

Numerical and Experimental Investigation of Internal Short Circuits in a Li-ion Cell

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Eric Darcy

National Renewable Energy Laboratory (Jan-Sep, 2010)
NASA-JSC

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project ID: ES109

Timeline

Project Start: 2009

Project End: 2014

Ongoing

Budget

• FY10: \$500K

FY11: Anticipated \$500K

Barriers

- Li-ion abuse tolerance and reliability
- Li-ion performance

Partners

- NASA-JSC
- Dow Kokam
- Battery Safety Consulting Inc.
- Battery Design LLC
- Sandia National Laboratories (SNL)
- U.S. Navy

Funded by Dave Howell, Energy Storage R&D Vehicle Technology Program, U.S. Department of Energy

Background

Internal Short Circuit (ISC), a Major Concern

 Because of its high specific energy and power density, the Li-ion battery (LIB) is a promising candidate to date for electric energy storage in electric drive vehicles (EDVs)

 Safety concerns regarding violent failure of the LIB system are a major obstacle to overcome for fast market acceptance of EDV technologies

• Thermal instability and flammability of the LIB components make them prone to catastrophic thermal runaway under some rare **ISC** conditions

 Many safety incidents that take place in the field are due to an ISC that is not detectable or predictable at the point of manufacture

Motivation

Barriers for Addressing Failures Due to ISC

- Evolving during Life: Latent defect gradually evolves to create an ISC while the battery is in use; inadequate design and/or off-limit operation causes Li plating, stressing separator
- Difficulty of Early Detection: Electrical and thermal signals of early stage ISCs are not easily detected in large-capacity LIB systems
- Complex Physics with Numerous Sensitive Factors: Behavior of a LIB with an ISC depends on various factors, including nature of the short; cell characteristics such as capacity, chemistry, electrical and configuration; and attributes of the pack where the cell is integrated
- Poor Reproducibility: To date, no reliable and practical method exists to create an on-demand ISC in Li-ion cells that produces a response that is relevant to the ones produced by field failures

Objectives

1. Model Investigation: Enhance knowledge of the complex physics of evolution and development of an ISC and subsequent cell responses using NREL's multiphysics ISC model

2. Test Method Development: Establish a relevant ISC test method by developing an on-demand short activation device to produce representative and reproducible ISCs in a active cell and relevant cell responses

3. Model+Test: Perform a synergistic study with combination of modeling and experimental approaches

Wax

Negative current collector (Al)

Cathode electrode

With combination of modeling
Separator

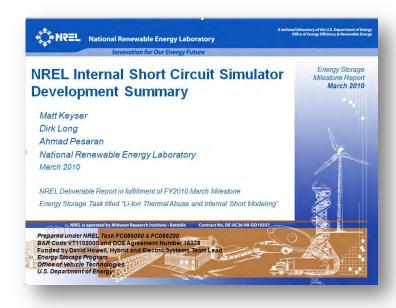
ISC device

Negative current collector (Cu)Anode electrode

Milestones

FY10 Milestone Report

 Matthew Keyser, Dirk Long, Ahmad Pesaran, "NREL Internal Short Circuit Simulator Development Summary"



FY11 Milestone Report - Due in September 2011

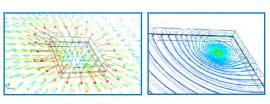
• "Li-Ion Abuse Response Modeling and Internal Short Circuit Simulation"

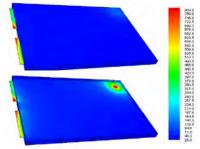
Approach

Focus of Modeling Study

Lead Investigator: Gi-Heon Kim

- Multiphysics ISC modeling
- Understanding cell behaviors





Model Validation Experiment Design

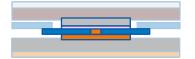
Focus of Testing Study

Provide Model Input

Confirm Model Assumptions

Lead Investigator: Matthew Keyser

- Develop relevant ISC in active cell
- Provide consistent and reproducible results





- Identify Critical Parameters
- Provide Complete Data Set for Non-Measurable Quantities



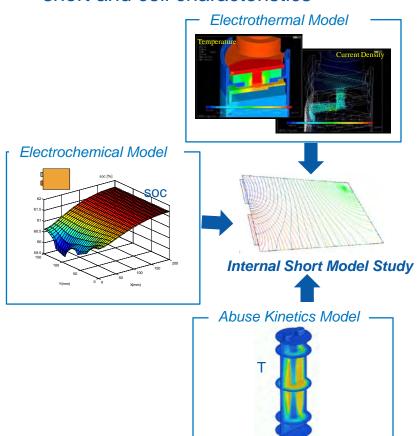


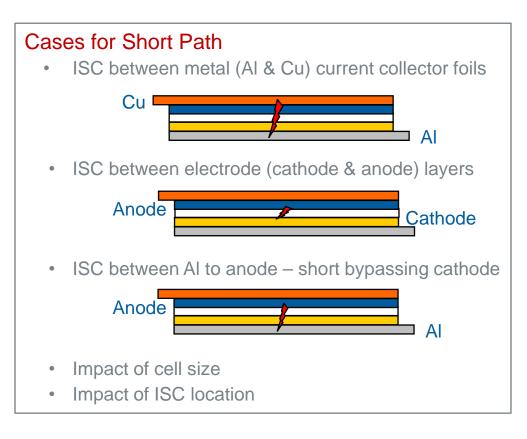
Photo Credits: Dow Kokam - Ben McCarthy

Approach – Modeling

Internal Short Circuit Modeling

- Perform multiphysics ISC model study using NREL's <u>electrochemical</u>, <u>electrothermal</u>, and <u>abuse reaction kinetics models</u>
- Predict cell responses and onset of thermal runaway corresponding to the nature of the short and cell characteristics

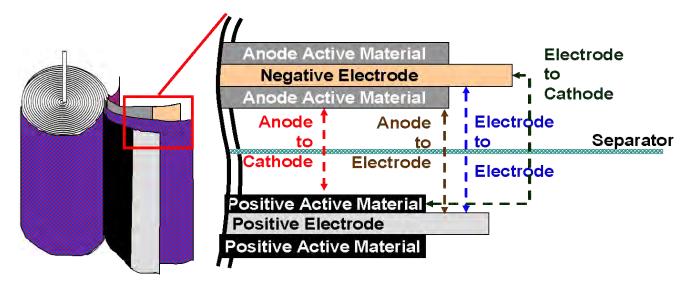




Approach – Testing

❖ Internal Short Circuit Instigator Device Development

- Small, low-profile and implantable into Li-ion cells, preferably during assembly
- Consistent and repeatable activation of internal short
- Electrolyte-compatible phase change material (PCM) for key component
- Triggered by heating the cell above PCM melting temperature



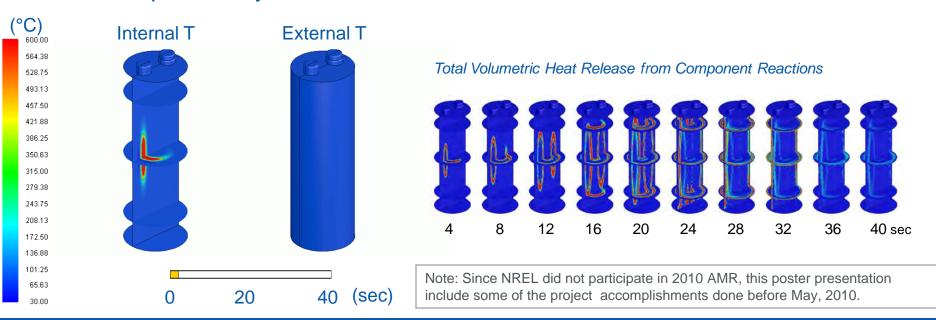
Spiral wound battery shown – can also be applied to prismatic batteries.

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

Previous Accomplishments

Technical Accomplishments

- Three-dimensional LIB abuse kinetics model was developed in support of DOE's ATD program, and the development was continued in the DOE's ABR program
- Previous study
 - ✓ Focused on understanding the interaction between heat transfer and exothermic abuse reaction propagation for a particular cell/module design
 - ✓ Provided insight on how thermal characteristics and conditions can impact safety events of LIBs



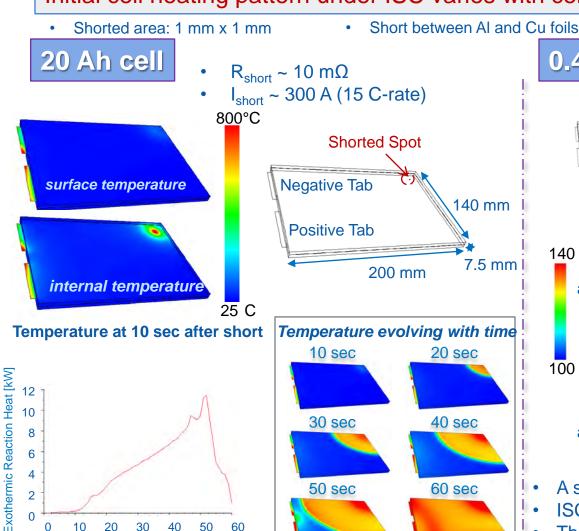
Accomplishments

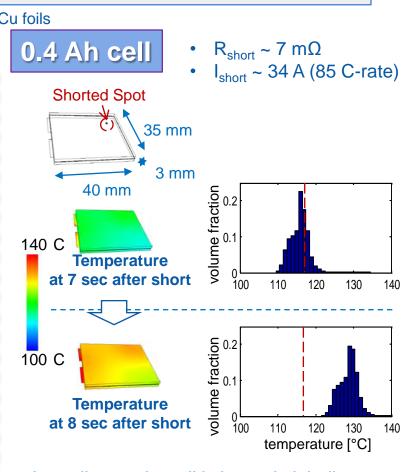
ISC Model Investigation

Impact of Cell Capacity

Technical Accomplishments

Initial cell heating pattern under ISC varies with cell capacity





- A small-capacity cell is heated globally
- ISC heating in a large cell is likely local
 - Thermally triggered "shut-down separator" may function effectively in a small cell

50

60

0

10

20

30

Time [sec]

Impact of Separator Integrity

25.5 C

Technical Accomplishments

Maintaining integrity of separator seems critical to delay evolution of the short

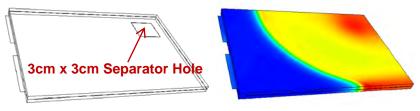
• Short between anode to cathode • 20 Ah capacity cell Shorted area: 1 mm x 1 mm • $R_{short} \sim 20 \ \Omega$ • $I_{short} \sim 0.16 \ A \ (< 0.01 \ C-rate)$ • Icm x 1cm Separator Hole current density field near short 43.1 C

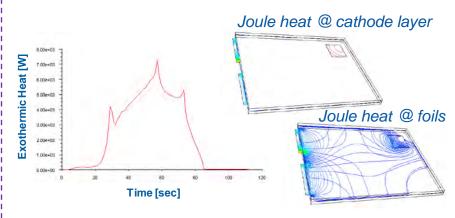
- Thermal signature of the short is hard to detect from the surface
- The short for simple separator puncture is not likely to lead to an immediate thermal runaway

Shorted area: 3 cm x3 cm

- $R_{short} \sim 30 \text{ m}\Omega$
- I_{short} ~ 100 A (5 C)

Temperature at 1 min after short





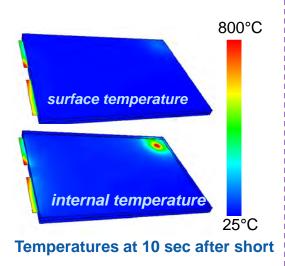
surface temperature

Electrical resistance of ISC varies with short path across electrodes

20 Ah capacity cell

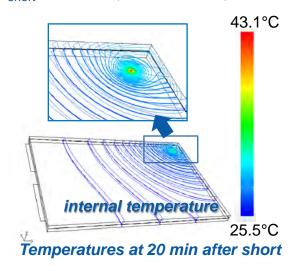
Short between Al & Cu foils

- $R_{short} \sim 10 \text{ m}\Omega$
- I_{short} ~ 300 A (15 C-rate)



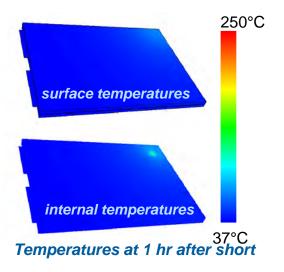
Short between anode and cathode

- $R_{short} \sim 20 \Omega$
- I_{short} ~ 0.16 A (<0.01 C-rate)



Short between anode and Al foil

- $R_{short} \sim 2 \Omega$
- I_{short} ~ 1.8 A (<0.1 C-rate)

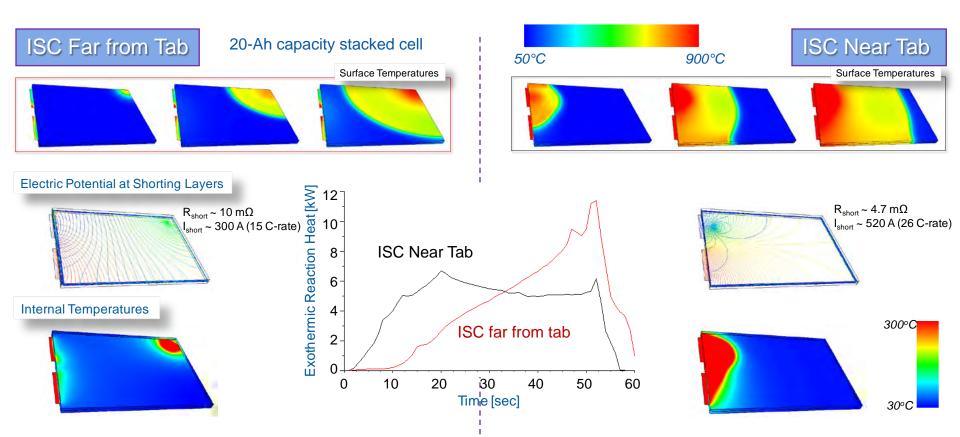


ISC bypassing cathode is likely to evolve into a hard short in relatively brief time

Impact of Short Location

Technical Accomplishments

Cell response varies with short location and cell electrical configuration



- For low-resistance ISC, near-tab ISC results in a smaller resistance because of shorter short-current path through shorting layers
- Pattern of local heating for convergence of short-current varies with location of short and internal electrical configuration of a cell

Accomplishments

ISC Test Method Development

NREL developed an on-demand activation device creating representative ISC

NREL's ISC instigator design

Anode to Cathode ISC Anode to Al ISC

Activated short with PCM wicked by battery separator

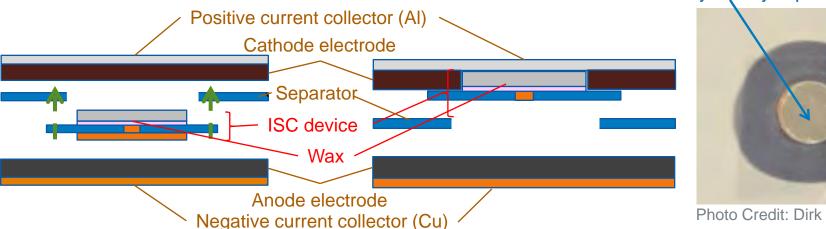


Photo Credit: Dirk Long, NREL

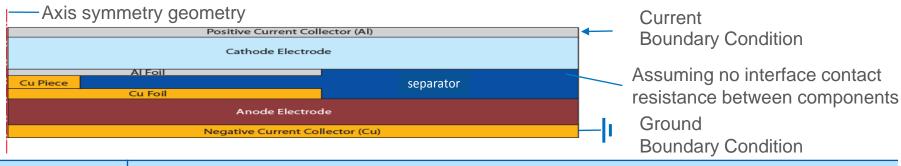
This device is applied for patent

- Triggered by heating the cell above PCM melting temperature (presently $40^{\circ}\text{C} 60^{\circ}\text{C}$)
- Initial device design focus is on anode-to-cathode active material short
- Improved device design focus is on anode-to-Al short

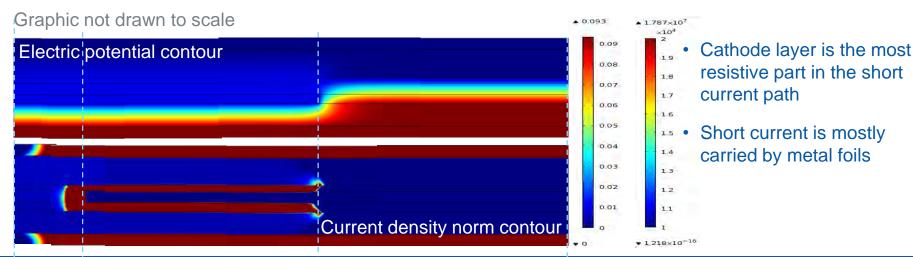
Characterizing the ISC Device

Technical Accomplishments

Model helps to understand characteristics of ISC device and short triggered



Property	Al pad	Cu pad	Cu piece	Positive current collector	Negative current collector	Cathode electrode	Anode electrode	Separator	
Electric conductivity [S/m]	3.541x10 ⁷	5.8x10 ⁷	5.8x10 ⁷	3.541x10 ⁷	5.8x10 ⁷	5	58	1x10 ⁻¹⁵	

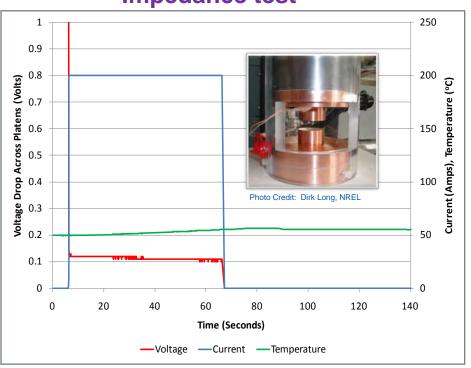


ISC Device Function Test

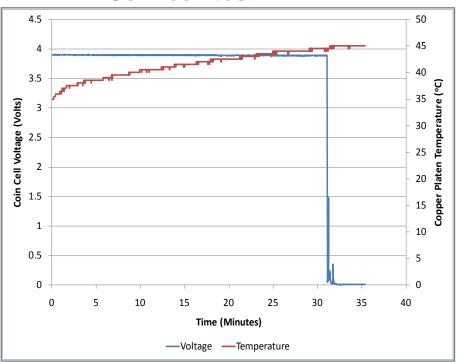
Technical Accomplishments

NREL ISC device consistently activated a short in laboratory testing

Impedance test



Coin cell test



Consistent Short Impedance ~ $0.5 \text{ m}\Omega$

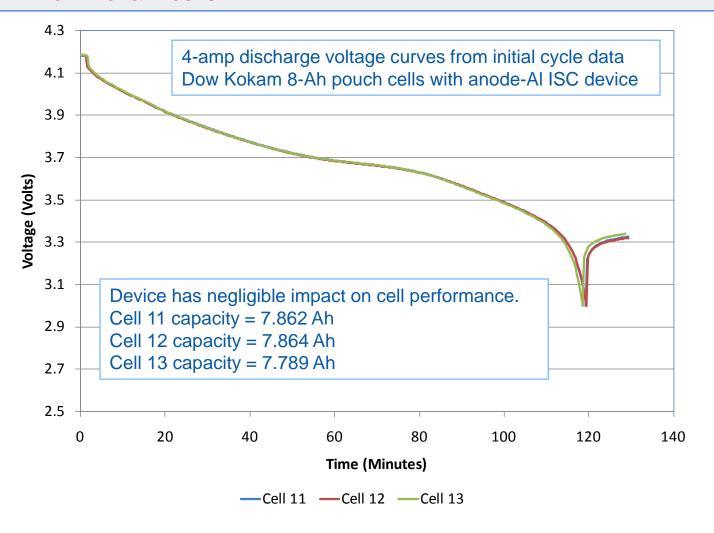
Reliable ISC Trigger in Coin Cells – 100% Success Rate

- In laboratory testing, the activated device can handle currents in excess of 200 A to simulate hard shorts (<5mΩ).
- Phase change from non-conducting to conducting has been 100% successful during trigger tests.
- Separator is an excellent wick for melted PCM.
- Nine of nine coin cells shorted with new ISC device design, shown here using a 42°C 44°C melting PCM.

ISC Device Implantation in a Large Cell

Technical Accomplishments

Implantation of NREL ISC device does not impact electrochemical performance of 8-Ah Dow Kokam cells



Implanting Anode-to-Cathode ISC in 8-Ah cells

Technical Accomplishments

ISC was consistently activated in 8-Ah stacked cells using NREL's ISC device

Implantation of ISC Device for Anode to Cathode short

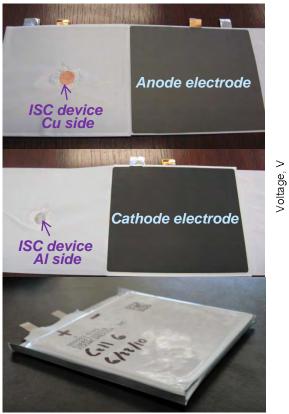
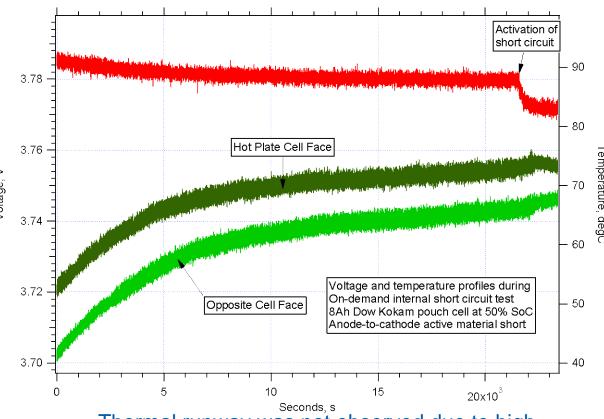


Photo Credits: Dow Kokam - Ben McCarthy

Shown here implanted inside a Dow Kokam 8-Ah pouch cell

Voltage Response to ISC



Thermal runway was not observed due to high impedance of the ISC between anode-to-cathode electrode surfaces

Implanting Anode-to-Al ISC in 8-Ah cells

Technical Accomplishments

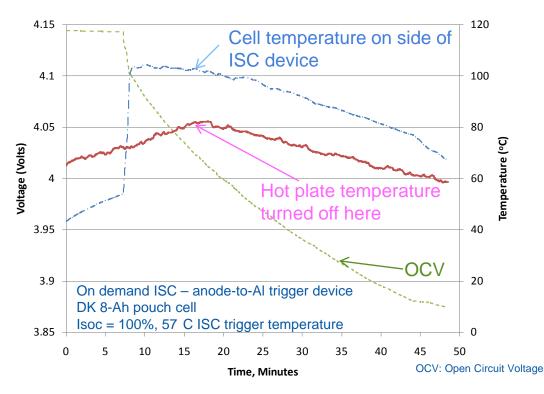
Anode-to-Al ISC implanted yielded lower impedance shorts in a 8-Ah cell

Implantation of ISC Device for Anode-to-Aluminum short



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

Voltage, Temperature Response to ISC



Detected a 55 C temperature rise in 80 seconds

 NREL's ISC device was easily implanted during the manufacturing process on DK's automated production line

Destructive Physical Analysis of Triggered Cell

Technical Accomplishments

Severe heat-affected zones were observed near the implanted short, subsequently creating separator holes in the adjacent layers









Photo Credit: Dow Kokam - Ben McCarthy

Inside pouch

Anode electrode Damaged separator

Unfolding the cell after the anode-to-Al short

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



Photos courtesy of Ben McCarthy, Dow Kokam

Collaborations

Dow Kokam

 Dow Kokam assembled ISC-implanted cells and tested them to evaluate NREL's ISC instigator device

NASA Johnson Space Center

- Eric Darcy of NASA-JSC, awarded by NASA's Innovation Ambassador Program, joined NREL's energy storage team (Jan ~ Sep 2010) and participated in the invention of NREL's ISC instigator device
- NASA-JSC also tested the ISC device at its facilities in Houston, Texas

Battery Safety Consulting, Inc.

- Dr. Daniel Doughty of Battery Safety Consulting, Inc. was subcontracted to submit a recommendation of Li-ion "Safety Roadmap" to DOE
- This document analyzes battery safety and failure modes of state-of-theart cells and batteries and makes recommendations on future investments that would support DOE's mission

Collaborations

Battery Design LLC

 NREL researchers are collaborating with Robert Spotnitz of Battery Design LLC to expand NREL's exothermic kinetics (empirical) model inventory

Sandia National Laboratories

 NREL researchers continue to discuss using SNL's test data for NREL's model development and validation with Christopher Orendorff of SNL

U.S. Navy

 NREL researchers continue to discuss using Naval Surface Warfare Center (NSWC) test data for NREL's model development and validation with Clint Winchester of NSWC's Carderock division

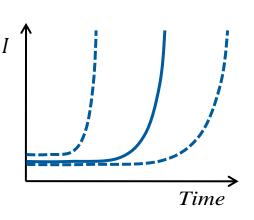
Future Work

NREL ISC Device

- Test cathode-to-Cu and Al-Cu collector shorts in stacked cells
- Implant and test ISC device in 18650 cylindrical cell designs (with NASA)
- Test the effectiveness of battery management systems in preventing collateral damage to cells neighboring the cell with an ISC
- Partner with cell manufacturers and auto industry to help them design safer LIB systems, which appears critical to realizing technologies for green mobility

ISC Evolution Study

- Understand initial evolution of an ISC using a controllable test fixture
- Investigate factors and conditions affecting the time scale for ISC development
- Quantify the sensitivity of the factors

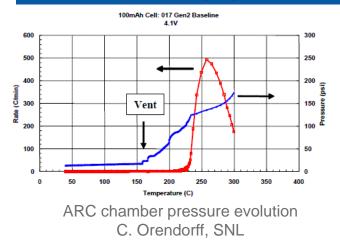


Future Work

Future Work / Deployment Strategy

Pressure Model

- Predict pressure evolving inside a battery container during thermal runway
- Understand cell venting mechanism
- Based on empirical correlations between temperature and volume of gas evolved from abuse reactions



Modeling Overcharge Mechanism

- Cathode Instability: Changes in the composition and lattice structure of the cathode host matrix during overcharge will be simulated
- Electrolyte Decomposition: The electrolyte decomposes due to the high voltage. The reactions taking place during this process will be included in the safety model
- Lithium Deposition: Lithium deposition during overcharge is usually assumed to take place when the anode voltage goes below 0V vs.
 lithium, whereas in this work we will explore the factors leading to the drop in the anode voltage

Summary – Model Investigation

- The multiphysics ISC model study was performed using NREL's electrochemical, electrothermal, and abuse reaction kinetics models
- Initial cell heating pattern under ISC varies with cell capacity
- Maintaining integrity of separator seems critical to delay evolution of the short
- The short for simple separator puncture is not likely to lead to an immediate thermal runaway
- Electrical resistance of ISC varies with short path across electrodes
- ISC bypassing cathode is likely to evolve into a hard short in relatively short time
- Cell thermal runaway response varies with short location and cell electrical configuration
- For low-resistance ISC, near-tab ISC results in a smaller resistance in a stacked cell because of shorter short-current path through shorting layers
- Pattern of local heating for convergence of short current varies with the location of the short and the internal electrical configuration of the cell

Summary — Test Method Development

- NREL has developed a small, low profile device for simulating ISCs in active Li-lon cells (applied for a patent)
- The ISC device was proven to activate a short consistently and repeatedly in laboratory tests
- To date, anode-cathode and anode-Al short-circuit cases have been tested in Li-ion coin and stacked pouch cells
- Implantation of NREL ISC device does not impact electrochemical performance of 8-Ah Dow Kokam cells
- The ISC device has shown great potential to produce results relevant to field failures caused by internal cell defects
 - Evaluation of ISC response of a cell no longer has to rely on lessrelevant crush tests
 - Results show 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

Publications and Presentations

- 1. G.-H. Kim, L. Chaney, K. Smith, A. Pesaran, E. Darcy, "Thermal Analysis of the Vulnerability of the Spacesuit Battery Design to Short-Circuit Conditions," 2010 Space Power Workshop, Manhattan Beach, CA, April 22, 2010.
- 2. G.-H. Kim, K. Smith, K.-J. Lee, A. Pesaran, "Integrated Lithium-Ion Battery Model Encompassing Physics in Varied Length Scales," The 3rd International Conference on Advanced Lithium Batteries for Automobile Application, Seoul, Korea, September 8–10, 2010.
- 3. G.-H. Kim, K.-J. Lee, L. Chaney, K. Smith, E. Darcy, A. Pesaran, "Numerical Analysis on Multi-physics Behaviors of Lithium-ion Batteries for Internal and External Short," 218th ECS Meeting, Las Vegas, NV, October 10–15, 2010.
- 4. G.-H. Kim, K.-J. Lee, L. Chaney, K. Smith, E. Darcy, A. Pesaran, "Prediction of Multiphysics Behaviors of Large Lithium-ion Batteries at Internal and External Short Circuit," Battery Safety 2010 in conjunction with 6th Lithium Mobile Power, Boston, MA, November 3, 2010.
- 5. E. Darcy, M. Keyser, D. Long, Y.S. Jung, G.-H. Kim, A. Pesaran, B. McCarty, "On-Demand Internal Short Circuit Device," 2010 NASA Aerospace Battery Workshop, Huntsville, AL, November 17, 2010.
- 6. M. Keyser, D. Long, Y.S. Jung, A. Pesaran, E. Darcy, B. McCarthy, L. Patrick, C. Kruger, "Development of a Novel Test Method for On-Demand Internal Short Circuit in a Li-Ion Cell," Large Lithium Ion Battery Technology and Application Symposium in conjunction with Advanced Automotive Battery Conference 2011, Pasadena, CA, January, 24–28, 2010.
- 7. E. Darcy, M. Keyser, D. Long, Y.S. Jung, A. Pesaran, B. McCarthy, "On-Demand Internal Short Circuit Device," 83rd Li Battery Technical/Safety Group Meeting, Key West, FL, February 16–17, 2011.

Technical Back-up Slides

Current abuse test methods may not be relevant to field failures

Penetration and Crush Tests Methods

- Army/Navy/FBI use nail/bullet penetration tests.¹
- NASA uses a crush test with a rounded rod.²
- Underwriters Laboratory (UL) uses a blunt nail crush test.³
- Motorola/Oak Ridge National Laboratory use a pinch (crush) test on pouch cells.⁴

Reliable, but not representative of field failures

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

Current abuse test methods may not be relevant to field failures

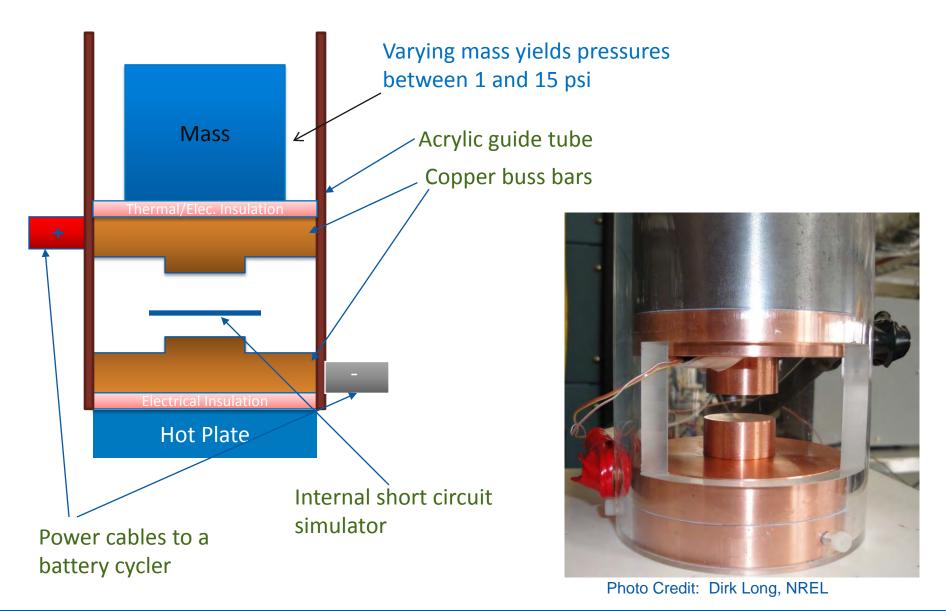
Contamination Test Methods

- BAJ⁵ and Celgard⁶ retrofitted a Ni particle into the jellyroll of a cell and triggered the event using a crush test.
- Sandia National Laboratories has tried several methods^{7,8,9}:
 - 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 retrofitted a metallic particle into the jellyroll of a cell and triggered the event by repeated charge/discharge cycling.¹⁰

More relevant, but with reliability and reproducibility challenges

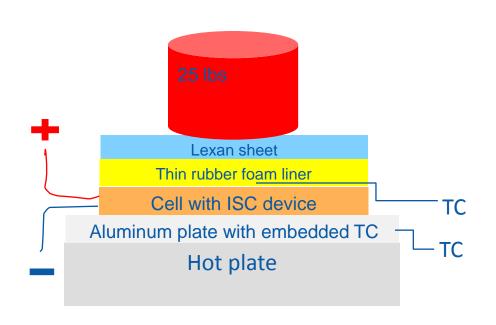
- 5. Battery Association of Japan, Nov 11, 2008, presentation on web.
- 6. S. Santhanagopalan et al., J. Power Sources, 194 (2009) 550-557.
- 7. Orendorff, C., et al., ECS Meeting, May 2009.
- 8. Orendorff, C., and Roth, E.P., USABC TT Meeting, Feb 2009.
- 9. Orendorff, C., et al., ECS Meeting, Oct 2010.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

Laboratory Test Fixture



Test Setup for Triggering ISC Implanted in a Cell

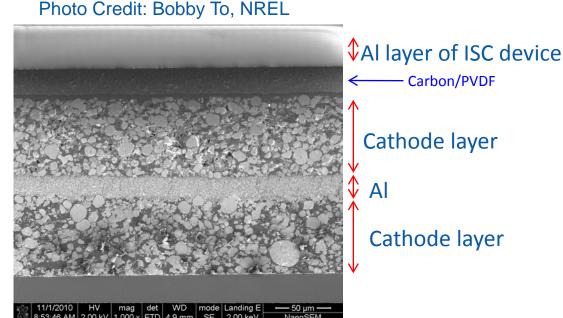
- Cell is charged to the appropriate state of charge.
- Hot plate provides the heating source.
- Cell is placed under compression (~1.6 psi).
- Al plate between hot plate and cell has an embedded thermocouple (TC).
- Thermocouple placed cell side opposite hot plate.
- Thin foam pad and Lexan plate placed between cell top and 25lb weight.
- Thin particulate bag encapsulates cell and its top TC (not shown for clarity).



Graphic is not to scale and for illustration only

Improving Interface Contact Resistance

- Part 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.



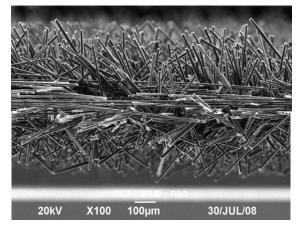


Photo courtesy of ESLI