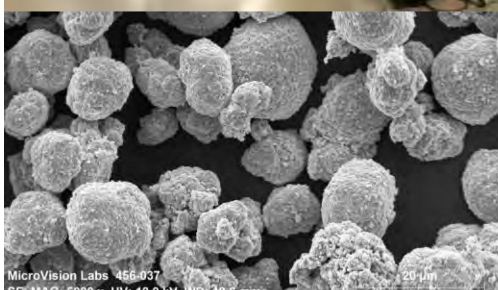
Lithium-ion Cell Internal Shorting:
1. Early Detection
2. Simulation



Battery Safety Council Forum 3
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For more information, contact
Brian Barnett at:
brian@camxpower.com
Mobile: 978-884-2220

CAMX Power
35 Hartwell Avenue
Lexington, MA
02421-3102

www.CAMXPOWER.com

These major activities at our company over the last decade have laid the foundation for our perspective that thermal runaways can be prevented and/or managed.

- Detailed post mortems of multiple Li-ion battery safety incidents.
- Investigation of mechanism of internal short formation and growth.
- Implantation of >1000 cells with small metal particles, monitoring short formation, growth, progression to thermal runaway.
- Development of FEA model, with heat transfer, subsequently with validation of model via wind tunnel measurements.
- Methodologies to trigger thermal runaway and to study cascading effects.
- High speed photography and data acquisition investigation for hard short formation (e.g., nail penetration) under a variety of conditions.
- Development of BMU technologies such as active cell balancing (licensed to major US electronics company, Analog Devices).

Early Detection:
Internal Short Detection Technologies

Some Perspectives on Battery Safety

The question of managing lithium-ion battery safety comes down to answering these questions: what are the triggers and how can they be managed?

Trigger	Why can this occur ?	Is this managed ?
Overcharge	Defective connections, failure of charging circuit	Yes, battery management system Yes, cell-level safety devices
Overheating from external sources	Battery pack placed too close to a heat source	Yes, cell-level safety devices open the cell at suitable internal pressure
Cell crushing creating massive internal shorts	Physical abuse of battery pack	Yes, design enclosures are built more tolerant to specific abuses
Internal short-circuits (a.k.a., field failures)	Internal-short caused by manufacturing defects	No (new technologies needed)
Cascading of thermal energy release	Affected cell can raise the temperature of surrounding cells	No (new technologies needed)

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Li-ion battery packs *can* be made inherently safe, with minimal impact on weight and volume, by developing key safety technologies.

Pre-emption
(Avoid thermal runaway)

Detection
(Warn of potential failure)

Intervention
(Stop thermal runaway)

Containment
(Minimize damage)

Fail-safe pack with minimal impact on weight, volume, and cost

Validation
(Because actual failures in the field are so rare, CAMX Power has been developed methods to generate “similar” internal short circuits - “Field Failure on-demand”).

CAMX Power has developed two different detection technologies capable of detecting developing internal shorts at levels well before they progress to thermal runaways, so actions can be taken to prevent safety incidents.

Pre-emption
(Avoid thermal runaway)

Detection
(Warn of potential failure)

Intervention
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Fail-safe pack with minimal impact on weight, volume, and cost

Validation

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CAMX Power has developed and demonstrated multiple intervention approaches which, activated after short detection, prevent thermal runaways.

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(Avoid thermal runaway)

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↕

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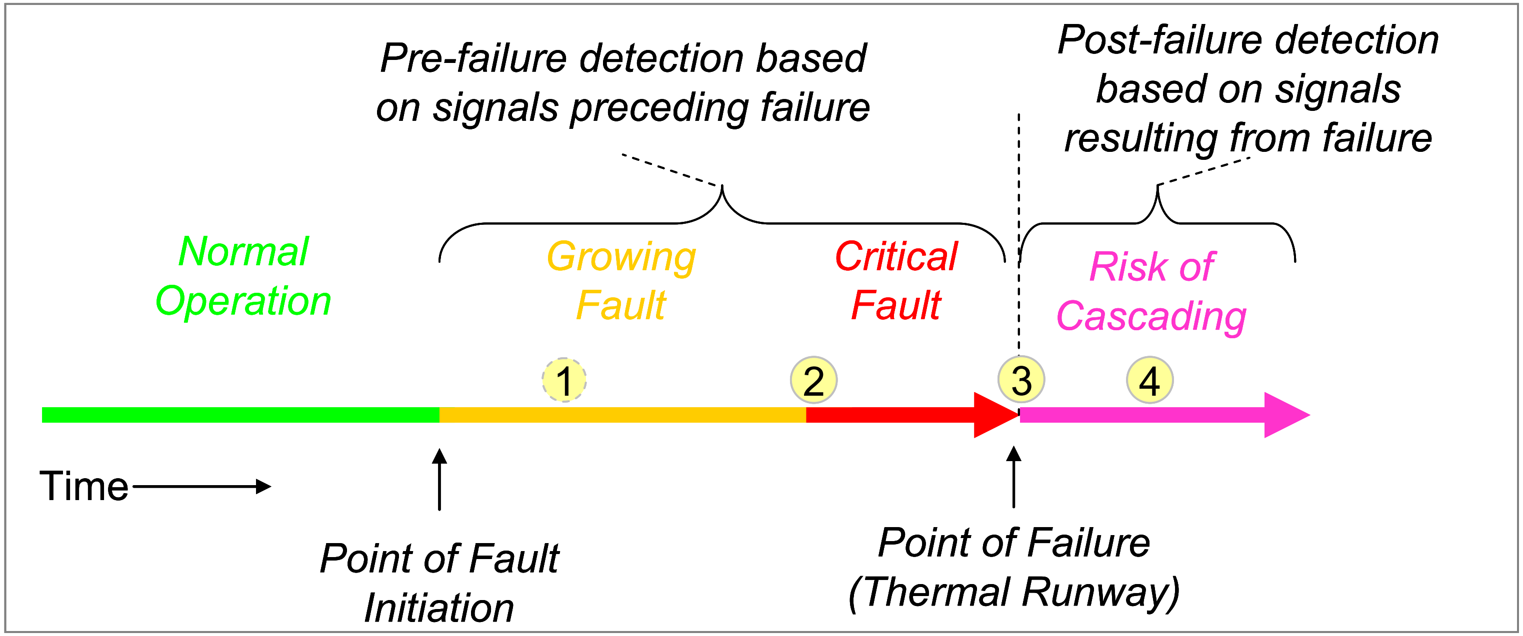
(Because actual failures in the field are so rare, CAMX Power has been developed methods to generate “similar” internal short circuits - “Field Failure on-demand”).

Challenges Associated with Internal Short Detection

Fault warning based on detecting smoke, particulate matter, or VOCs may not provide sufficiently early warning to deploy effective intervention strategies.

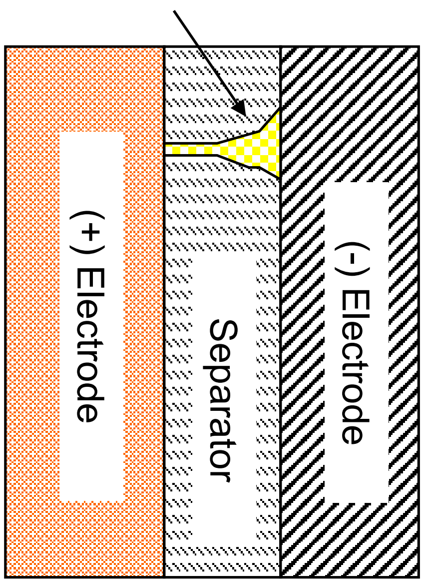


- More often than not, these signals come after the most serious failure has already commenced (i.e., stage 4 in the figure).
- *Our approach is based on delivering warning in advance of a failure by detecting signals associated with a growing internal fault in a cell.*

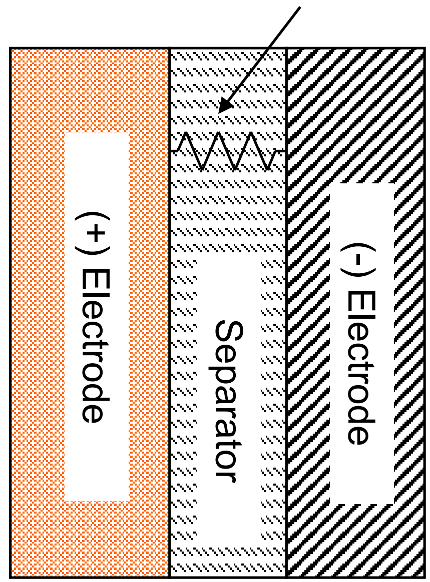
The use of external load resistances to simulate an internal short can be understood from the equivalent circuit for an internal short circuit between electrodes of a cell:

Conducting structure (e.g., dendrite) introducing electronic conductivity (short) between electrodes

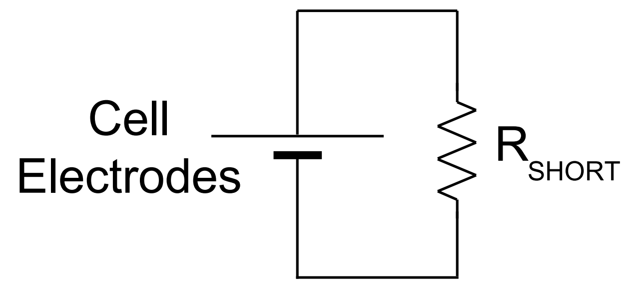
The internal short creates a connection between cell electrodes of resistance R_{SHORT}



(a) Example of an internal short: a dendritic metallic bridging structure



(b) An internal short represents a resistive element connecting the cell electrodes.



(c) The equivalent circuit shows how a resistance across the cell terminals replicates an internal short of that resistance. This equivalency holds as long as short resistance is large with respect to cell internal resistance, a condition met by five to seven orders of magnitude or more for the resistances we have presented in testing.

The resistance of a growing internal short is virtually invisible against the internal resistance of the cell, with which it sits in parallel.

- A 1000 ohm short in a 18650 cell of typical 50 milliohm resistance, changes the resistance presented at the terminals to 49.998 milliohms, a change far smaller than temperature, SOC effects, etc.

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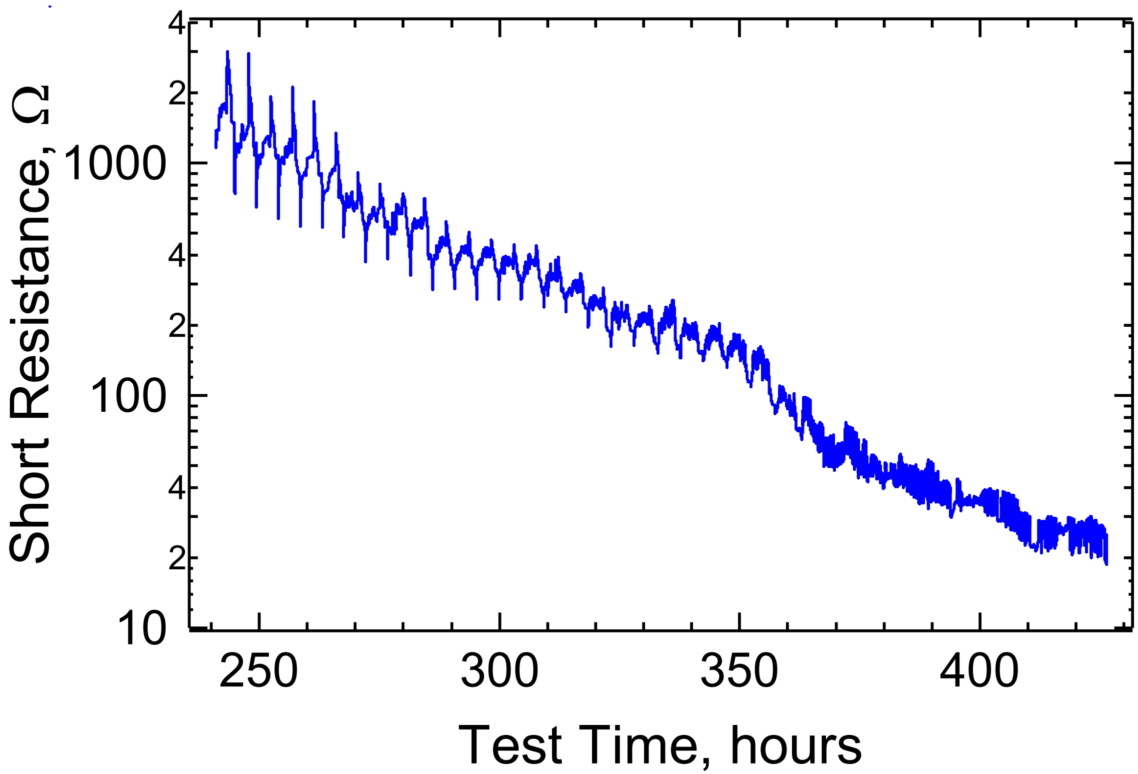
- In, for example, a 1 milliohm PHEV cell, a 1000 ohm short changes the internal resistance to 0.999999 milliohms.

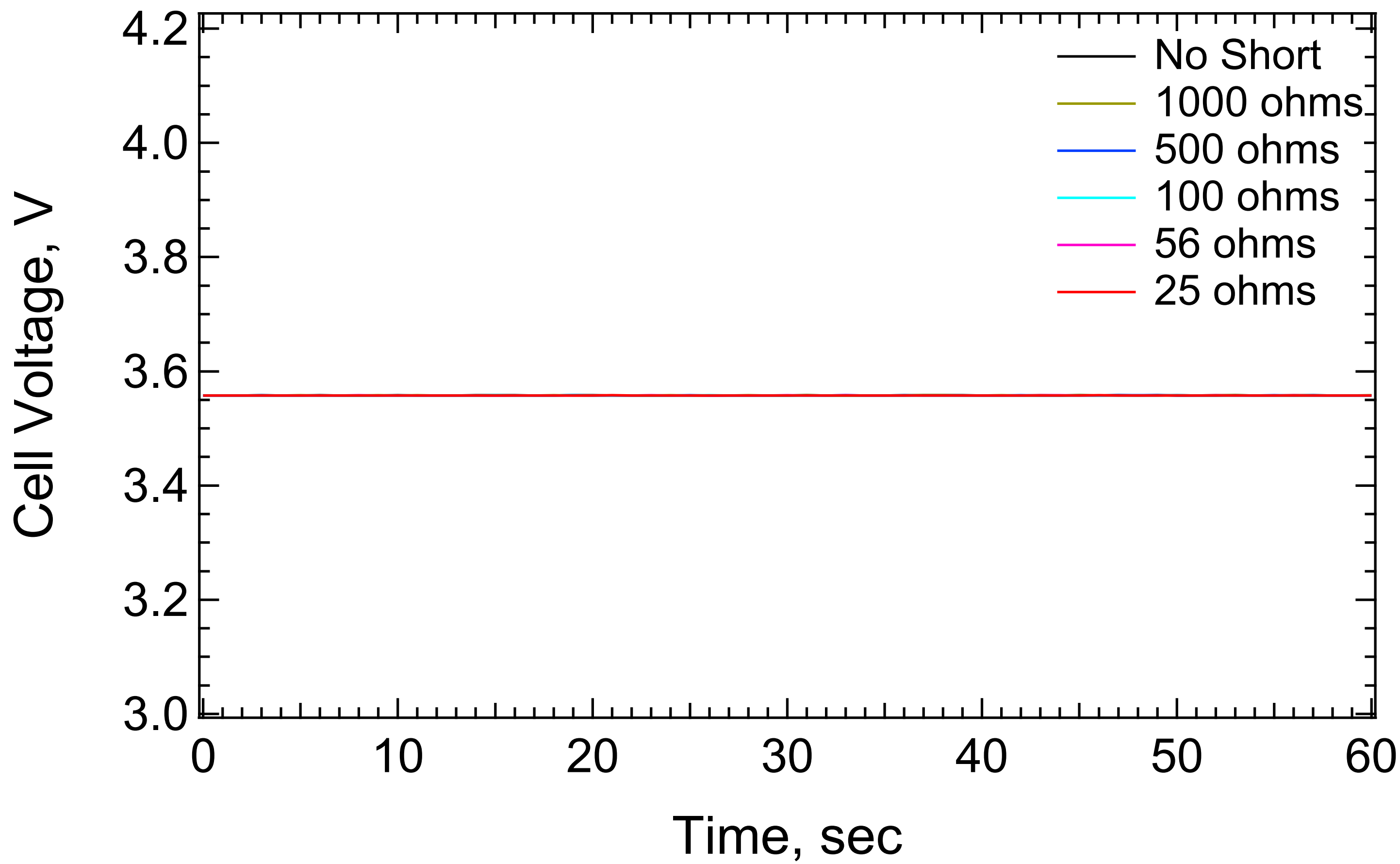
An internal short may develop over multiple cycles and/or over a long period of time, remaining virtually invisible to battery management for most of its life.



Characterization of an internal short produced in a lithium-ion cell in CAMX Power labs by implantation of a metal particle, monitored as it grows through multiple charge-discharge cycles using CAMX Power internal short detection technology.

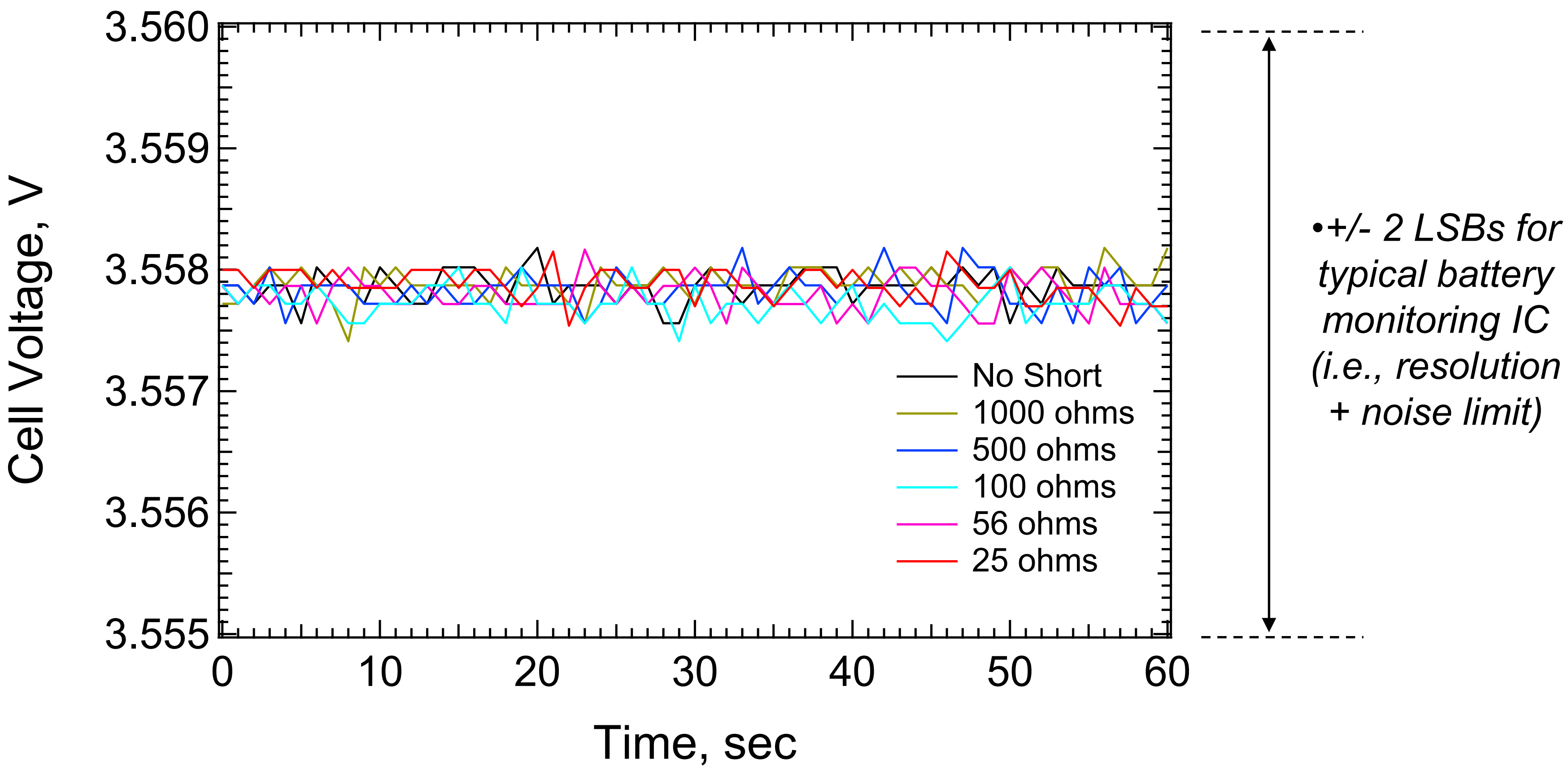
- *Short resistance is initially >1000 ohms, at detection threshold, giving rise to only a few milliamps of current – a level extraordinarily difficult to discern from the currents of normal charge and discharge in cells, which are three orders of magnitude larger.*

Voltage monitoring (battery cycler with 16 bit resolution) is too insensitive to rapidly detect internal shorts.



Any effects of the shorts on cell voltage are indistinguishable from the no-short condition: the six voltage traces overlap.

Detail of voltage traces shows that any differences resulting from shorts are below limits imposed by measurement resolution and noise. Typical BMS ICs are a factor of 16 *less* sensitive.



Note that identifying a trend in voltage indicative of an internal short requires more than observing just a one-bit-above-noise-floor change.

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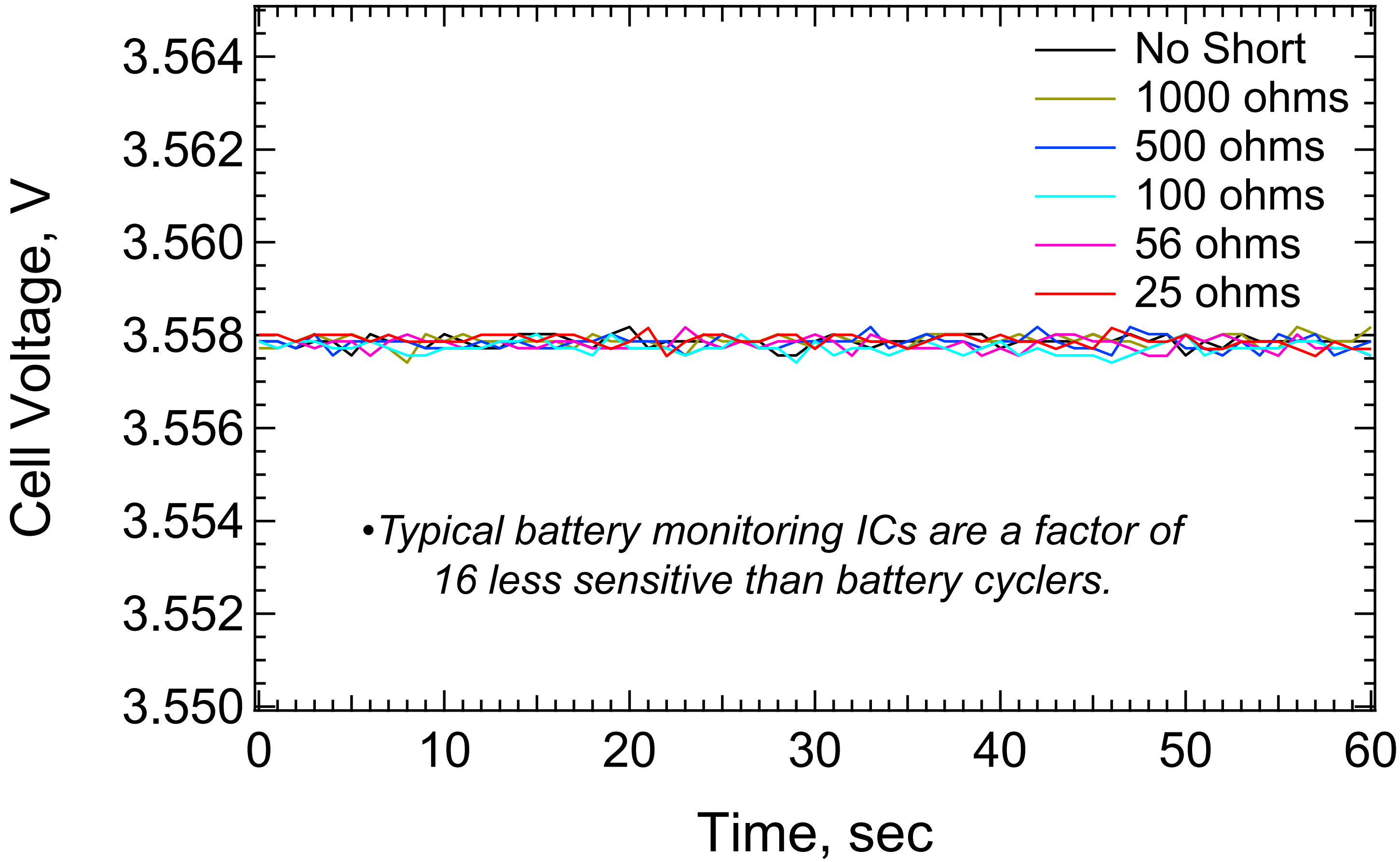


Rapid detection of internal shorts requires a different, significantly more sensitive detection technique.

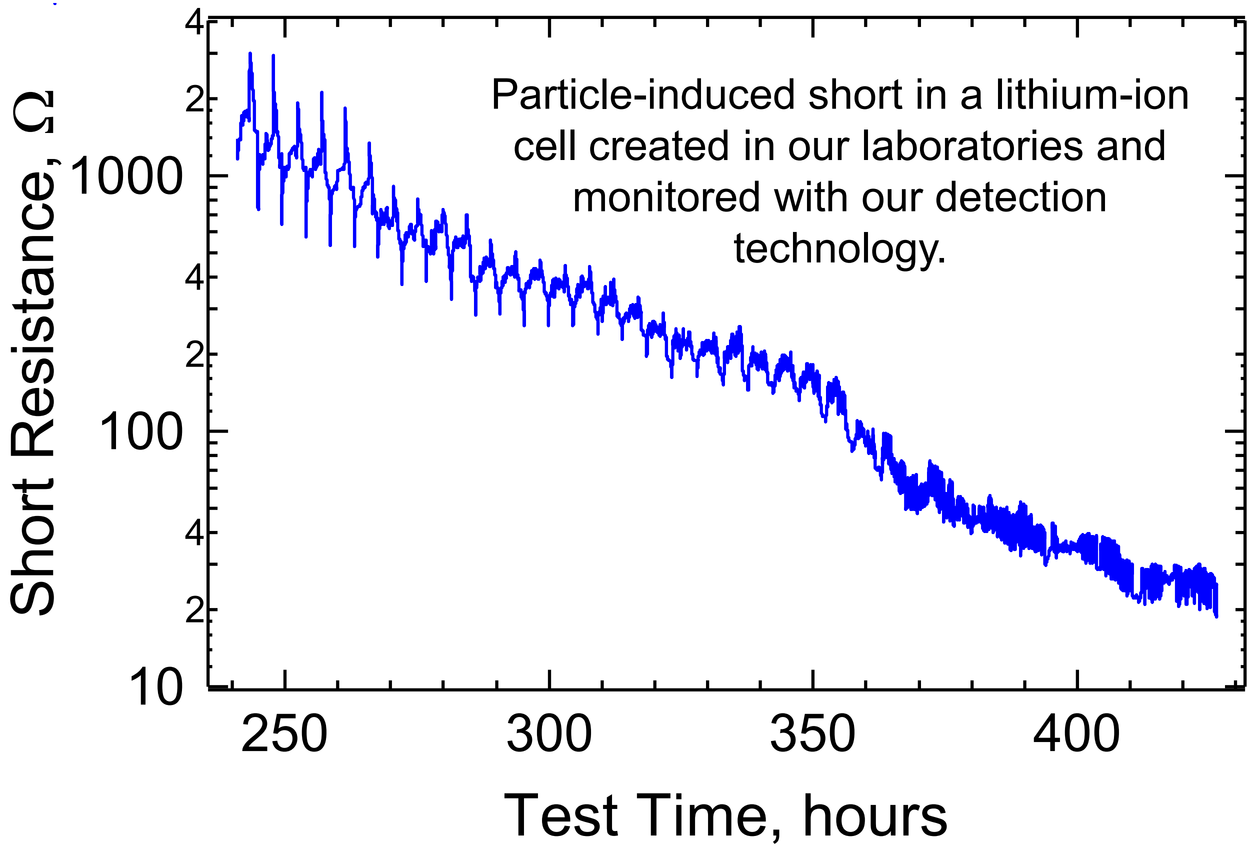
Typical approach for cell voltage monitoring at rest to infer the presence of short is not suitable for rapid, advance detection of growing internal shorts.

Magnitude of the short resistance	Time needed to make an unambiguous determination of short presence in a 25 Ah cell		
	Typical BMS IC*	CAMX Power Short detection technologies	
		Universal Technology	Real Time Technology
1000 Ω	26-42 hours	300 seconds	Real time
100 Ω	2.6-4.2 hours	30 seconds	Real time
10 Ω	0.26-0.42 hours	20 seconds	Real time

* Time required to acquire data to 10X minimum resolution (e.g., enough data to allow assessment /quantification of rate of voltage change) assuming ideal, noiseless performance. Real performance of BMS ICs may yield slower detection results. Voltage measurement resolution based on examples of typical BMS ICs from major manufacturers. Voltage resolution range used in calculation was 0.376-0.61 mV (specified for two different major commercial BMS products).

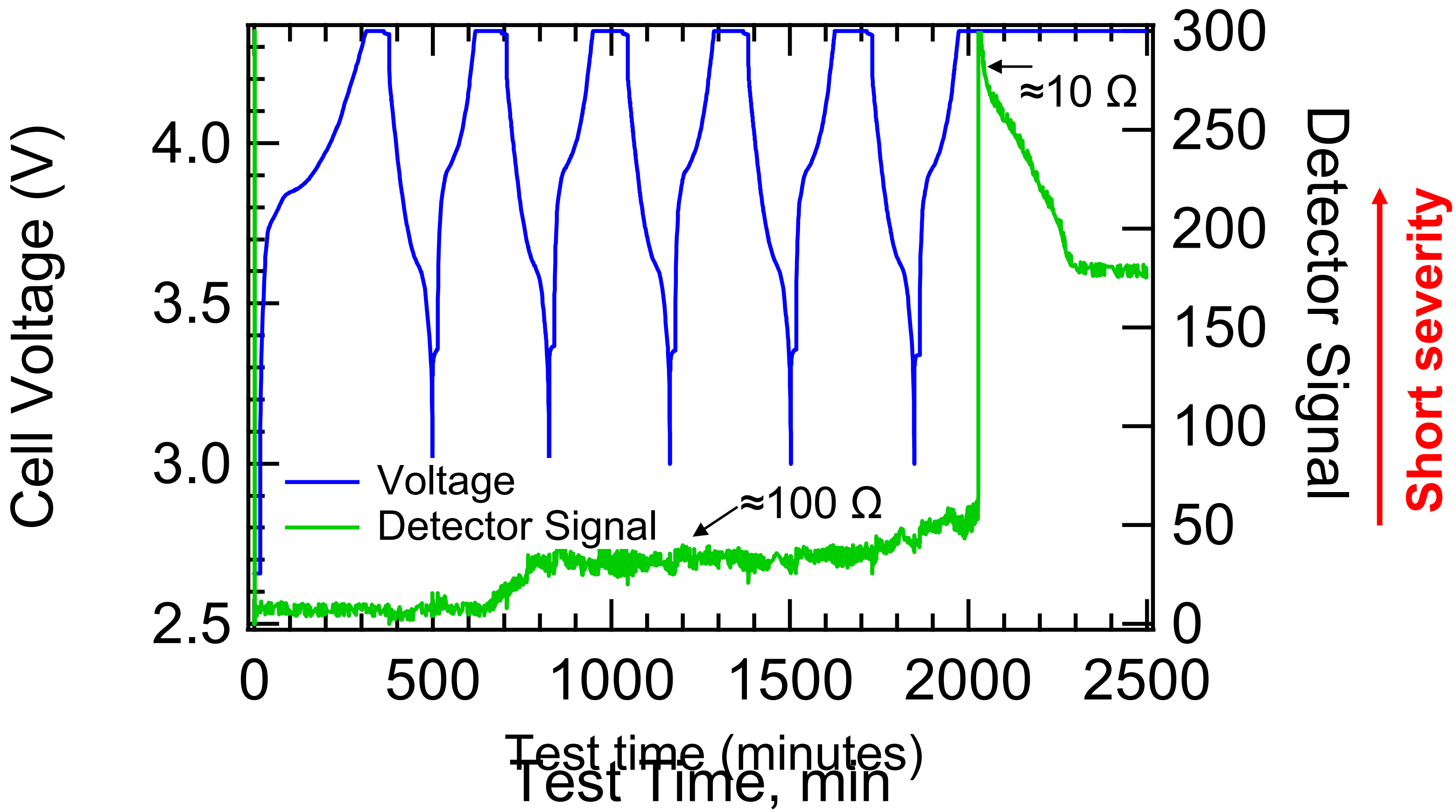
Dynamics of growing internal shorts and the need for early detection

An internal short may develop over multiple cycles and/or over a long period of time, remaining virtually invisible to battery management for most of its life.



➢ ***The short is present and growing long before reaching dangerous levels. Modeling work we have carried out, and experimentally confirmed, places the threshold for thermal runaway in an 18650 cell at approximately 4Ω.***

As internal shorts grow in severity, they can undergo sudden, sharp increases in magnitude, posing immediate risk of thermal runaway.



➢ ***Detection of internal shorts while they are still small affords opportunity for productive intervention to avert a thermal runaway.***

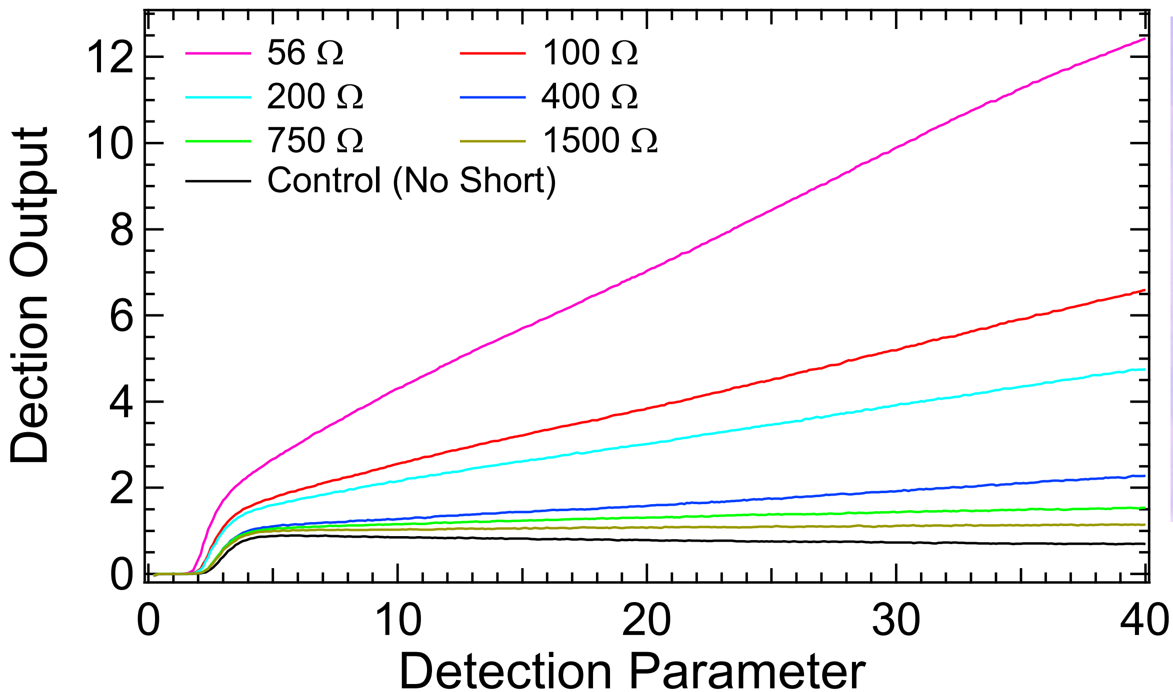
Technologies for Internal Short Circuit Detection in Li-ion Cells and Packs

CAMX Power has developed two different technologies for detection of internal shorts: both are non-invasive, cell chemistry-agnostic, and tested (to-date) from -30 to +55°C.

- Universal Detection Technology
  - Low cost, works for any cell configuration.
  - Minimally disruptive, easily integrates into BMS.
  - No changes in the pack.
  - Performs monitoring diagnostic while battery is at rest.
- Real Time Detection Technology
  - Real time monitoring including over automotive duty cycles, charge/discharge and rest.
  - Detailed SOH monitoring on each cell.
  - Non-invasive and chemistry agnostic over full automotive temperature range.

Both systems are ready for implementation in battery packs: CAMX Power is now working with major automotive companies on demonstration.

The CAMX Power internal short circuit detection technology provides sensitive monitoring for internal shorts and can detect and quantify shorts (even minor shorts) in the 1000 ohm range.

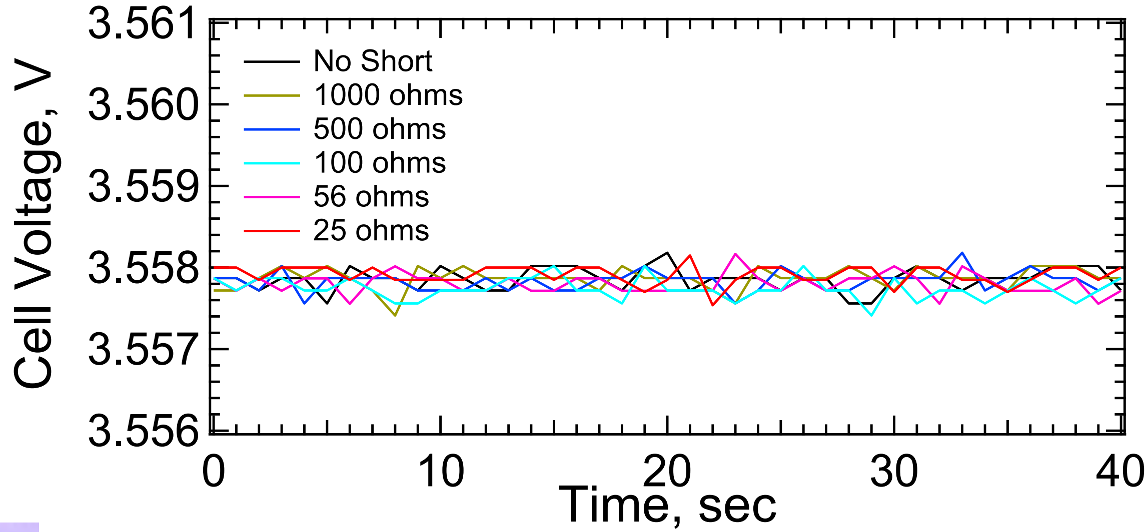


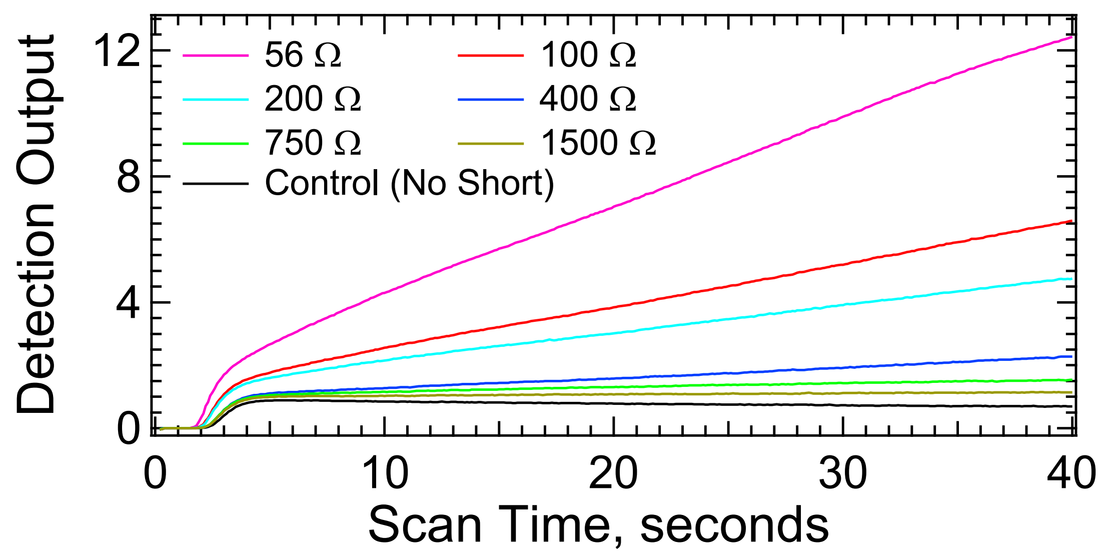
CAMX Power

The prototype on the right is part of a technology demonstration now underway at a major automotive manufacturer.

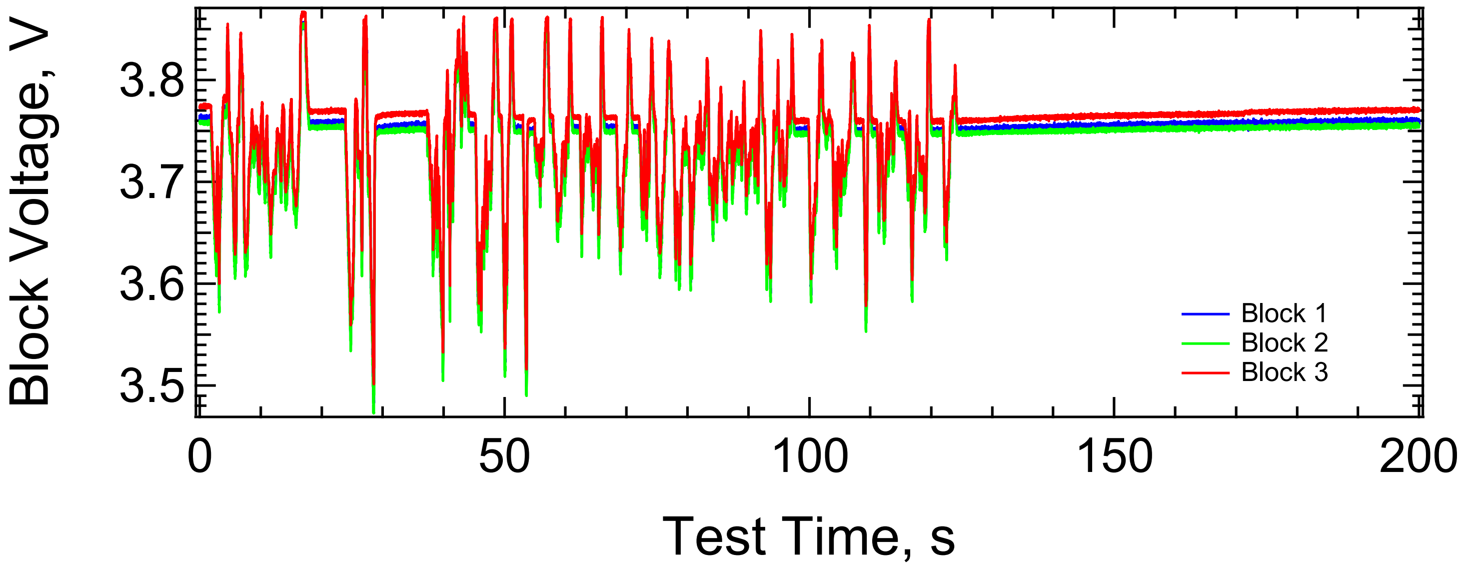
Voltage monitoring is too insensitive to rapidly detect internal shorts.

Battery cycler with 16 bit resolution





Automotive drive cycles pose one of the most challenging detection environments.



- *Standard BMS monitoring does not reveal the presence of a short*

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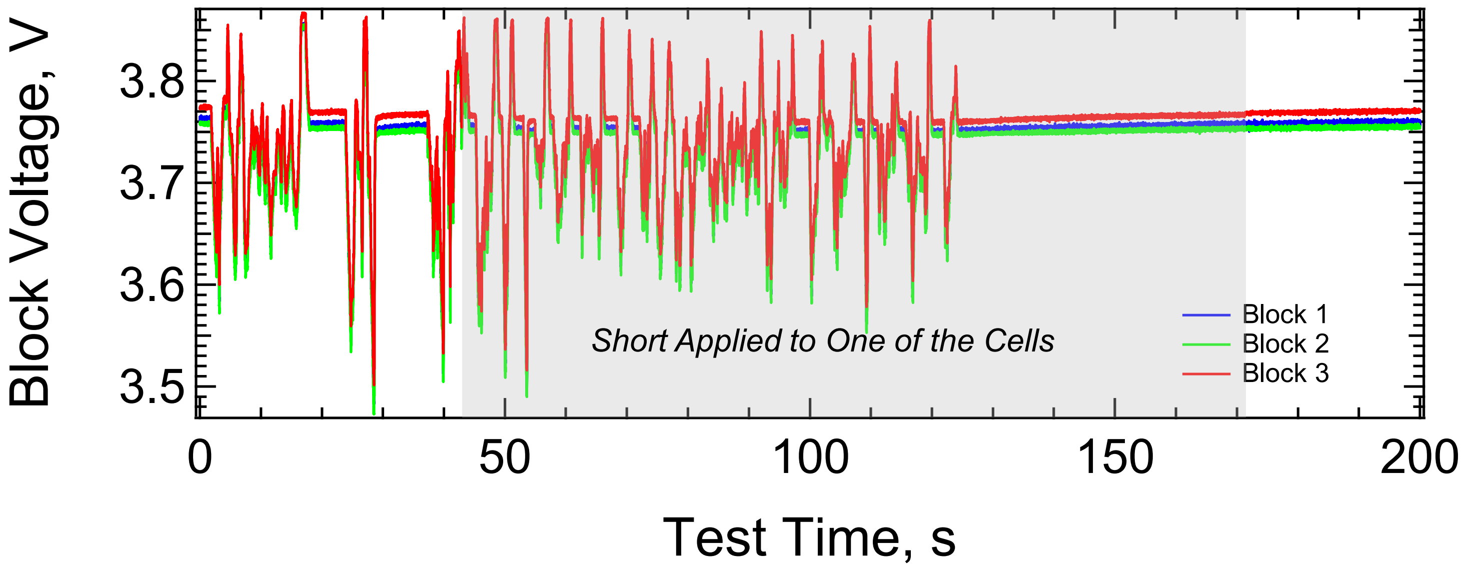

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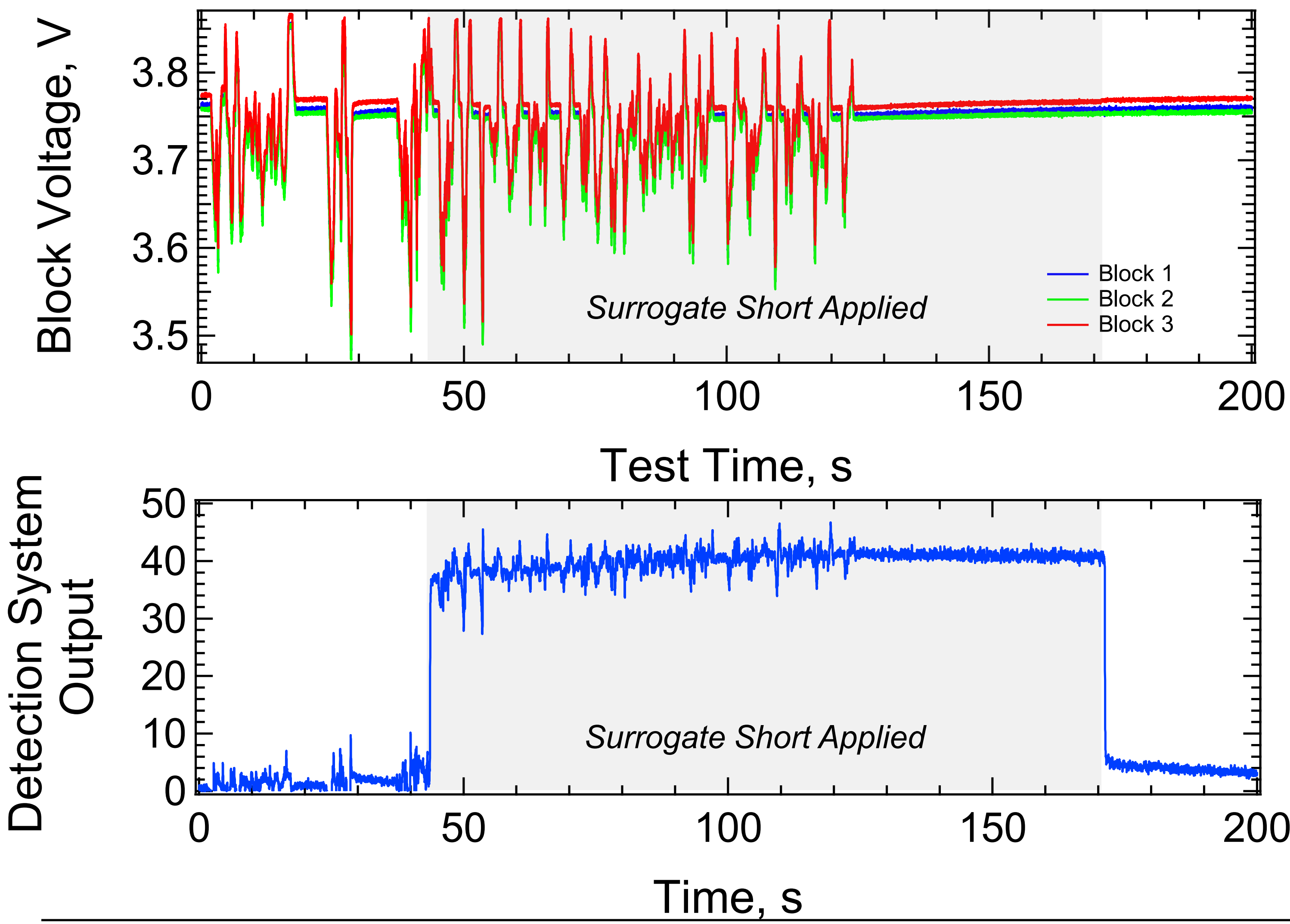


- *Standard BMS monitoring does not reveal the presence of a short*
- *CAMX Power detection technology does*

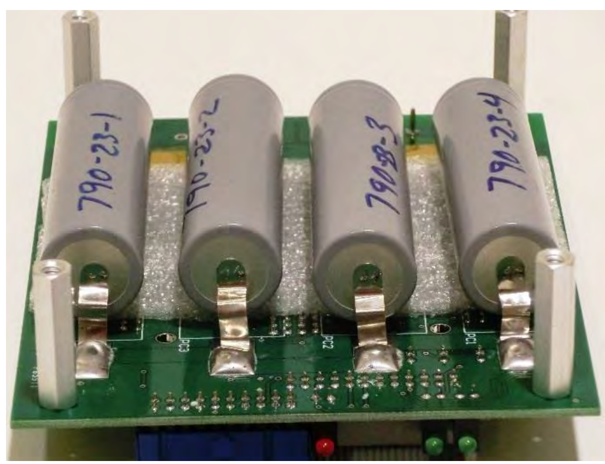
Internal Short Circuit Detection Technology: Selected Example of Implementation Activities

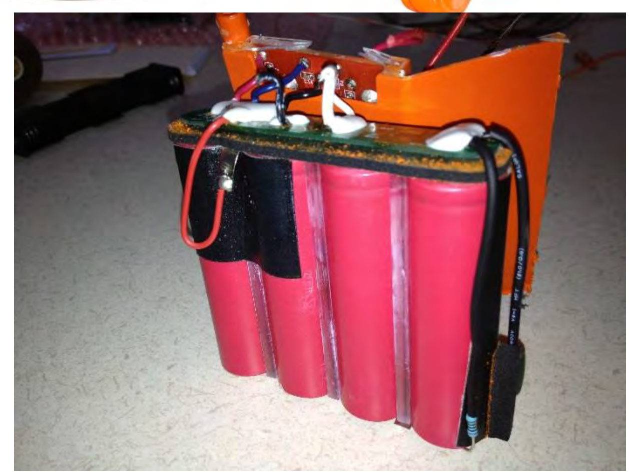
We have adapted our Real Time Detection Technology for detecting internal short circuits in cap lamps worn by miners.

- Li-on based batteries (e.g., in cap lamps) are extensively employed in mining today.
- Internal short circuits in these batteries can pose a significant danger.
- Early warning of growing internal short circuits can enable intervention and prevent catastrophic/cascading failures.

NLT Eclipse

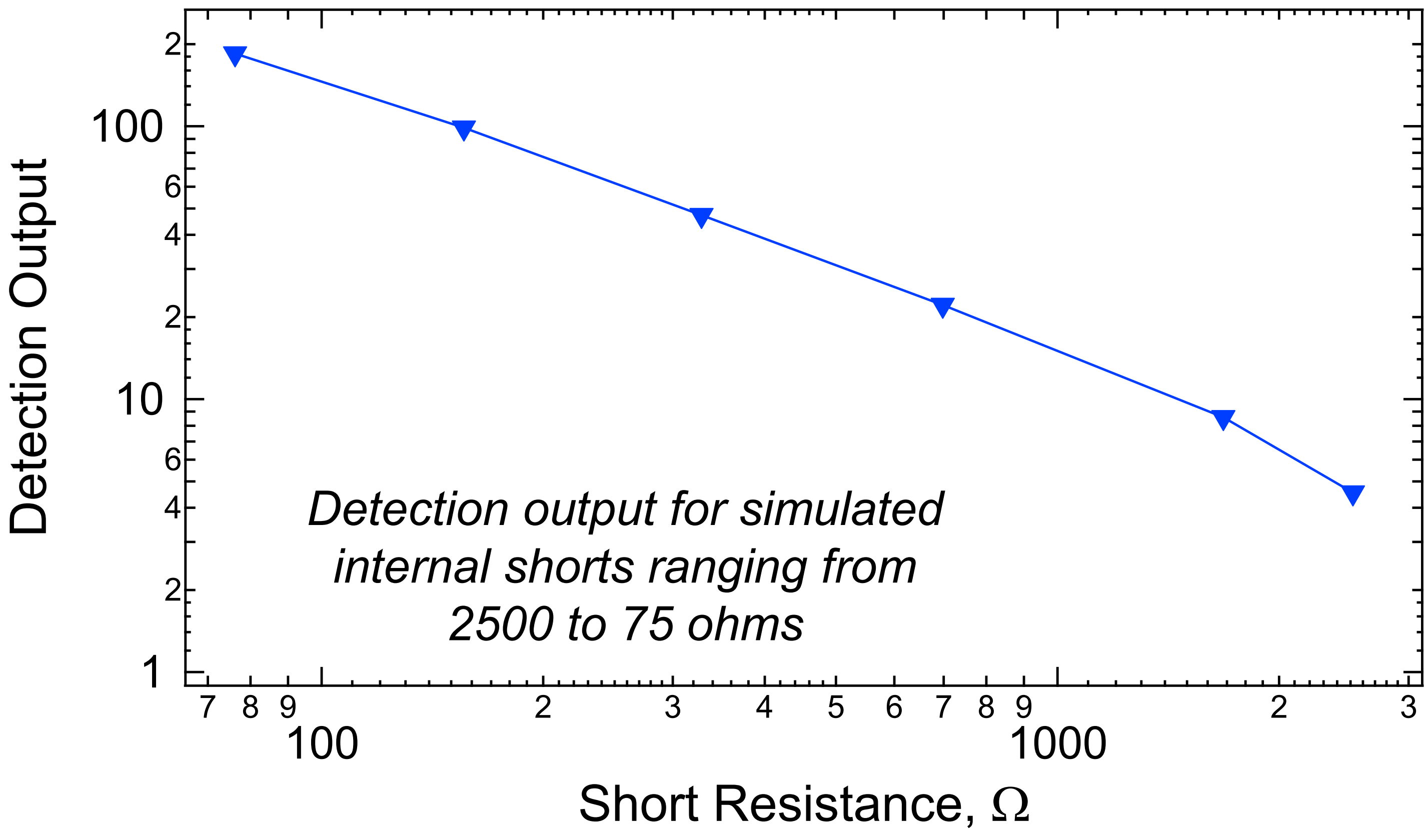
Initial prototype board with CAMX Power electronics to demonstrate internal short detection





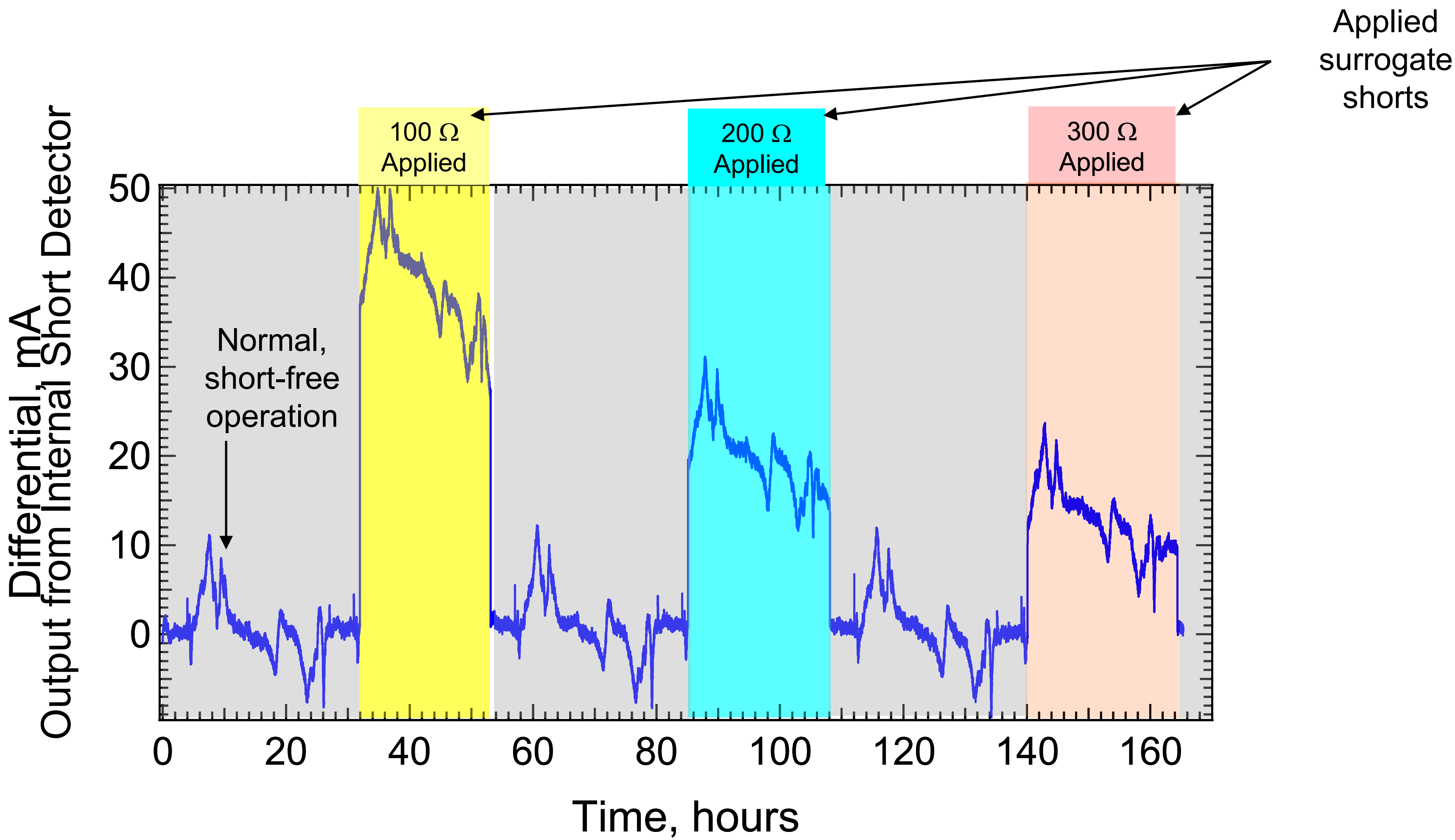
"The findings and conclusions in this presentation have not been formally disseminated by the National Institute for Occupational Safety and Health and should not be construed to represent any agency determination or policy. Mention of any commercial product does not imply endorsement."

In testing under realistic field use charge-discharge profiles, our technology was able to definitively detect internal short circuits in the battery systems that power miner's cap lamps as minor as 2500 ohms.



➢This testing confirmed the accuracy and freedom from false positives and false negatives for the cap lamp battery detection implementation

Our technology can provide real-time detection of internal short circuits in cells used in the miner's cap lamps.



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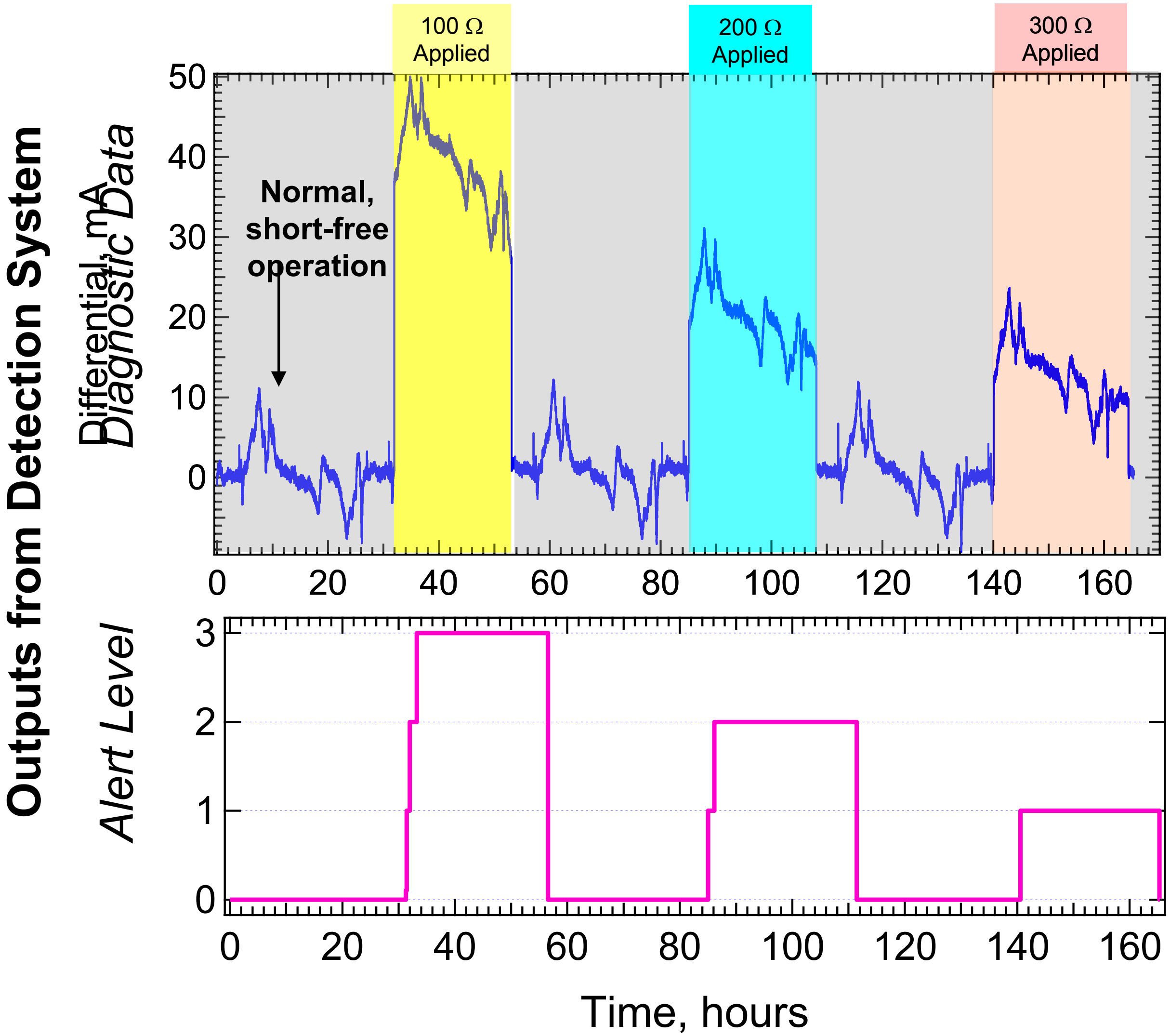
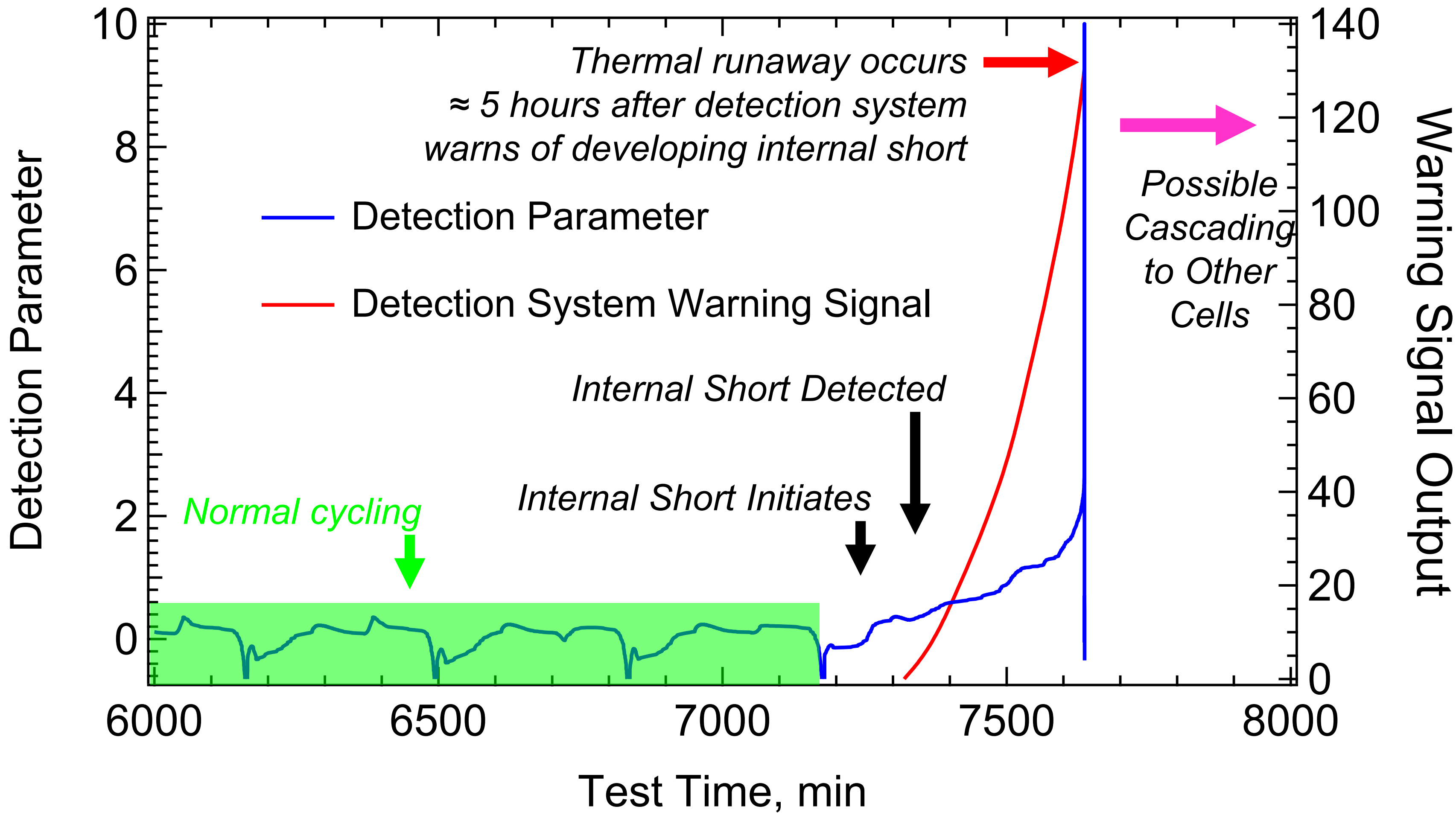


- Detects internal shorts whether the battery is being charged, powering the cap lamp, or at rest.
- Can activate interventions upon detection of an internal short.

The CAMX Power short detection has been shown to deliver warning well in advance of occurrence of thermal runaway:



- **Detection of a building fault *before* it triggers a runaway affords opportunity to avoid the runaway altogether**

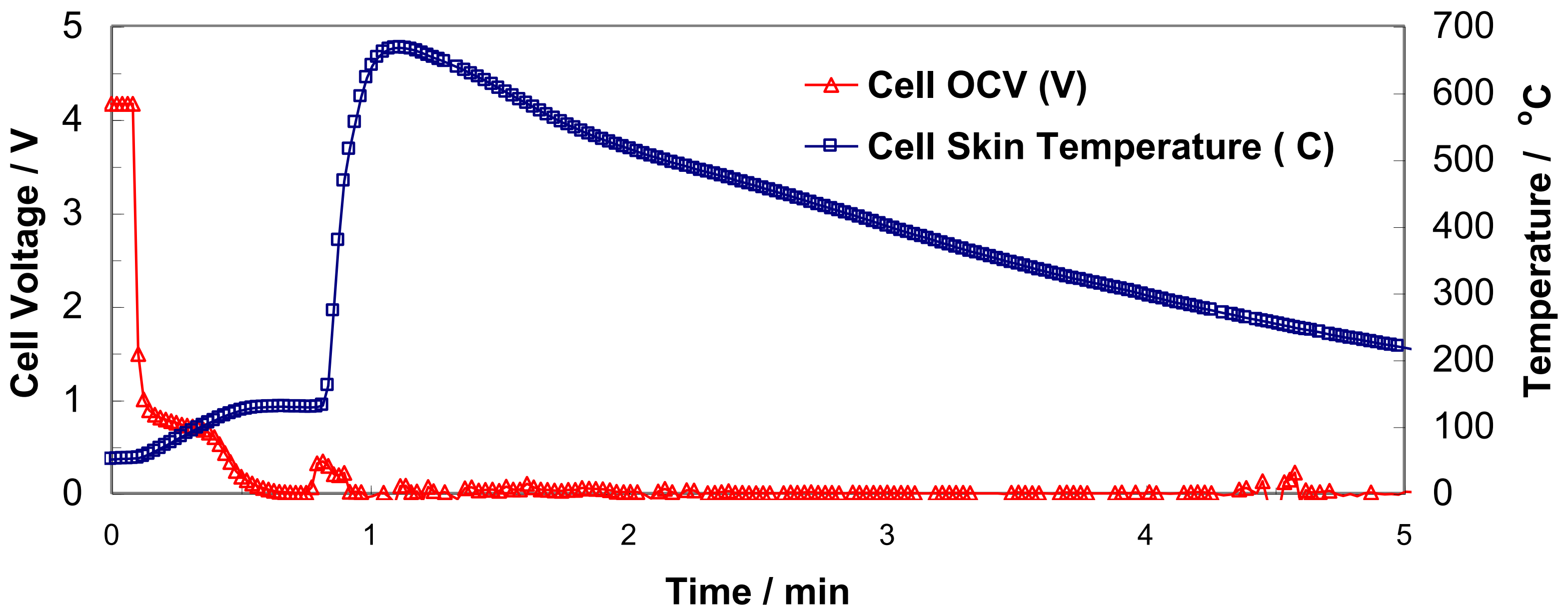
Simulation

(carried out via computer and multiple lab-based methods)

Let’s watch thermal runaway …

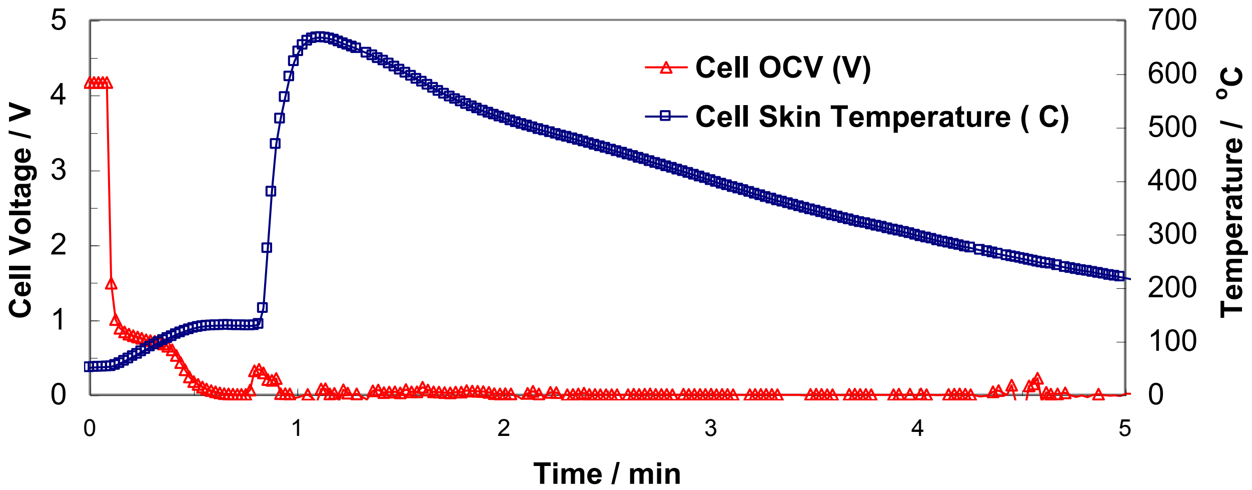
What does a thermal runaway look like … if you were there?

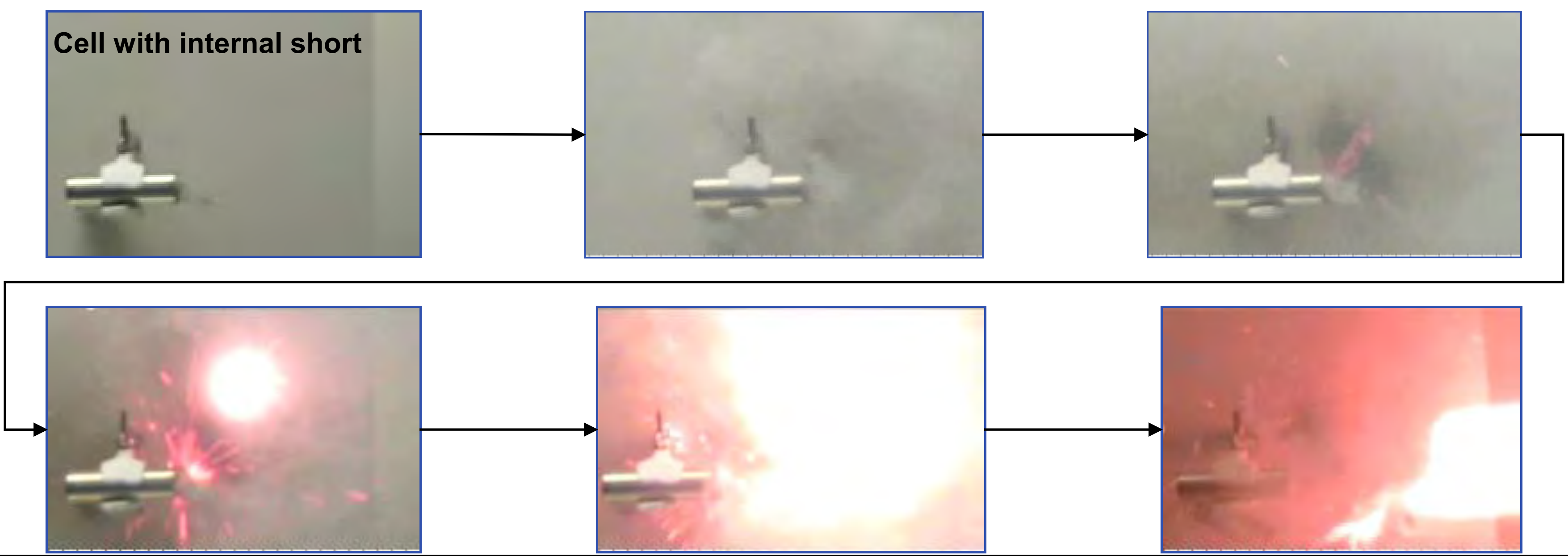
Lithium-Ion Cell: Stimulated to a Thermal Runaway



LG 2.6 Ah, 20 Watts Heater

Peak temperatures are very impressive – in this case, nearly 700ºC.





A combination of non-invasive evaluation and post-mortem examination can help reconstruct the progression of the safety incident.

Detailed multi-party audits of a large number of actual Li-ion safety incidents.

Images removed for reasons of confidentiality

Note the beads of condensed aluminum !

Images removed for reasons of confidentiality

Note the condensation of beads of aluminum !

Images removed for reasons of confidentiality

(CAMX Power test with commercial cell, below)

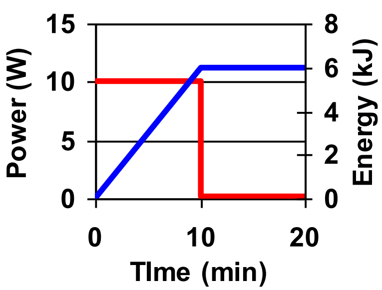
Simulating Thermal Runaway

(a validated FEA model)

CAMX Power has augmented a commercial FEA program with subroutines for transient 3-d simulations of safety-related field-failures.

Inputs:

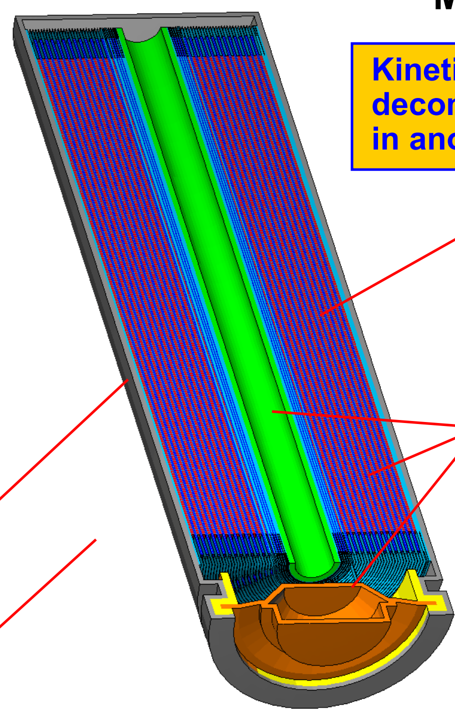
Heat generation associated with a short circuit:



Boundary conditions:

- Surface heat transfer coefficient
- Ambient temperature

Model properties:



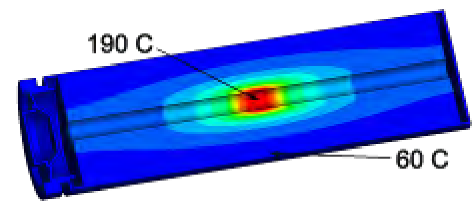
Kinetic models for thermal decomposition reactions in anode and cathode

Thermal properties for all cell constituents:
- density
- specific heat
- conductivity

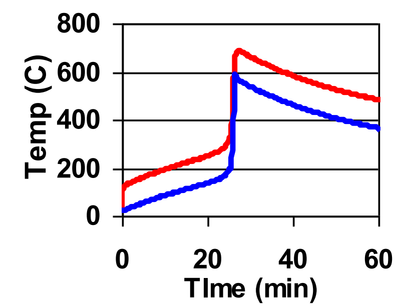
3-D transient FEA model with coupled decomposition rates & heat transfer

Outputs:

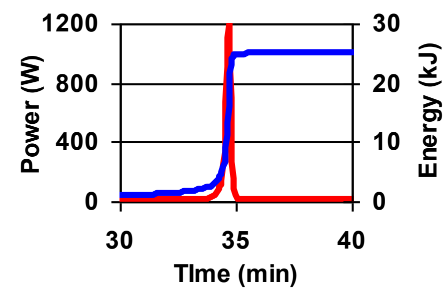
- Distribution of T, Q_{dot} at selected time intervals.



- Temperature histories at



rates, surface heat loss, etc.



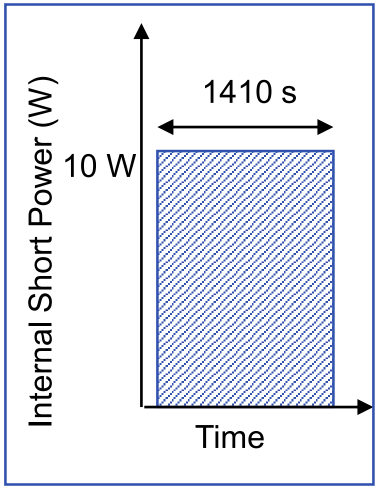
Li-ion cells contain energetic materials, which are stimulated to release heat in a field-failure.

Process	Temperature Range (ºC)	Energy release[1]	Energy release in an 18650 cell
Decomposition at anode	80 -120 150 - 300	300 – 450 J/ g-anode 1200 – 1400 J/g-anode	~ 9.6 – 13.3 kJ
Decomposition at cathode	150 - 300	1500 – 1800 J / g-cathode	~ 16.8 – 30 kJ
Self-reaction of salt with solvent	250 - 400	900 J/g electrolyte	~2.5 – 5.4 kJ
Complete combustion of solvent[2]	Auto-ignition temperature ~ 450	18 kJ / g solvent	**90 – 126 kJ**

[1] Approximate values estimated from DSC and ARC testing of cell components: charged anodes and cathodes, and typical electrolyte compositions;

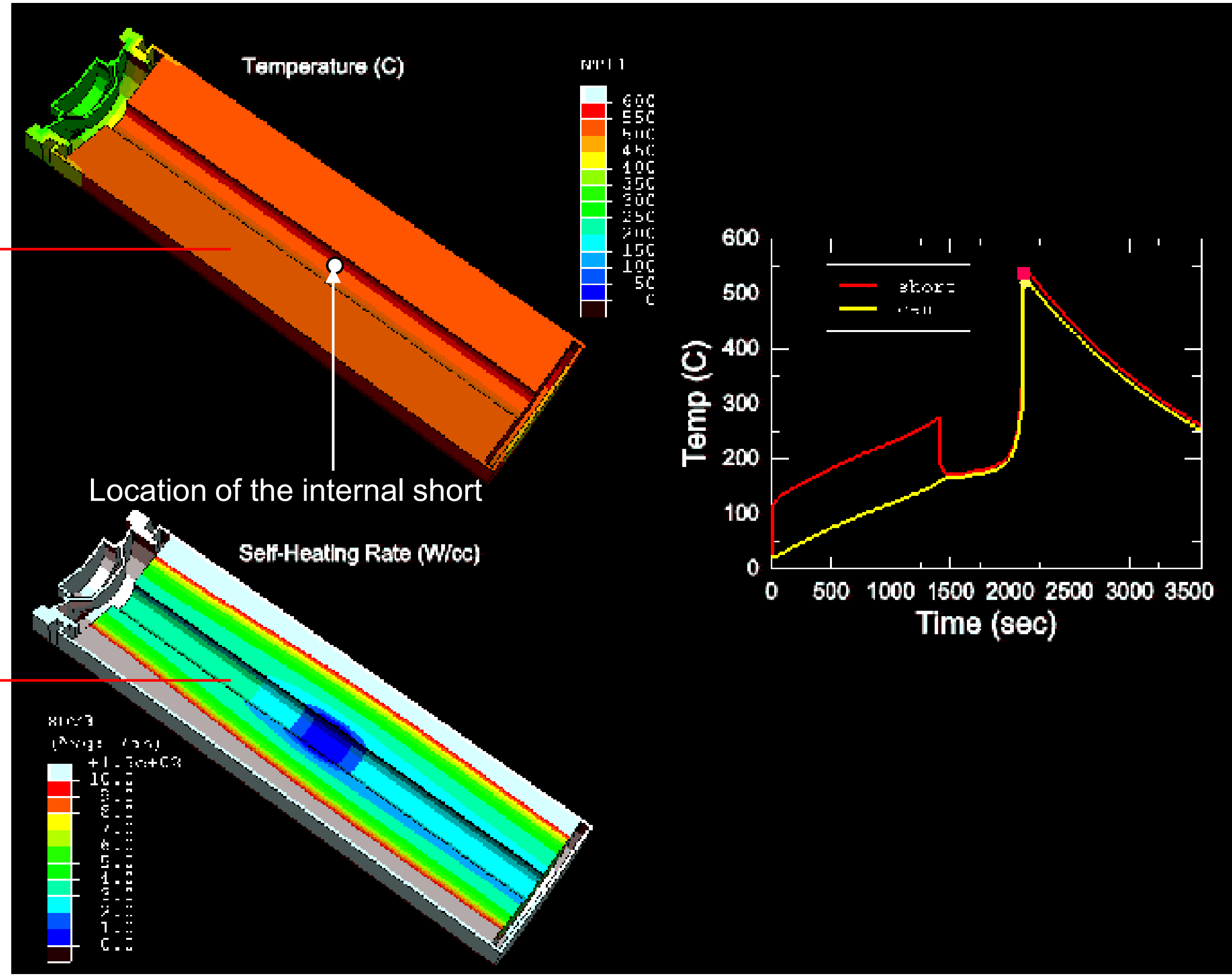
[2] Please note that there is insufficient oxygen available inside an 18650 cell to effect complete combustion of the solvent. However, if vented at high temperatures or vented in the presence of an ignition source the solvent can burn outside the cell.

FEA simulations show the temperature evolution and heat release profiles when an internal short results in a thermal runaway.

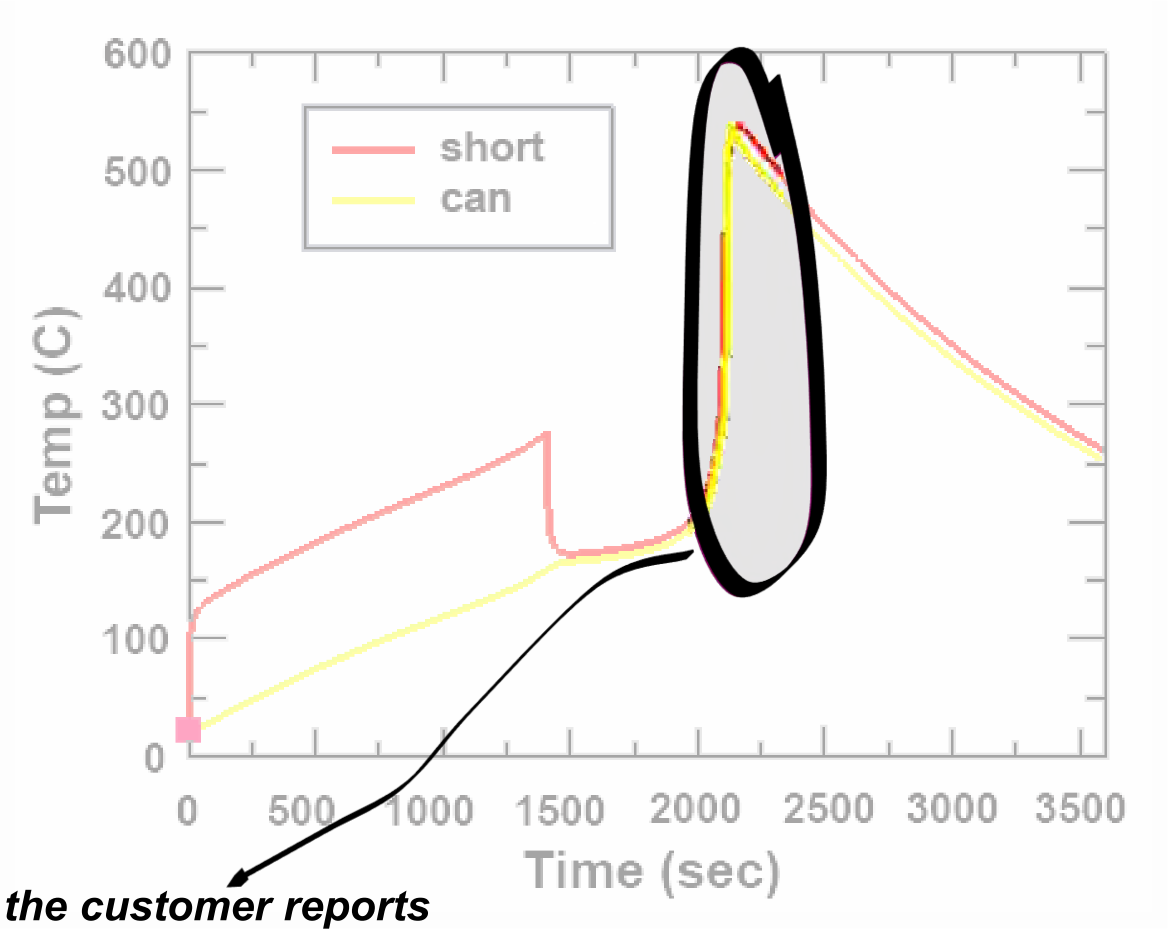


Temperature distribution

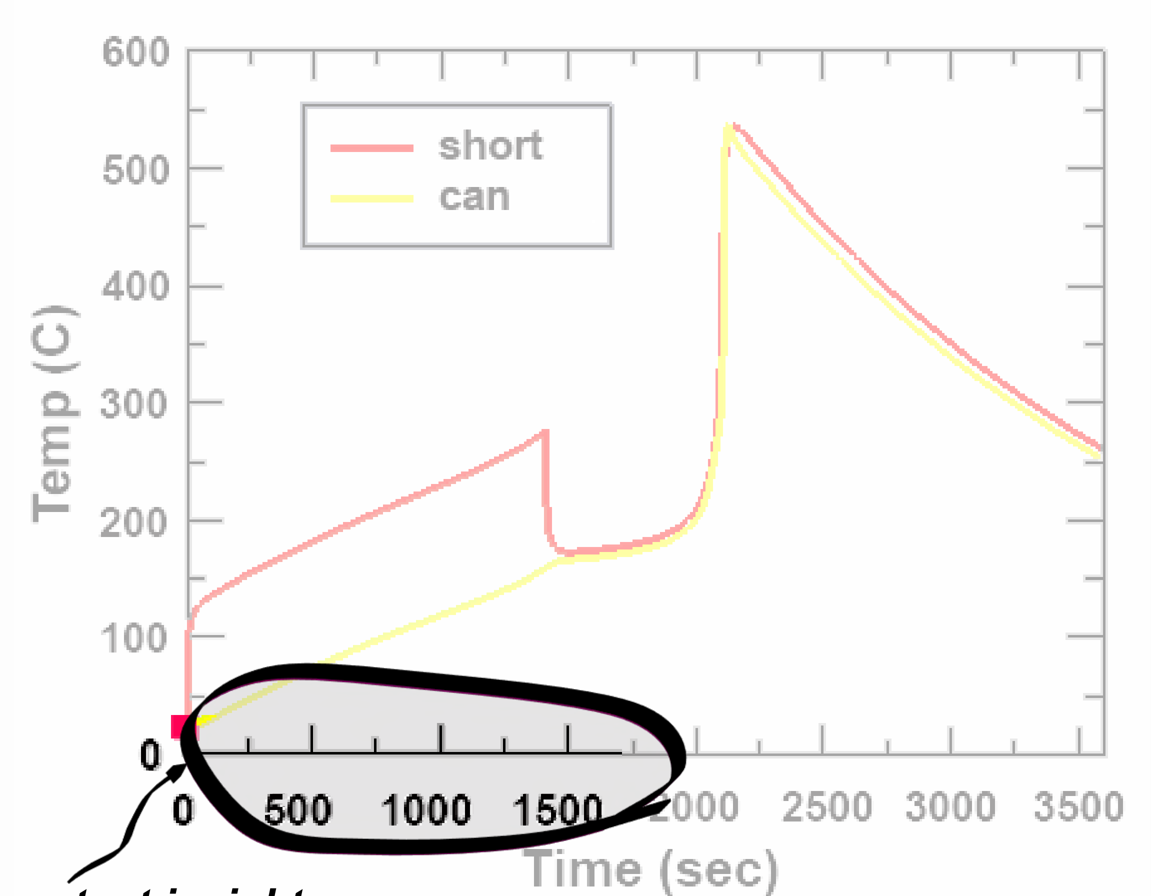
Distribution of heat generation from thermal decomposition reactions



B.Barnett, D.Ofer, R.Stringfellow, S.Sriramulu (Safety Issues in Li-Ion Batteries) in: Robert A. Meyers (Ed.), Encyclopedia of Sustainability Science and Technology, Springer Science, 2012

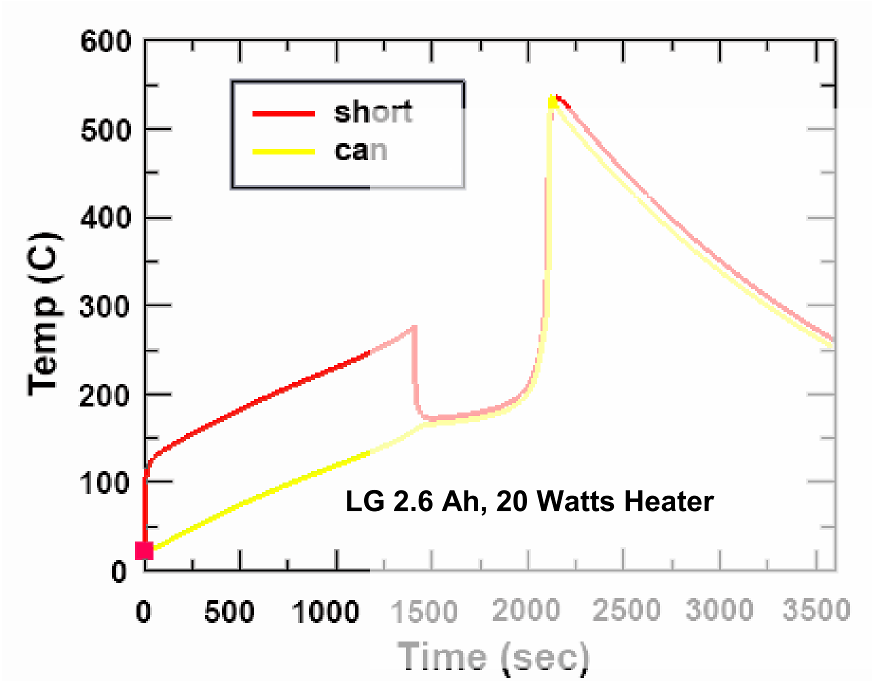


This is what the customer reports

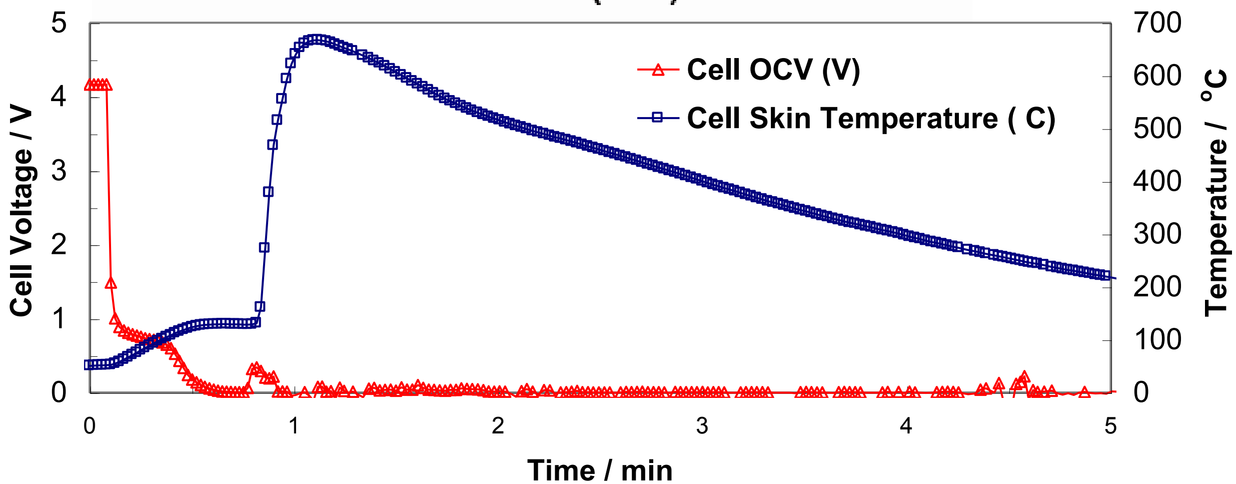


This is an important insight

- Regardless of the input power, we appear to have several minutes before thermal runaway is inevitable, i.e., we exceed threshold power and then exceed threshold energy
- Intervention may be possible, but can be very difficult.

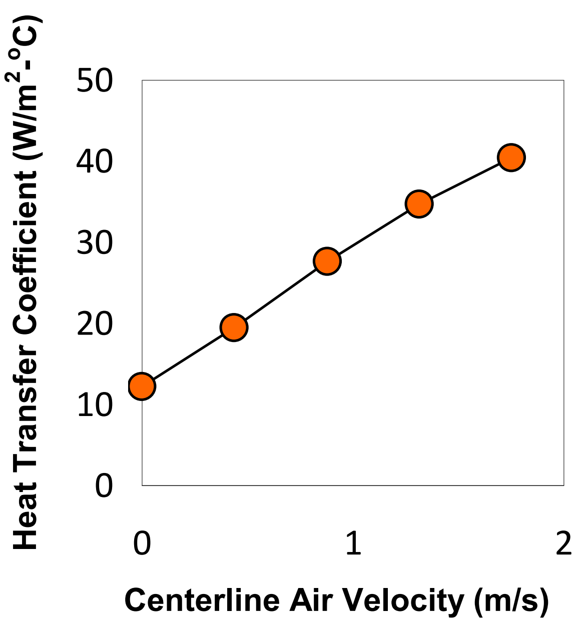


Simulation



Experimental Data

We designed and installed a wind tunnel for battery safety tests, where the heat transfer experienced by cells can be controlled.



cell

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Mechanism of Internal Short Formation

Many mechanisms have been proposed as being responsible for initiating an internal short circuit from foreign metal particle contamination in cells:

1. Dissolution of foreign metal particle from cathode → plating at the anode → growth of metal dendrite from anode surface to cathode → shorting of cell

2. Dissolution of foreign metal particle from the cathode → plating at the anode → promotion of Li deposition → Li-dendrite growth → shorting of cell

3. Foreign metal particle moves during charge/discharge cycling to a position close to separator → punctures separator after several cycles → shorting of cell

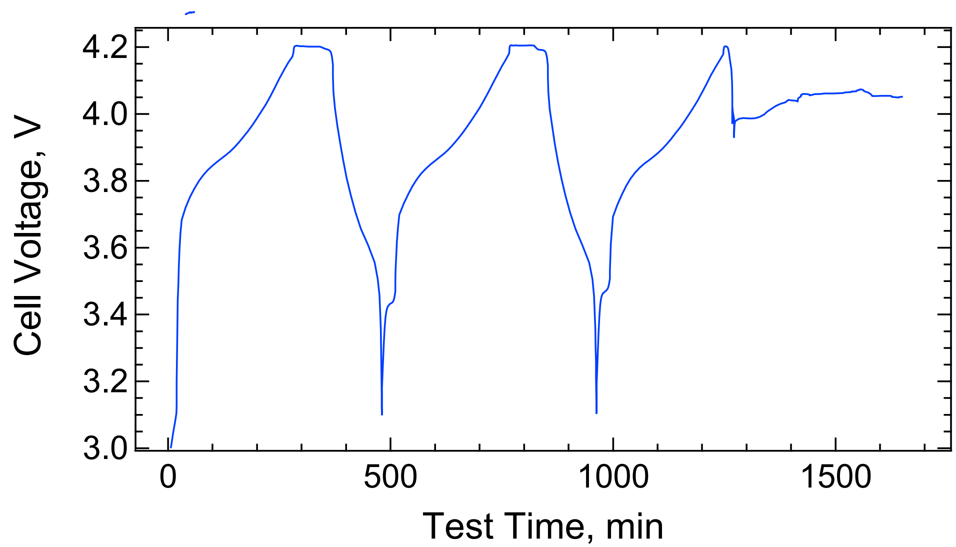
4. Unintentional overcharge due to faulty BMU → Li deposition on anode → repeated overcharging results in Li dendrite growth → shorting of cell

Our work to-date suggests that pathway 1 is the most likely precursor to thermal runaway.

We performed a large number of coin cell studies to understand the mechanism, as well as the kinetics of metal dissolution and plating, for different metals.

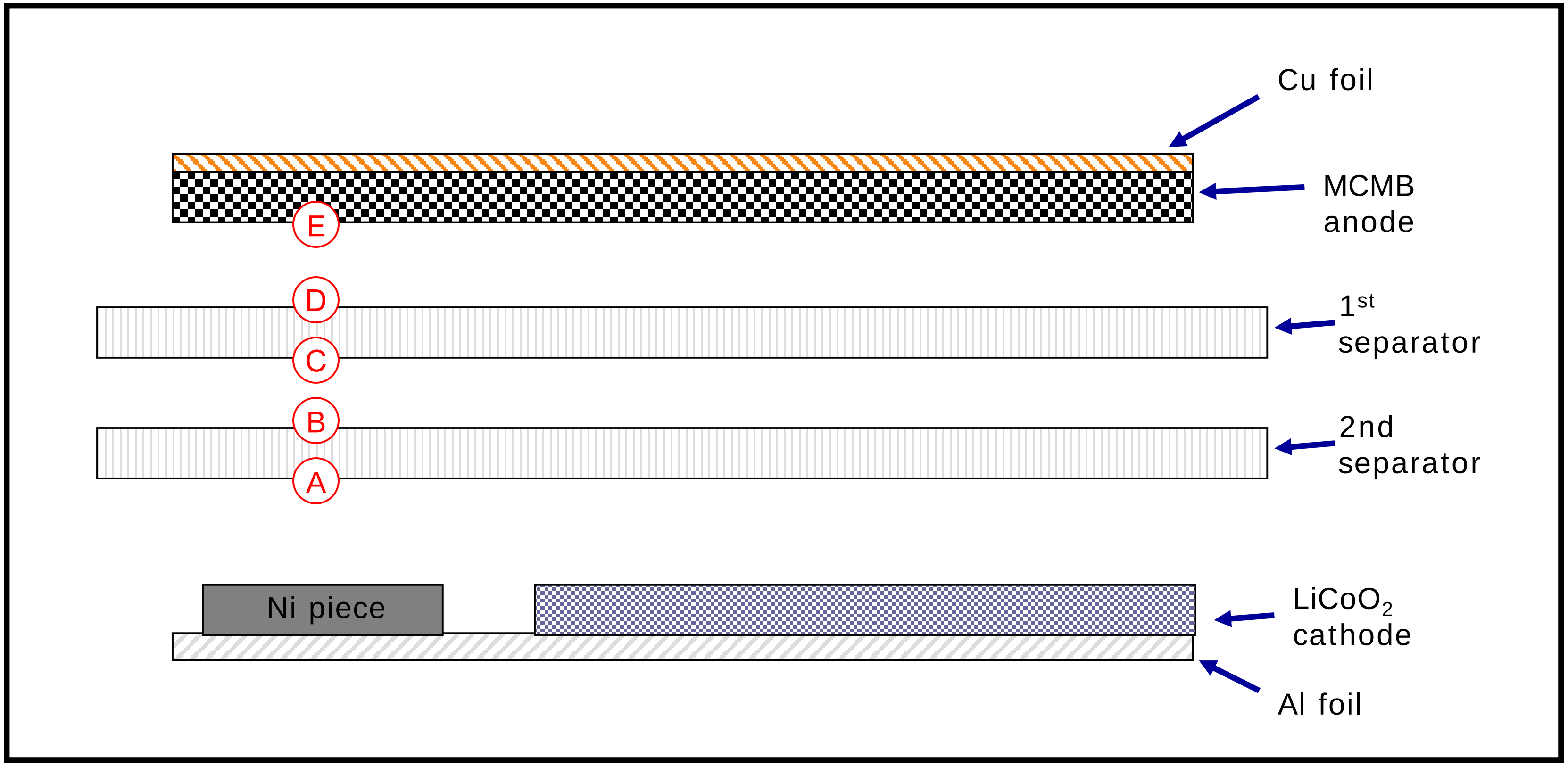
Position of Particle

Coin cell test configuration with metal particle placed at the cell center



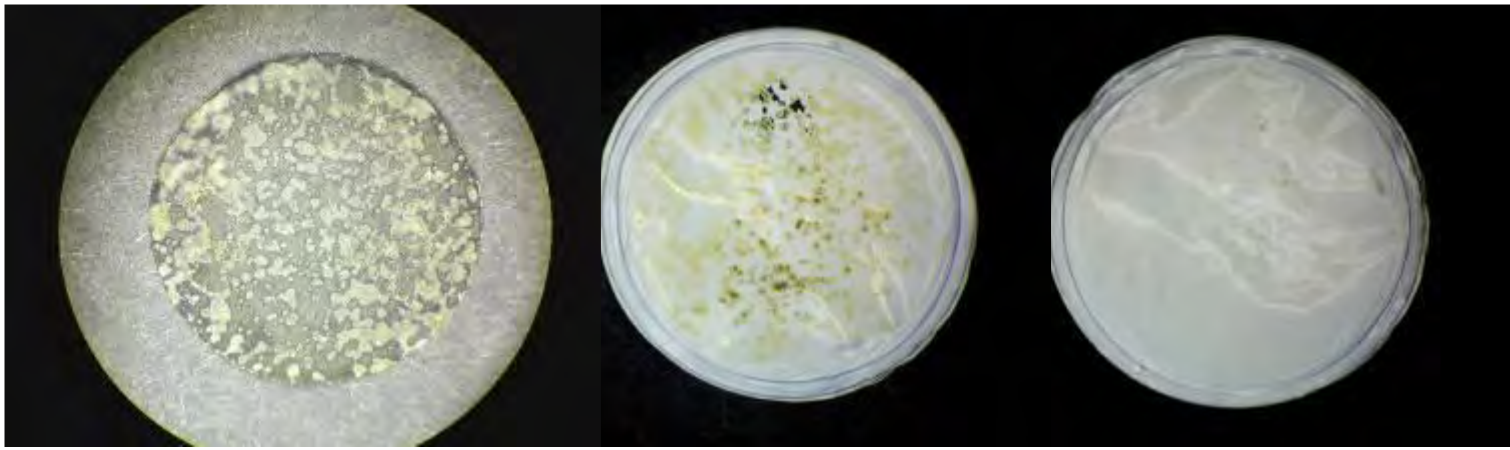
Short-circuited coin cells were disassembled for post-mortem analysis by optical microscopy and EDS.

Materials from regions (A~E) in the figure below were analyzed :

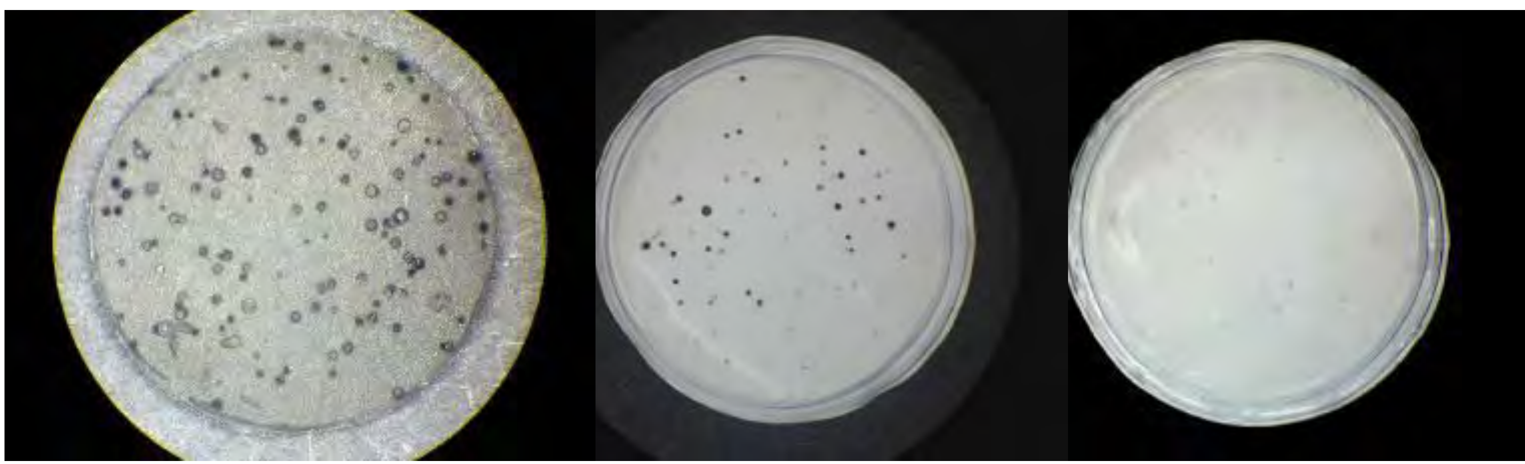


Different metals behave differently in the Li-ion cell. However, to date, little is known about metal dissolution and plating in Li-ion cells.

Fe particles in the cathode. Post-mortem after 1st charge.

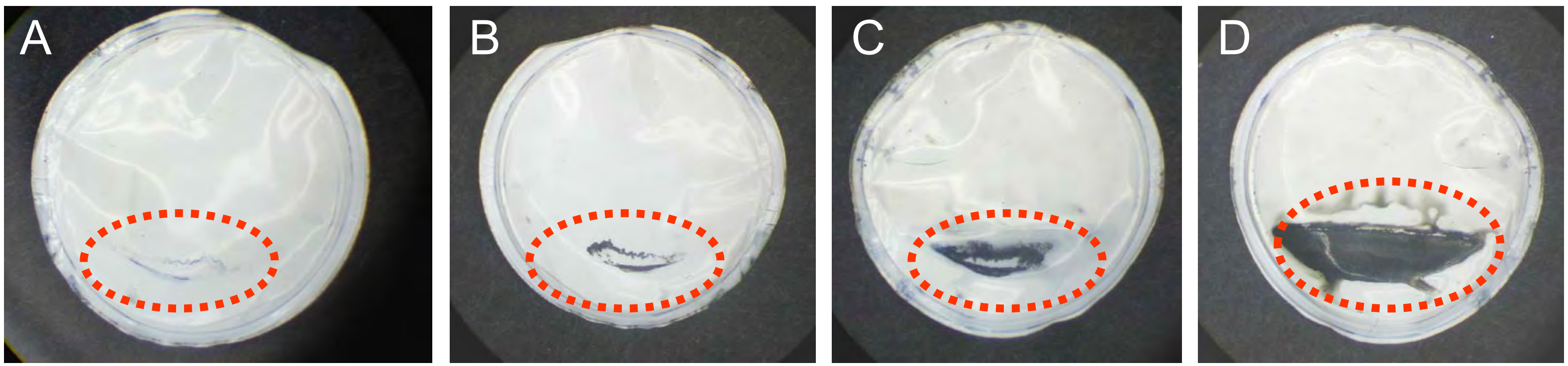


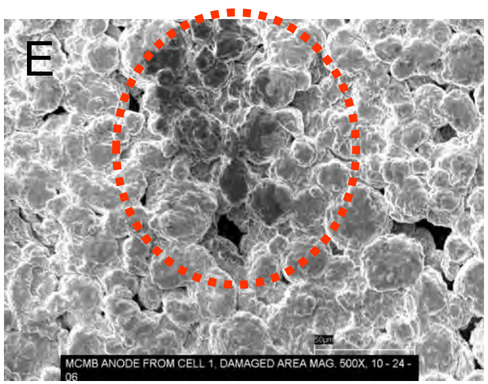
Ni particles in the cathode. Post-mortem after 1st charge.

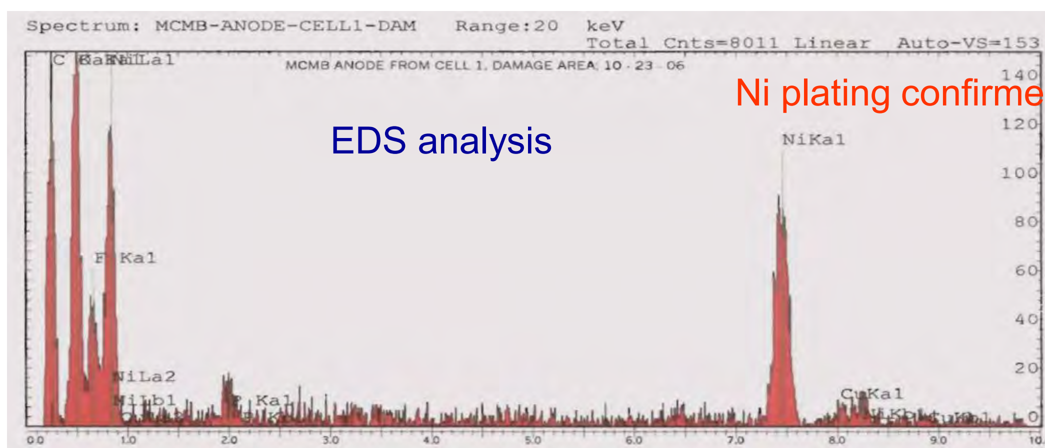


MCMB Anode | Separator, anode side | Separator, cathode side

Post mortem analysis clearly showed the formation of a nickel deposit: the deposit on anode side of the separator was larger than that on the cathode side, implying non-uniform growth of the deposit.

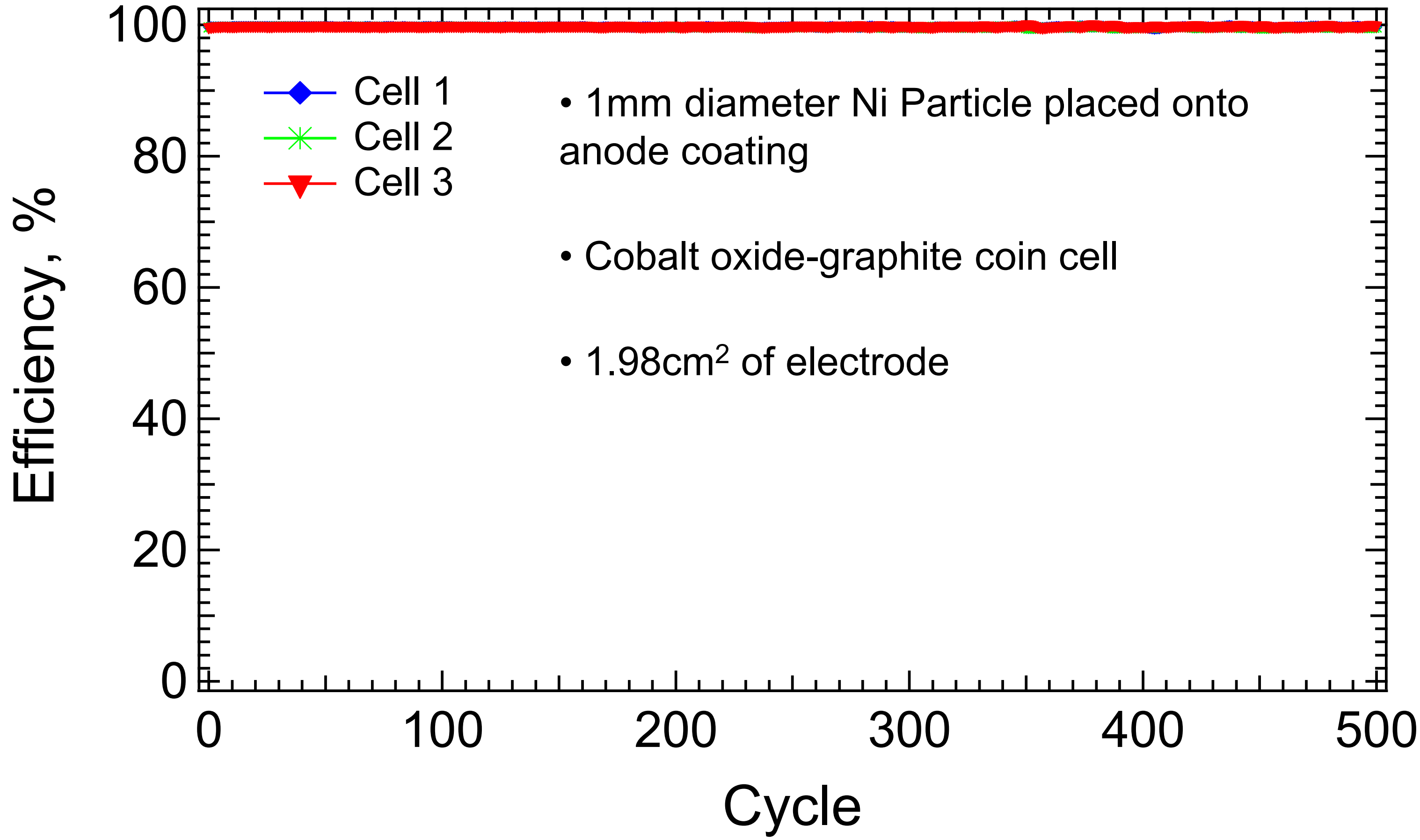




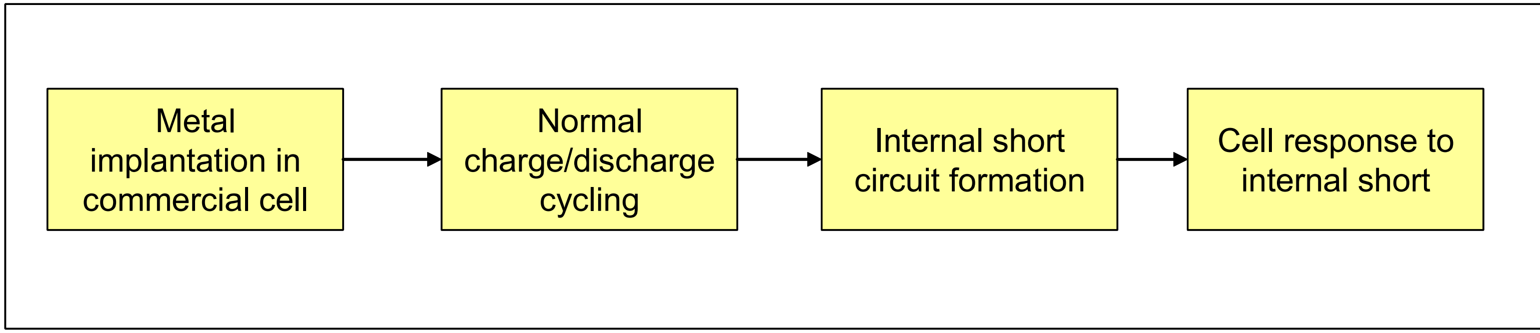


Note) EDS chart showed is for spot E on anode, but EDS charts for the spots A through D are very similar to this.

In tests where a nickel particle was placed on the *anode* coating, no shorting was observed in over 500 cycles



Some years ago we developed a technique (since enhanced) for introducing a latent flaw in 18650 cells involving the following steps.



- Implantation of metal particles in 18650 cells:
  - Disassembly of the cell
  - Unwinding of the jelly roll
  - Placement of a foreign metal particle in contact with cathode or cathode substrate
  - Rewinding of the jelly roll
  - Sealing of the jelly roll into a test fixture
- Normal charge/discharge cycling to cause metal dissolution, plating, and shorting through deposit growth.

We successfully created an internal short during normal cycling in more than 75 % of the cells implanted with metal particles.

Summary Observations on 52 commercial 18650 cells (capacity > 2.4 Ah) implanted with metal particle in early work circa 2009

Observed Response of Commercial 18650 cells During Normal charge/Discharge cycling Following Metal Particle Implantation	Number of cells exhibiting response
Cell experienced thermal runaway with temperatures > 600°C	15
Cell temperature exceeded 130°C, but did not go into thermal runaway and was subsequently inoperable	24
Cell showed some evidence of internal short formation, but appeared to cycle normally	13

The mechanism described below may explain the differences in the deposition patterns previously observed for Fe and Ni.

Fe Particles

- Fe spontaneously dissolves at the potential of the uncharged cathode in the uncycled full cell. Probably:
- Before the MCMB anode was formed, the Fe^{y+} diffused away from the cathode
- Once the anode formation began, Fe^{y+} deposition at the anode occurred
- The diffuse deposition pattern at the anode reflects the spreading of the Fe^{y+} from the cathode

Implications

- If all of the Fe in the cathode dissolves and spreads before the cell has been formed, then it would be less likely that a small particle could form a short during the formation (and subsequent cycles)

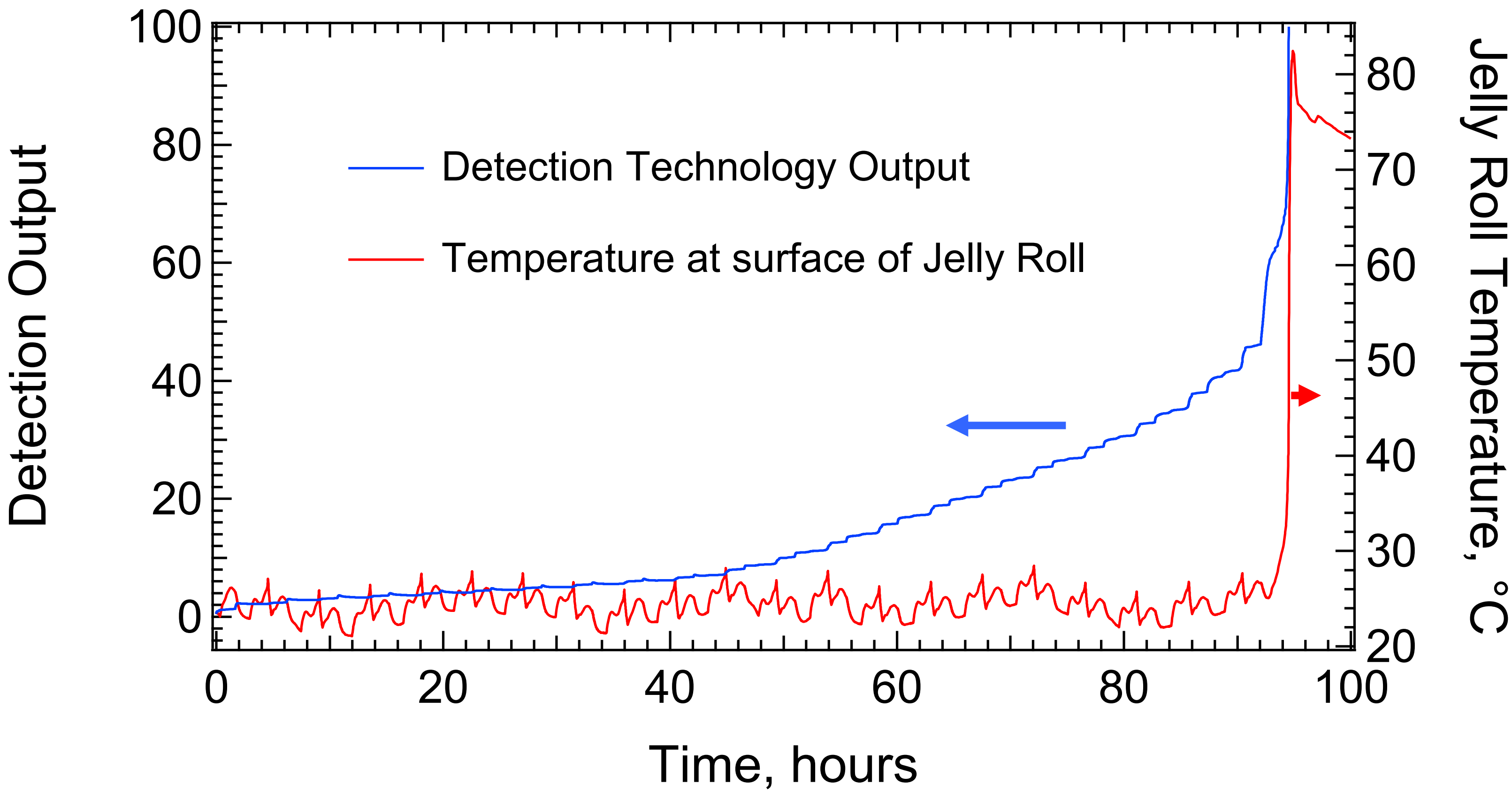
Ni Particles

- Spontaneous Ni dissolution is very slow
- Significant amount of Ni dissolution occurs only when the cell is at high SOC;
- Under these conditions, the anode has been formed and able to reduce the Ni^{2+}
- The more concentrated deposition patterns for Ni is because Ni deposition at the anode occurs before the Ni^{2+} has a chance to diffuse away

Implications

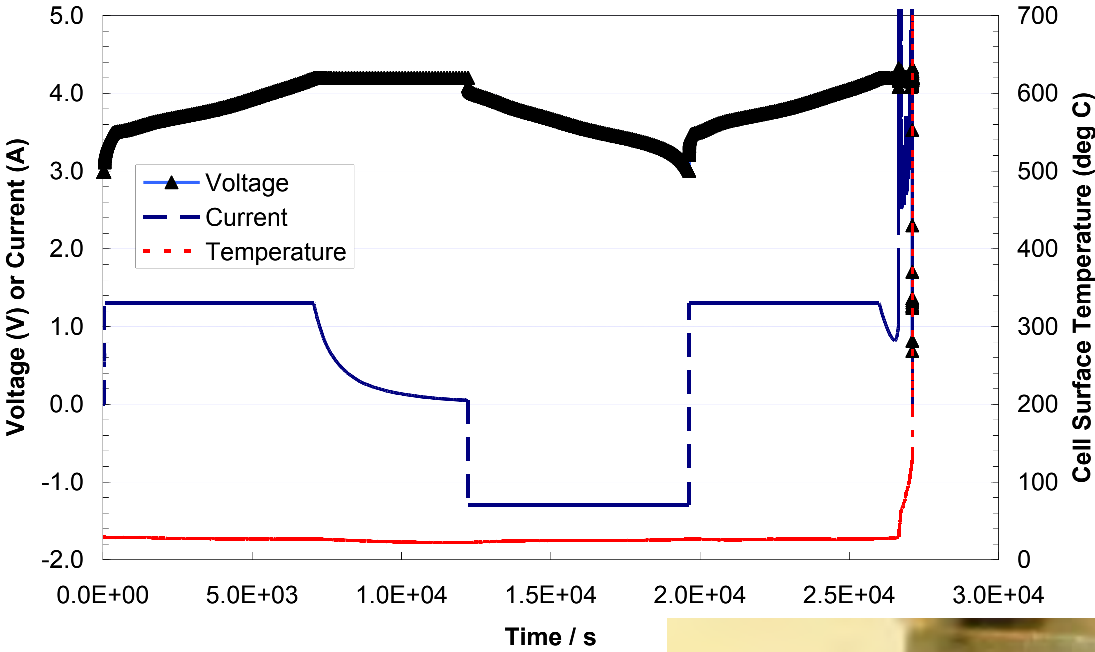
- Higher probably of not being ‘caught’ in the formation cycles

This 18650 cell failed due to a nickel particle-induced internal short at cycle 21, but the short was present and growing for many cycles prior to the failure.



The CAMX Power technology detected the internal short over ten cycles prior to cell failure, providing advance warning while the short was still small not afforded by cell voltage, current, or temperature monitoring.

Thermal runaway in a Li-ion cell induced using unique CAMX Power particle implantation methodologies.



a) This cell ran away after a particle was implanted. Aluminum beads indicate cell temperatures exceeding 660^{o}C.

b) Runaway in this cell resulted in aluminum melting (beads can be seen on the end of the jellyroll) and partial ejection of the jellyroll core.

We successfully demonstrated that we can induce thermal runaway during normal operation of an 18650 cell (≥ 2.6 Ah).

This cell ran away after a particle was implanted. Aluminum beads indicate cell temperatures exceeding 660^{o}C.

Runaway in this cell resulted in aluminum melting (beads can be seen on the end of the jellyroll) and partial ejection of the jellyroll core.

We have succeeded in creating an internal short AND a thermal runaway after many charge-discharge cycles in an 18650 cell.

Why Mechanically Induced Shorts Are NOT the Same As Particle-Induced Shorts

Commercial NCM cells experienced violent thermal runaway in a nail penetration test.

* Commercial 18650 cell, charged to 4.2 V

t = 126 ms
after nail
penetrated
the can wall

t = 158 ms
after nail
penetrated
the can wall

t = 190 ms
after nail
penetrated
the can wall

During the nail penetration test, it is not uncommon to observe explosions within 200 ms of nail penetration.

Our experimental setup allows us to characterize the nail penetration process in detail.

Fast nail, 8 cm/s

Analysis of the nail penetration data shows that the outcome in the nail penetration is governed by phenomena in the vicinity of the nail.

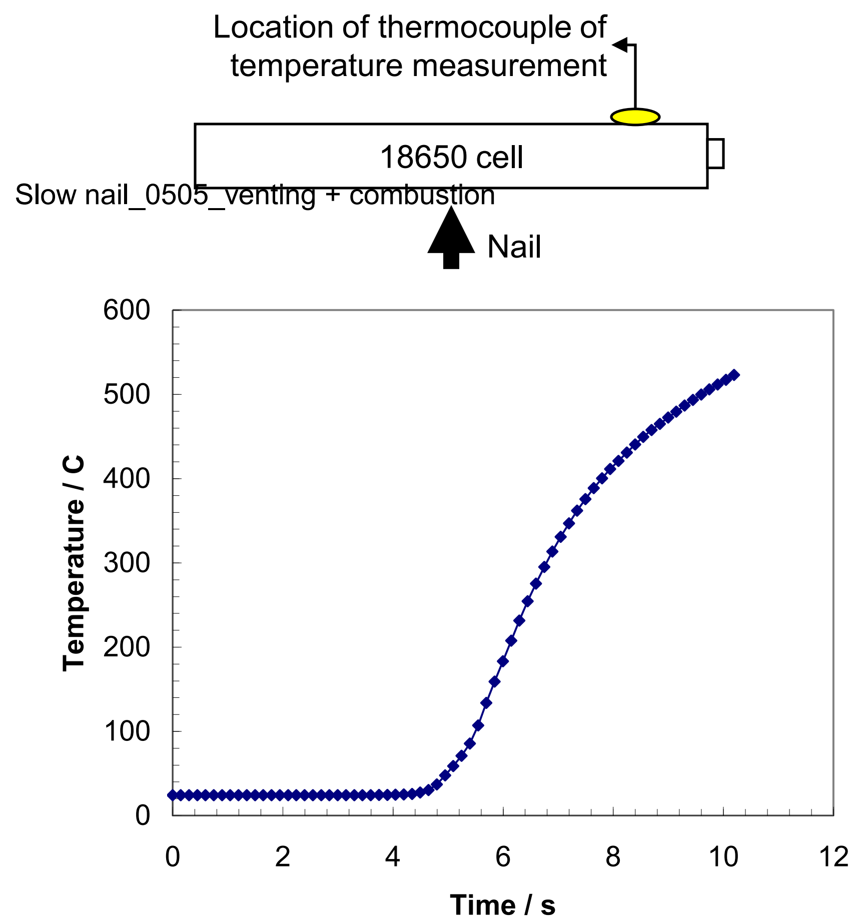
During the nail penetration test, venting and explosions occur typically < 500 ms

t = 126 ms after nail penetrated the can wall

t = 158 ms after nail penetrated the can wall

t = 190 ms after nail penetrated the can wall

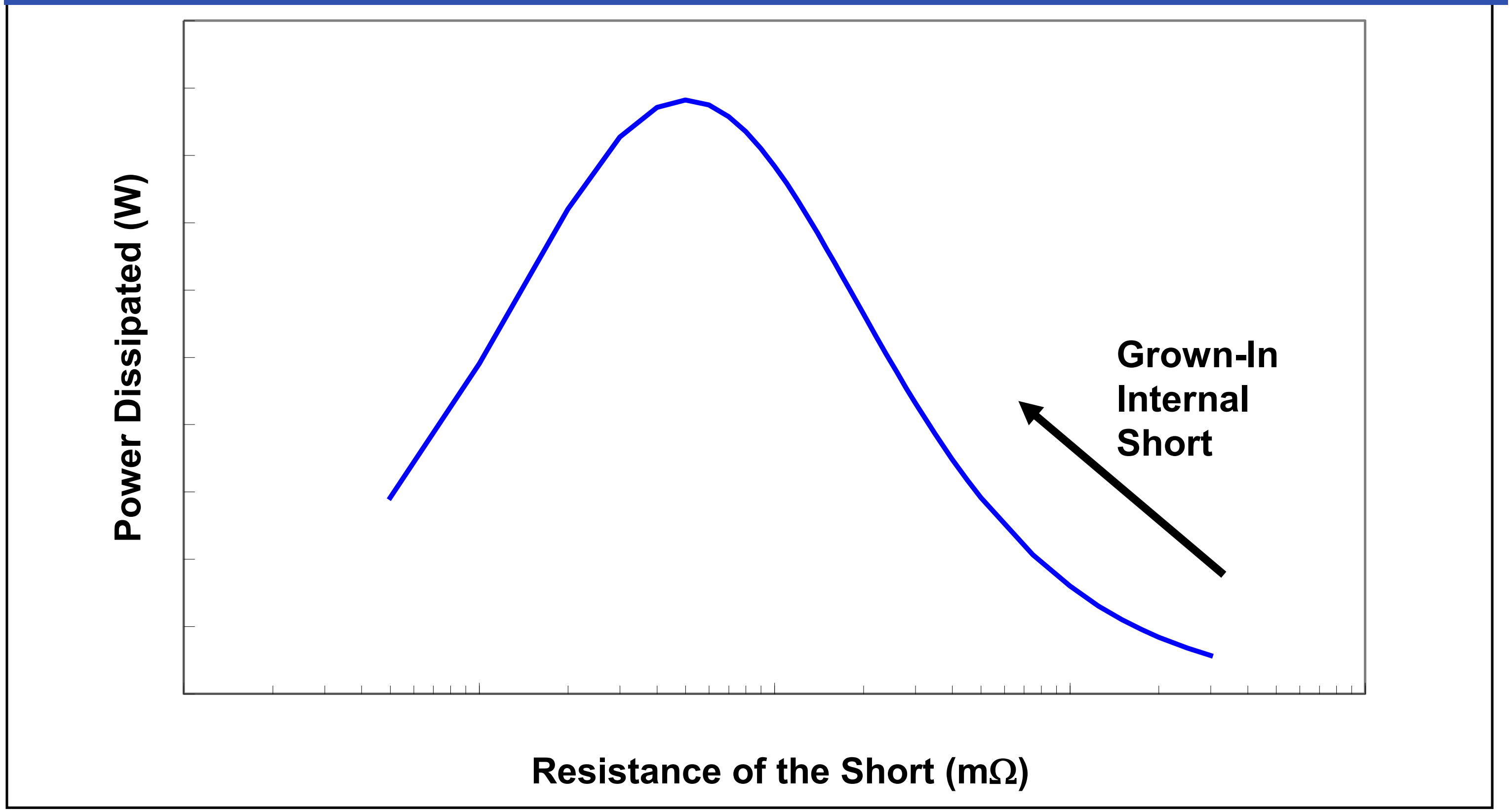
However, the cell surface temperature barely increases in this short time period.



A "grown-in" internal short-circuit begins from infinite/high resistance and matures to lower resistances, heating the cell, until the cell is "dead" or a thermal event occurs …

Power Dissipated in the Short

Depiction of the expected power dissipation through an internal short circuit as a function of the short resistance and cell power capability



… but the nail penetration short (s) can initiate with extremely low short resistance, with little cell heating possible before an explosion occurs.

CAM X Power