Lithium Ion Battery Safety

November 15, 2016
New England Section ECS
Northeastern University

Boston POWER

- Background
- Some Basics
- Tools to Study Safety
- Approaches to Prevent Propagation

Boston-Power Introduction

MISSION	Support adoption of green technologies to drive environmentally sustainable economic growth through developing and manufacturing high-volume advanced lithium-ion products and solutions
MARKETS	China EV Passenger (Eco-EV), Commercial (eTruck) / fleet (eTaxi) vehicles Global EV and ESS EV: Construction, Mining, Fleet Vehicles, Personal Vehicles ESS: Renewable Energy Storage Systems (Residential, C&I) Global Small Format Packs Asset Tracking, Sensors, Lighting, Etc..
FACTS	Founded 2005 – Private Key Investors: GSR, Oak, FAM State of the art manufacturing plant in Liyang, China 100+ patents issued; >200 patent filings



Boston-Power Products and Solutions

CELL / BLOCK PRODUCTS

Industry leading cell performance in terms of density, temperature range, cycle life and fast charge capability

MODULE SYSTEM PRODUCTS

Semi-Custom Cell-to-Module system for quickly and easily integrating Boston-Power cells into large format modules

PACK SOLUTIONS

Fully customized solutions integrating Boston-Power cells into large format modules and packs (China focused)

Swing and Sonata Cells

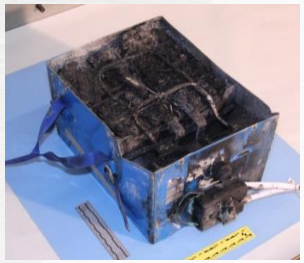
Ensemble ™ Module System

Custom Module and Pack Solutions

Li-ion Safety in the News

- Across markets

Portable	Transportation	Aerospace
• Laptop battery recalls • (2006) Sony 65M cells • (2007) Nokia 46M cells • (2015) Hoverboards • (2016) Samsung Galaxy Note7 est. $5Bil	• (2012) Volt (NHSTA) • Tesla Road Debris • Bus fires in China	• (2008) Navy Adv. Seal Delivery System • (2013) Boeing Dreamliner • (2016) DARPA RoboSimian (JPL)



- Yet we hear less about ICE car fires in the US - ~150,000 per year (10% of all fires) with on average of 209 civilian deaths and $536M in direct property damage (NFPA) per year
- Increasing shipping regulations (IATA & ICAO) of Li-ion cells and products plus more restrictive exceptions by carriers

Size of battery packs increasing

- Potential magnitude of incidents increasing
- Portable device packs <100Wh because of shipping regulations
- Transportation
  - Cars: <100 kWh in volume production today
  - Buses: as high as 300-400 kWh
  - Ferries: largest reported 4.16MWh (Scandlines)
- Stationary
  - Home: <20 kWh
  - Grid: 10's of MWh
- Large systems have fire suppression and thermal management

AES Dayton Power & Light, AES has 2.5 TWh of installed capacity

Background

Some Basics

Tools to Study Safety

Approaches to Prevent Propagation

Lithium Ion Cell Chemistry Options

Design	Features	Cell Chemistry		
		Anode	Cathode	V
Energy	• Higher energy materials • Higher energy electrode designs	Gr	NCA-NCM	3.65
	• Blended with Ni materials	Gr	LMO	3.7
Power	• High rate materials • Thinner and more porous/conductive electrodes • More tabs and larger A_x conductors	Gr	LFP	3.25
	• For faster charge and longer cycle life	LTO	LFP/LMO/ NMC	1.8-2.85

Lower Voltage and Energy Density

Electrode Components

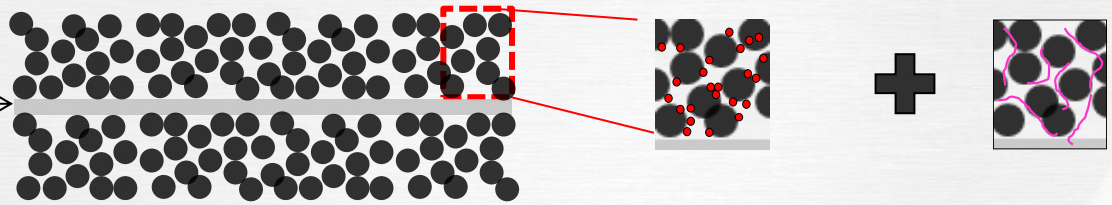
Cathode

Active materials

Conductive additives

Binders

Al foil



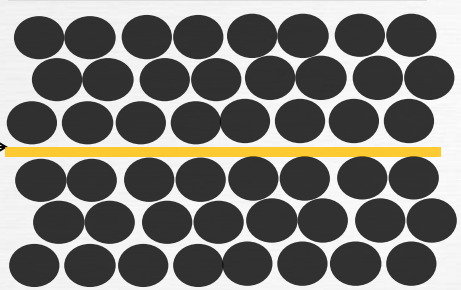
Separator

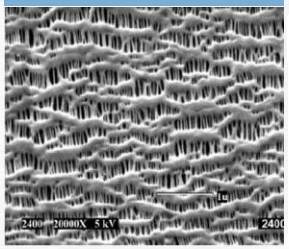
Poly-olefin

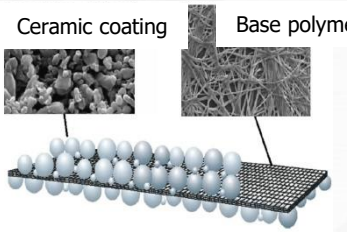
Ceramic Coated

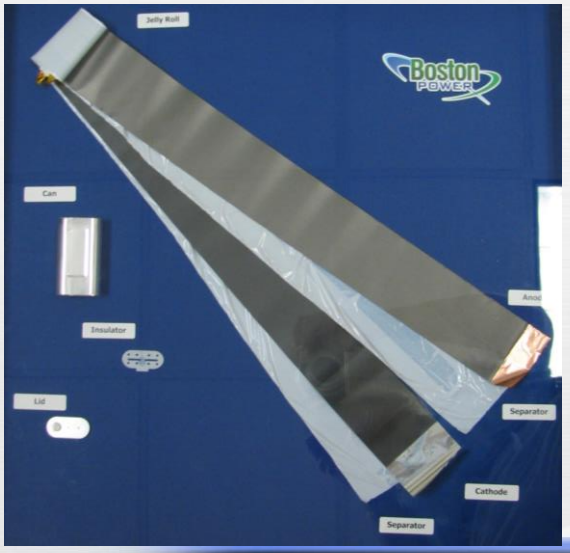
Anode

Cu foil







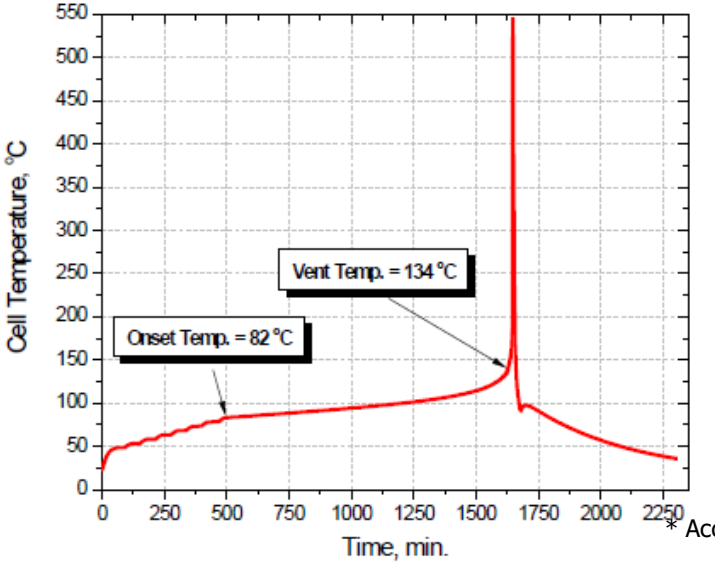


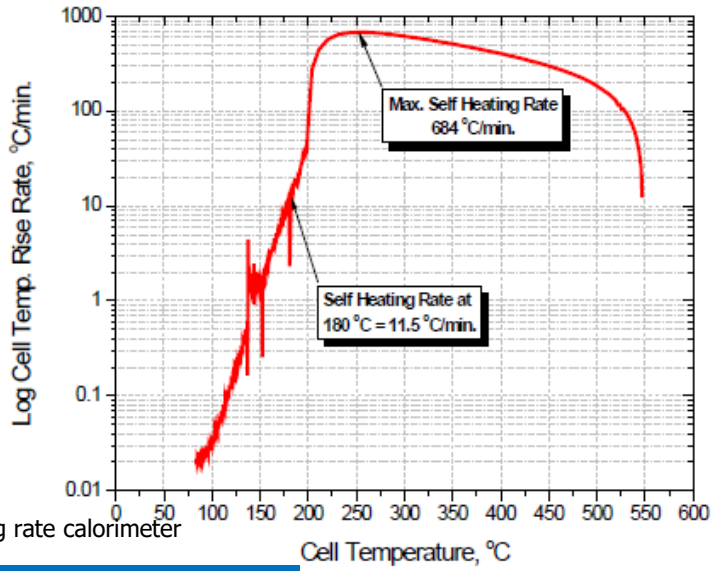
Foil thickness (μm): 10-15
Particle Sizes (μm): 5-20
Electrode thickness (μm): 100-150

Separator thickness (μm): 9-25
Composition: PP, PE, PP/PE/PP, ceramic coatings
Porosity (%): 40-60

Thermal Runaway (TR)

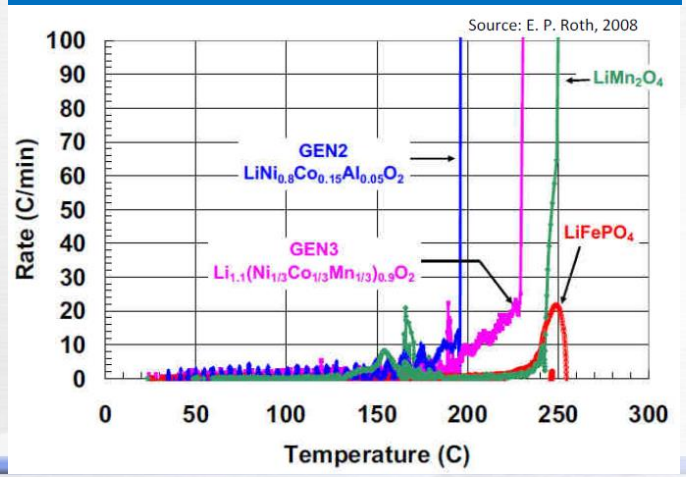
Thermal Runaway Typical ARC* Results





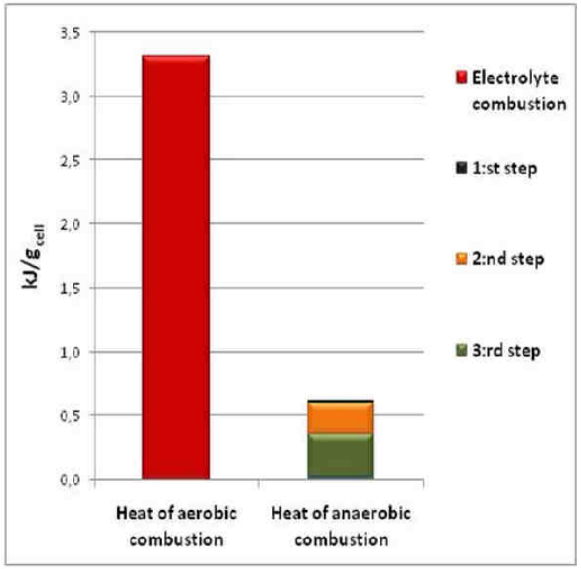
* Accelerating rate calorimeter

Cathode – Electrolyte DSC



Electrolyte – Selected Properties

Electrolyte Energy



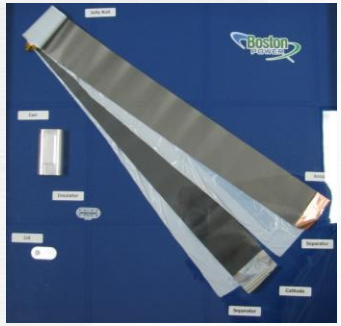
al., *Thermal study of organic electrolytes with fully charged cathodic materials of lithium-ic*
., *A review of Li-Ion Cell Chemistries and their Potential use in Hybrid Electric Vehicles*, 200

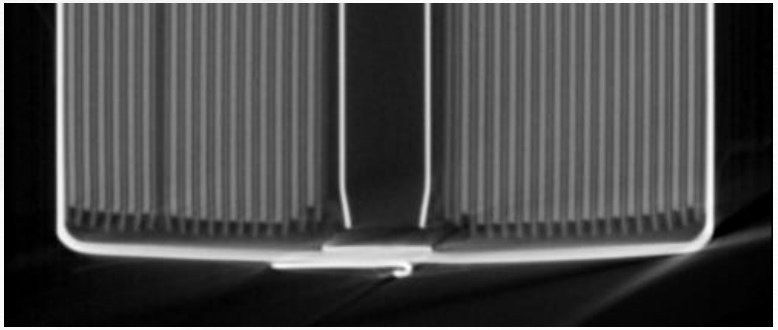
Property	Units	Range
Boiling Point	°C	90-250
Vapor Pressure	Torr	90-250
Flash Point	°C	18-145
Auto-ignition T	°C	~450
Heat of Combustion	kJ/ml	-16 to -21

- For volume estimate - ~0.5cc/Wh
  - 0.5L/kWh
- Base Solvents (carbonates)
  - PC, EC, DMC, DEC, EMC
  - Optimized for widest possible thermal operational range (-40°C - 70°C)
  - Highly flammable
  - Highly moisture sensitive ($LiPF_6$ and H_2O will generate HF)

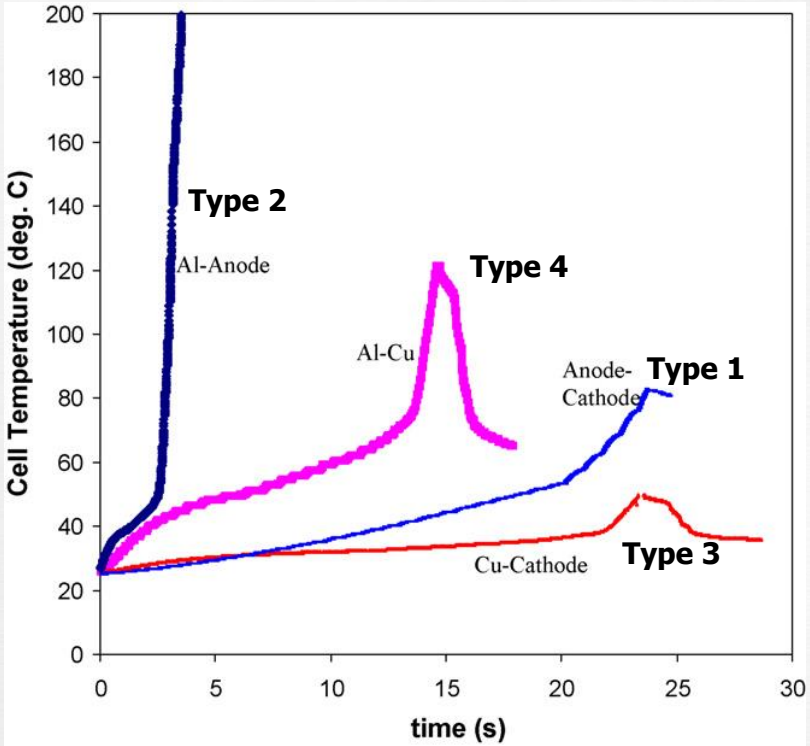
Causes of TR and internal shorts

- Cell Design (Impedance, thermal, ease of assembly, tolerances, materials, ...)
- Cell Manufacturing (maintenance, environment, …)
  - Particle Contamination (size, material, morphology, location)
  - Physically pierce the separator or dissolve to form dendrite
  - Electrode alignment (winding), damage during jellyroll insertion
  - Soldering leads to terminals (heat damage to separator)
- Electrical Abuse
  - Overcharge (Li plating, electrolyte decomposition, cathode damage)
  - Overdischarge (Cu dissolution)
  - Short Circuit
- Thermal Abuse
  - Poor electrical connections
  - Fires (burning fuel, ..)
- Mechanical Abuse (cyclic, impact)
- Human factors





Internal short-circuits - Impact of Location



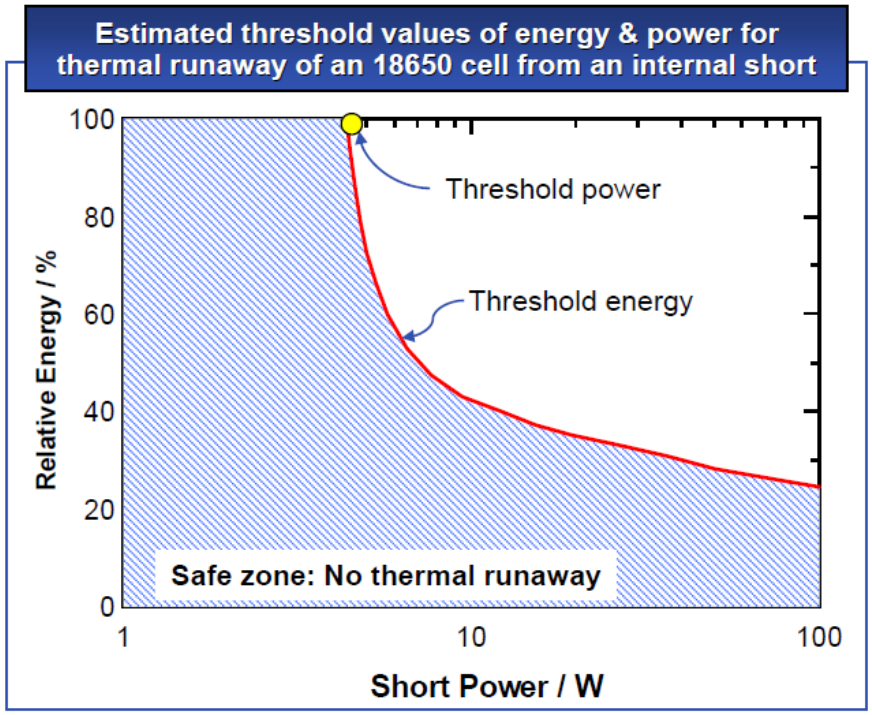
Local temperature after various types of short-circuit scenario in a lithium ion cell

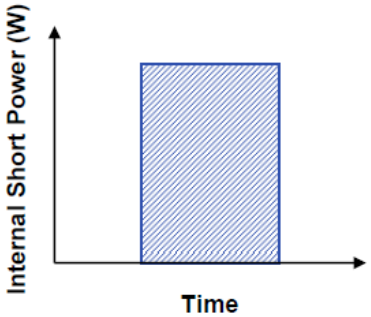
Journal of Power Sources 194 (2009) 550–557

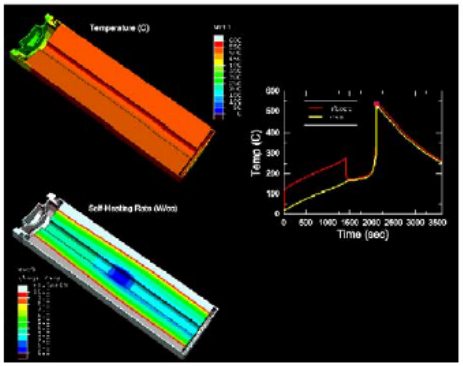
NREL – A Pesaran, et al

Type	Location
1	Anode-Cathode
2	Al-Anode
3	Cu-Cathode
4	Al-Cu

Thermal Conditions for TR







* For a 2.6 Ah 18650 cell with an external heat transfer coefficient of 10 W/m^2-K. The threshold values depend on the external heat transfer coefficient, cell design & chemistry.

CAMX Power

C McCoy, S Sriramulu, B Barnett, Li-ion Battery Safety Technologies and Their Implementation, Int'l Battery Seminar, Ft Lauderdale (2016)

Boston POWER

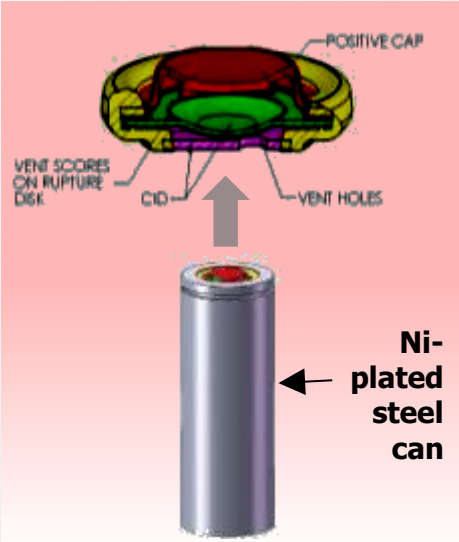
Safety devices used in cells

	PTC	Shut down separator	CID	Vent	Rupture
	Positive Thermal Coefficient	3 layered separator	**C**urrent **I**nterruption **D**evice		Less catastrophic
Mechanism	▪ **Thermal switch** ▪ **Resettable** ▪ **Protect from overheating**	▪ Pores shut down at high temperature	▪ Pressure fuse ▪ Non-resettable ▪ Protect from pressure buildup due to gas generation	▪ Pressure activated ▪ Score in can wall ▪ Rupture disc	▪ Lid Seal ▪ Aluminum vs. steel for 18650
Devices Protects Against	▪ **External short circuit** ▪ **Over temperature**	▪ Overcharge ▪ Over temperature ▪ Internal shorts with temperature increase <150 ºC	▪ Overcharge ▪ Over temperature	▪ Explosion	▪ Explosion

Adds resistance to cell, i.e., 10mΩ

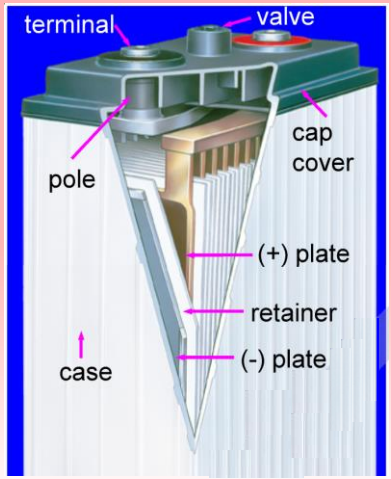
Safety features differ across form factors

Cylindrical



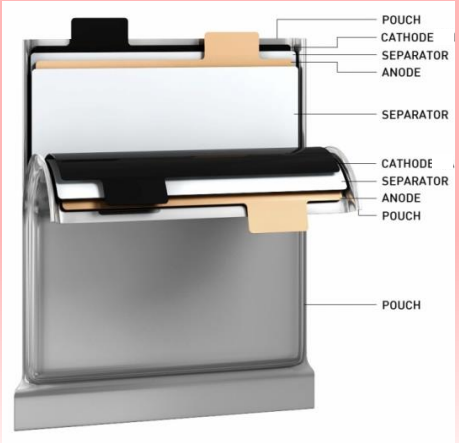
- Crimp sealed cap
- Nickel plated steel cans
- Safety features typically in lid
  - CID
  - Vent
  - PTC (if used)
- Bottom can vents

Prismatic



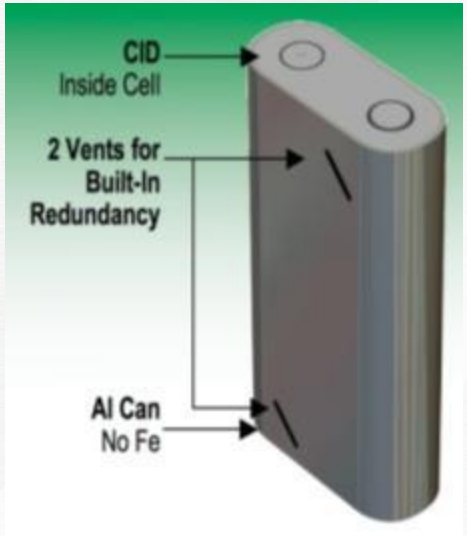
- Plastic or steel housing
- No CID
- Vent in lid
- Many internal connections
- May have poor thermal dissipation

Polymer



- Soft packaging requires mechanical support
- Leakage risk (seals)
- Ballooning upon overcharge
- CID not possible
- Risk of "Dry out" due to uneven stack pressure

Swing Cell

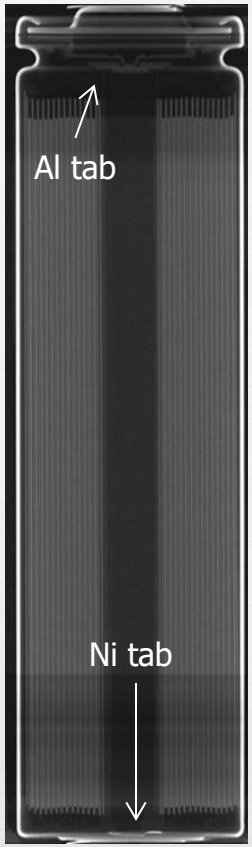


- Laser welded lid
- Aluminum can
- CID
- 2 Vents

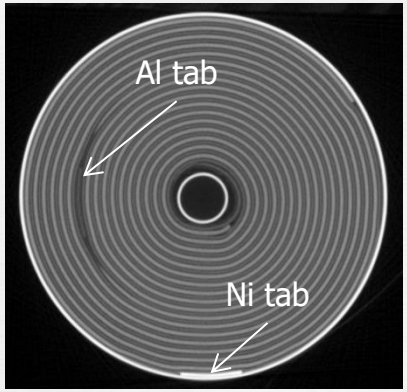
Wound Cell Design (tabs, taping, alignment)

18650 Cell Example

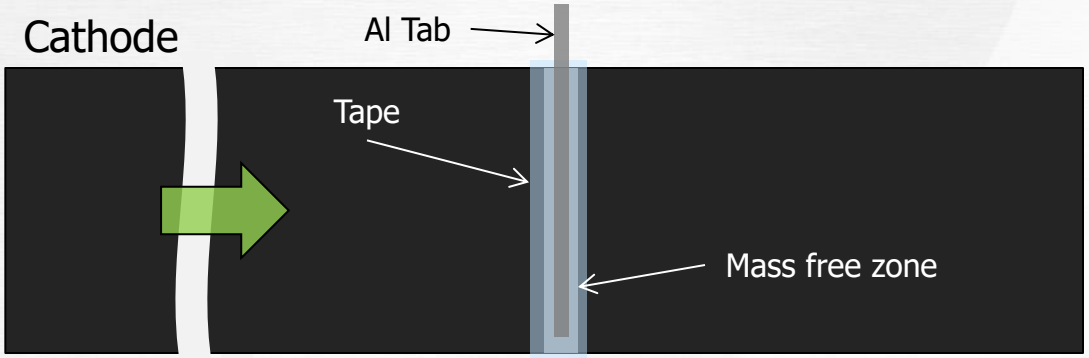
X-ray side view



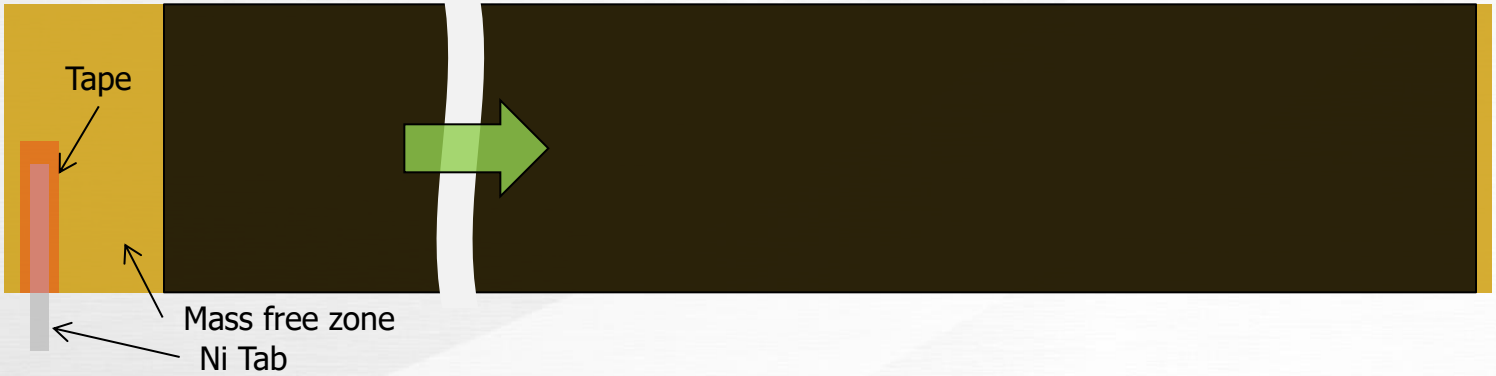
X-ray top view



Cathode

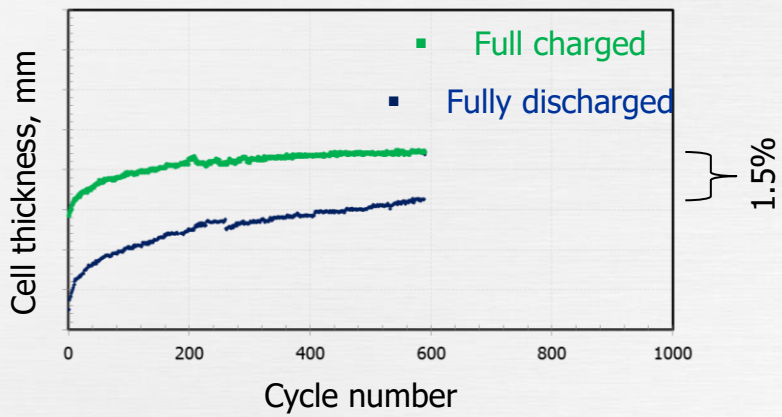


Anode

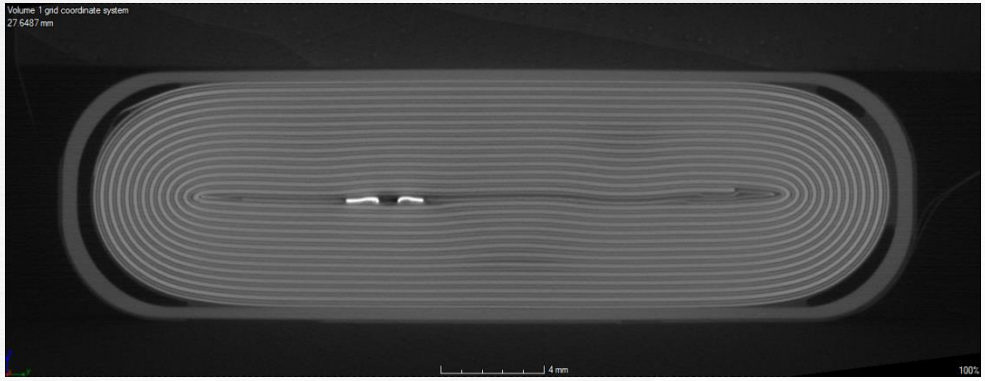


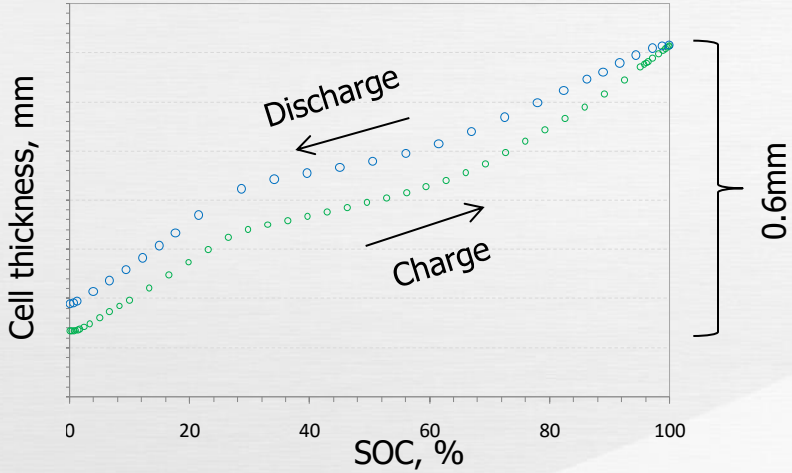
Dynamic structure with cycling

Rigid enclosure exposed to volumetric excursions both within a given cycle and over the cell life

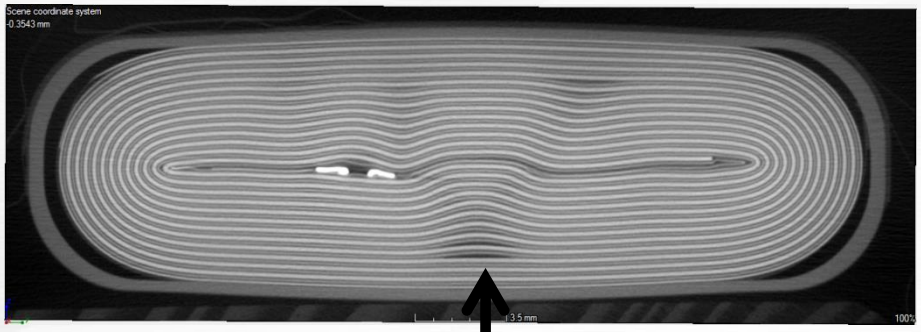


Fresh 103450 cell





After 200 HT cycles



Gaps

Background

Some Basics

Tools to Study Safety

Approaches to Prevent Propagation

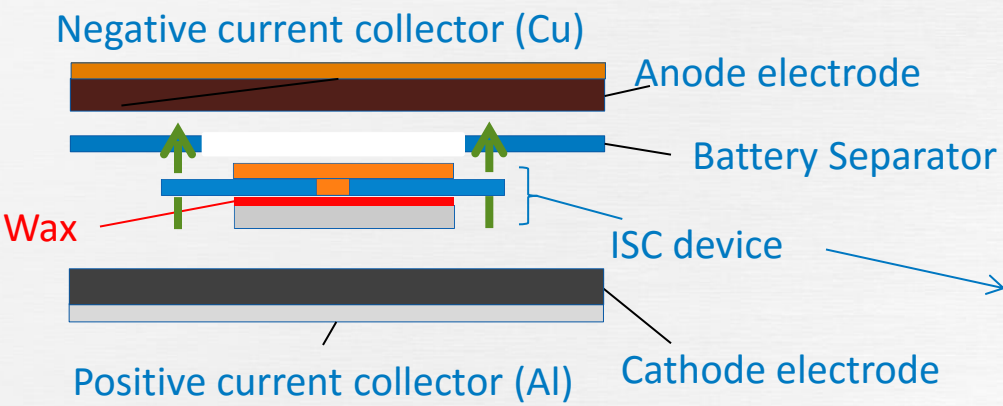
NREL/NASA Internal Short Circuit(ISC)

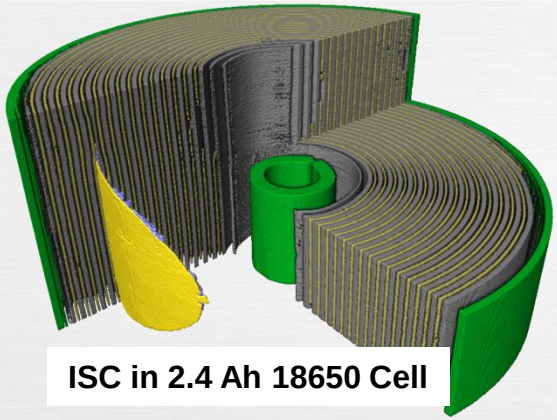
- **Objective**: Establish an improved ISC cell-level test method that
  - Simulates an emergent internal short circuit
  - Capable of triggering the four types of cell internal shorts
- **Motivation**: Current internal short abuse test methods, e.g., crush, nail, overcharge, local heating ..) may not be relevant to field failures
- US Patent#9,142,829
  - NREL – Matt Keyser, Dirk Long, and Ahmad Pesaran
  - NASA – Eric Darcy

2016

- NREL has delivered more than 1000 ISC devices to NASA and partners for the to study of separators, non-flammable electrolytes, electrolyte additives, fusible tabs, propagation, …
- Material for discussion of ISC devices provided by Matt Keyser and Eric Darcy

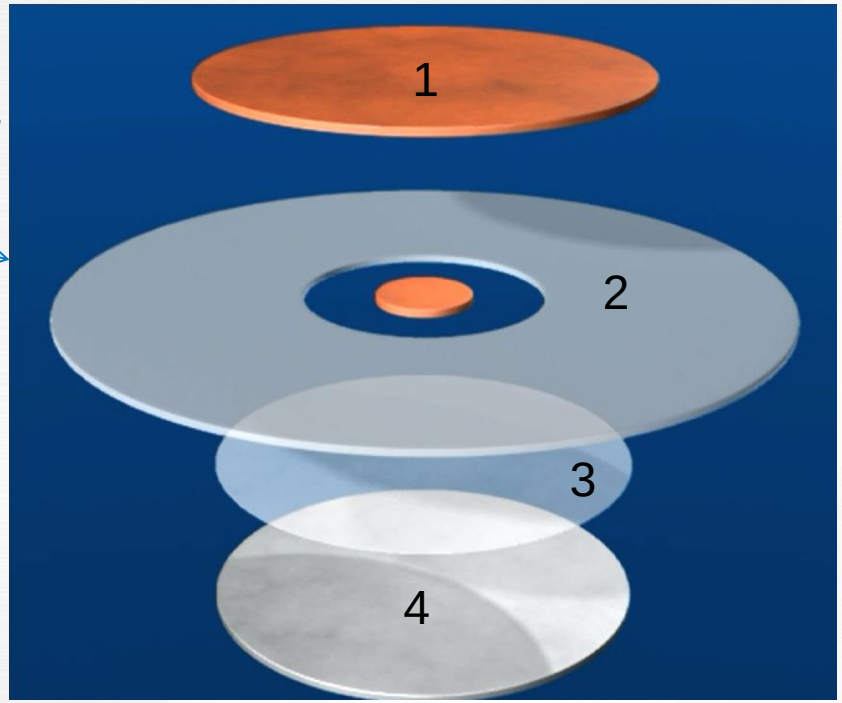
NREL/NASA ISC Design





ISC in 2.4 Ah 18650 Cell

US Patent #: 9,142,189



Top to Bottom:

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

Examples of ISC Results

Type 2 vs Type 4 ISC with Shutdown Separator

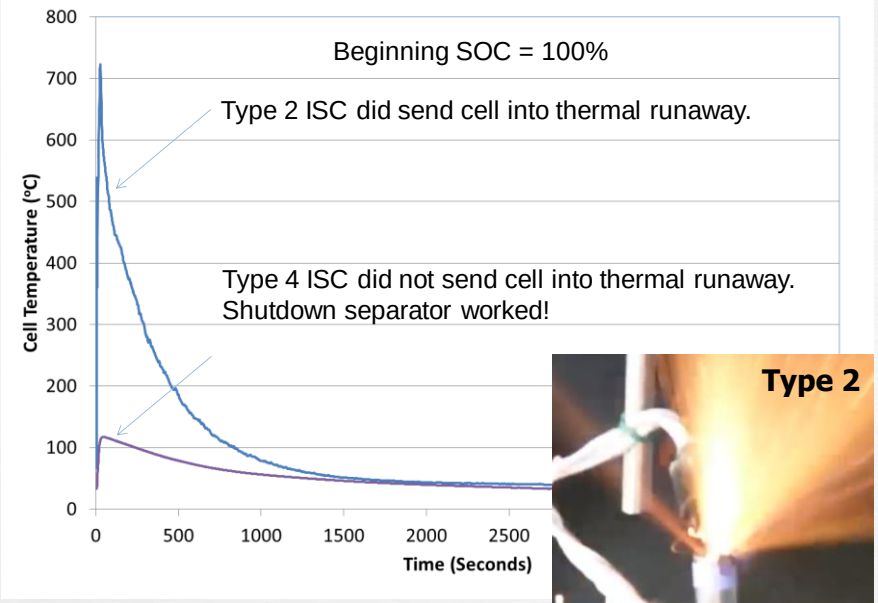
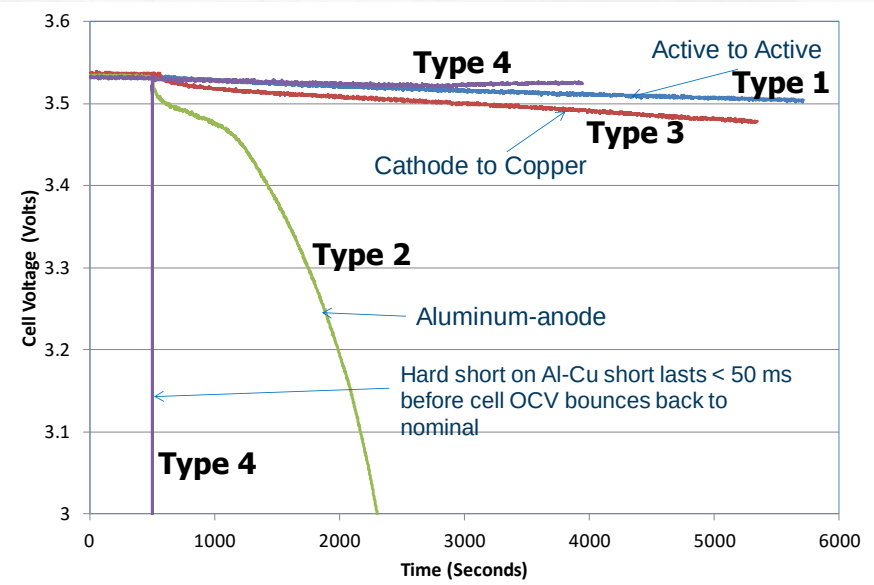


Photo Credit: Eric Darcy, NASA

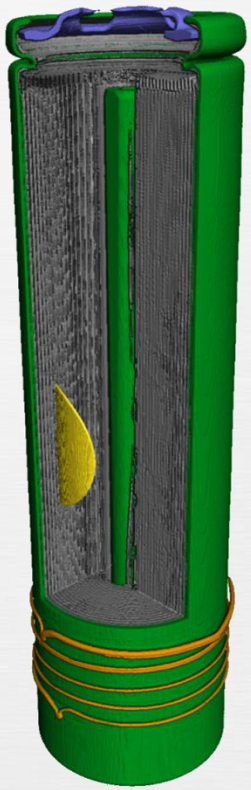
ISC Type Comparison in Dow Kokam 8Ah Cell

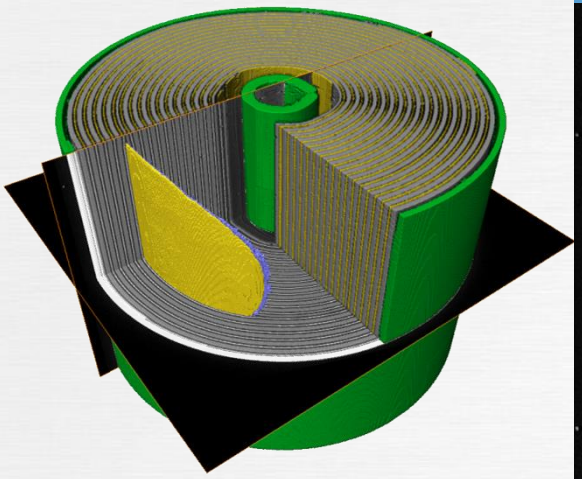


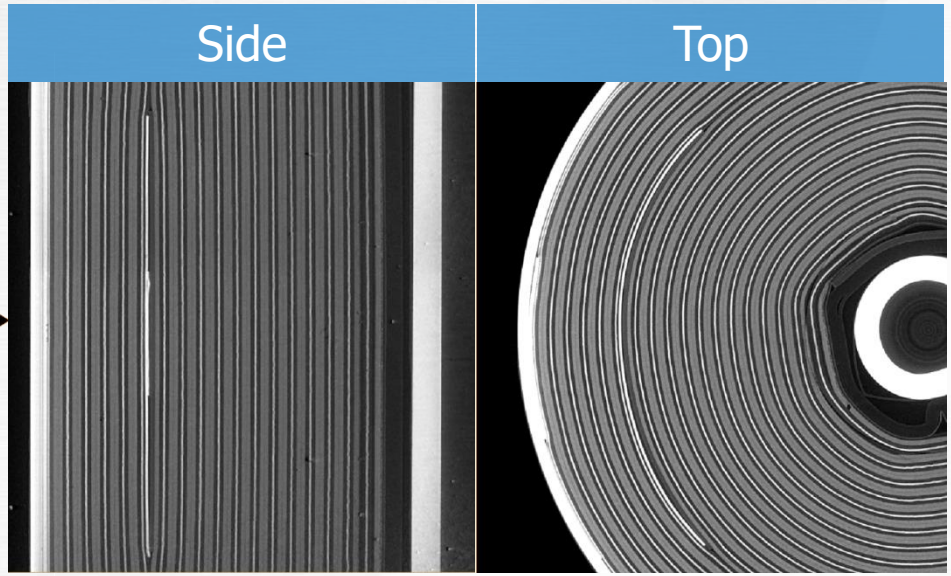
Imaging of thermal runaway events

- Thesis research conducted by Donal Finegan, PhD with advisor Professor Paul Shearing at University College of London (UCL)
- High speed high resolution radiography used to collect 3D images of lithium-ion cells undergoing thermal runaway
- Cells used in thermal runaway study provided by Matt Keyser (NREL) and Eric Darcy (NASA)
- Reference for the material which follows in preparation – D.P. Finegan et al.

ISC devices imbedded in a 18650 cell



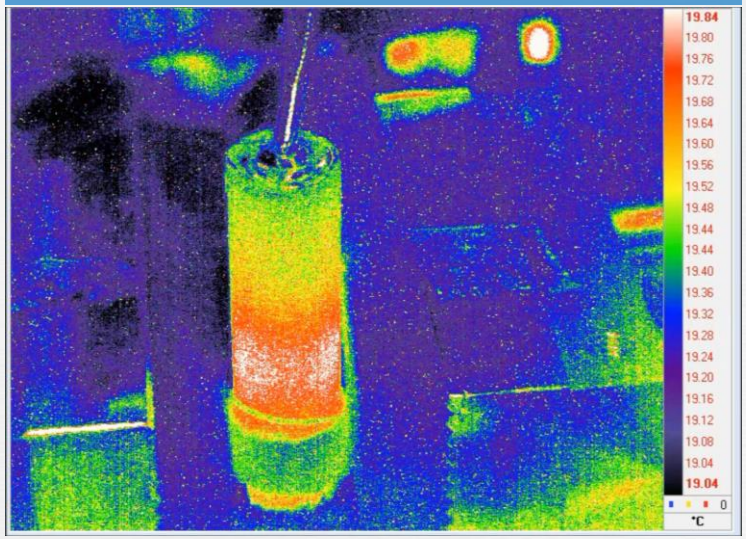




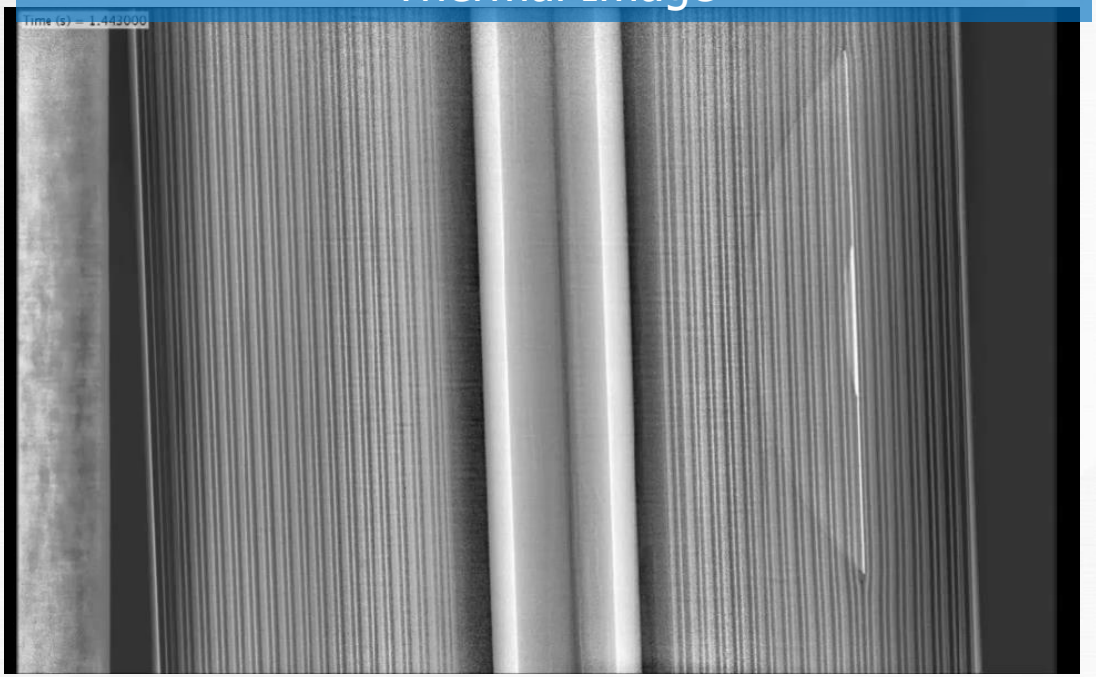
- 3D reconstructions and individual slices showing the placement of the ISC device in the test cell

Imaging of a TR event

Thermal Image

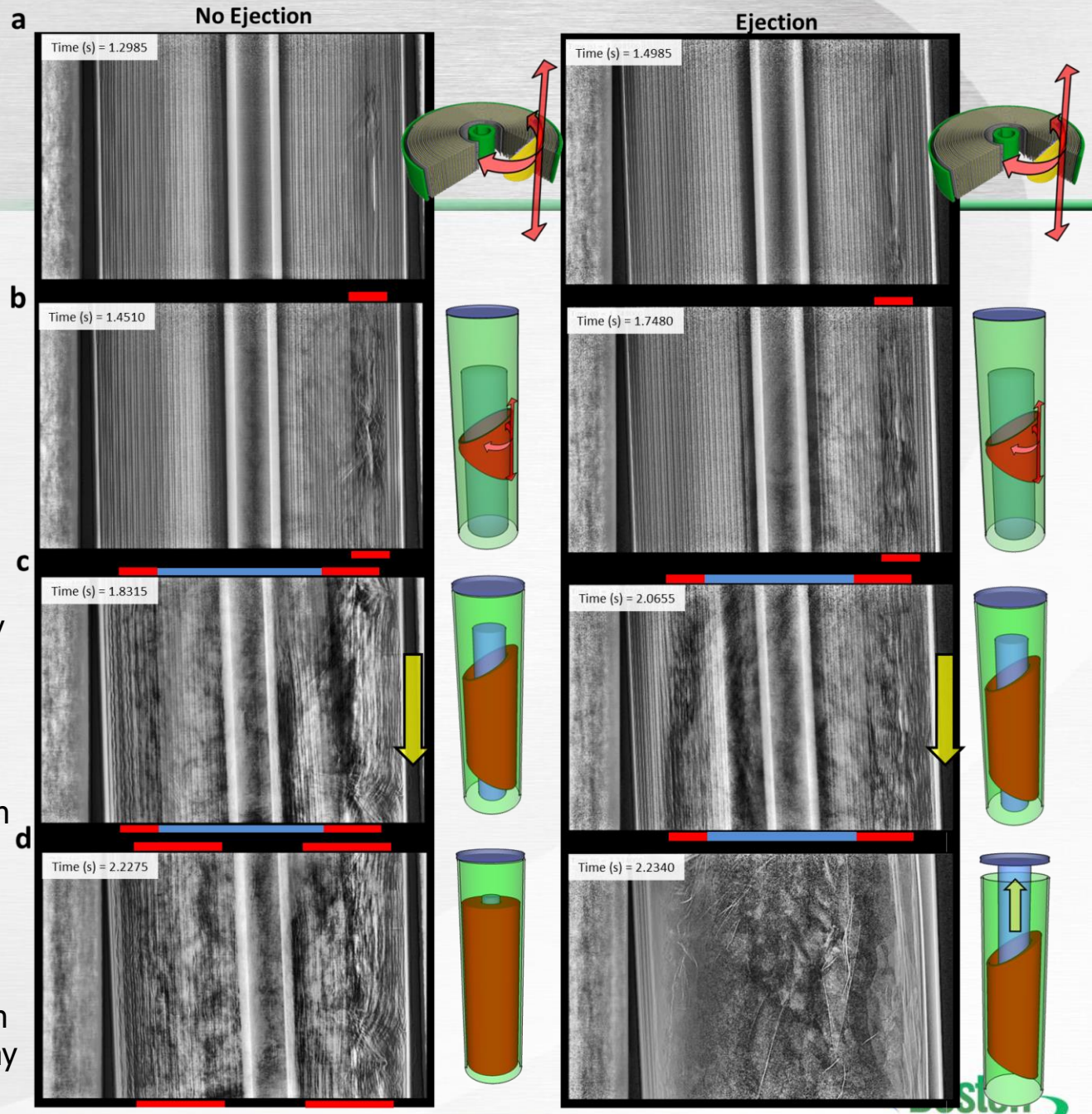


Thermal Image



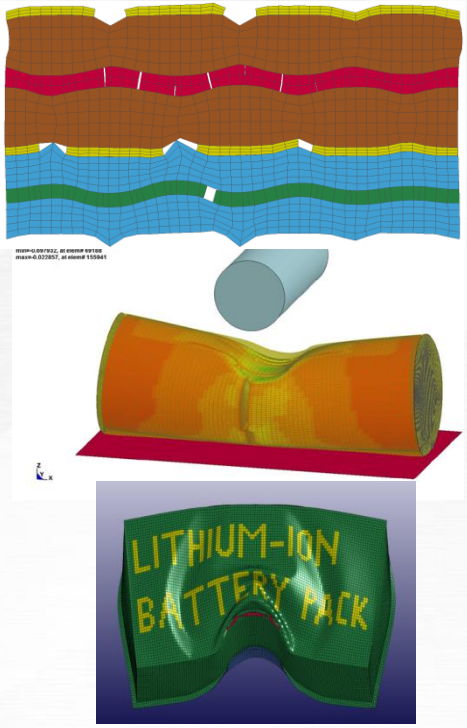
- Simultaneous thermal and X-ray imaging capturing TR initiated with ISC device – less than 60 seconds to "completion"
- Time stamped radiography video taken at 2000 fps at the ESRF (European Synchrotron Radiation Facility, Grenoble, France) beamline ID19

- Propagation occurs fastest in the longitudinal and azimuthal direction
- The red region in the 3D illustration indicates the reaction zone at that time during propagation
- The inner blue cylindrical core is representative of the intact core of the electrode assembly
- The reaction zone creates a fluidized layer (red) around an intact cylindrical core (blue)
- The intact core (blue) can then shift up towards the vent causing clogging, leading to ejection of the contents
- Alternatively, the entire electrode assembly can remain in the cell and thermal runaway continues to completion



MIT Battery Safety and Crashworthiness Consortium

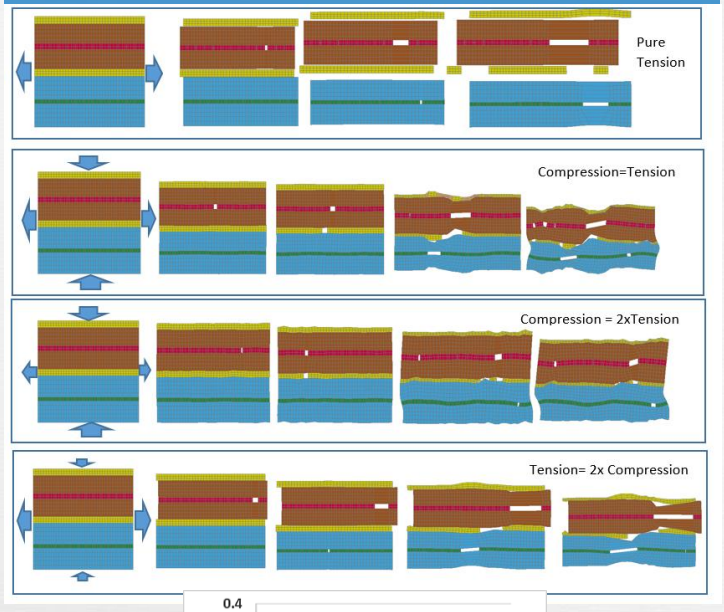
- Goal: Predict internal shorting of batteries during the mechanical deformation of a vehicle crash
  - Determine how much deformation/force a cell can tolerate before forming a short
  - Develop finite element modeling tools (and experimental methods) to
    - Identify best properties for electrode/separator components
    - Design of electrode structure and cell casing (materials and geometry)
    - Design of pack housing, connections, body-in-white(BIW)
- Impact and Crashworthiness Lab (ICL), MIT
  - Director of ICL – Prof Tomasz Wierzbicki (wierz@mit.edu)
  - Co-Director of ICL Battery Consortium – Prof Elham Sahraei (elhams@mit.edu)

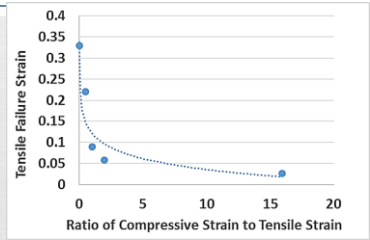


Prediction of Material and Cell Failure

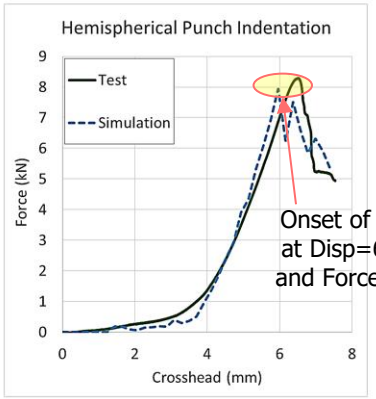
- Representative Volume Element (RVE) micro model developed to study various loading scenarios and component properties (friction between layers, layer thicknesses, …)
  - 0.307mmx0.307mm section of electrode/separator stack

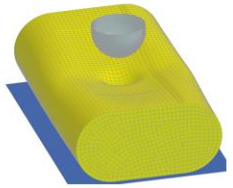
RVE

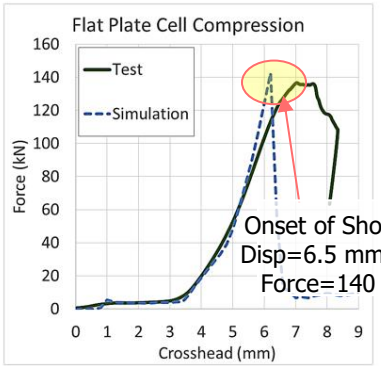


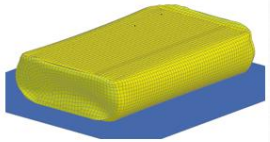


Macro Model



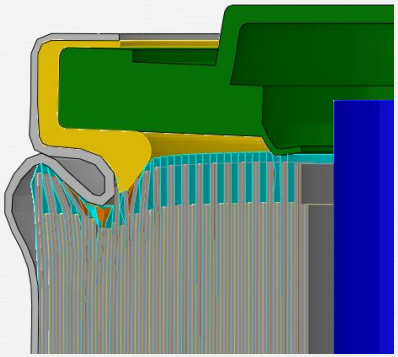




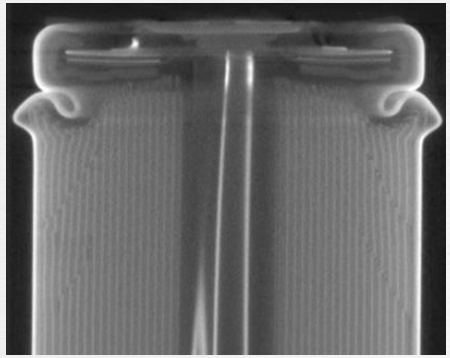


Elham Sahraei

FEM of Axial Compression of 18650 Cell

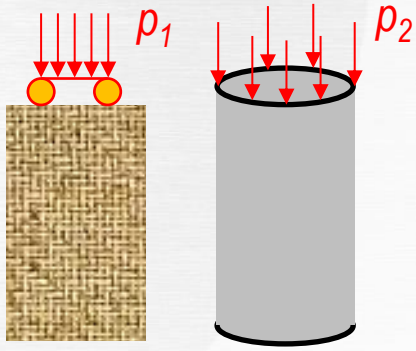


Finite Element simulation



Micro CT scan

Battery tests and disassembling



Analytical solution

- 3 mm intrusion deformed the crimp region of the lid-seal seal fracturing the separator resulting in an internal short
- Clarified the sequence of axial compression – mechanisms at different deformation stages
- Modeling performed by Juner Zhu (MIT ICL PhD student)

Background

Some Basics

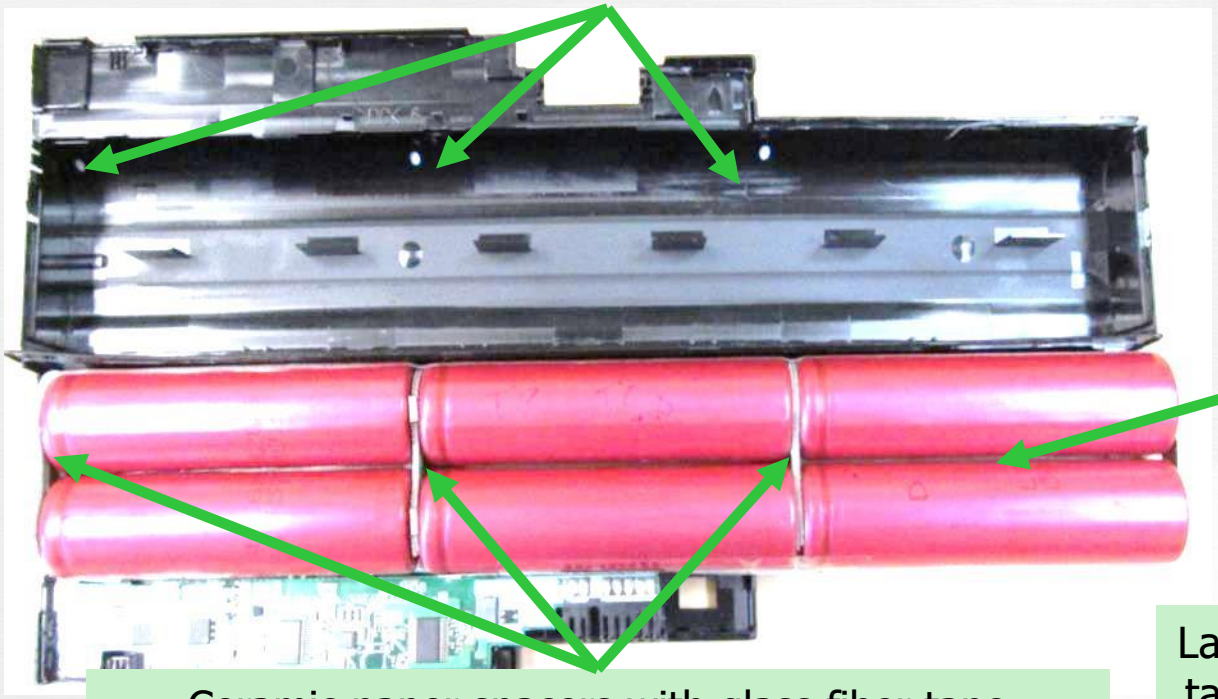
Tools to Study Safety

Approaches to Prevent Propagation

Lessons* from laptop pack designs (2004)

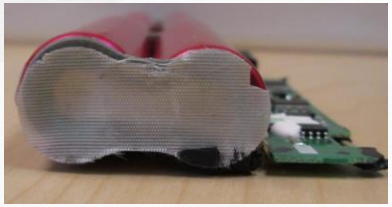
Openings in plastic housing facing computer

Ceramic spacers between cells act as **heat barriers** and combined with hidden housing openings under label **redirect hot effluent** into computer



1mm space between cells **reduces heat conduction** between cells to reduce propagation

Ceramic paper spacers with glass fiber tape



Layer of glass fiber tape beneath cells redirects effluent away from bottom of battery pack and end user

* P. Partin, Director of Product Development, Boston-Power

Pack Safety Integration

Safety Layer	Description	Key Elements
1 Prevention	Prevention of a failure by addressing root causes. Should prevention fail, move to:	• DFMEA and Fault Tree Analysis • Robust battery management system BMS • Battery thermal management BTM • Crashworthiness design • Pack-level short circuit protective fuse
2 Detection & Counter Measures	Provides early warning of a failure, and initiates active counter measures. If counter measures fail, move on to:	• BMS fault detection and countermeasures
3 Containment	Containment of the failing component to avoid cascading of the problem into a sub-system safety incident. If containment fails, then move to:	• Module-level Thermal Pulse Barriers • Cell-level Fusing (fusible-links)
4 Damage Limitation	Prevent collateral damage by limiting damage to the failed sub-system itself. If limitation fails, then move to:	• Pack-level Firewalls • Pack controlled exhaust system (PACE)
5 Evacuation	Provide time and means for vehicle occupants and bystanders to safely evacuate/escape	• Pack Enclosure Design and Construction Material • Thermal Shield between pack and vehicle

Battery Management in Safety

- Monitoring of cell voltage, temperature, and current/power **LIMITS**
  - Overcharge (max voltage (>4.2V), time limit on charging, temperature)
  - Overdischarge (min voltage (<2.75V) during discharge, low OCV)
  - Low temperature charging limits on I and V
  - High temperature limits on charging and discharge
- Fault Detection
  - "An opportunity for innovation"
  - Internal shorts
    - Increase self-discharge rates – observed as ΔOCV or increased balancing current to that cell
    - Cell impedance << Internal Short
    - Large parallel arrays further complicate detection of single cell fault
  - Warning time of a short may be extended or very limited, i.e., on the order of minutes

Fault Levels and Counter Measures

Fault detection is an important function of the battery management system

FAULT CATEGORY	DESCRITPION	COUNTER MEASURE EXAMPLES
WARNING 	One or several battery pack parameters are outside of the design specification	Battery pack can still operate safely without restriction, but the vehicle should be brought in for inspection
ALARM 	One or several battery pack parameters are at a level that could compromise safety	The pack can operate with power limitation (limp home mode), but cannot be restarted / recharged after the vehicle has been stopped
EMERGENCY POWER-OFF (EPO) 	One or several battery pack parameters are at a level that presents an immediate and significant safety concern	The BMS alarms the vehicle operator to stop the vehicle and then disconnects the battery. The vehicle cannot be restarted or recharged after the battery has been disconnected

Controlling Propagation

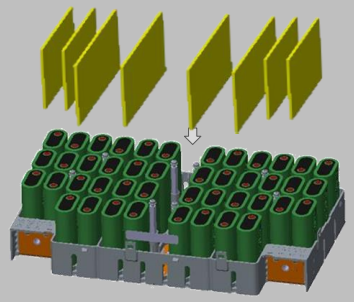
- **Containment**- Keeping adjacent cells below target temperature is critical
  - Thermal barrier – spacing or thermal barrier material (cells expand)
  - Conduct heat away
    - Heat sink (passive) – metal or plastic mass
    - Active cooling – liquid channels, heat pipe with fan
  - Redirect hot ejecta (gases, flame, liquid) away from adjacent cells
    - Are vent(s) reliable? Or do random can wall ruptures occur?
  - Fusing to prevent shorting of adjacent parallel cells (xP) and heating
- **Damage Limitation**
  - Firewalls
  - Suppression – put out flame and cool system with "water"

M Keyser, E Darcy, Driving Factors for Achieving Safe, High Performing Li-ion Battery Designs, More Electric Aircraft USA, Seattle (August 2016)-

Containment – Thermal Pulse Barrier

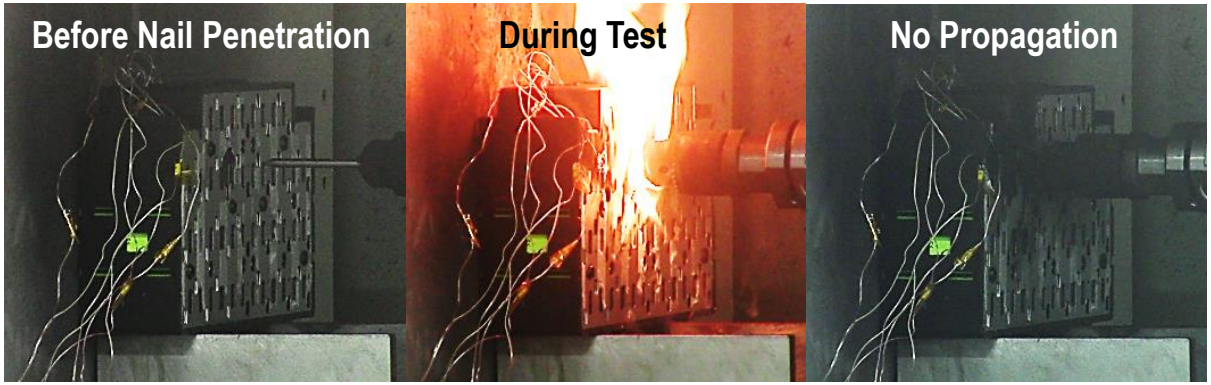
- Thermal pulse barriers can help protect against propagation
- The design employs automotive grade thermal barrier material between neighboring cells

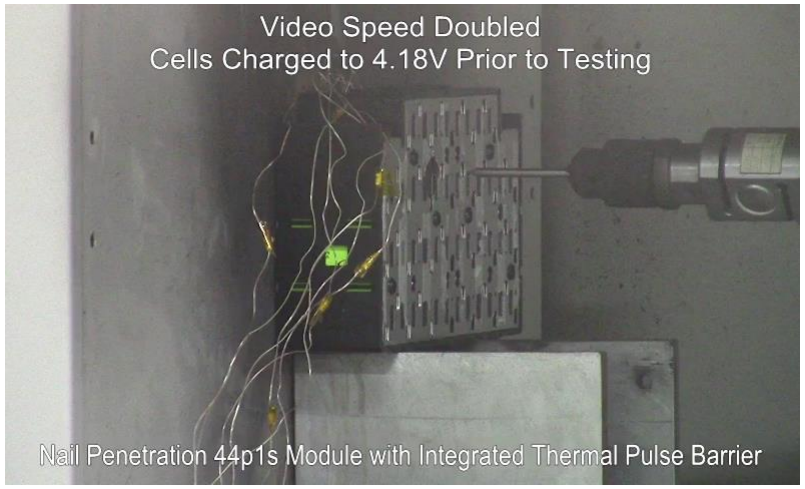
Thermal Barrier Material



0.85kWh (44p1s) Module

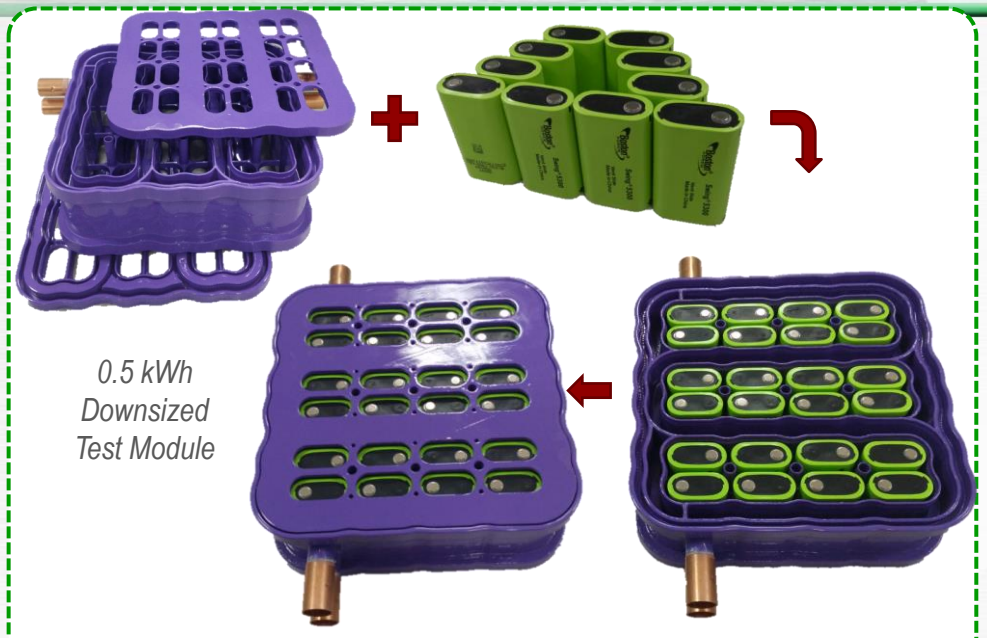
Nail Penetration Testing of Module



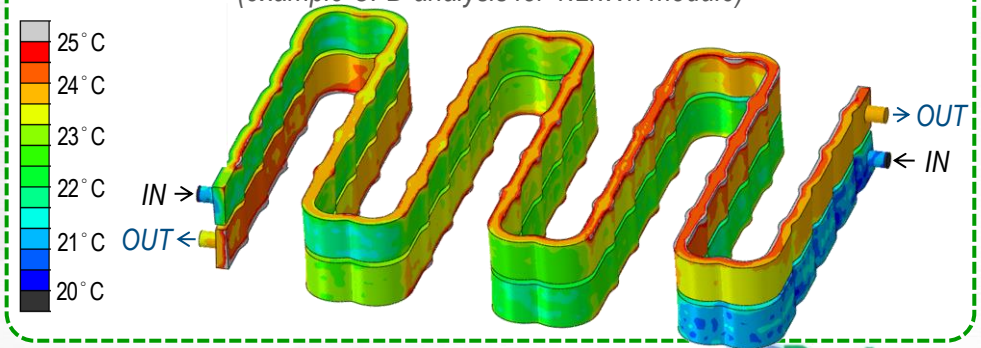


Containment - Heat Dissipation

- Unique cell-module design with cooling jacket integrated in high-tech polymer module housing
- Joint development program with Covestro AG* (Germany based world-leading supplier of high-tech polymer materials)
- Numerous thermal management benefits, but the design effective at stopping propagation in preliminary tests



Dual cooling-jackets counter-flow design for thermal uniformity (example CFD analysis for 1.2kWh module)

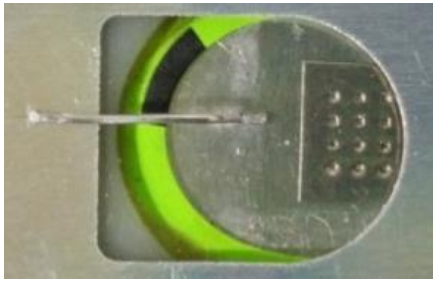


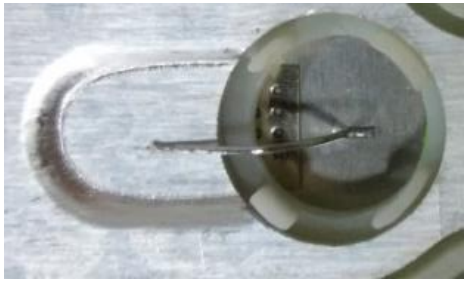
* *Covestro AG was formerly the Material Sciences Division of BAYER AG before being spun off as a separate company in October 2015*

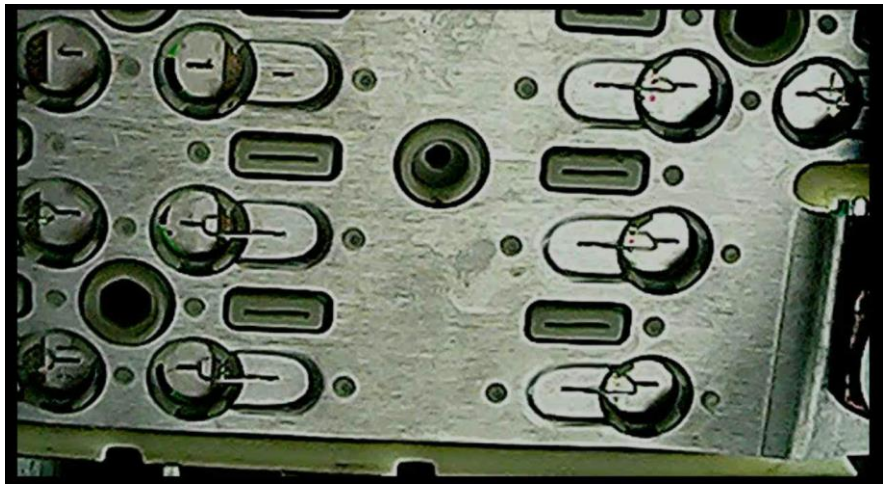
Containment – Fusible Link Connections

- Wire-bonded aluminum wire provide overcurrent fuse for each cell in a parallel array
- Protect against local, module or cell short circuits
- Prevents inrush from neighboring cells thereby suppressing cell-to-cell cascading
- Cost savings and increased automation compared to conventional nickel-tab designs

Overcurrent Fuse for Each Cell

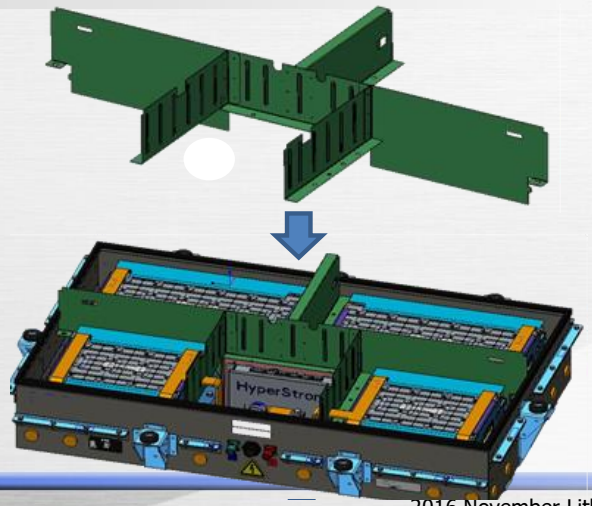






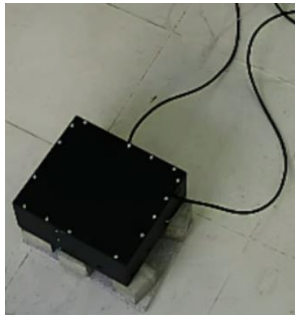
Damage Limitation–Firewalls and Exhaust

- Firewalls can help contain a thermal incident within a section of the pack
- Pack controlled exhaust system (PACES) allows hot gases and combustible material from the affected section to vent away from the pack
- Suppression with a liquid media is also an option which can extinguish the fire and cool the system



Scaled-down Pack Testing of Firewalls and PACE

Scaled-down Pack before Thermal Runaway (TR)

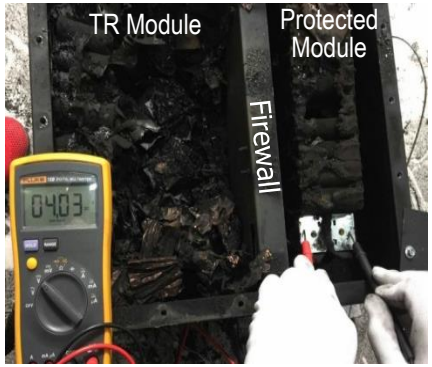


PACE vents heat away and firewall shields rest of pack

After TR, no propagation and enclosure intact

Before:
Both Modules at 4.1V

After:
Protected Module 4.03V



Acknowledgements

- Boston-Power
  - JR Linna
  - Phil Partin
- NASA
  - Eric Darcy
  - Sandeep Yayathi
- NREL
  - Matt Keyser
- MIT
  - Elham Saharei

Thank you!

Eric Carlson
ecarlson@boston-power.com