On-Demand Internal Short Circuit Device

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2010 NASA Aerospace Battery Workshop

Nov 17, 2010, Huntsville, AL

Why are Li-ion cell shorts a 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 long 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 cell short conditions.**
- **Despite extensive QC/QA, standardized industry safety testing, and over 18 years of manufacturing learning, 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 COTS cells screened for spacecraft applications[2]**
- **What about with custom large cells?**
  - Not enough data exists to build statistically useful probabilities

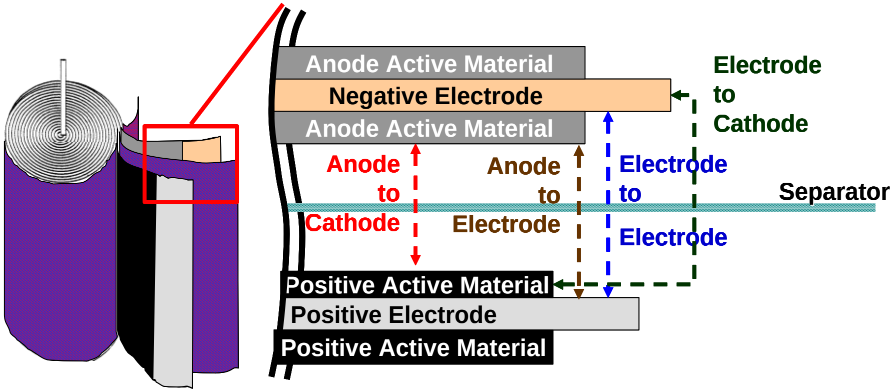
Aftermath of an external short incident

Aftermath of a suspected internal short incident

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

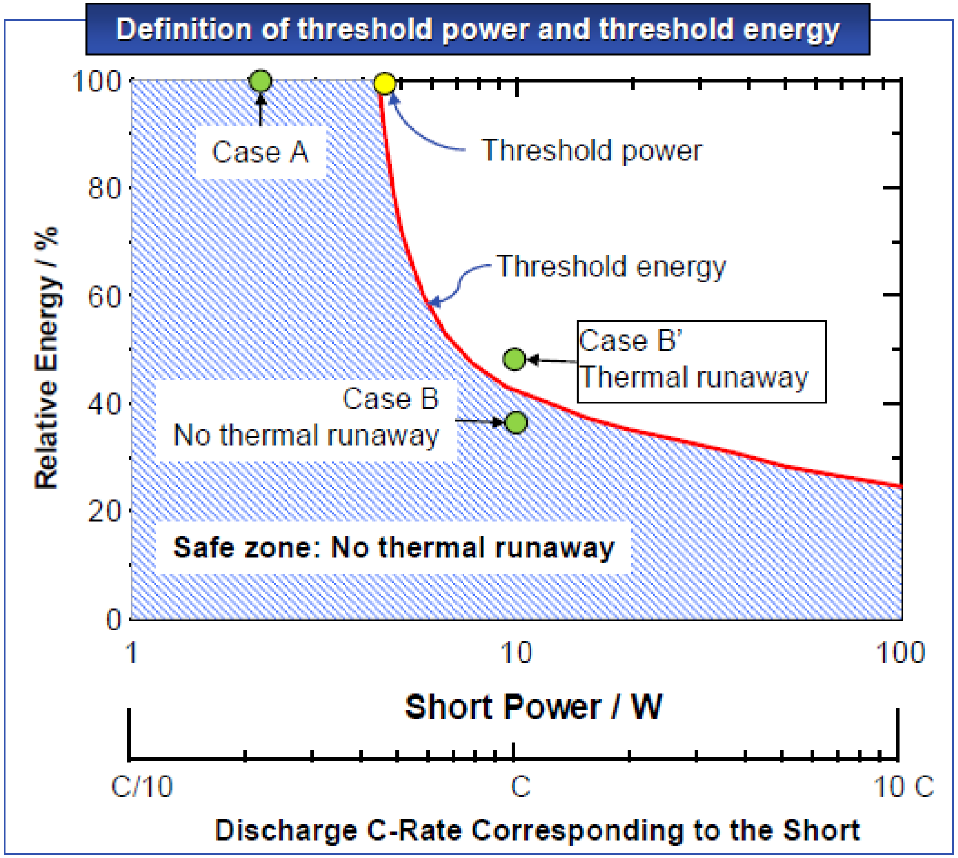
Objectives

- **To establish an improved cell-level test method that;**
  - Simulates an emergent Internal Short Circuit (ISC) by detailing the cell assembly and test conditions that replicate catastrophic field failures behavior due to a cell latent defect
    - Capable of triggering the 4 types of cell internal shorts
  - Produces consistent and reproducible results and
  - Can establish the locations and temperature/power/SOC conditions for given cell design where an ISC will result in thermal runaway
  - Provide relevant data to validate internal short circuit models



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

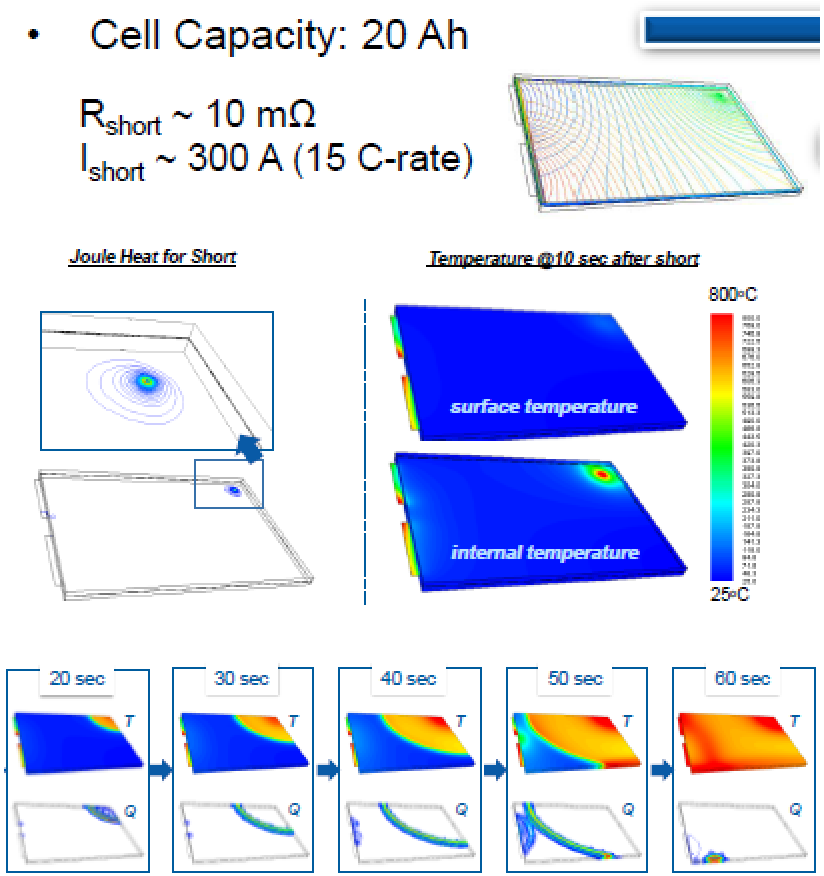
Thermal Abuse Models



TIAX safe zone mapping model

- Cell Capacity: 20 Ah

R_{short} ~ 10 mΩ
I_{short} ~ 300 A (15 C-rate)



Gi-Heon Kim Model (NREL)

Motivation

Field Failures Mechanisms

- **Latent defect (built into the cell during manufacturing) gradually moves into position to create an internal short while in the field**
  - Sony[3] concluded that metallic defects where the cause of their 1.8 million battery recall in '06
- **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 and 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 relevant to the ones produced by field failures**

3. Nikkei Electronics, Nov. 6, 2006

Description of Previous Efforts & Shortcomings

Penetration & Crush Tests - reliable but not representative of field failures

- **Army/Navy/FBI use nail/bullet penetration tests[3]**
- **NASA uses a crush test with a rounded rod[4]**
- **UL uses a blunt nail crush test[5]**
- **ONL/Motorola uses a pinch (crush) test on pouch cells[6]**

3. Lyman, P. and Klimek, P., 69th Lithium Battery Technical/Safety Meeting, Myrtle Beach 2004

4. Jeevarajan, J. , 2008 NASA Aerospace Battery Workshop, Huntsville, AL.

5. Chapin, T. and Wu, A., 2009 NASA Aerospace Battery Workshop, Huntsville, AL

6. Maleki, H. and Howard, J.N., J. of Power Sources, 2008

Descriptions (cont.)

Contamination Methods – More relevant, but with reliability and reproducibility challenges

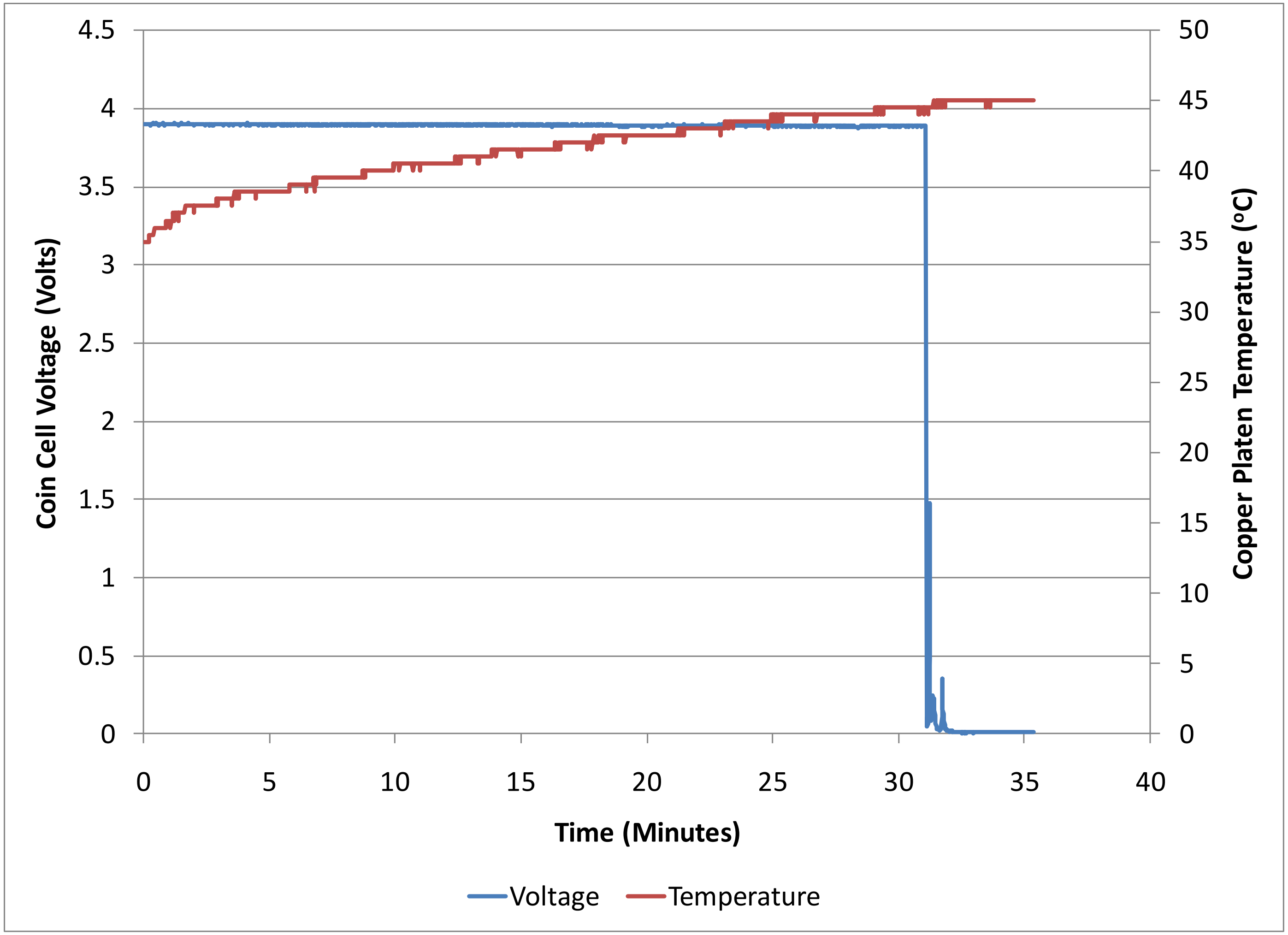
- **BAJ[7] and Celgard[8] retrofit a Ni particle into the jellyroll of a cell and triggers the event by crush test**
- **SNL[9,10,11] has tried several methods**
  - Building cells with Ni particle contamination and combined with sonication, thermal ramp, or overcharge to trigger the short
  - Implanting low melting indium (In) alloy in the separator combined with heat trigger
- **TIAX[12] retrofits a metallic particle into the jellyroll of a cell and triggers the event by repeated charge/discharge cycling**
- **SAFT[13] assembles the cell with a micro-heater (tungsten wire) next to separator sandwiched between anode and cathode**

7. Battery Association of Japan, Nov 11, 2008 presentation on web
8. S. Santhanagopalan, et. al., J. of Power Sources, 194 (2009) 550-557
9. Orendorff, C., et.al, ECS Mtg, May 2009
10. Orendorff, C. and E.P. Roth, USABC TT Meeting, Feb 2009
11. Orendorff, C., et.al, ECS Mtg, Oct 2010
12. Barnett, B., et.al, 2010 Power Sources Conference
13. Kamen, N. and Robinson, W., SAFT Patent Disclosure not filed, offered to the gov't, and reported at the 2010 SPW

NREL Cell Internal Short Development

- **Internal short device design**
  - Small, low profile and implantable into Li-ion cells preferably during assembly
  - Key component is an electrolyte compatible phase change material (PCM) sandwiched between thin foils of Al and Cu
  - Triggered by a raising the cell above PCM melt temperatures (presently 40 – 60 °C range)
- **Initial device design focus is on anode-to-cathode active material short**
  - In laboratory testing, the activated device can handle currents in excess of 100 amps to simulate hard shorts (<10 mohms)
  - Phase change from non-conducting to conducting has been 100% successful during trigger tests
  - Separator is an excellent wick for melted PCM
- **9 out of 9 tests with Li-ion coin cells assembled with the device have successfully shorted on demand**

Internal Short Development - Coin Cell



9 of 9 coin cells shorted with new ISC device design. Here using a 42-44 °C melting PCM.

Implantation of ISC device for active-active short

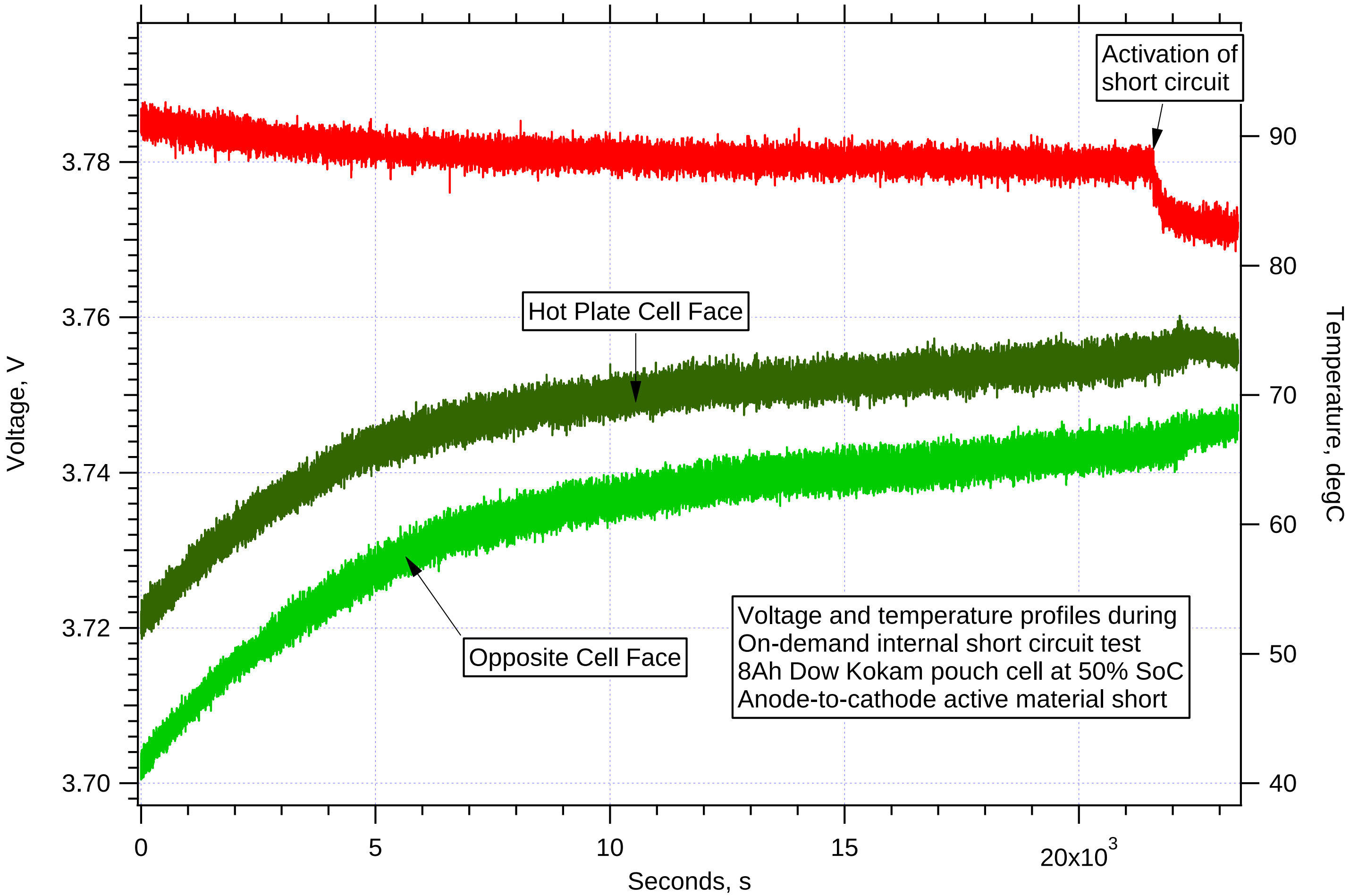
Cu side of ISC device interfaces anode, Al side interfaces cathode.

Here implanted inside a Dow-Kokam 8Ah pouch cell design

Cell Internal Short Development

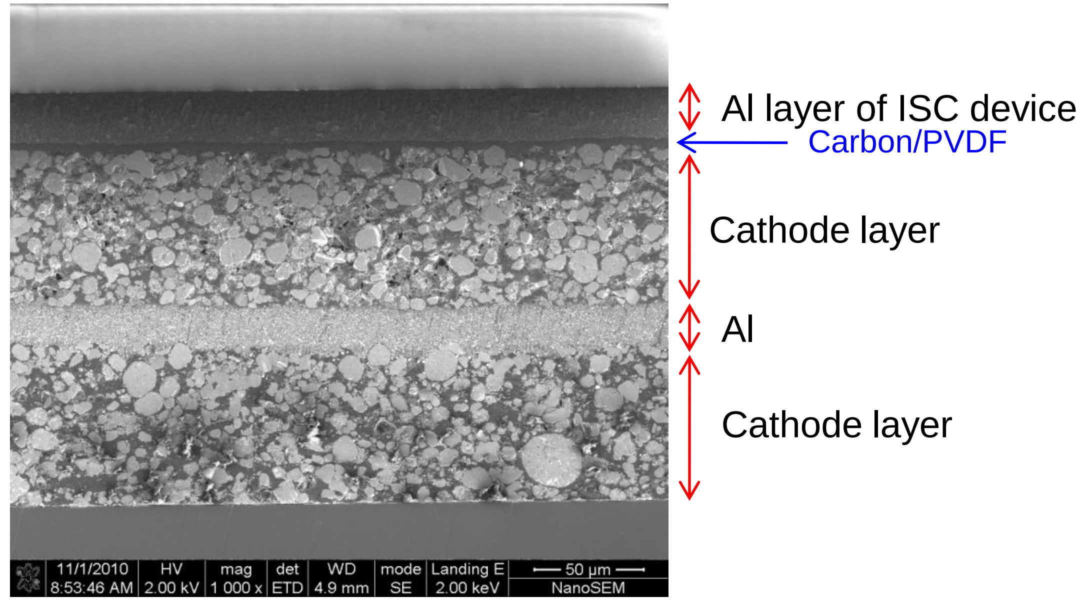
- **Design of the device uses a flexible PCM resulting in a device that is compatible with automated cell stacking/winding equipment**
- **Partnered with Dow-Kokam (DK) to have cells assembled and tested with the new ISC device**
- **First 33 cell stacks were successfully implanted with the device in an anode-to-cathode short position and demonstrated nominal charge and discharge capacities**
- **First 2 cells triggered produced high impedance shorts**
  - Tests performed at 10% and 50% SoC with similar results
  - Root cause of high impedance found to be high interface contact resistance between the active electrode materials and surfaces of the ISC device

Plot of voltage response to ISC



Improving Interface Contact Resistance

- **Cathode active material contact resistance with the pure Al foil pad of our device is on the order of ~1 ohm and is driving the resistance of the anode-to-cathode short**
  - A metallic contaminant pressed into the cathode material during manufacturing would have much better contact resistance as field failures have demonstrated
- **Looking at advanced materials for improving contact resistances**
  - Carbon/PDVF deposited on Al (pictured)
  - High conductivity micro carbon fibers (pictured)
- **Bonding Al disc onto the cathode active material during electrode coating**



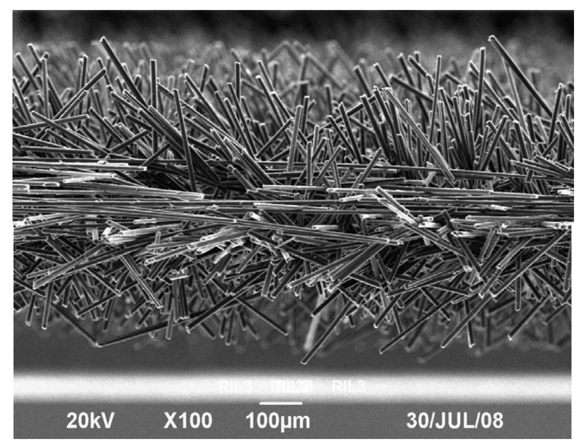
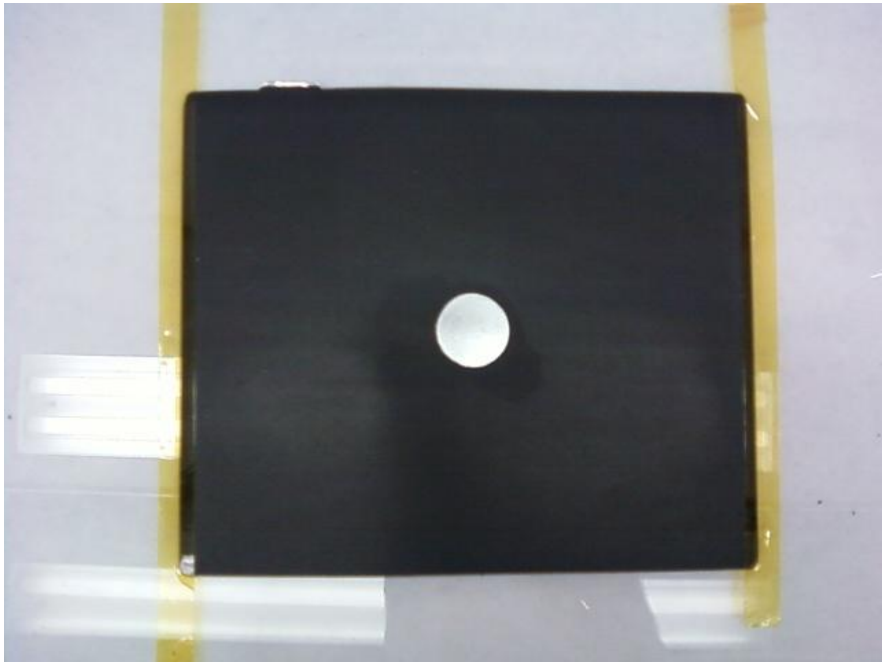


Photo courtesy of ESLI

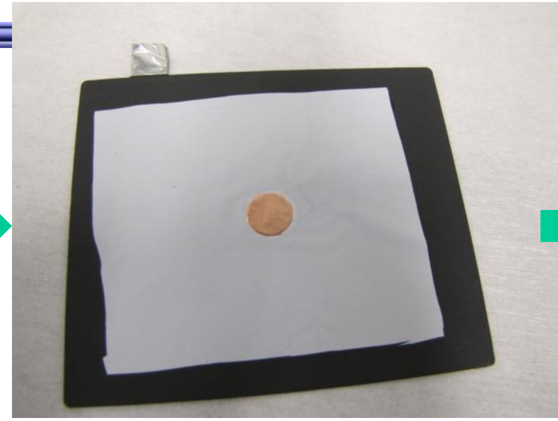
Anode-to-Al short

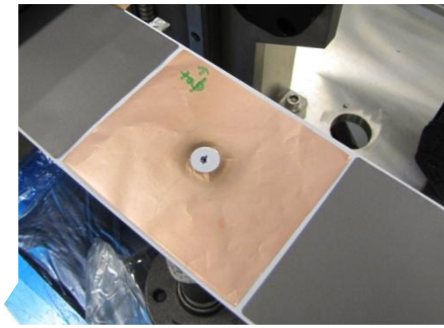
- **Use NMP to remove cathode coating from center portion of double sided cathodes (DSC)**
- **Replaced thin Al pad on ISC device with one that matches the thickness of the cathode coating**
- **Dry conductance tests indicate ~150 mohms from Al current collector to Cu current collector using an activated ISC device**
- **Implantation done at DK**



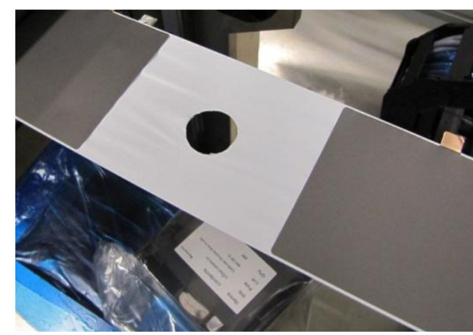
Double Sided Cathode with active material removed to expose Al current collector

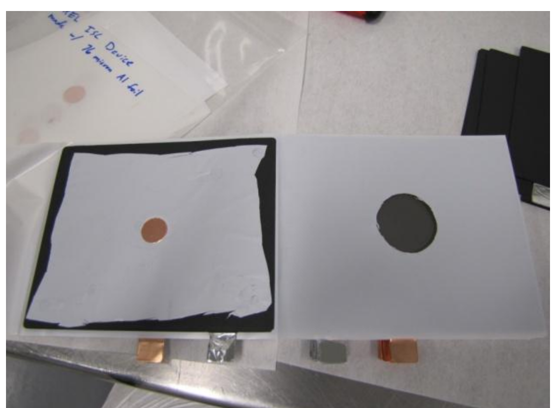
Anode-to-Al Short



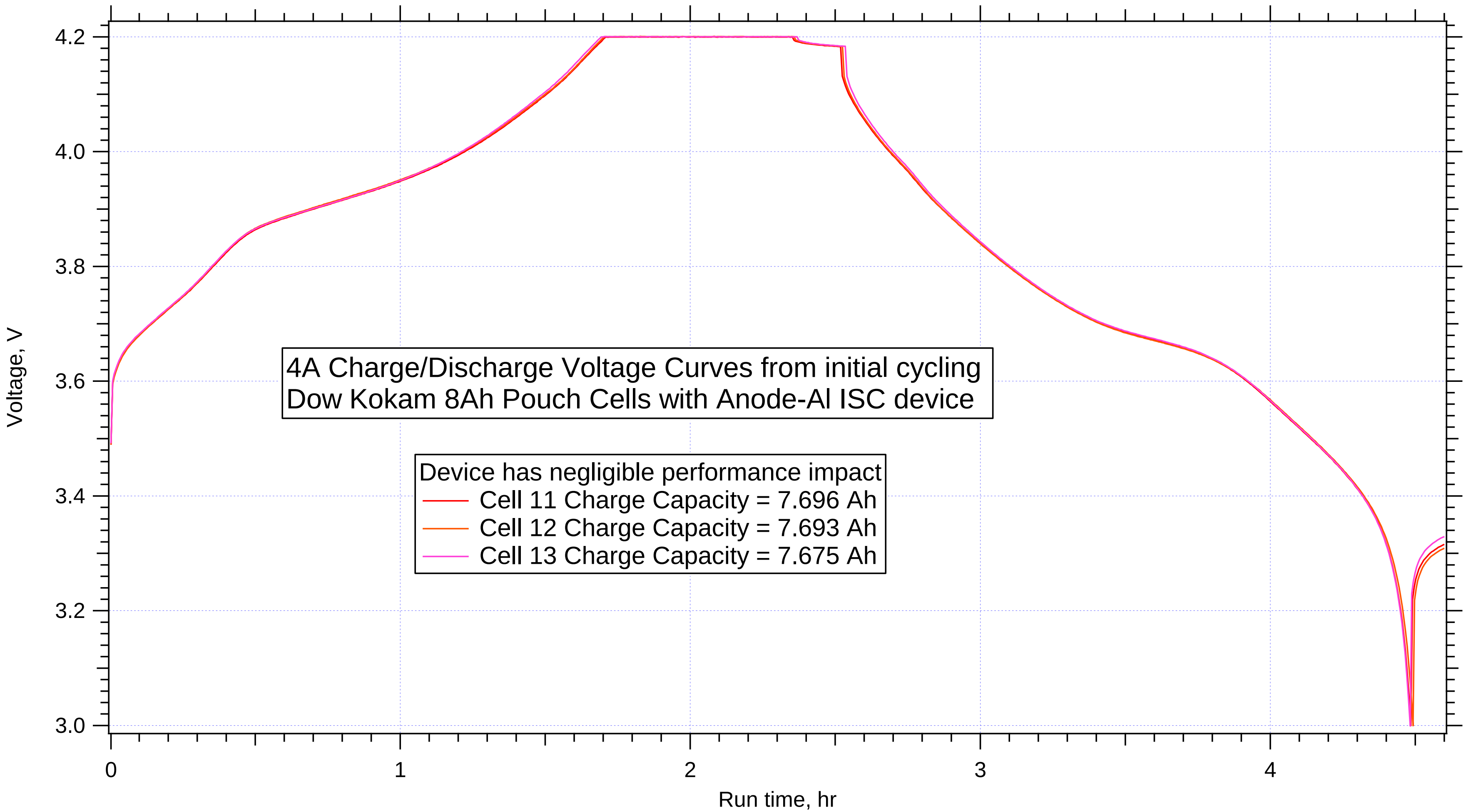


- **DK lightly glues the custom ISC device to the modified cathode, lines up the separator hole with a template to center the separator hole, and then allows stacking to proceed**

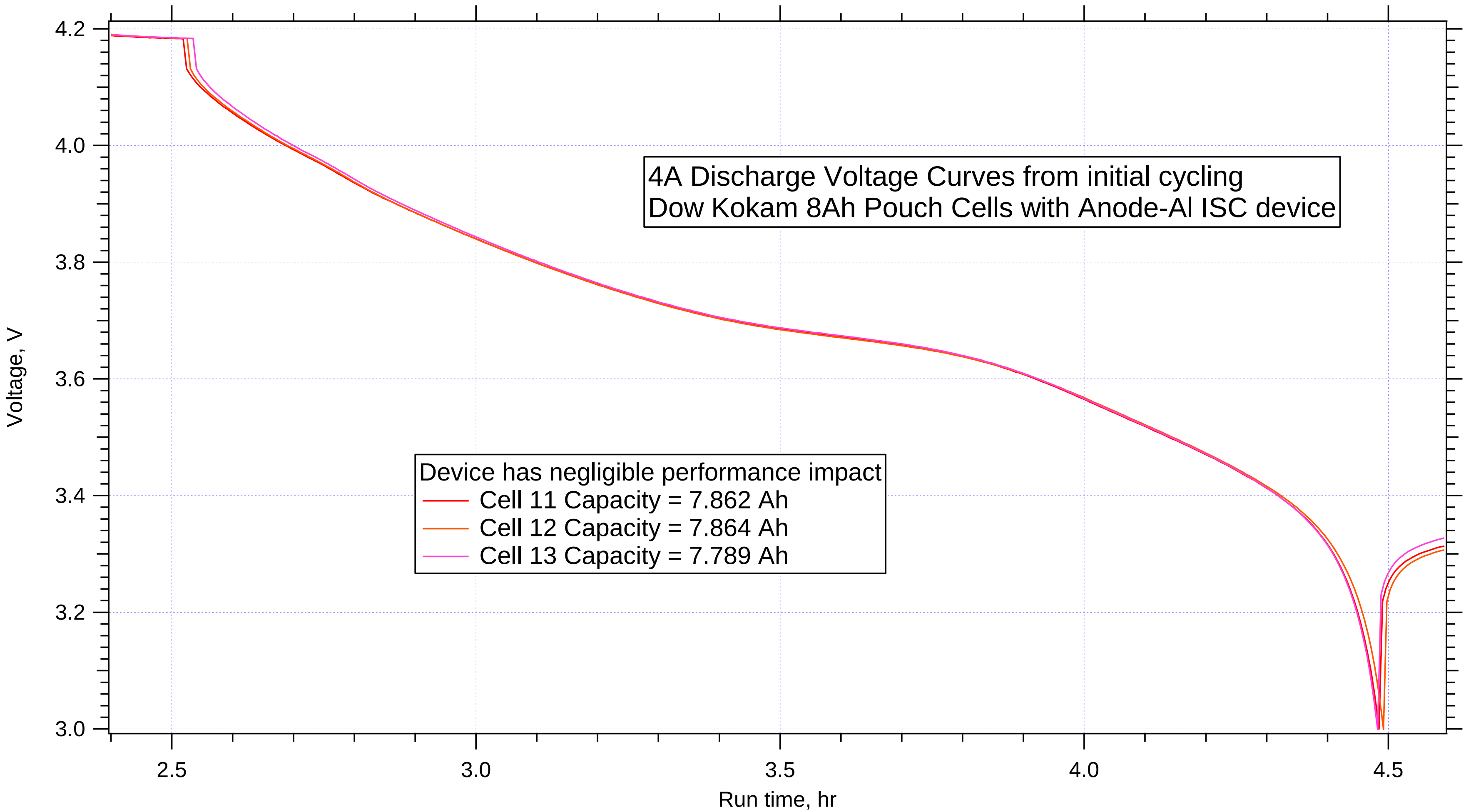




Nominal Capacity Cycling after Implantation

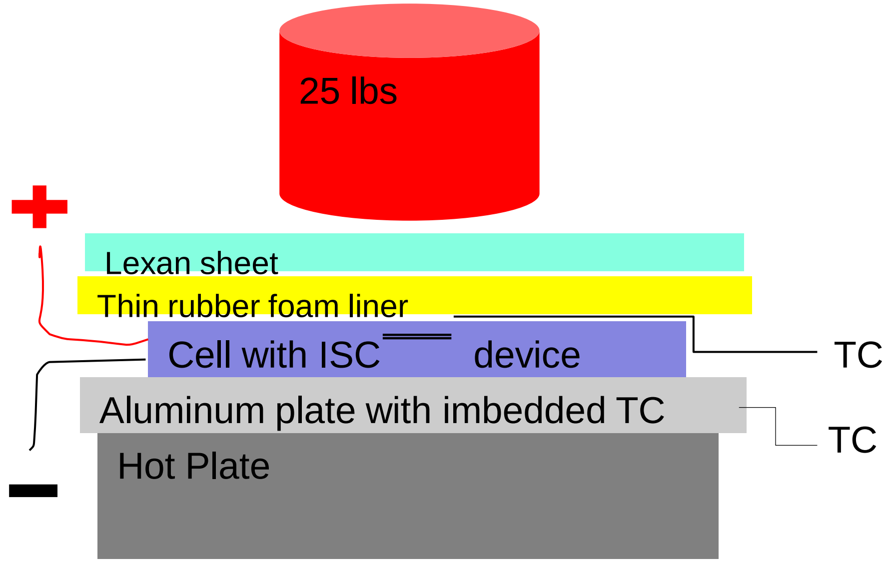


Nominal Capacity Cycling after Implantation



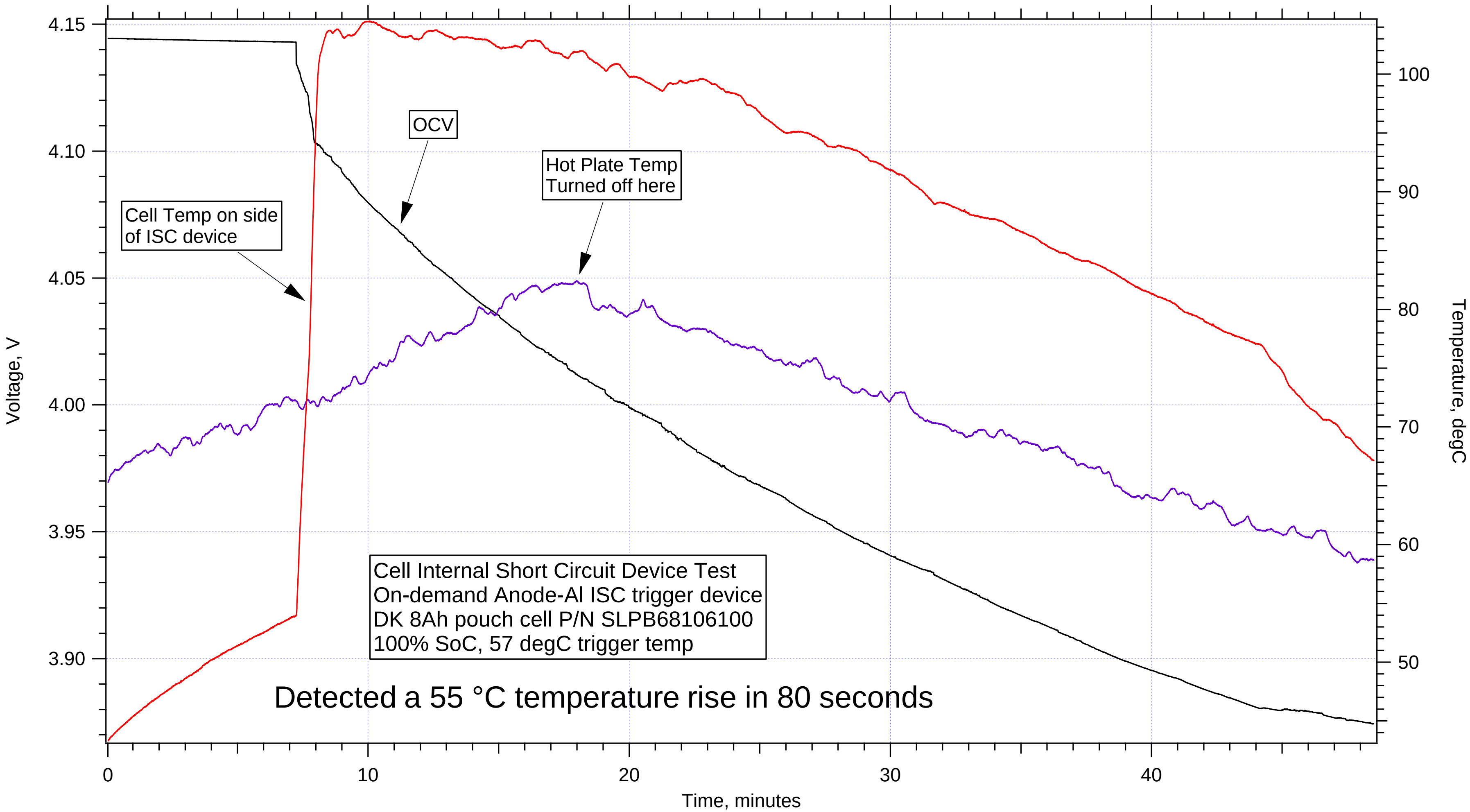
Trigger Test Set-up

- **Cell is charged to the appropriate SoC**
- **Hot plate provides the heating source**
- **Cell is placed under compression (~1.6 psi)**
- **Al plate between hot plate and cell with an imbedded thermocouple**
- **Thermocouple placed cell side opposite hot plate**
- **Thin foam pad and lexan plate placed between cell top and 25 lbs weight**
- **Thin particulate bag encapsulates cell and its top TC (not shown for clarity)**

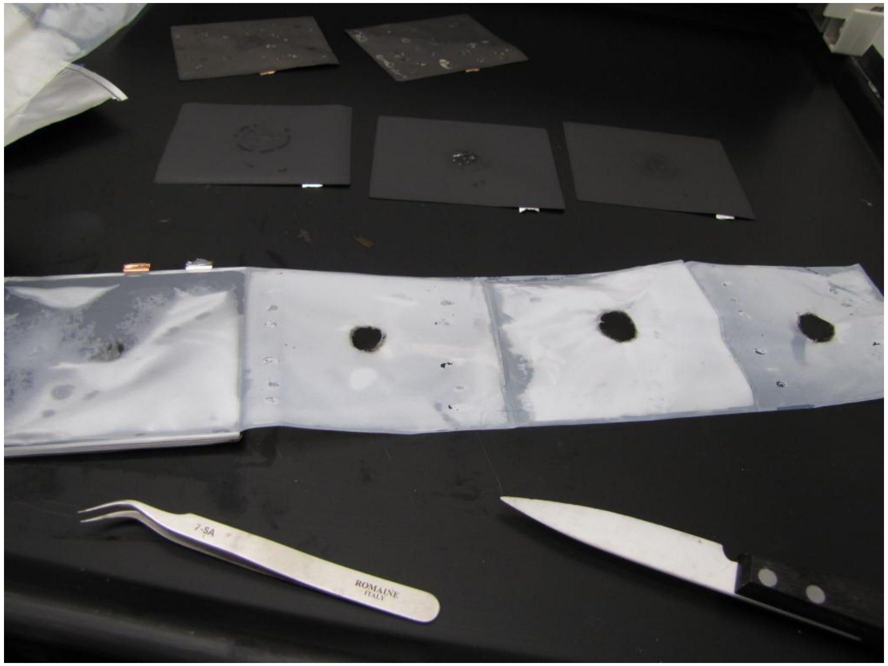


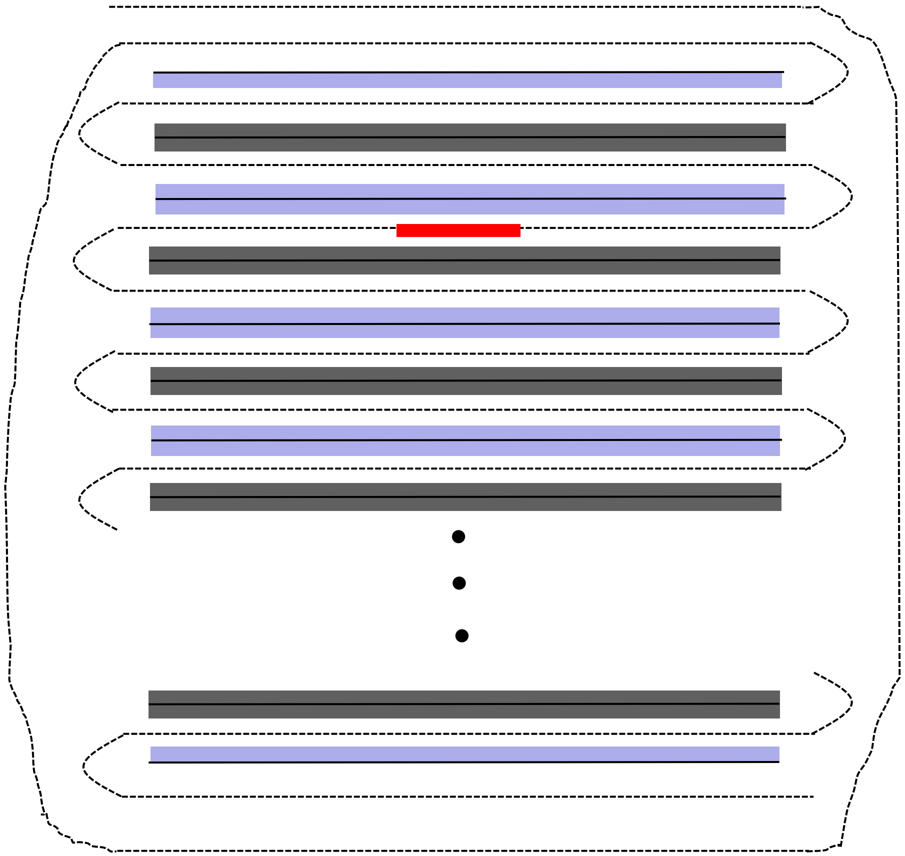
Graphic is not to scale and for illustration only

Plot of voltage, temp response to ISC



DPA evidence

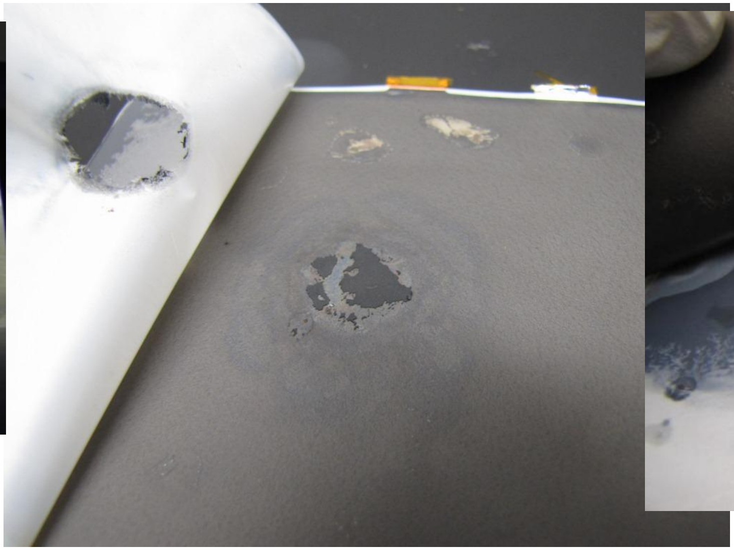


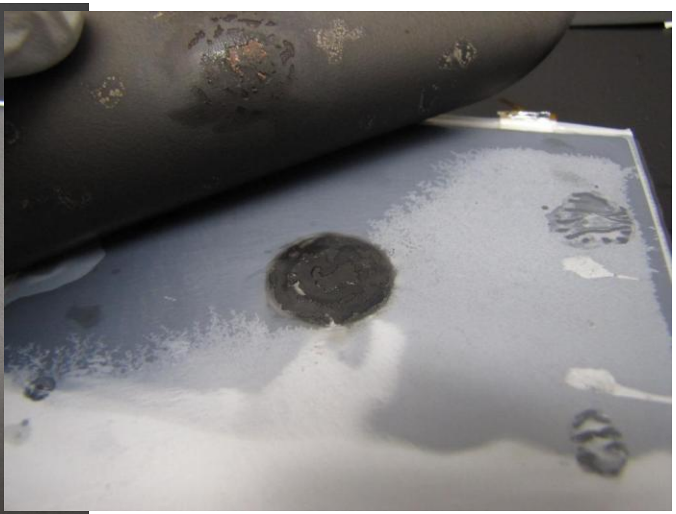


Anode-Al short without any improvements to interface contact resistances

- **Severe heat effected zones in 8 electrode layers in vicinity of ISC device and on inside of pouch laminate side near short**
- **Tabs stayed intact**

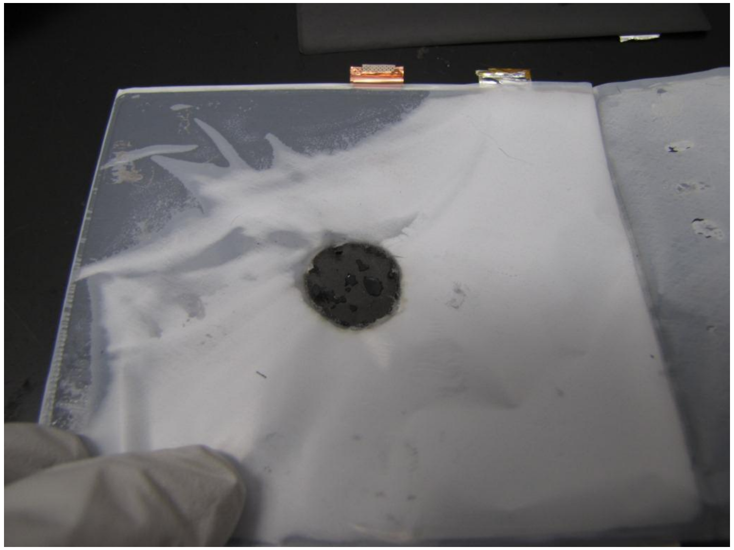
DPA Evidence (cont.)





Unfolding the cell after the Anode-Al short

Anode and cathode sandwiching the ISC were not yet separated to prevent damage



Summary Conclusions

- **Small, low profile, flexible, and implantable device has been demonstrated to be reliable in triggering on-demand internal cell short circuits**
  - Device has never failed to activate
  - Anode-cathode and Anode-Al short circuit tested to date
  - Anode-Al short caused a rapid 55 °C temperature rise in an 8Ah Dow-Kokam cell design, but does not induce thermal runaway
  - Must reduce bottleneck resistances to get hard shorts
    - Currently investigating several very promising redesign options to lower key interface resistances
- **However, much was learned from ISC device/cell component impedance measurements**
  - Cathode active material-to-device interface has highest impedance
  - Suggests that metallic particle contamination after electrode calendaring may only yield high/med impedance shorts if only bridging anode-to-cathode active materials
    - Suggests that metallic particle contamination mitigation measures during mixing, slurry coating, and calendaring could be most important for safety
    - After calendaring, particle defects may only yield soft anode-to-cathode shorts
    - However, this may not be true for collector-to-collector shorts
- **Anode-to-Al short yielded lower impedance shorts**
  - As predicted previously by others[14] this type of short is more likely to drive cell into thermal runaway
    - ~150 mohm short at ISC device caused damage in 8 electrode layers and the inside of closest pouch layer
  - Cathode-to-Cu and Al-Cu collector shorts remain to be tested

14. S. Santhanagopalan, et al., J. Power Sources (2009)

Conclusions (cont.)

- **Device has excellent promise to produce results relevant to field failures caused by cell defects**
  - Comparison of the abuse tolerance of various cell designs will be possible
  - Results have promise to guide and validate future cell design improvements
    - Advanced electrode coating and separators, etc
  - Validation of cell abuse models will no longer have to rely on results from less relevant crush tests
  - Results have promise to guide and focus cell production line defect and contamination mitigation measures
  - Current device designs can be used with Li primaries using carbonate electrolytes (MnO_2, FeS_2, CF_x)
  - With further maturation, we could verify by test the effectiveness of a given battery thermal management system at preventing collateral damage to cells neighboring one with an internal short circuit
- **Implantation and testing in an 18650 cell design is planned as the next development step**

Acknowledgements

- **NREL for providing a great place to work on this technology with their energy storage group**

- **Dow-Kokam for being willing to be first to implement this idea**