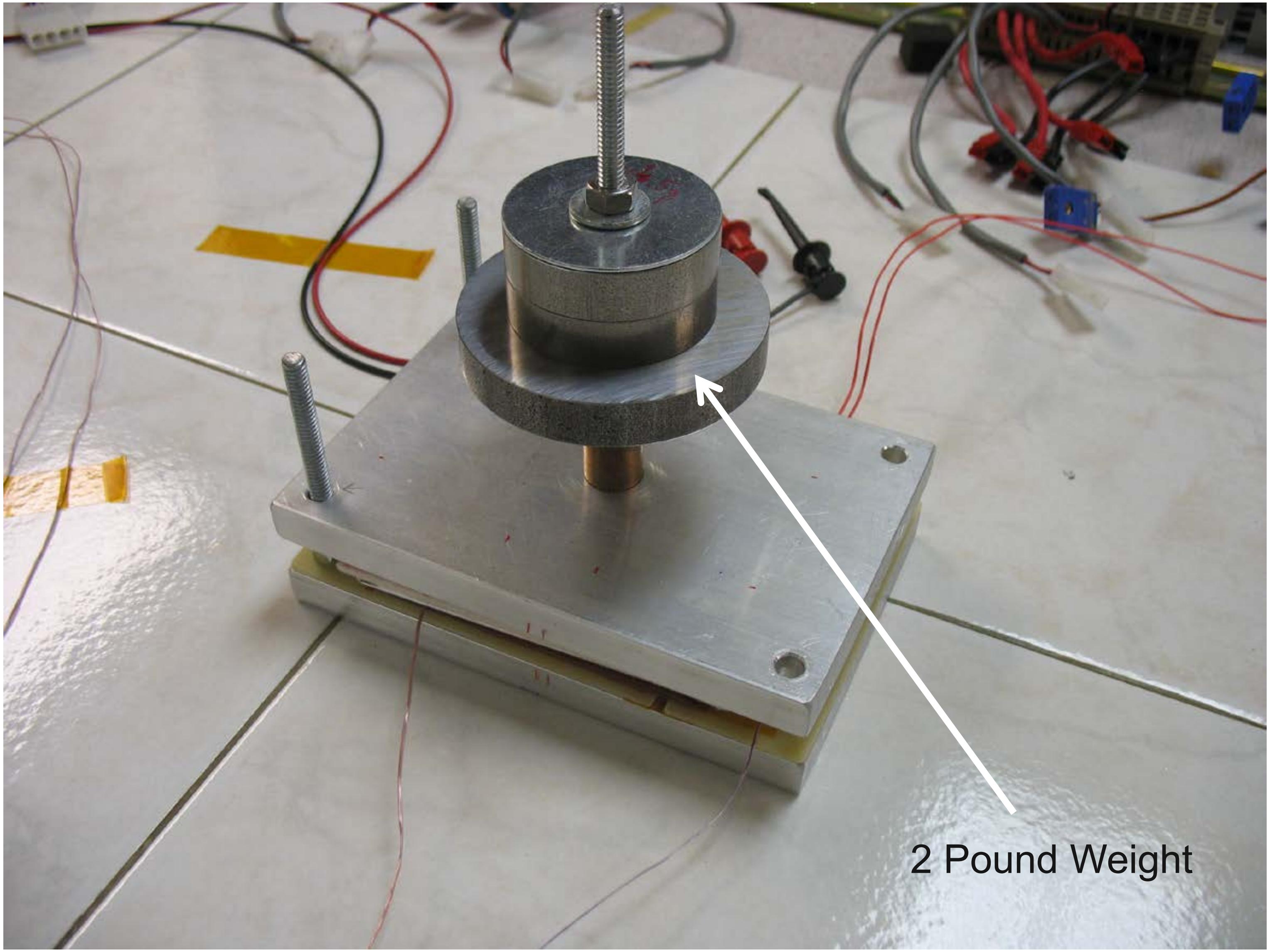
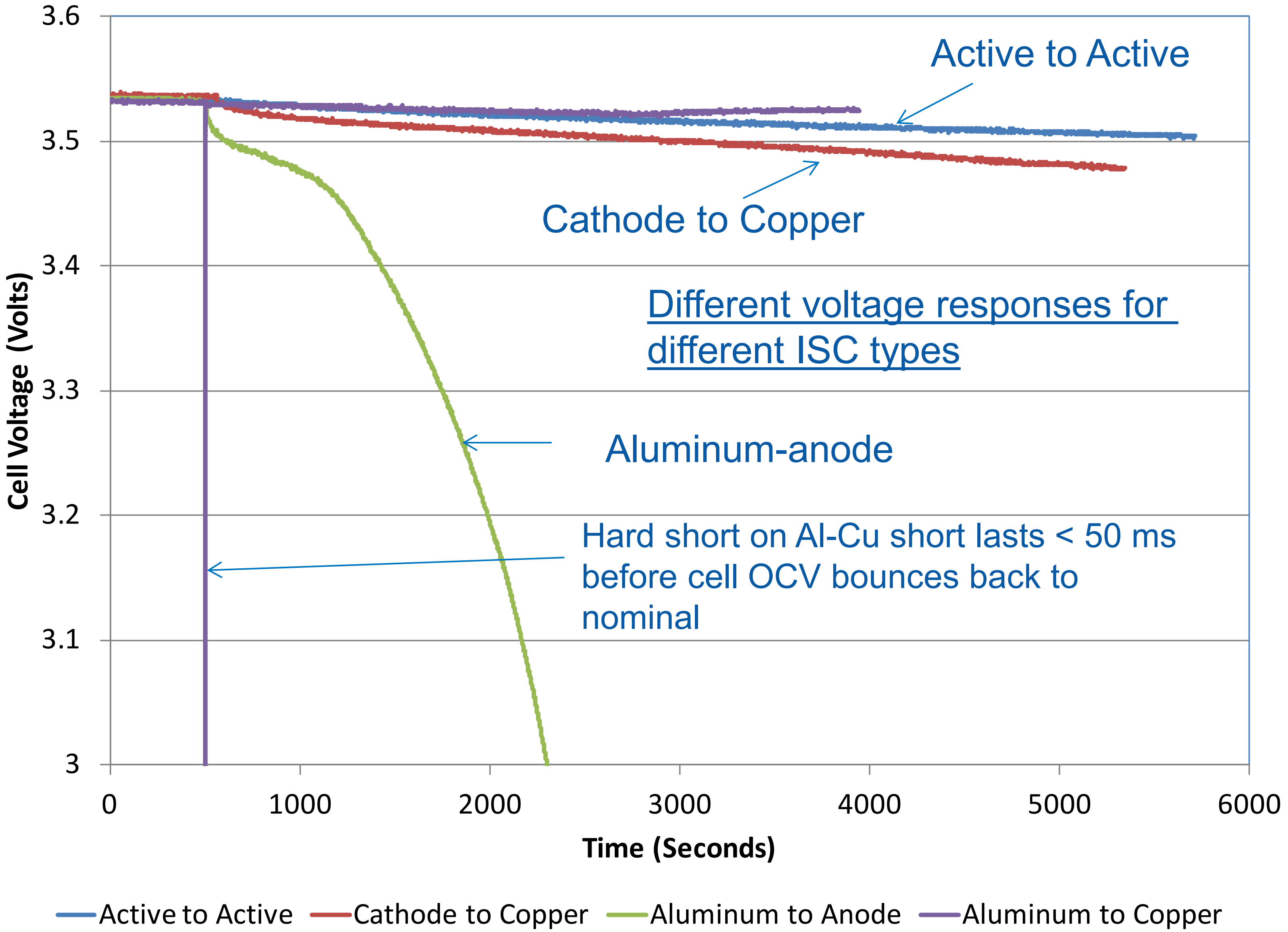
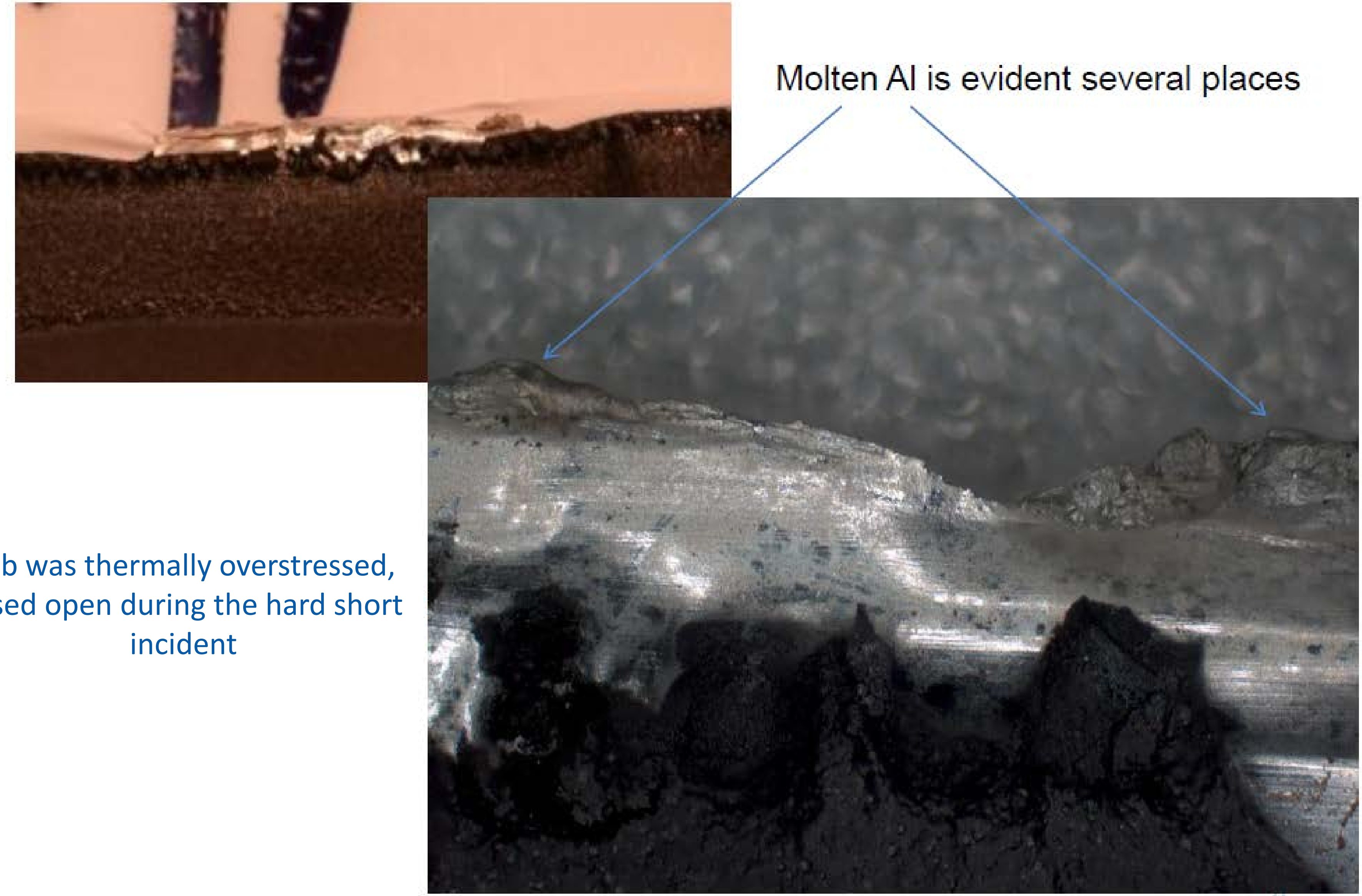


Photo Credit: Brad Strangways, Symmetry Resources Inc.

DK 8 Ah Cell Activation at 10% SOC



Macro Image of Cathode Cell Tab – Al to Cu ISC



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

Photo Credits: Eric Darcy, NASA

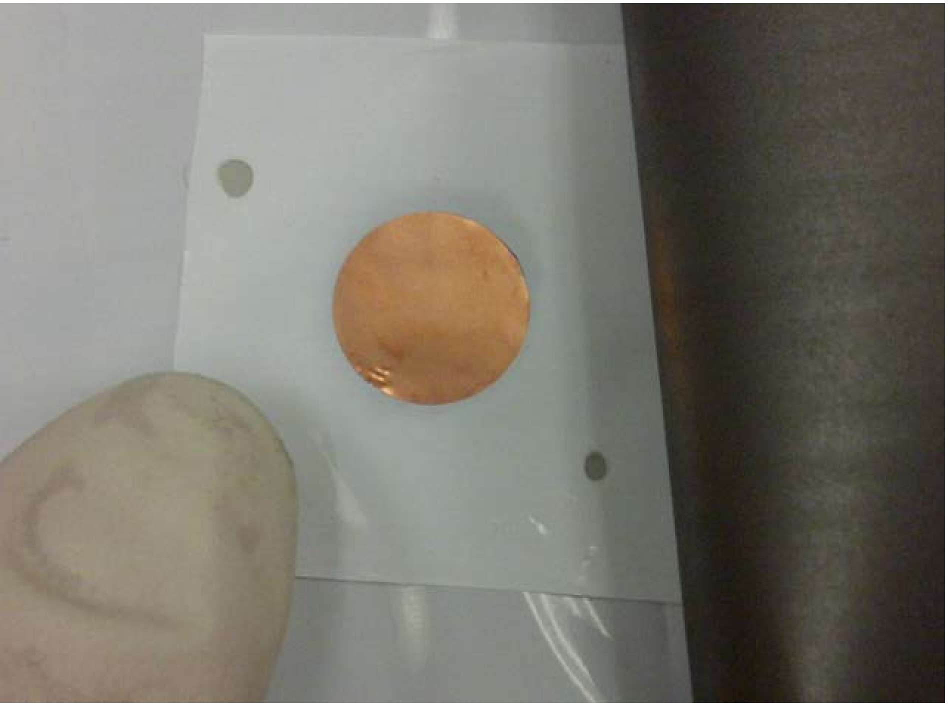
Dow Kokam Testing Summary

- The microcrystalline wax used in the ISC appears to be stable in the Dow Kokam electrolyte. Of the 50 cells placed in storage in November 2011, only three cells showed large voltage degradation when tested in September 2012.
- For FY12, 90% of the cells passed formation that were fabricated at Dow Kokam with the ISC.
- All four ISC types activated under test at 10% SOC:
  - It was determined that pressure is needed on the area of the ISC to:
    - Ensure that the wax flows from between the aluminum disc and copper puck.
    - Ensure the ISC components remain in contact.
  - The voltage and thermal response of the cell was different for all four types of ISCs.
- Future Testing:
  - Test cells at 100% SOC.
  - Test cells with new type of ISC device to eliminate the need for pressure on ISC during activation -100% successful in dry activation.
  - Vary location of ISC device to determine spatial effect – middle of stack and outside of stack.

ISC Device Implantation

- 8 Ah Pouch Cell
- 18650 Cylindrical Cell – 2.4 Ah

ISC Implantation – Active to Active



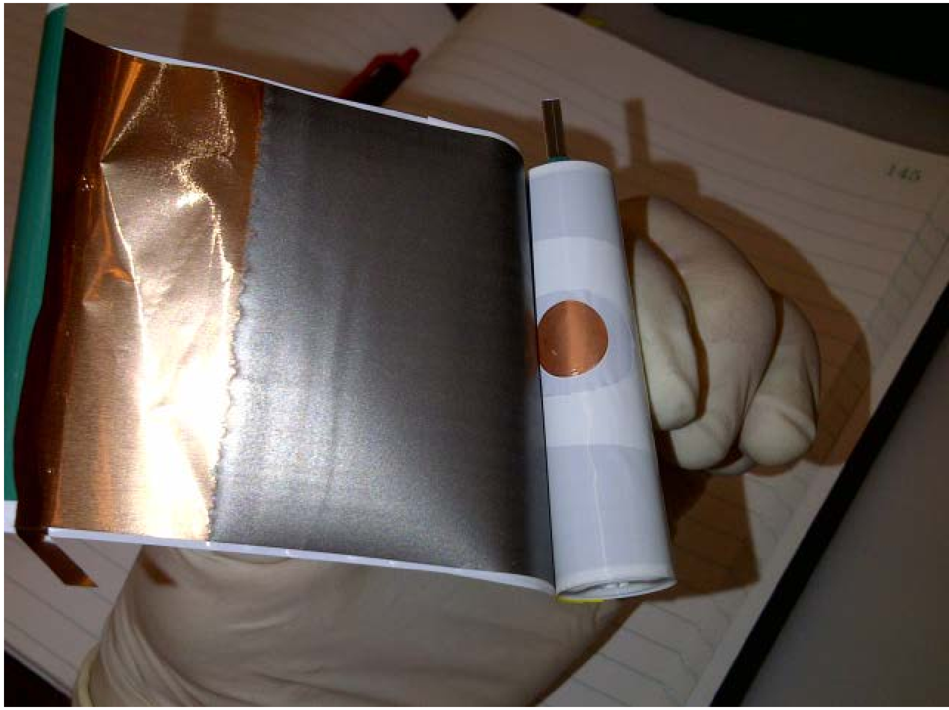
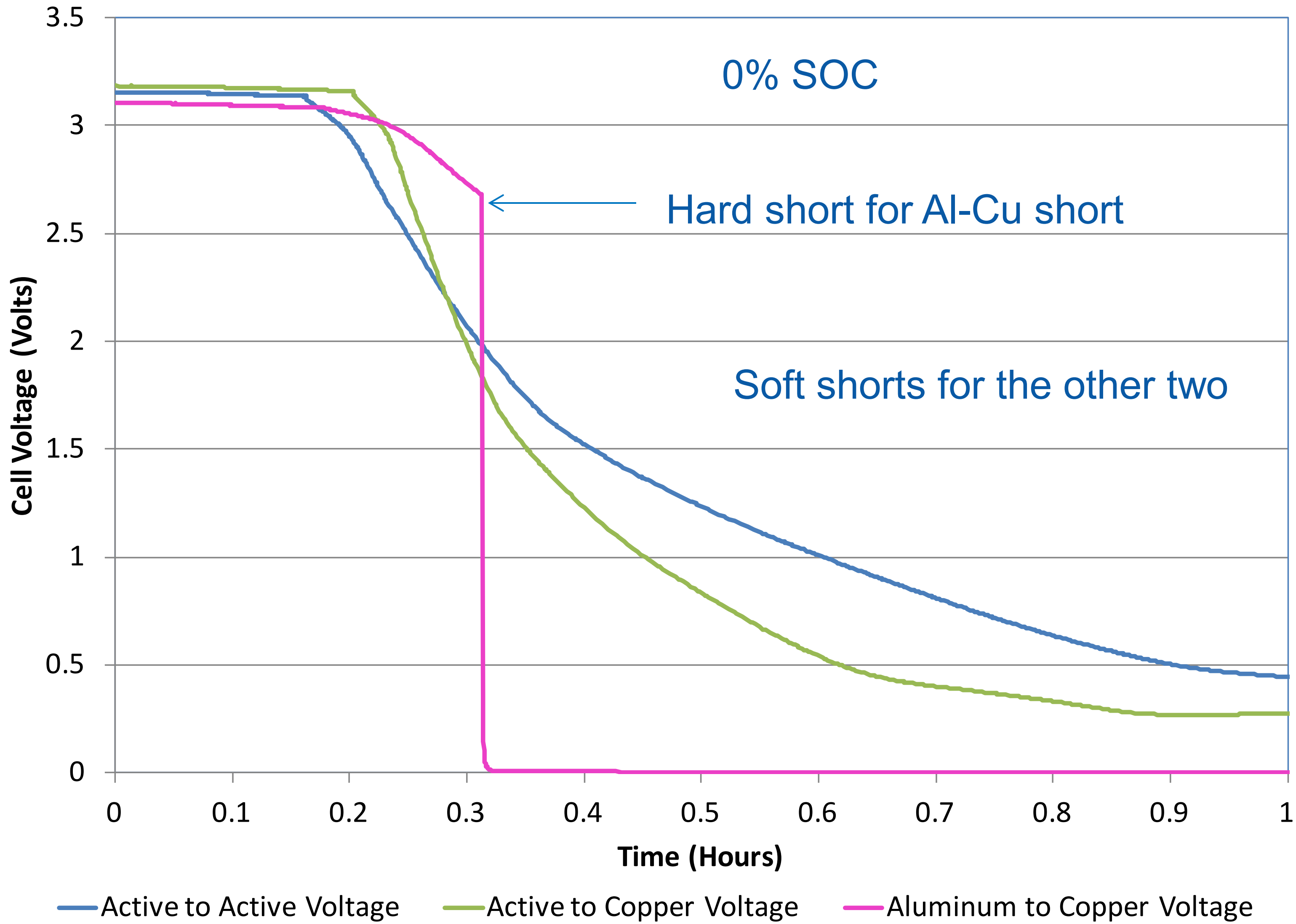


Photo Credits: Mark Shoesmith, E-One Moli

1st Round of Testing

Round	Active To Active (Type 1)	Aluminum To Active (Type 2)	Active To Copper (Type 3)	Aluminum To Copper (Type 4)	0% SOC Activation	100% SOC Activation	Shutdown Separator
1	**X**	**X**	**X**	**X**	**X**		X
2				X		X	X
3				X		X	
4		X		X		X	X

Results – 1st Round of Testing with 18650 Cells



Aluminum to anode voltage profile missing because cell shorted during formation

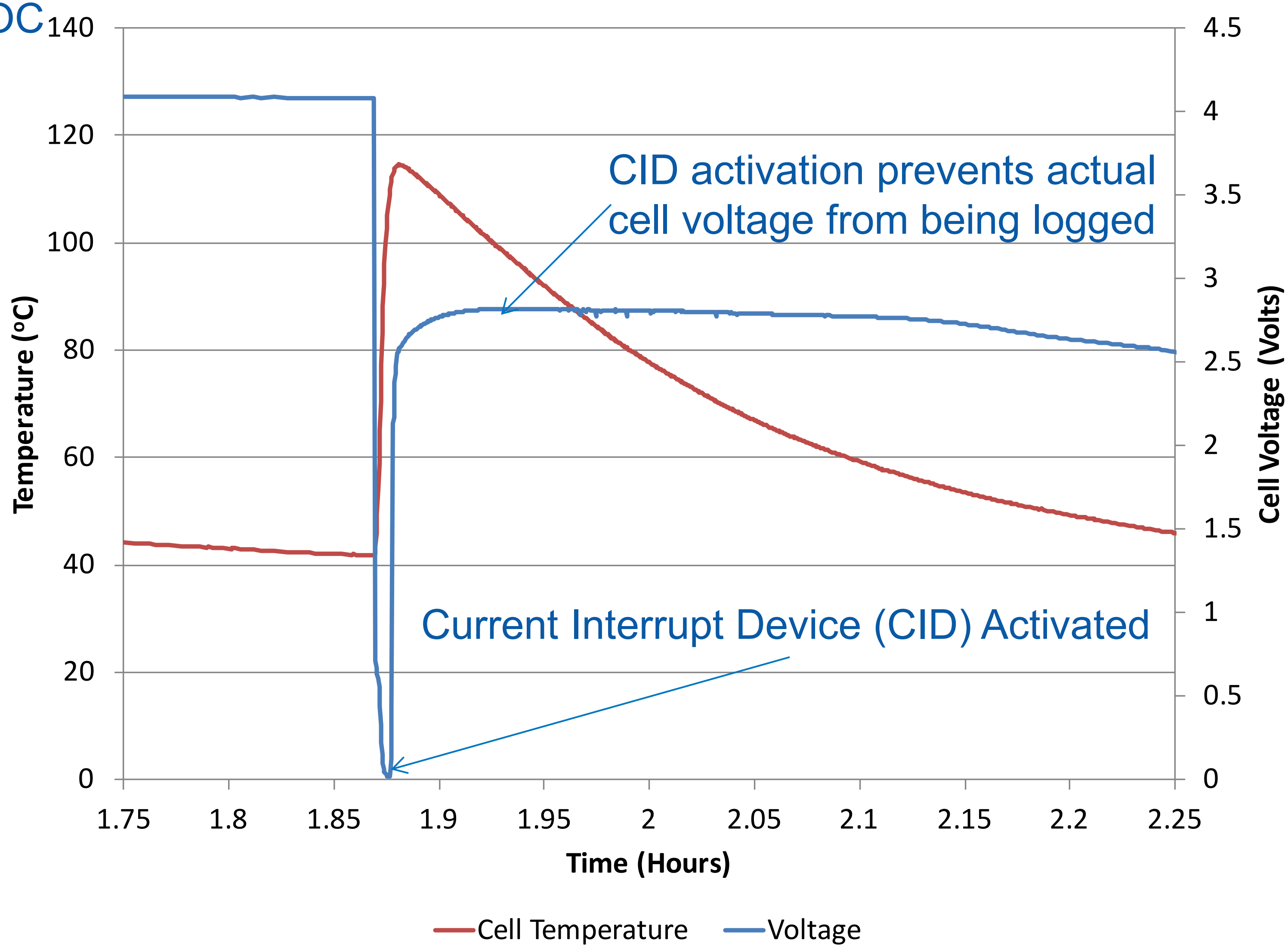
2nd Round of Testing

Round	Active To Active (Type 1)	Aluminum To Active (Type 2)	Active To Copper (Type 3)	Aluminum To Copper (Type 4)	0% SOC Activation	100% SOC Activation	Shutdown Separator
1	X	X	X	X	X		X
2				**X**		**X**	**X**
3				X		X	
4		X		X		X	X

- Cells tested at 100% SOC
- Standard shutdown separator used in cell – PP/PE/PP

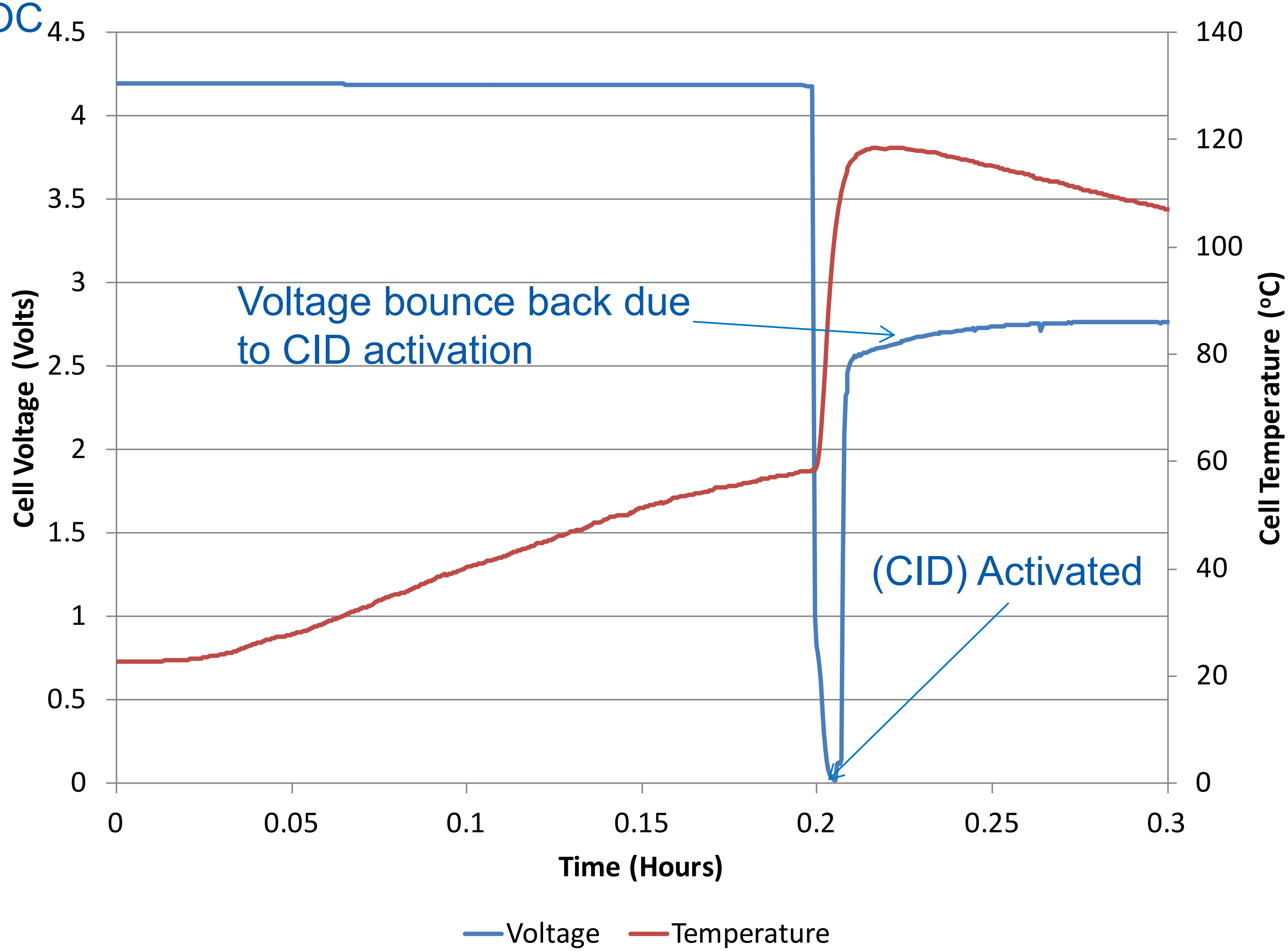
2nd Round – Foil to Foil ISC Activation

At 100% SOC
Type 4 ISC
Cell 702



2nd Round – Foil to Foil ISC Activation

At 100% SOC
Type 4 ISC
Cell 801

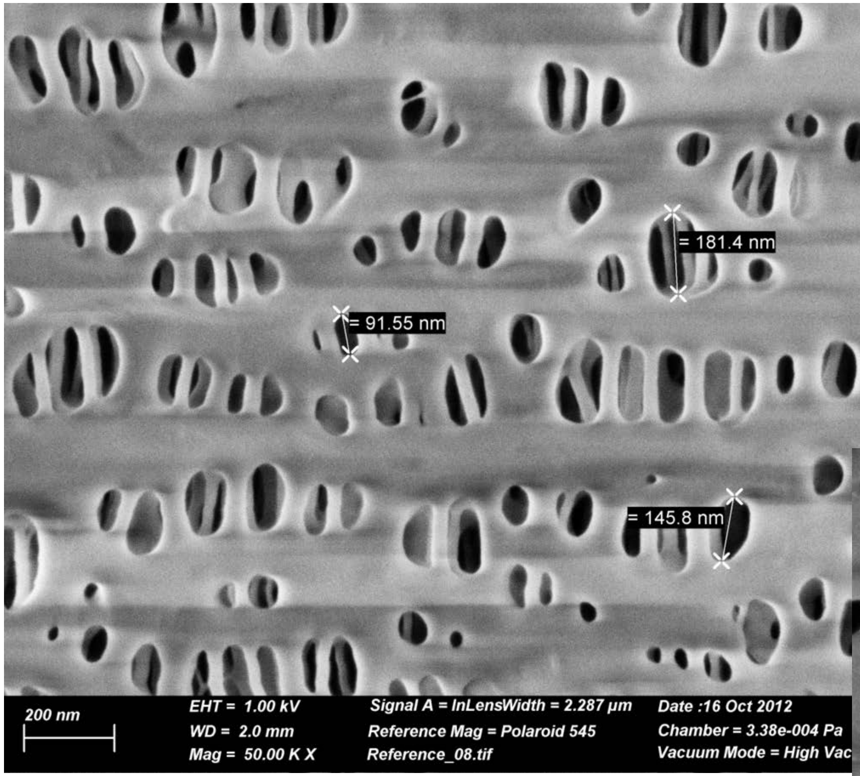


Cell 801 DPA – 2nd Round of Testing

Photo Credits: Mark Shoesmith, E-One Moli

- Cell 801, CID activated. Recovery voltage is likely not a cell measurement.
- Jellyroll measurements: 0.0V,
- Separator is shutdown and adhered to the cathode indicating high internal temperature. Separator is a shutdown separator – polypropylene/polyethylene/polypropylene (PP/PE/PP). The PE melts at a lower temperature than the PP and thus fills the pores in the PP layers.

Separator from cell DPA vs Control Separator



PP/PE/PP separator extracted from unwetted jellyrolls

PP/PE/PP separator extracted from cell 801 with activated ISC device showing reduced “shutdown” porosity

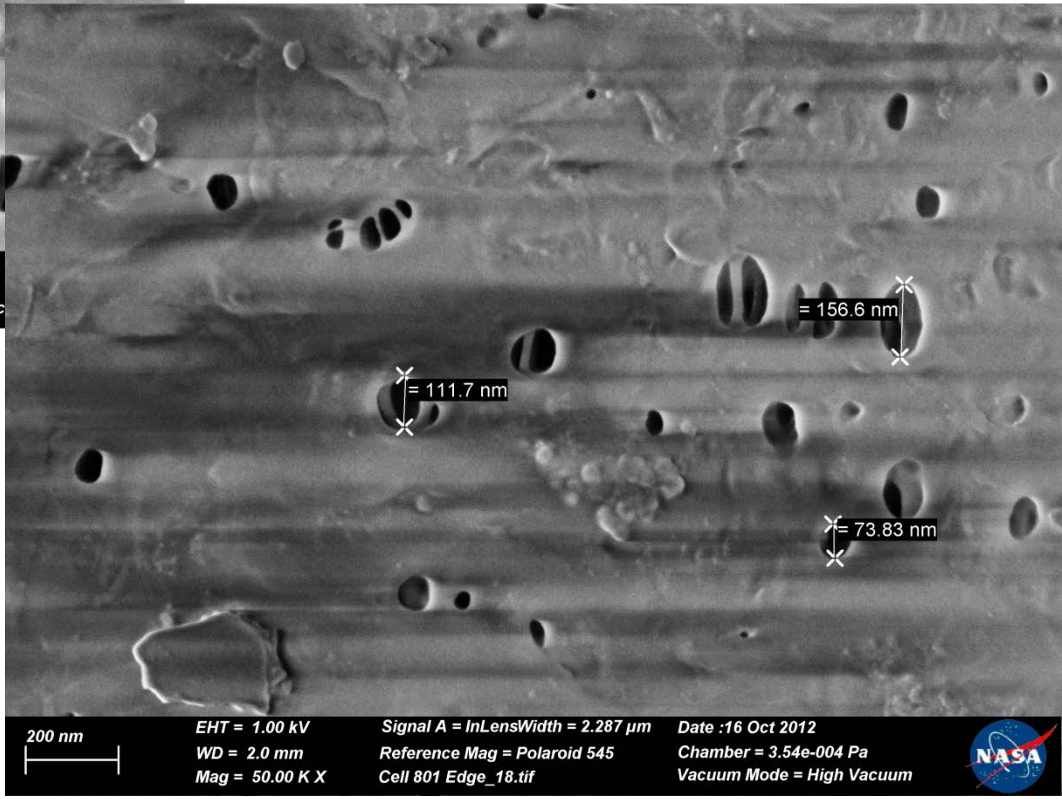


Photo Credits: Eric Darcy, NASA

Cell 801 DPA – 2nd Round of Testing

Photo Credits: Mark Shoesmith, E-One Moli

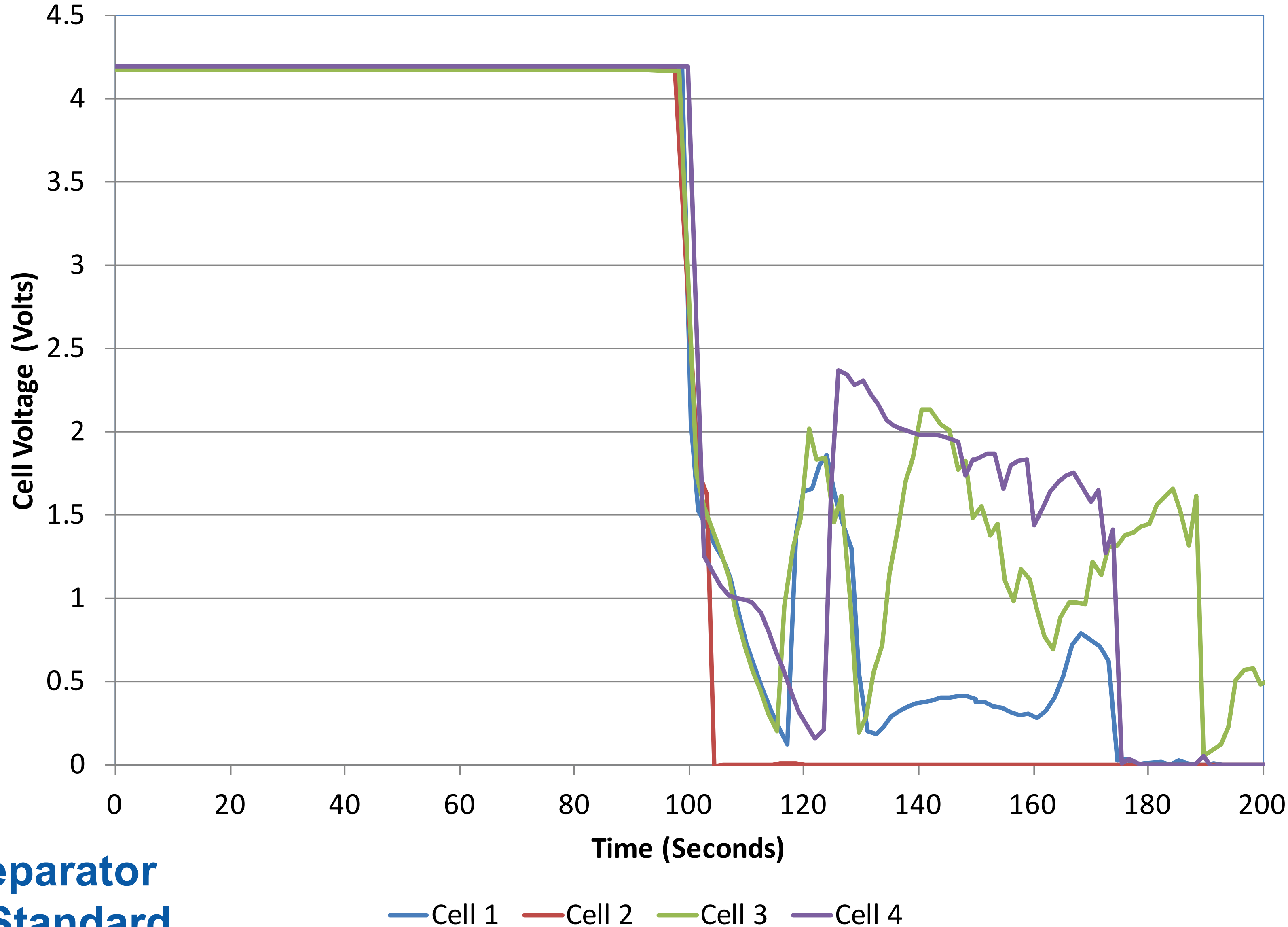
- No obvious cuts in cathode foil
- Area of charged anode still visible. Indicating separator shutdown has limited the internal discharge to a fraction of the cells capacity.
- Due to the separator shutdown, the full energy of the cell was not discharged otherwise the temperature achieved by the cell would have been much higher.

3rd Round of Testing

Round	Active To Active (Type 1)	Aluminum To Active (Type 2)	Active To Copper (Type 3)	Aluminum To Copper (Type 4)	0% SOC Activation	100% SOC Activation	Shutdown Separator
1	X	X	X	X	X		
2				X		X	
3				**X**		**X**	**X**
4		X		X		X	X

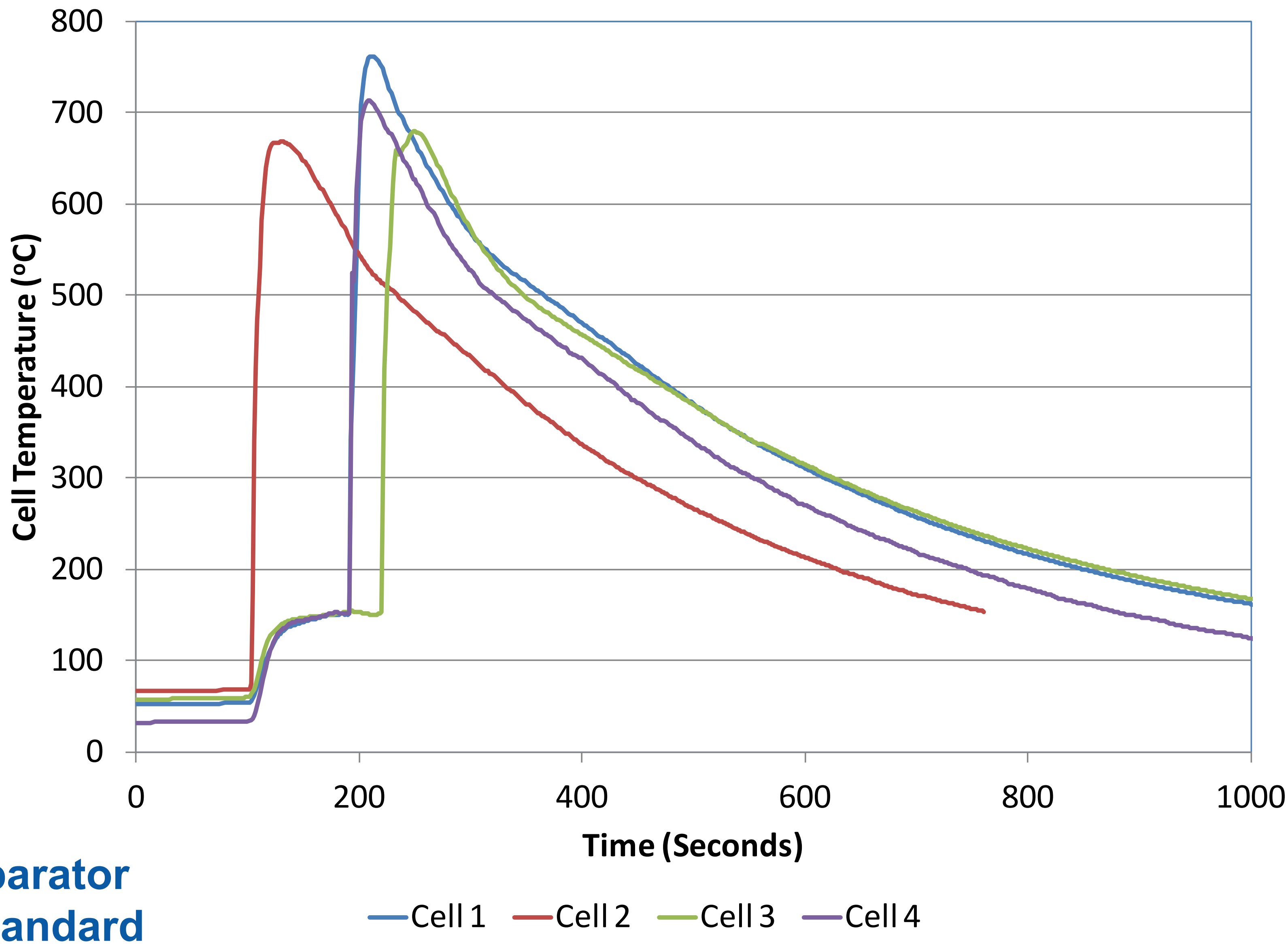
- Improved ISC Design
- Four (4) cells implanted with ISC design
- 100% of cells passed formation and initial cycling
- 100% of cells activated in oven testing
- **Non-standard separator used in tests – PP separator only. Cell abuse tolerance not representative of standard cell.**

Aluminum to Copper ISC Activation – 18650 Cell No Shutdown Separator – 100% SOC



PP Separator
Non-Standard

Aluminum to Copper ISC Activation – 18650 Cell No Shutdown Separator – 100% SOC



PP Separator Non-Standard

Aluminum to Copper ISC Activation – 18650 Cell Image Time Sequence – 100% SOC

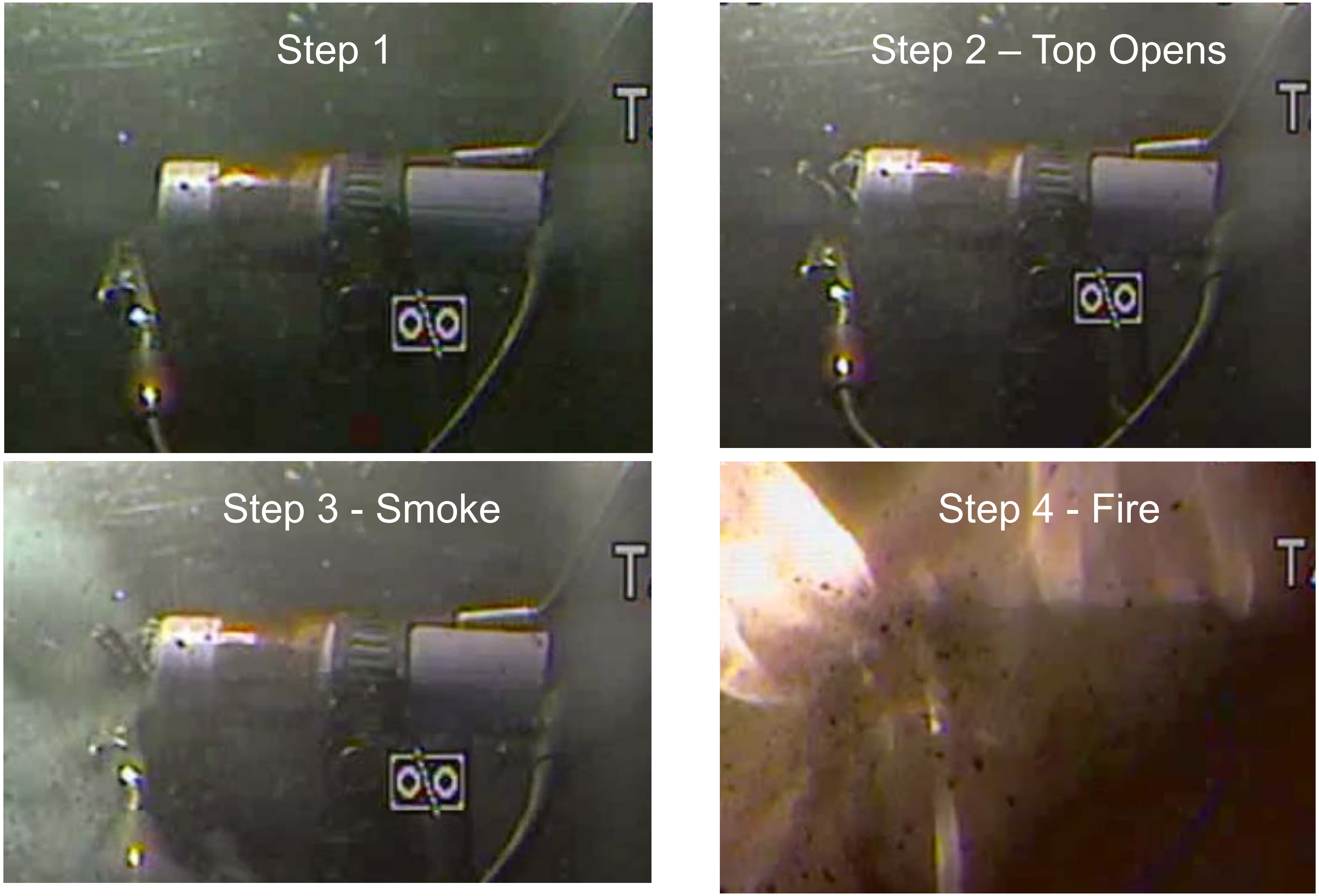


Photo Credits: Mark Shoesmith, E-One Moli

PP Separator Used - Non-Standard Separator

4th Round of Testing

Round	Active To Active (Type 1)	Aluminum To Active (Type 2)	Active To Copper (Type 3)	Aluminum To Copper (Type 4)	0% SOC Activation	100% SOC Activation	Shutdown Separator
1	X	X	X	X	X		X
2				X		X	X
3				X		X	
4		X		X		X	X

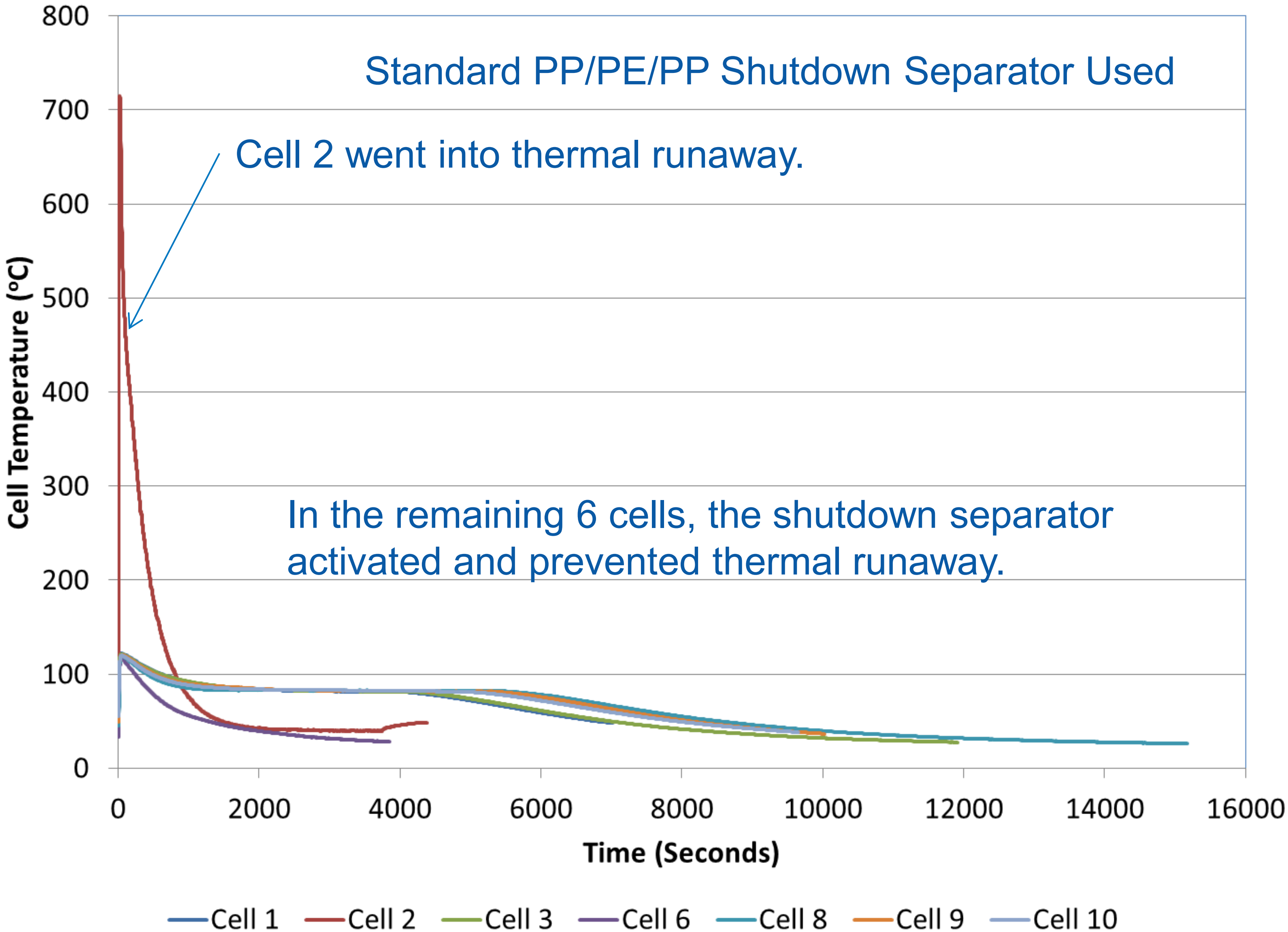
- 4th Round of testing was done to look at repeatability of ISC activation.
- Standard Shutdown Separator – PP/PE/PP
- 10 Cells of both type 2 and type 4 were tested.
- **Cells went through 10 full discharge/charge cycles before activation – all showed nominal capacity and coulombic efficiency during cycling.**

4th Round - Type 4 Repeatability Study

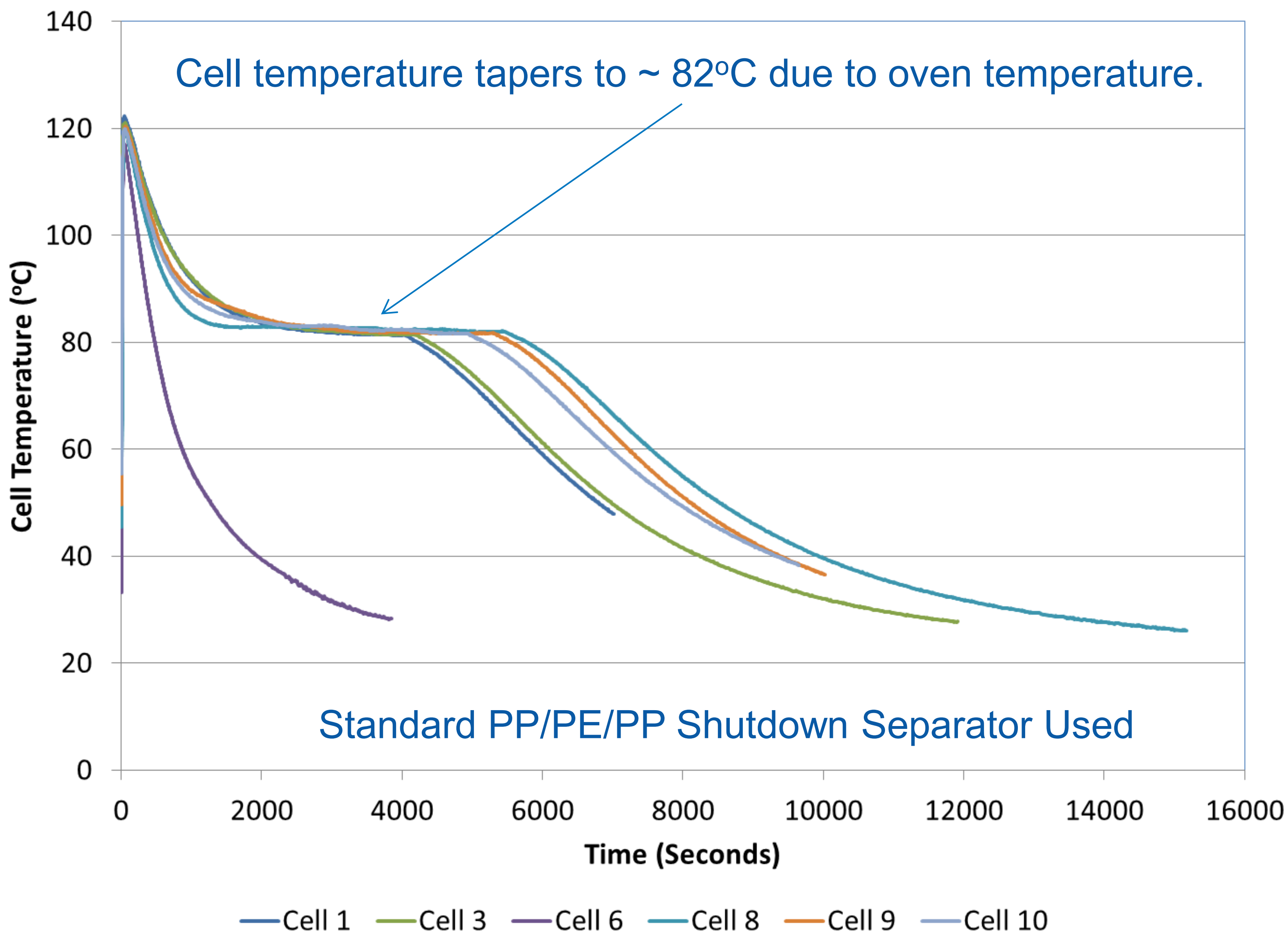
Cell	Successful Formation	Successful Activation?	Thermal Runaway?
1	Yes	Yes	No
2	Yes	Yes	Yes
3	Yes	Yes	No
4	Yes	No	-
5	Yes	No	-
6	Yes	Yes	No
7	Yes	No	-
8	Yes	Yes	No
9	Yes	Yes	No
10	Yes	Yes	No

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

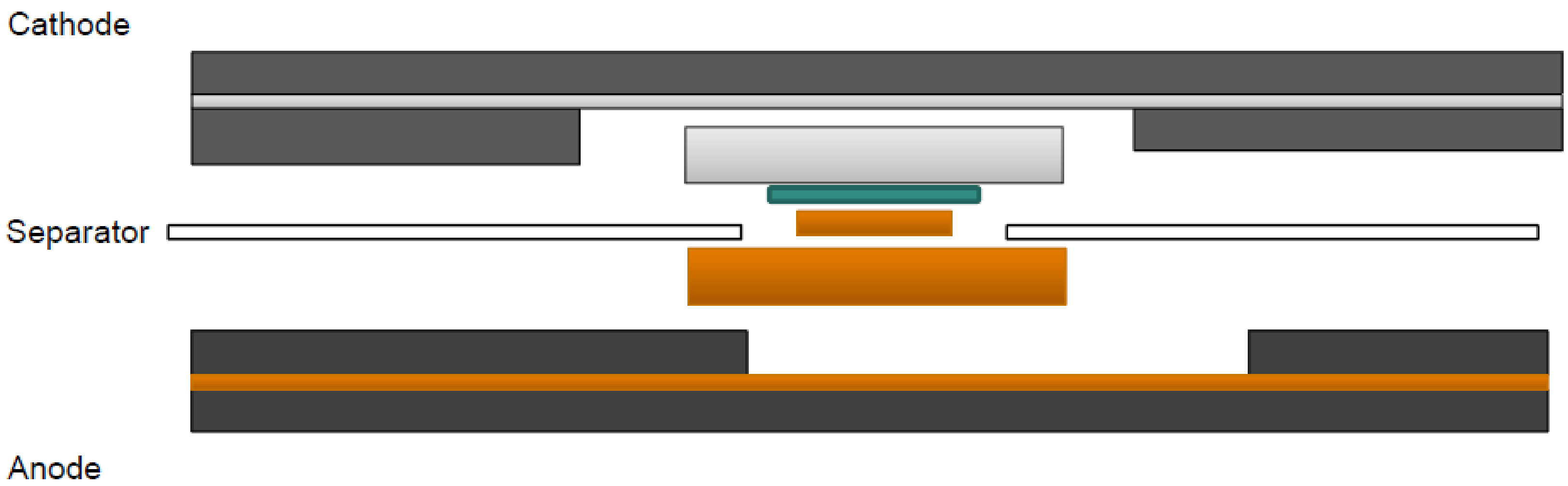
Type 4 ISC – Successful Activation



Type 4 ISC – Successful Activation Except Cell 2



Type 4 – Thermal Runaway Event



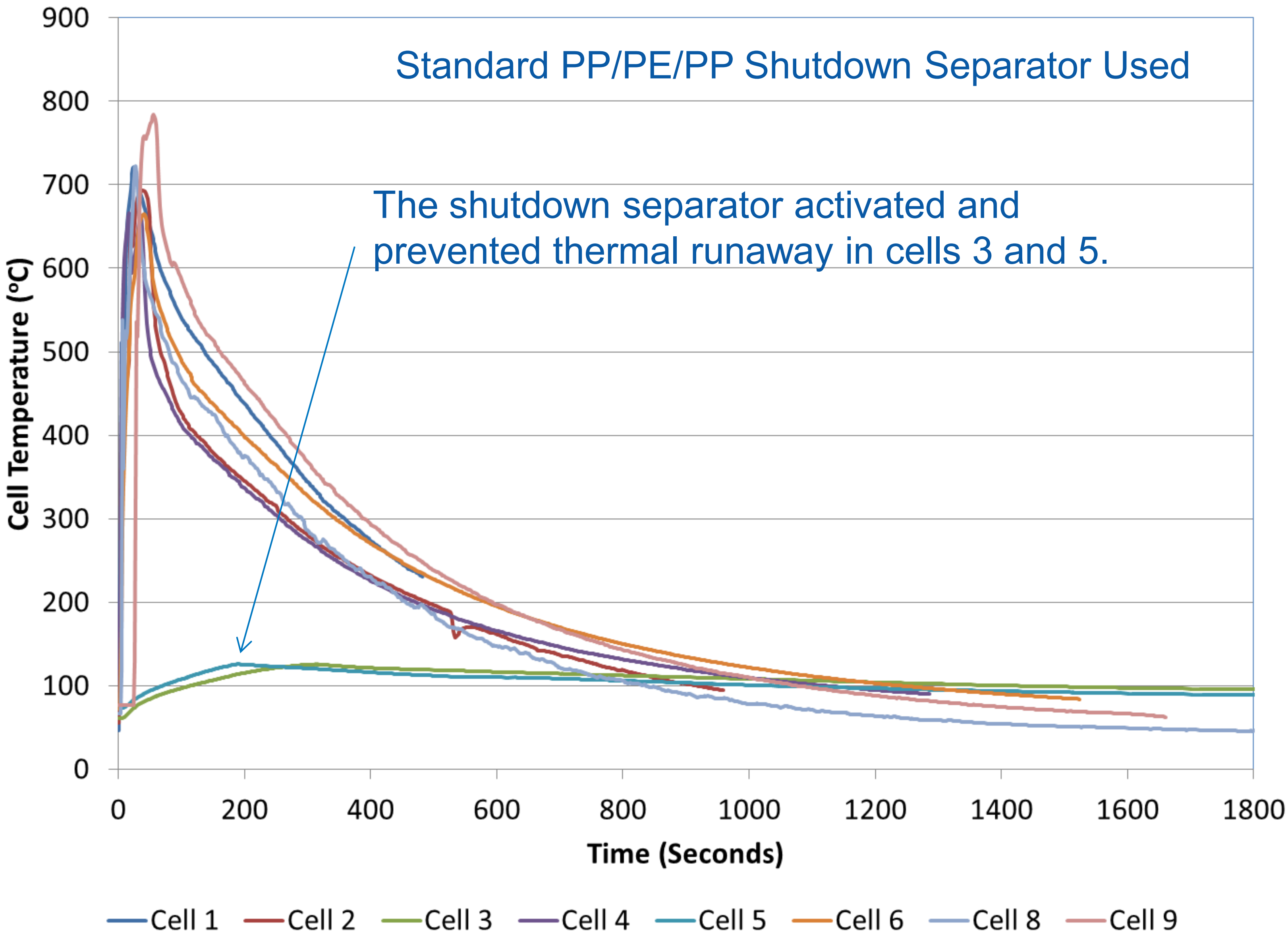
- **Analysis of similar cell showed two alignment issues**
  - ISC device overlapped active graphite (Created a Type 2 Short)
  - Active cathode overlapped bare anode foil which may have caused lithium plating to occur on Cu collector.
- **Difficult to retain proper alignment in a manual implantation process**

4th Round - Type 2 Repeatability 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



E-One Moli Observations (1/2)

- 1st Round - The ISC in the E-One Moli activation tests are showing different results for the different types of ISCs.
  - Soft short in the cathode to copper foil ISC
  - Soft short in the cathode active to anode active ISC
  - Hard short in the aluminum foil to copper foil ISC.
- 2nd Round - When the foil to foil ISC was activated at 100% SOC:
  - The current interrupt device activated due to pressure build up within the cell.
  - But shutdown separator prevented the cell from going into thermal runaway.
- 3rd Round - Foil to foil ISC was with a non shutdown separator (3rd round - non standard separator used in cell):
  - All four cells made it through formation – improved ISC design.
  - All four cells went into thermal runaway upon ISC activation
  - All four cells had similar thermal responses to the ISC activation.

E-One Moli Observations (2/2)

- 4th Round – 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 the performance of safety improvements to the cell – for example, shutdown versus non-shutdown separator.

Our Path Forward…

Need to mature our device design to significantly reduce the rate of premature failures and improve its reliability for the following purposes:

1. Determine optimum size and shape of ISC – to date, no optimization of ISC components have been performed.
2. Working with others, fabricate many ISC device cost effectively and distribute them to cell developers for evaluation.
3. Reassure cell users and manufacturers that our device will reliably perform when implanted in larger number of cell designs with perhaps larger fomat,
4. The design can be adapted to be a relevant representation of all 4 types of internal short circuit circumstances in the widest possible range of cell designs,
5. The results can be trusted to determine which cell designs are most tolerant or most vulnerable to the internal short circuit hazard and why,
6. The results will focus the manufacturing mitigation measures to prevent defects and metallic contamination to those areas that most effectively need it.
7. And lastly, the results will help the method gain acceptance for becoming an established Li-ion cell industry test standard that will lead to safer lithium cell and battery designs.

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  - Dave Howell
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  - *Chad Kruger*

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