Development of a Novel Test Method for On-Demand Internal Short Circuit in a Li-Ion Cell

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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.

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

Aftermath of an external short incident

Aftermath of a suspected internal short incident

Photos Credit: NASA – Eric Darcy

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

Previous Efforts & Shortcomings

Penetration and Crush Tests Methods

- Army/Navy/FBI use nail/bullet penetration tests[4].
- NASA uses a crush test with a rounded rod[5].
- Underwriters Laboratory (UL) uses a blunt nail crush test[6].
- Motorola/ Oakridge National Laboratory use a pinch (crush) test on pouch cells[7].

Reliable, but not representative of field failures

4. Lyman, P., and Klimek, P., 69th Lithium Battery Technical/Safety Meeting, Myrtle Beach 2004
5. Jeevarajan, J., 2008 NASA Aerospace Battery Workshop, Huntsville, AL
6. Chapin, T., and Wu, A., 2009 NASA Aerospace Battery Workshop, Huntsville, AL
7. Maleki, H., and Howard, J.N., *J. Power Sources*, 2008

Previous Efforts & Shortcomings (cont.)

Contamination Test Methods

- BAJ[8] and Celgard[9] retrofitted a Ni particle into the jellyroll of a cell and triggered the event using a crush test.
- Sandia National Laboratory[10,11,12] 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[13] retrofitted a metallic particle into the jellyroll of a cell and triggered the event by repeated charge/discharge cycling.

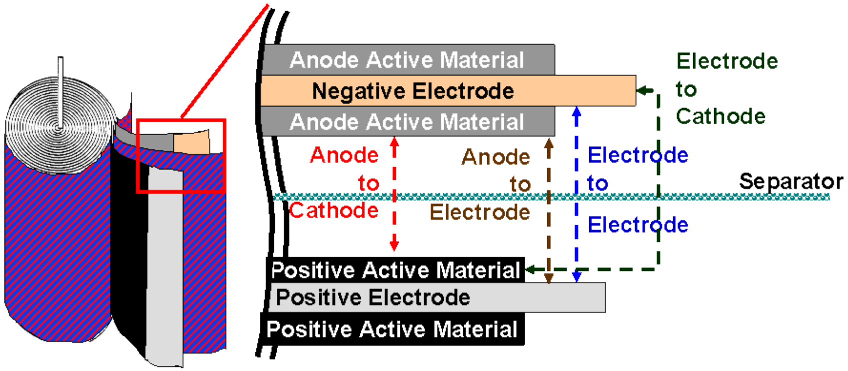
More relevant, but with reliability and reproducibility challenges

8. Battery Association of Japan, Nov 11, 2008 presentation on web
9. S. Santhanagopalan et al., *J. Power Sources*, 194 (2009) 550-557
10. Orendorff, C., et al., ECS Meeting, May 2009
11. Orendorff, C., and Roth, E.P., USABC TT Meeting, Feb 2009
12. Orendorff, C., et al., ECS Meeting, Oct 2010
13. Barnett, B., et al., 2010 Power Sources Conference

Objectives

Establish an improved ISC cell-level test method that:

- Simulates an emergent internal short circuit (ISC) by detailing the cell assembly and test conditions that replicate catastrophic field failure behavior due to a latent cell defect
  - Capable of triggering the four types of cell internal shorts
- 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

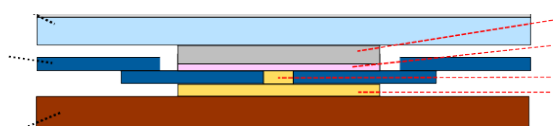


Spiral wound battery shown – can also be applied to prismatic batteries.

NREL Cell Internal Short Circuit Development

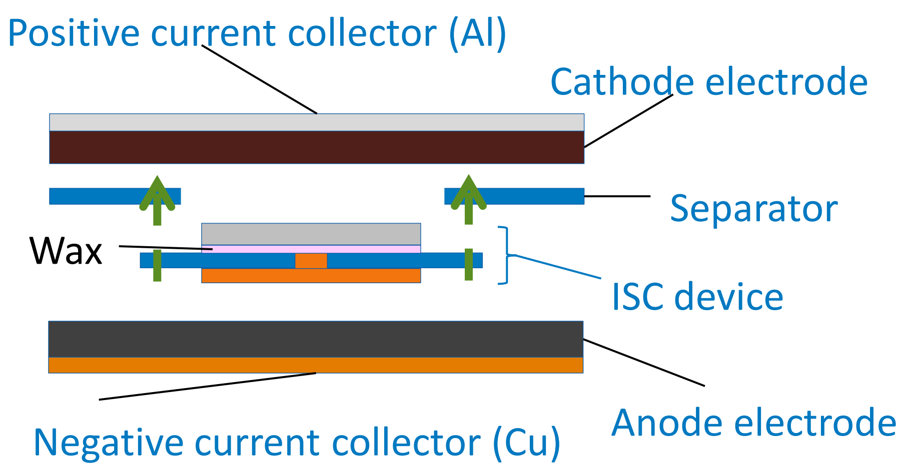
Internal short circuit device design

- 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)
- In laboratory testing, the activated device can handle currents in excess of 200 A to simulate hard shorts (<5 mohms).
- Phase change from non-conducting to conducting has been 100% successful during trigger tests.



Patent application filed for the ISC Device

NREL Internal Short Design



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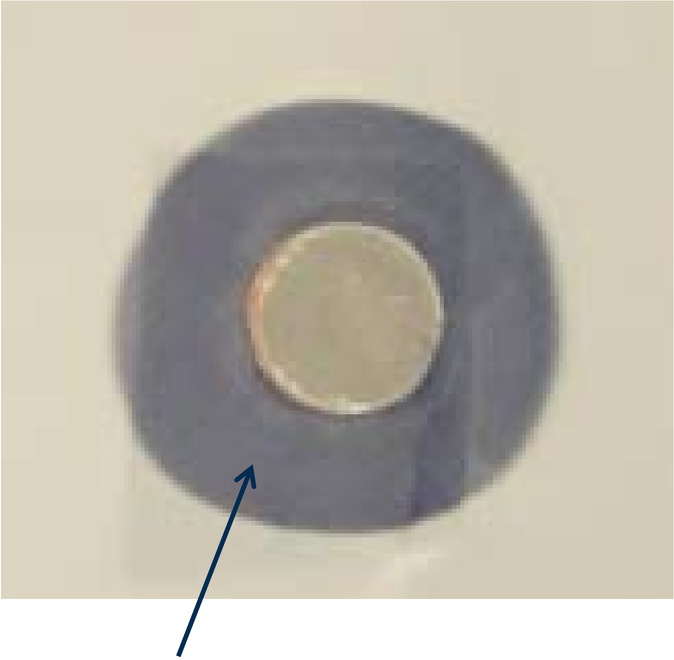


Activated short with PCM wicked by battery separator

Photo Credit: NREL – Dirk Long

Laboratory Test Fixture

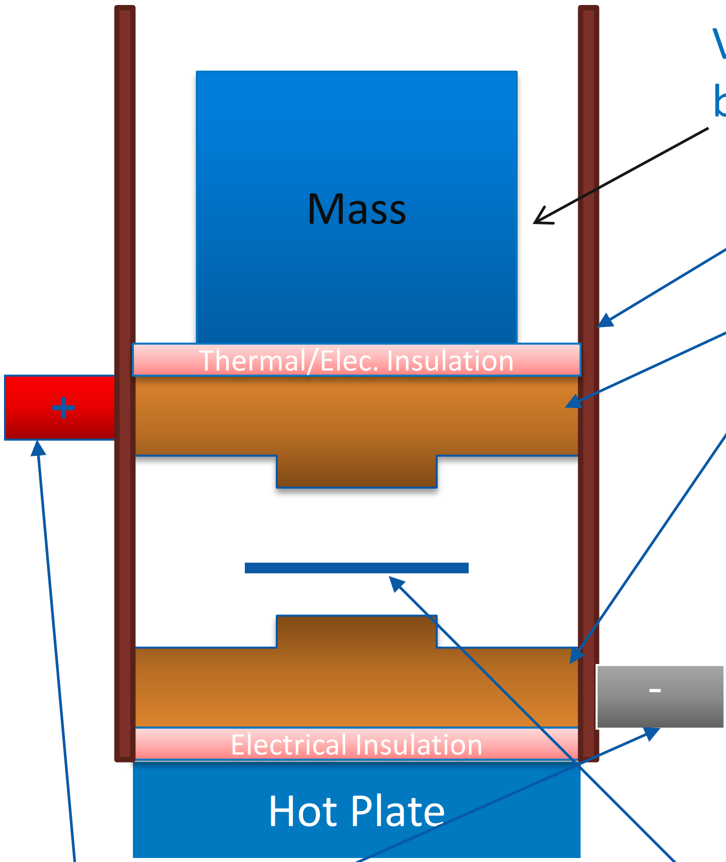
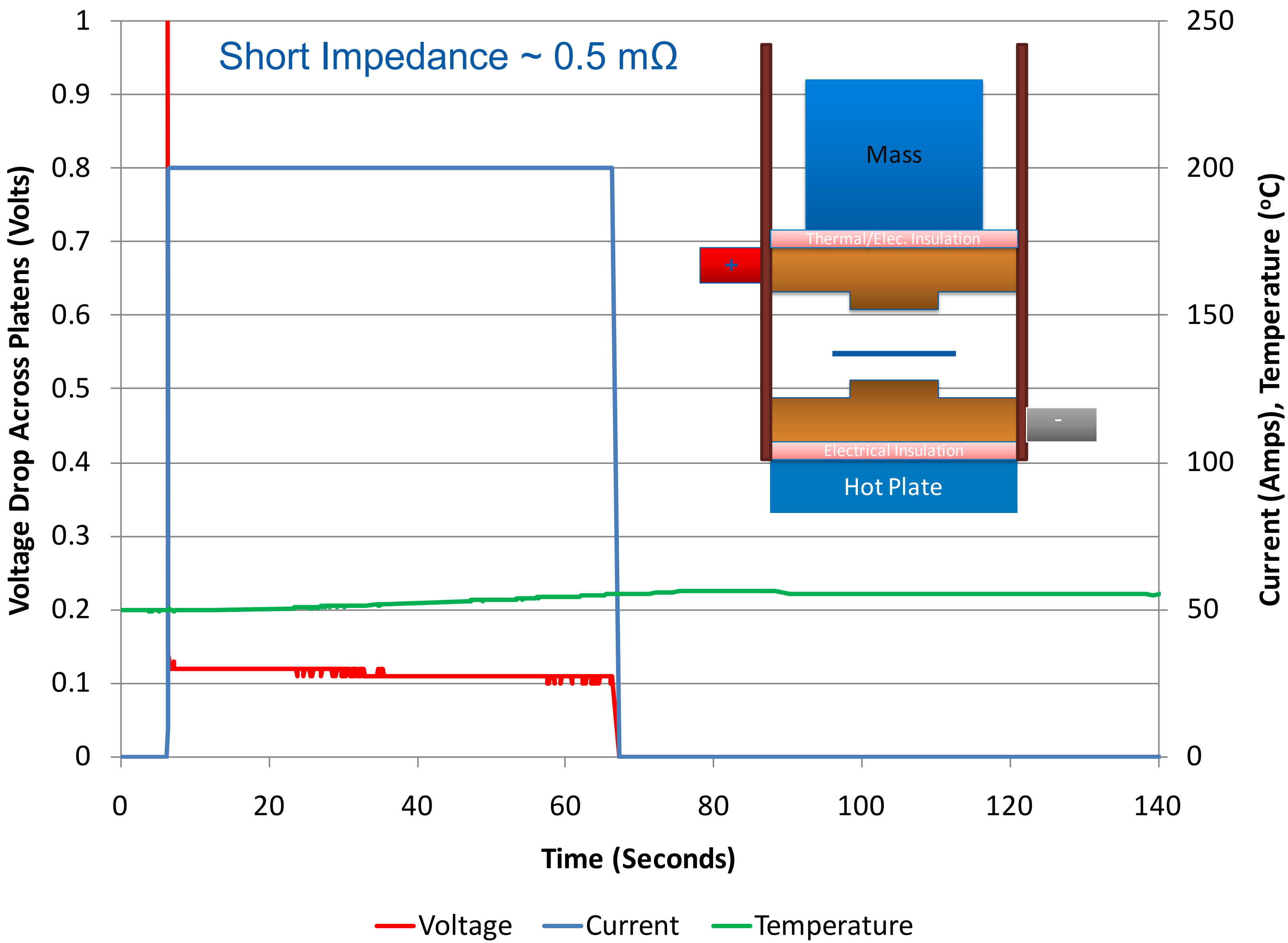
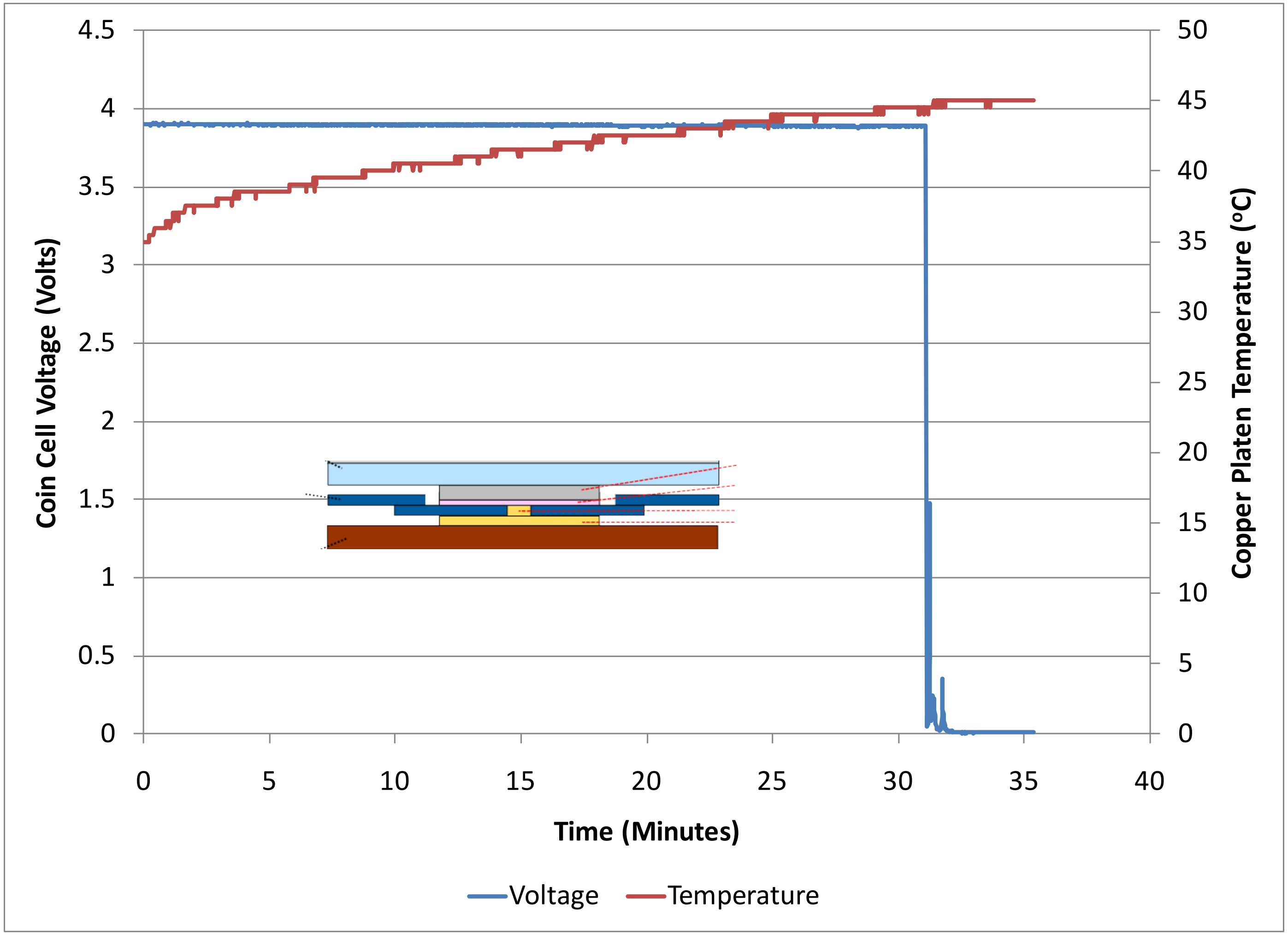


Photo Credit: NREL – Dirk Long

Laboratory Test Fixture – Internal Short Test



Internal Short Circuit – Coin Cell Tests



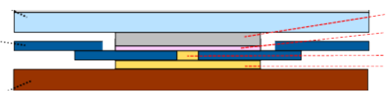
Nine of nine coin cells shorted with new ISC device design, shown here using a 42 – 44°C melting PCM.

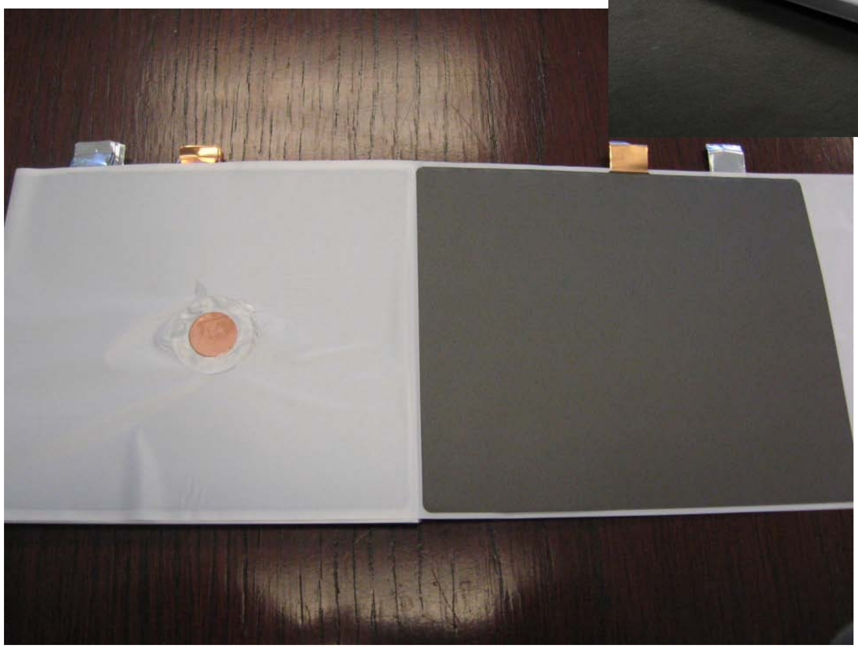
Cell Internal Short Circuit Development

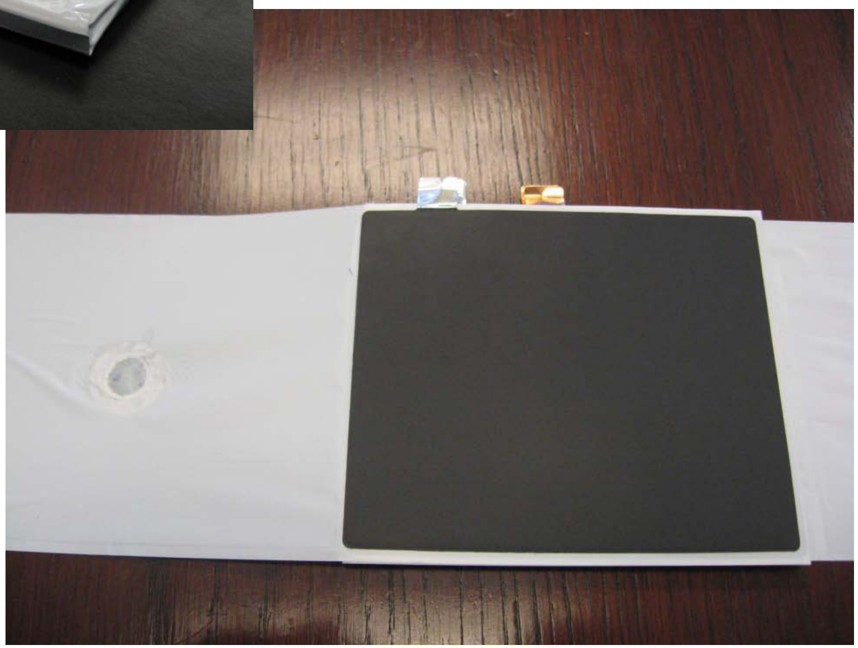
- NREL partnered with Dow-Kokam (DK) to have cells assembled and tested with the new ISC device.
- Design of the device uses a flexible PCM, resulting in a device that is compatible with automated cell stacking/winding equipment.
- To date, over 50 cells have had the device implanted into it. All cells show nominal capacity and voltage curves.

ISC	Cathode	Anode	Al Current Collector	Cu Current Collector	Comments
1	X	X			Completed
2		X	X		Completed
3	X			X	Results in 4 Weeks
4			X	X	Results in 1 Week

Implantation of ISC Device for Active-Active Short





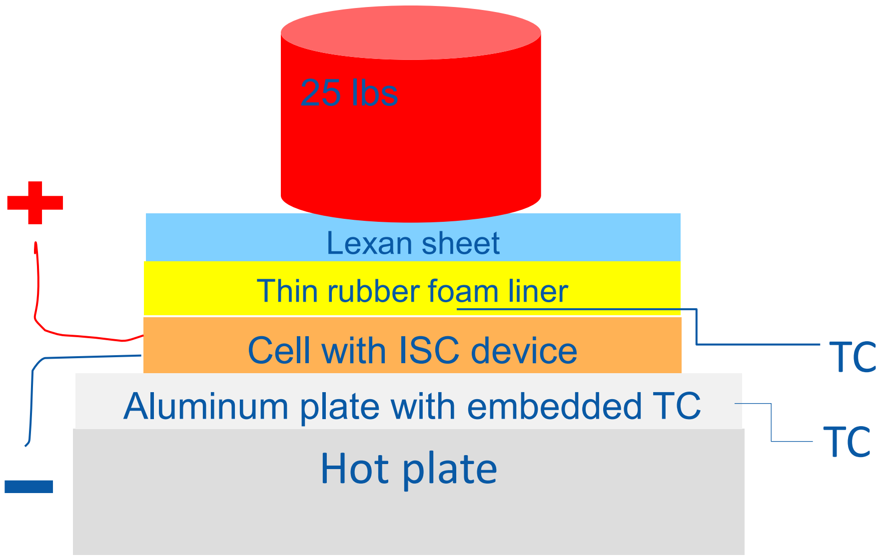


Cu side of ISC device interfaces anode, Al side interfaces cathode; shown here implanted inside a Dow-Kokam 8-Ah pouch cell design.

Photo Credits: Dow Kokam – Ben McCarthy

Test Setup for Triggering ISC Implanted in a Cell

- 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 has an embedded thermocouple (TC).
- Thermocouple placed cell side opposite hot plate.
- Thin foam pad and Lexan plate placed between cell top and 25-lb weight.
- Thin particulate bag encapsulates cell and its top TC (not shown for clarity).



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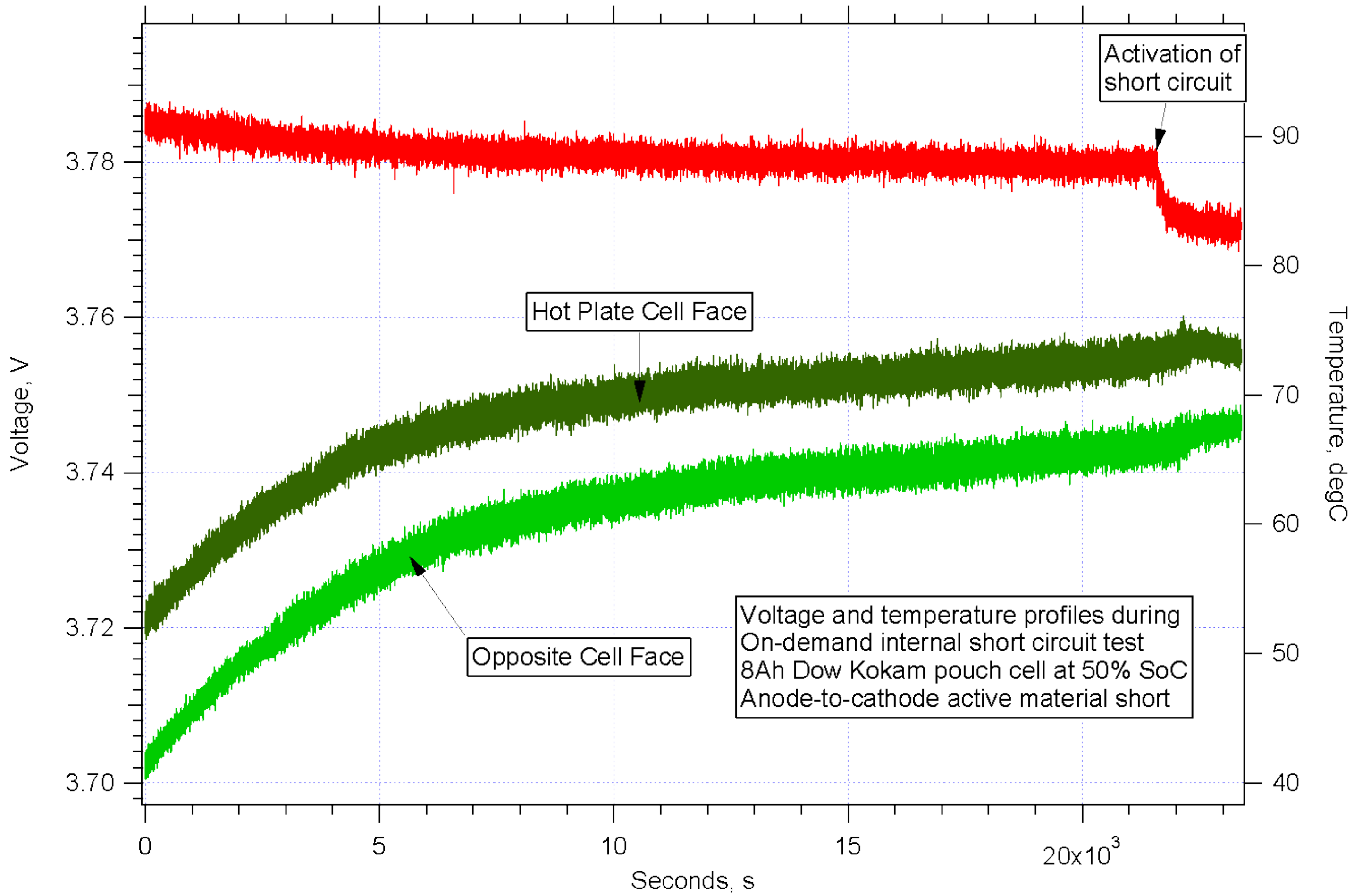
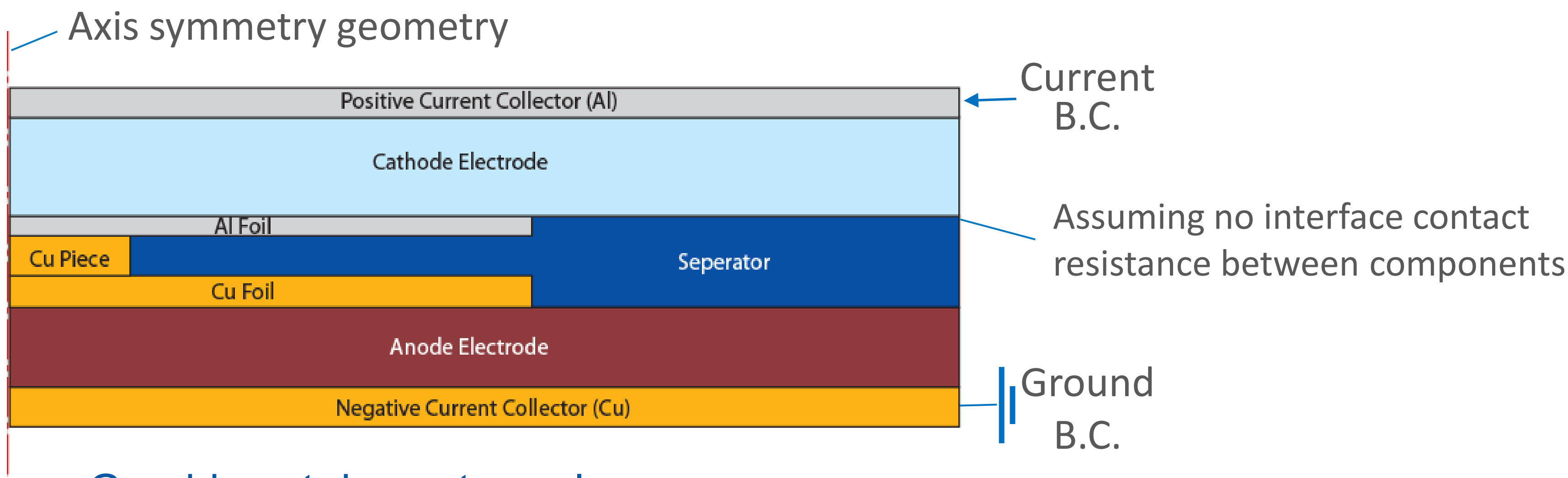
Voltage Response to ISC – Active to Active



Impedance Model of the ISC Device



Graphic not drawn to scale

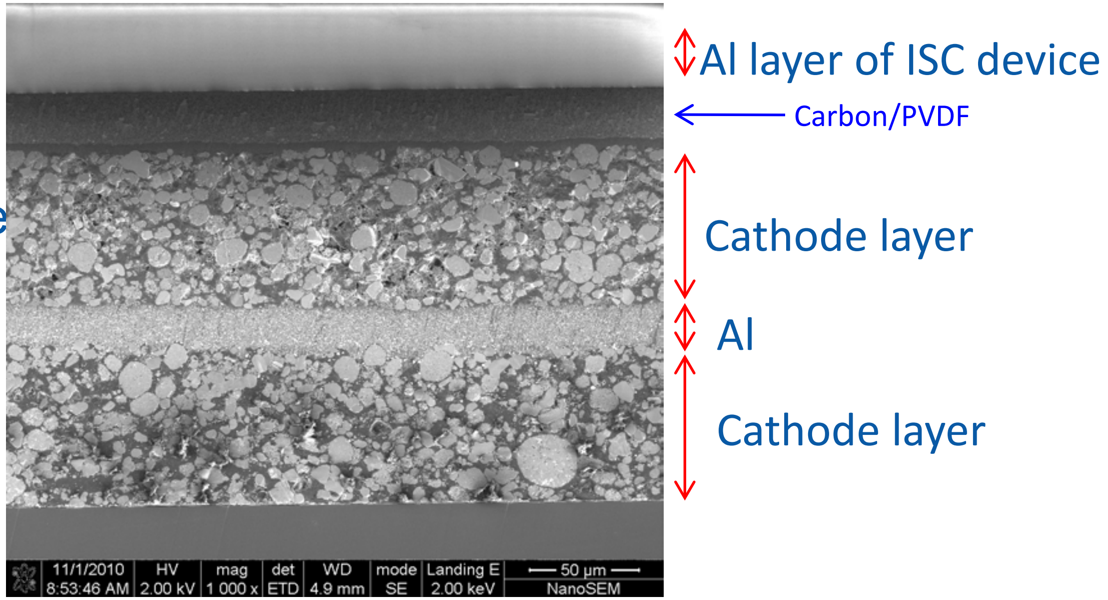
Property	Al-pad	Cu-pad	Cu-piece	Positive current collector	Negative current collector	Cathode electrode	Anode electrode	Separator
Electric conductivity [S/m]	3.541×10^{7}	5.8×10^{7}	5.8×10^{7}	3.541×10^{7}	5.8×10^{7}	5	58	1×10^{-15}

Cathode active material is most resistive component
Interface contact resistances must be determined by test

Improving Interface Contact Resistance

- Cathode active material contact resistance with the pure Al foil pad of our ISC is on the order of ~1 Ω 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/Polyvinylidenefluoride (PVDF) deposited on Al (pictured)
  - High-conductivity micro-carbon fibers (pictured)
- Bonding Al disc onto the cathode active material during electrode coating.

Photo Credit: NREL – Bobby To



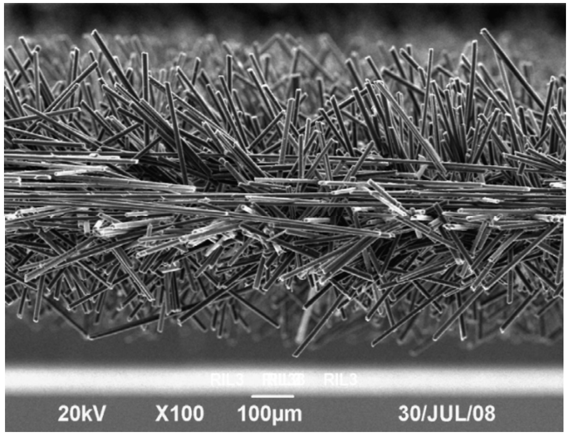


Photo courtesy of ESLI

Anode-to-Aluminum Current Collector Short

- Used NMP to remove cathode coating from center portion of double-sided cathodes.
- 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.
- Implanted a ISC device in a cell at DK labs.

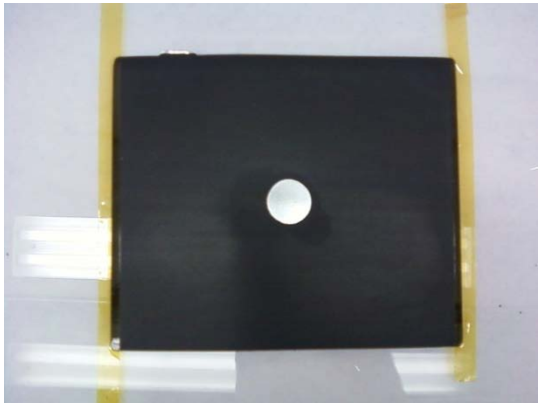
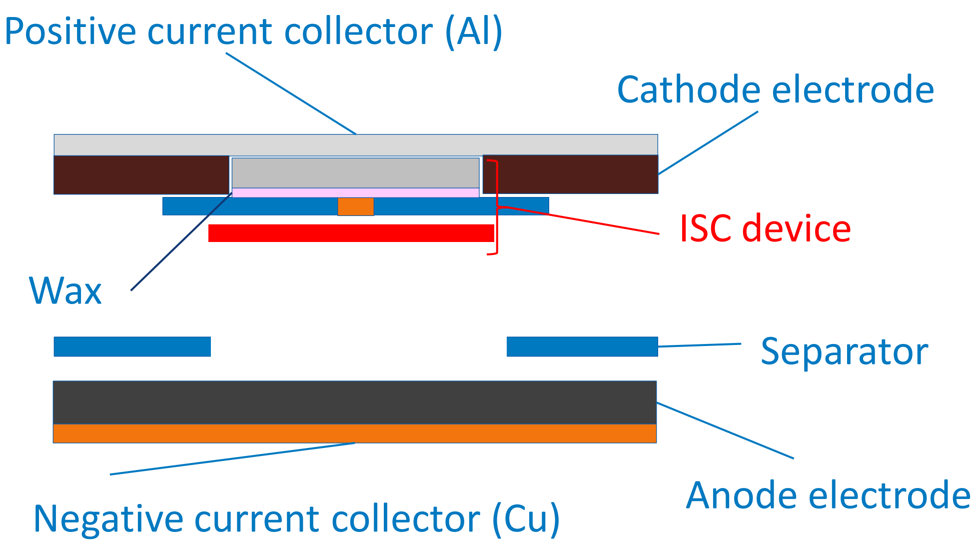


Photo Credit: NREL – Yoon Seok Jung



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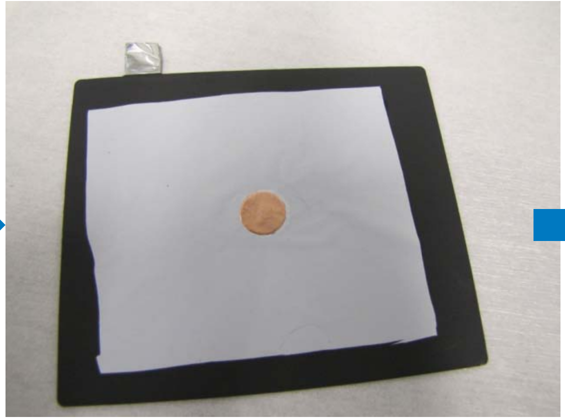
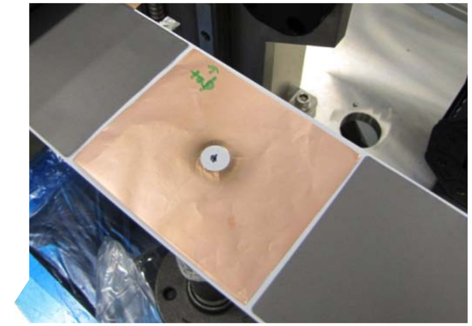
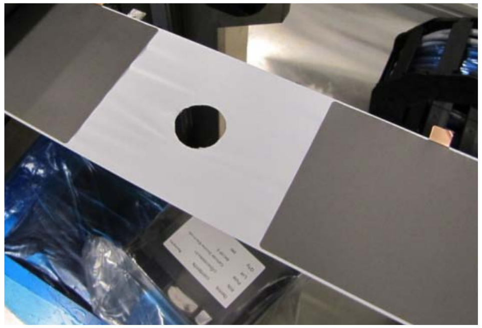
Anode-to-Al Short





DK lightly glued the custom ISC device to the modified cathode, lines up the separator hole with a template to center the separator hole, and then allowed stacking to proceed.



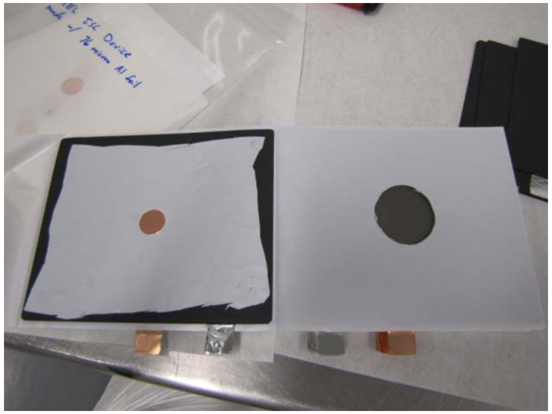
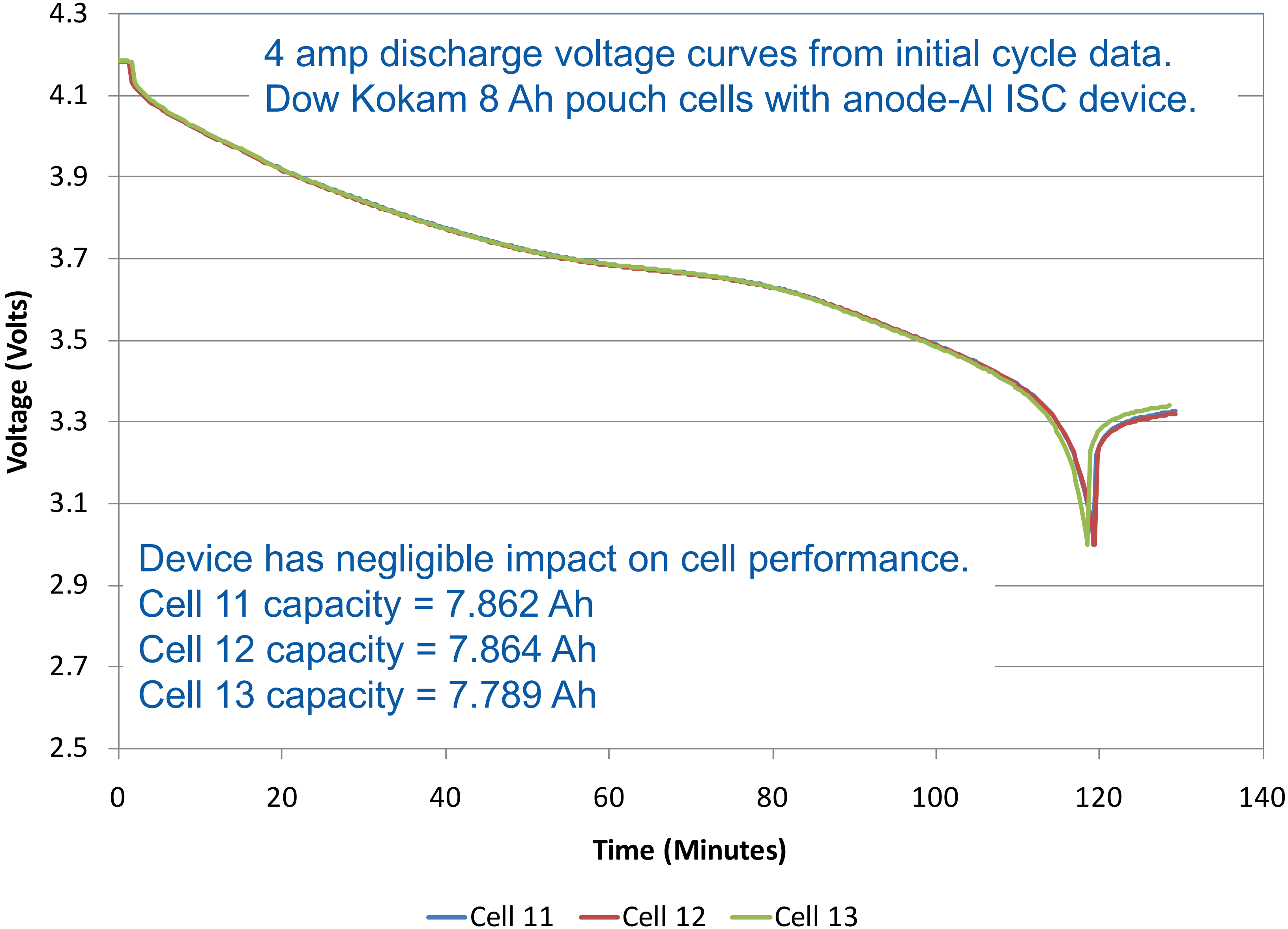
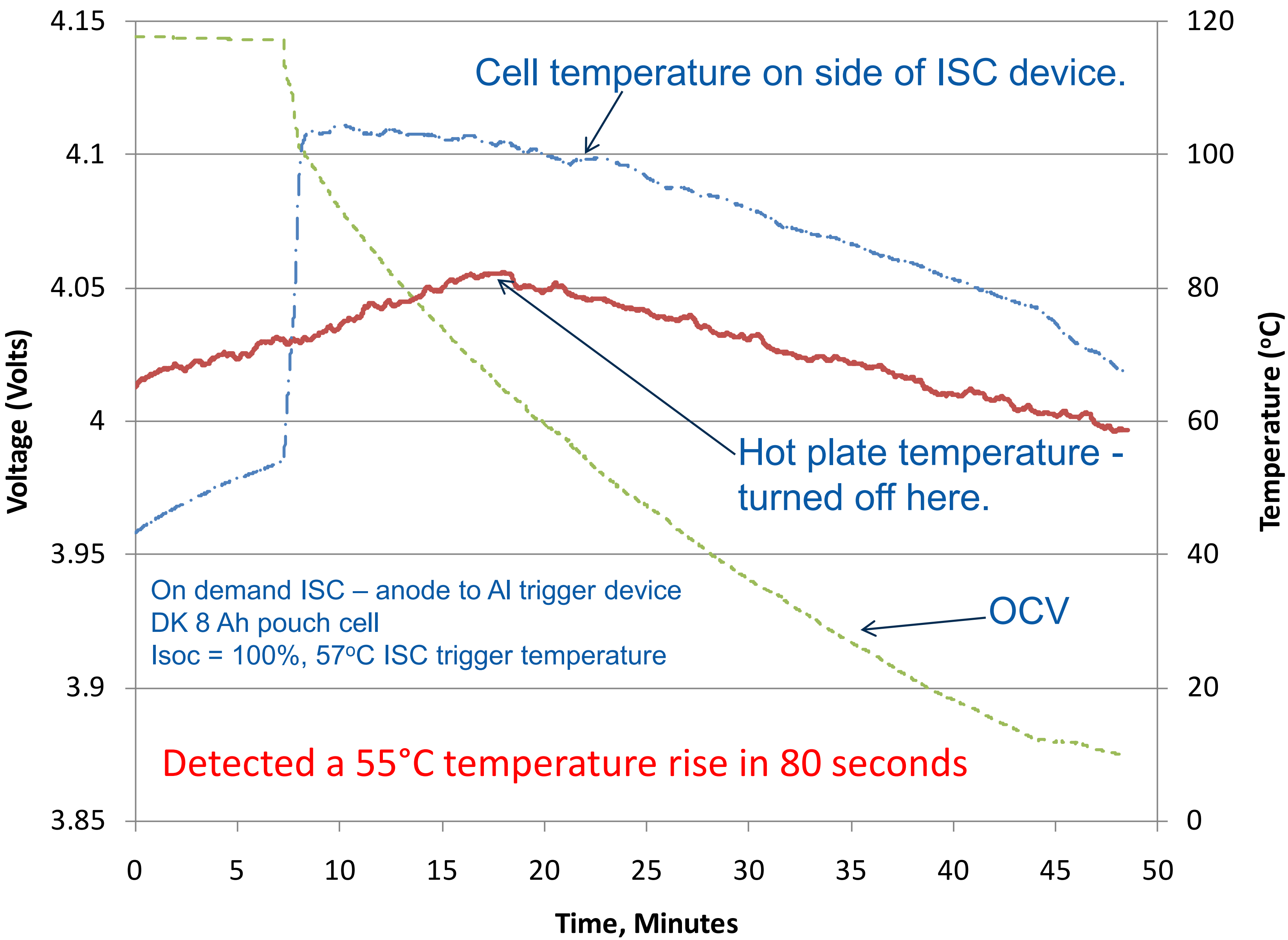


Photo Credits: Dow Kokam – Ben McCarthy

Nominal Capacity Cycling after Implantation



Voltage and Temperature Response to ISC



Results of Destructive Physical Analysis

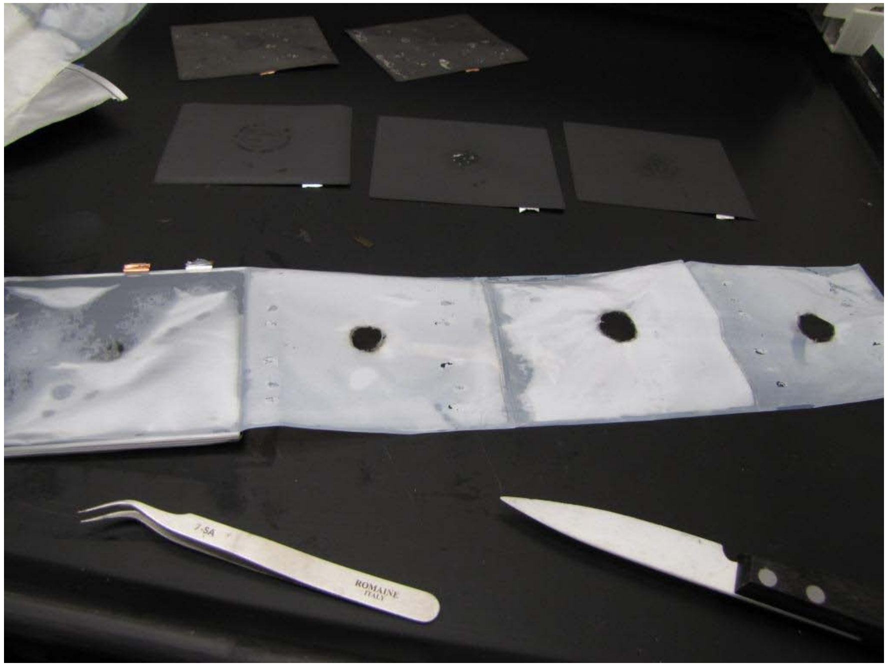
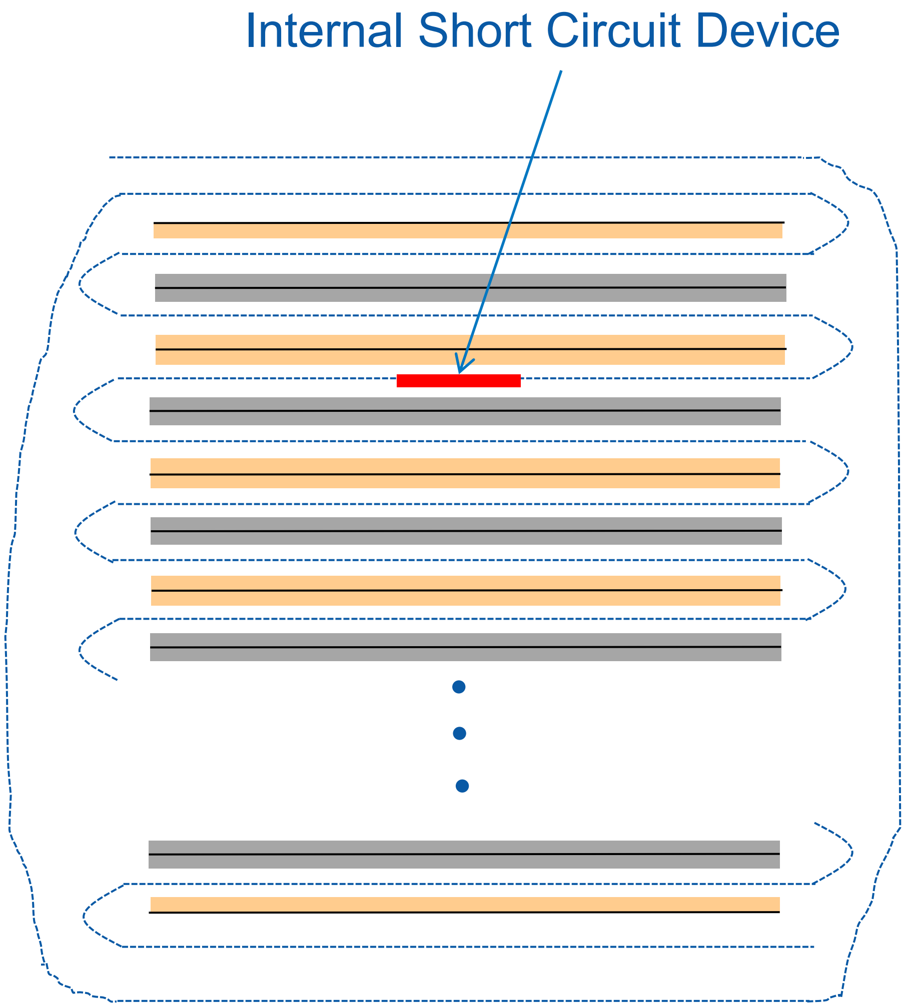


Photo Credit: Dow Kokam – Ben McCarthy

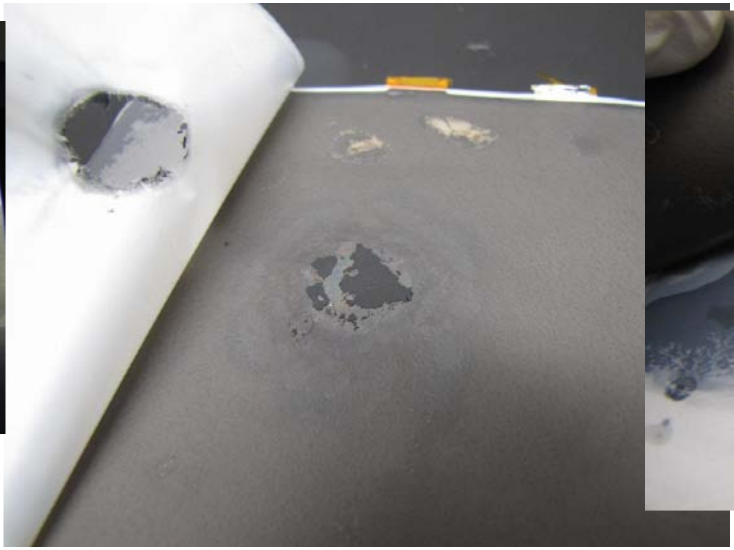
Anode-Al short without any improvements to interface contact resistances

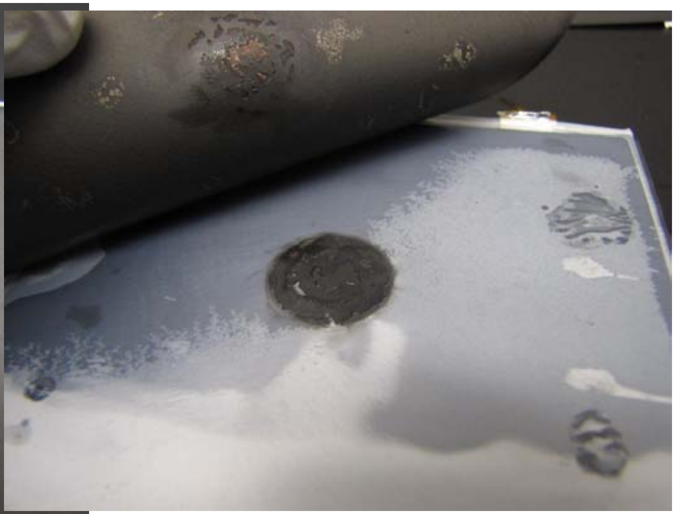
Severe heat-affected zones in eight electrode layers in vicinity of ISC device and on inside of pouch laminate side near short.

Tabs stayed intact.



Destructive Physical Analysis Evidence (cont.)





Unfolding the cell after the Anode-Al short

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

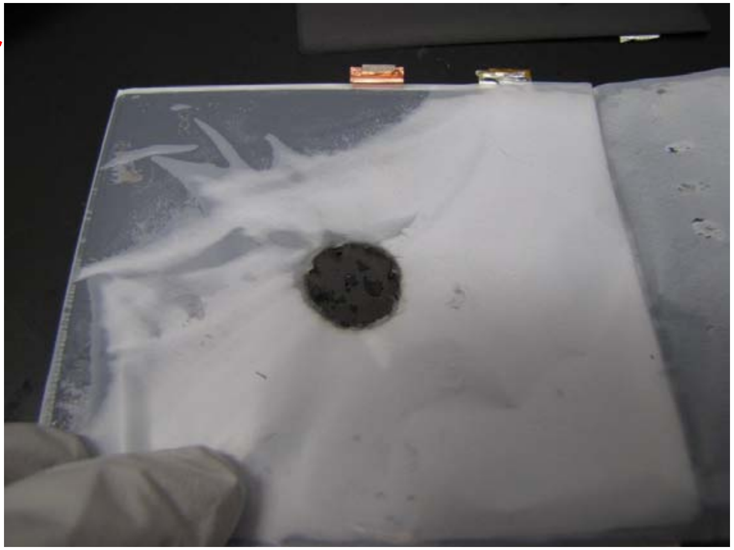


Photo Credits: Dow Kokam – Ben McCarthy

Observations

- A small, low profile, flexible, and implantable device has been demonstrated to be reliable in triggering on-demand internal short circuits
  - PCM activation has never failed to activate.
  - Anode-Al short caused a rapid 55 C temperature rise in an 8-Ah Dow-Kokam cell design, but did not result in thermal runaway.
  - High contact resistances prevented hard shorts and thermal runaway.
    - Currently investigating several very promising redesign options to lower key interface resistances.
- Although thermal runway was not achieved, 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.
- 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 significant damage in eight electrode layers and the inside of closest pouch layer.

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

Summary and Planned Work

- NREL/NASA has developed a small, low profile device for simulating internal short circuit (ISC) in Li-Ion cells.
- An patent application has been filed for the ISC device.
- To date, anode-cathode and anode-Al short-circuit cases have been tested in coin and stacked pouch cells
- The ISC device has shown great potential to produce results relevant to field failures caused by internal cell defects
  - Evaluation ISC response of a cell no longer has to rely on less relevant crush tests.
  - Results have promise to guide and focus cell production line defect and contamination mitigation measures.
  - Comparison of the abuse tolerance of various cell designs will be possible.
- Planned Work:
  - With further maturation, we plan to further test the effectiveness of the ISC device in triggering a thermal runaway
  - Test Cathode-to-Cu and Al-Cu collector shorts in stacked cells
  - Implant and test ISC device in 18650 Li-Ion cell designs
  - Test the effectiveness of battery managements systems in preventing collateral damage to cells neighboring one with an internal short circuit.

Acknowledgments

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  - Dave Howell

- Dow-Kokam for being willing to be the first to support us with evaluation of NREL ISC device

- Support and contributions by NREL colleagues
  - Gi-Heon Kim
  - Kyu-Jin Lee
  - Shriram Santhanagopalan
  - John Ireland