Understanding Safety-Related Field Failure (not Abuse) of Lithium-Ion Cells

Presentation at the 2008 NASA Aerospace Battery Workshop

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Major effort is required to improve the ways we address safety in lithium-ion batteries, before serious mitigation of lithium-ion safety incidents can occur.

- Safety incidents threaten the business, environmental and social benefits and opportunities associated with lithium-ion.
- The battery community does not have adequate tests to evaluate safety as it relates to the safety incidents that have taken place or could take place.
- Safety is a system issue – it cannot be judged from measurements of single components.
- Models can play an important role, when used judiciously with appropriate experimental data, to guide development of safer lithium-ion cells and batteries.

Major effort is required to improve the ways we address safety in lithium-ion batteries.

- Despite extensive (1) QC/QA, (2) standardized industry safety testing, and (3) a decade or more of manufacturing learning, major recalls have taken place and incidents still occur.
- Safety incidents that take place in the field almost always originate due to an internal short (that was not detectable or predictable at the point of manufacture).
- Safety incidents take place on the order of one in 10 million cells *for the most experienced manufacturers* (well beyond six sigma).
- Internal shorts will never be completely eliminated.
- Conditions leading to thermal runaway in safety incidents develop during “normal” operation in the field, after some time in the field, and are not detectable at the point of manufacture.
- Evidence for temperatures in excess of 660C is routinely found in safety incident post mortems.

What happens in a Field Failure?
How is it different from abuse?

Post mortems of cells from lithium-ion safety incidents frequently reveal beads of condensed aluminum – cell temperature must have exceeded 660 °C!

(Note: pictures have been removed for reasons of confidentiality)

The "standard" abuse tests and materials-level tests employed by the battery industry do not predict when safety-related field failure will occur.

Whether or not thermal runaway follows from an internal short cannot be determined solely from component-level measurements because:

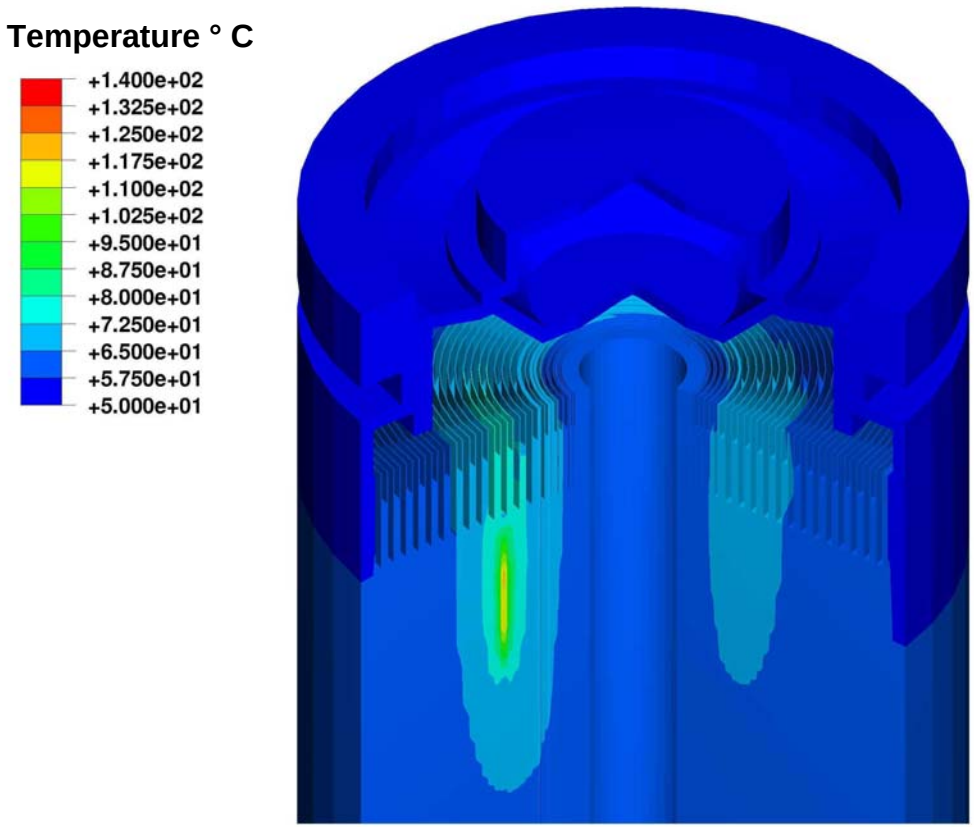
1. **An internal short results in a highly non-homogeneous temperature distribution;**

2. **Whether thermal runaway follows from this non-homogeneous temperature profile is determined by a complex interaction among instantaneous values of temperature, concentrations, and rates of reactions.**

- These are precisely the reasons why field failure is a different process than abuse tolerance.
- Unfortunately virtually all our traditional safety tests are abuse tests.

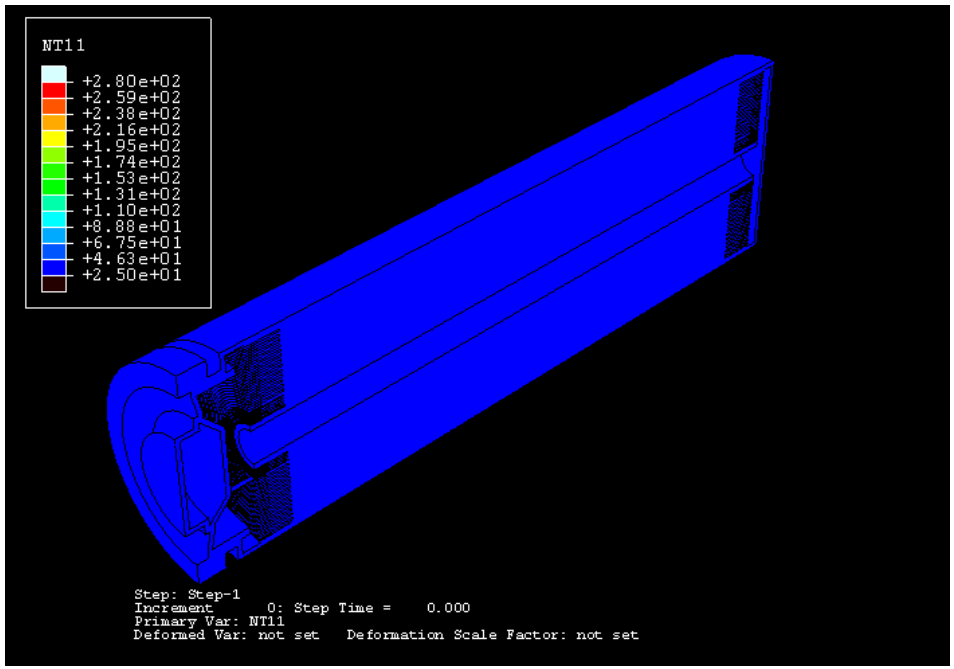
An internal short leads to a highly non-homogeneous temperature distribution within the cell.

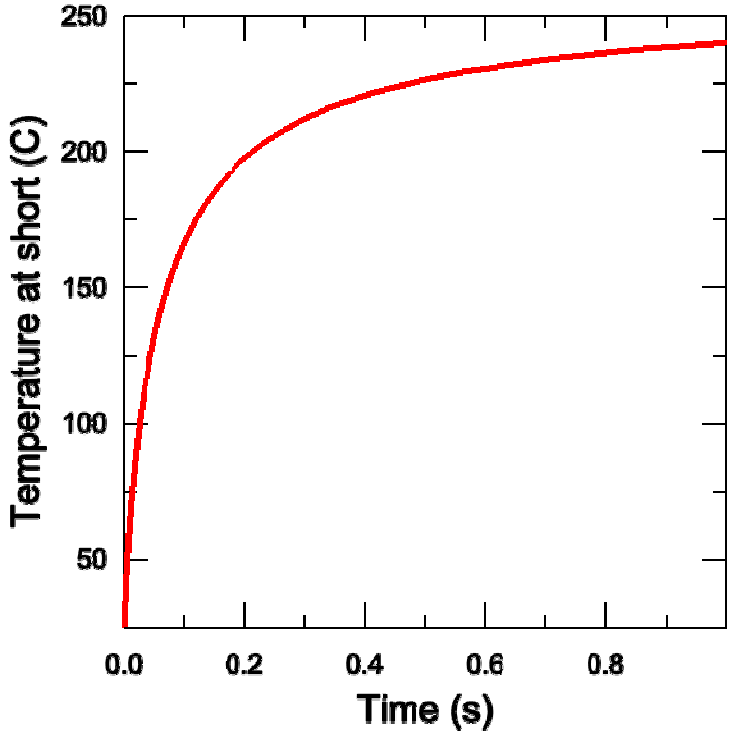
Temperature Profile in an 18650 Immediately following an internal short circuit



Simulations show that the thermal energy of an internal short by itself is sufficient to increase the local temperature by 200ºC in less than a second.

Simulated Temperature Rise Caused by Internal Short





18650 cell charging at 0.7 C-rate which develops an internal short of diameter 100 μm at time 0.

There are important differences between safety-to-withstand abuse, versus safety-to-withstand field failures.

Abuse Tolerance

- Predictable
- Common to all cells
- Can/should be evaluated at the cell level
- Various chemistries can/should be evaluated for relative abuse tolerance
- Time constants relatively long
- Can be augmented by protection devices

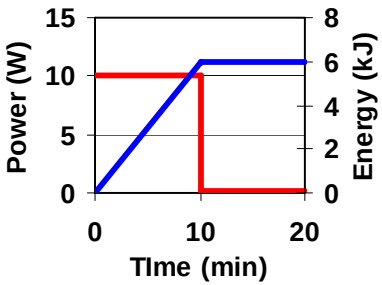
Field Failures

- Not predictable
- One-in-a-million (or less)
- Difficult to evaluate at the cell level, or through QC
- Materials must be evaluated for relative kinetics, pressures
- Much higher temperatures can occur *quickly*
- PTC, CID, shutdown separators, electronic controls are not effective

For a given set of initial and boundary conditions, the model calculates the time-dependent temperature distribution following an internal short-circuit.

Inputs:

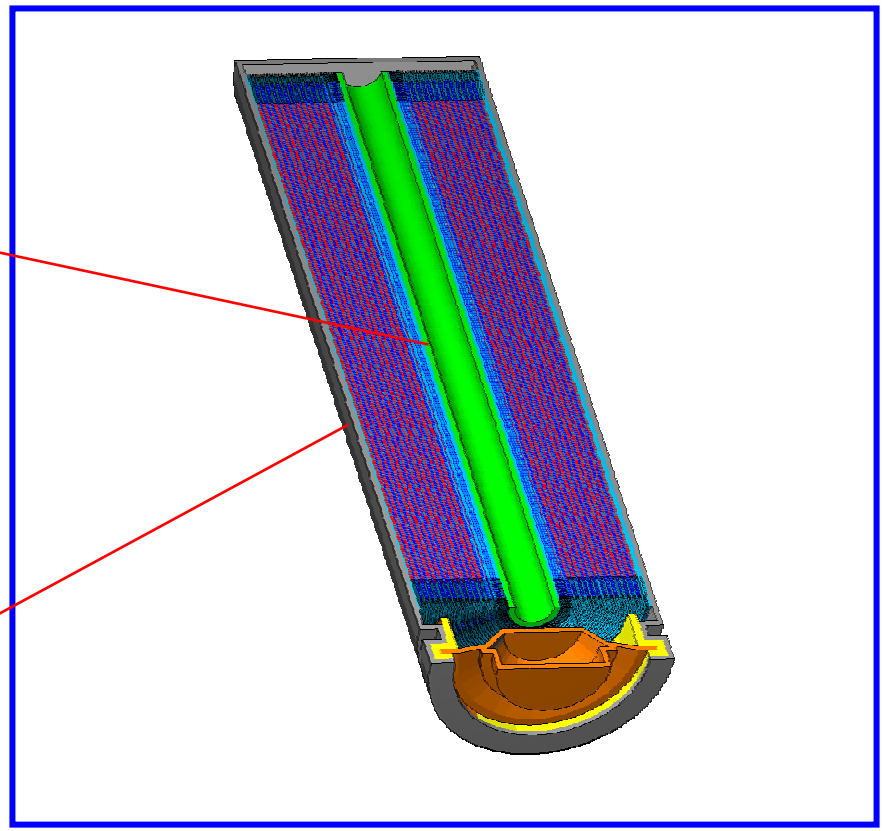
Heat generation associated with a short circuit:



Boundary conditions:

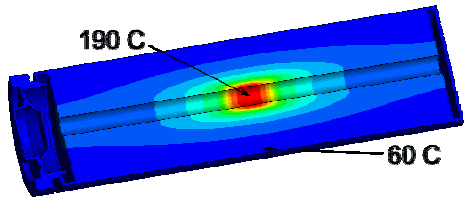
- Surface film coefficient
- Sink temperature

Transient FEA model with coupled decomposition rates & heat transfer

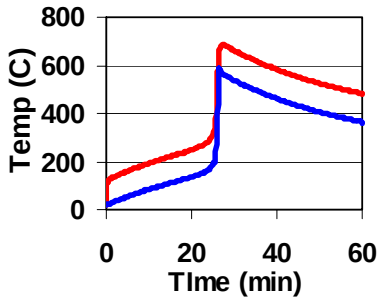


Outputs:

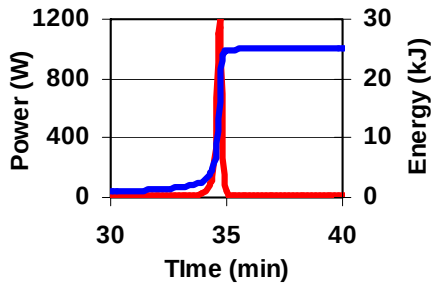
- Distribution of T, Q_{dot} at selected time intervals.



- Temperature histories at selected points in the cell.



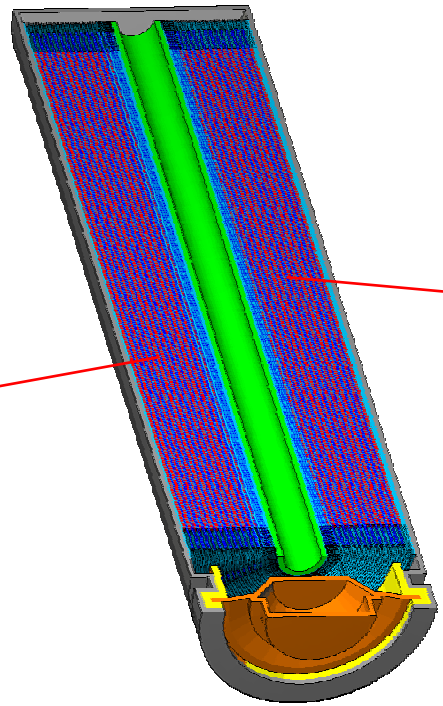
- Total cell heat generation rates, surface heat loss, etc.



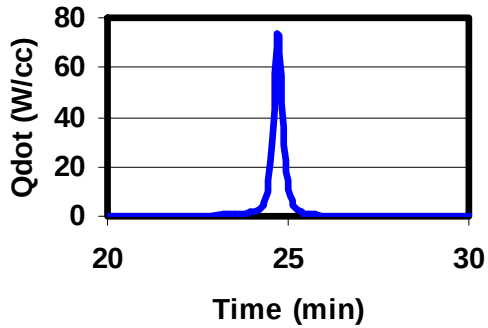
The model incorporates measured or calculated thermal properties of all cell components, and has routines to estimate the local heat release from the anode and cathode as a function of temperature and time.

- **Thermal properties for all cell constituents are defined as input to the model:**
  - **Density**
  - **Specific heat**
  - **Conductivity**
- **Many of the active material parameters have been measured from 18650 cells; others are taken from literature**
- **Jellyroll constituents can be modeled individually or as a composite**

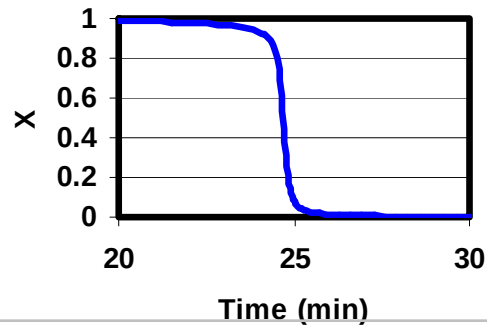
2-D or 3-D FEA model



- **For both the anode and cathode, the rate of heat release is defined at each material point based on the local temperature.**



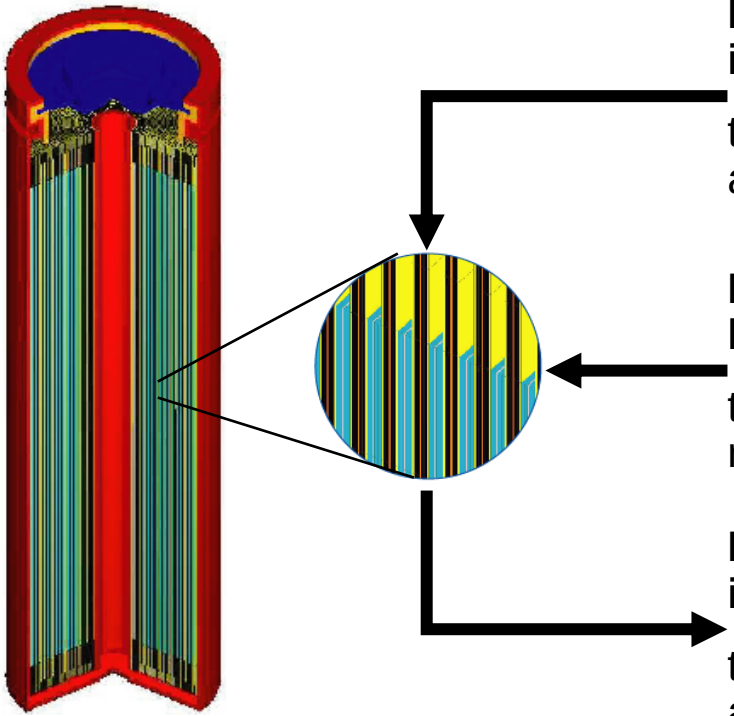
- **State variables that track the evolution of species concentration are calculated and updated during each time step.**



Thermal propagation is determined by a complex relationship between instantaneous values of temperature, concentrations, and rates of reactions, all variable as f(T) at all points in the system.

Propagation occurs when for a given volume within the cell at any instant:

Rate of Heat in + rate of heat generation > rate of heat out



Heat into the volume is determined by instantaneous local values of:

temperature gradient, temperature, specific heat, and thermal conductivity

Heat generation is determined by instantaneous local values of:

temperature, concentrations of reactants, heat of reaction(s)

Heat out of the volume is determined by instantaneous local values of:

temperature gradient, temperature, specific heat, and thermal conductivity

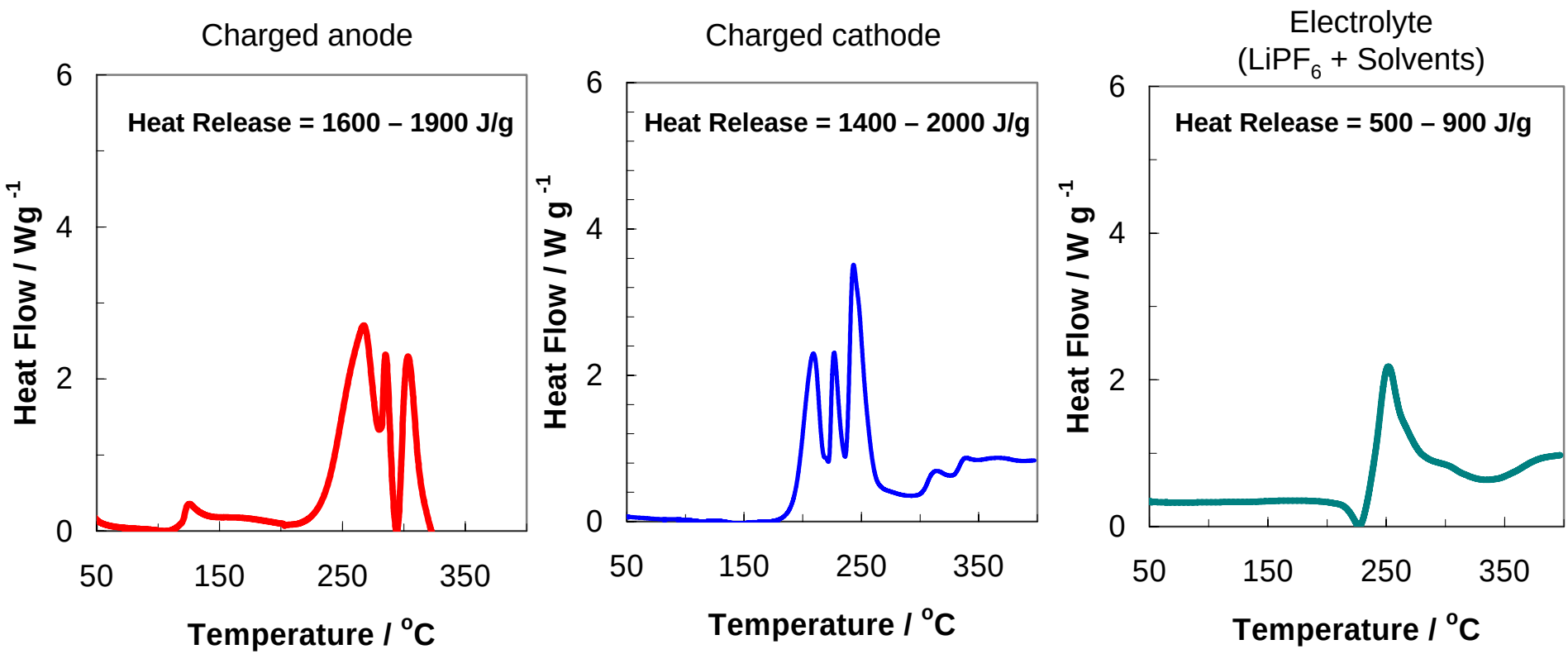
Li-ion cells contain energetic materials, which are stimulated to release heat in a field-failure.

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.

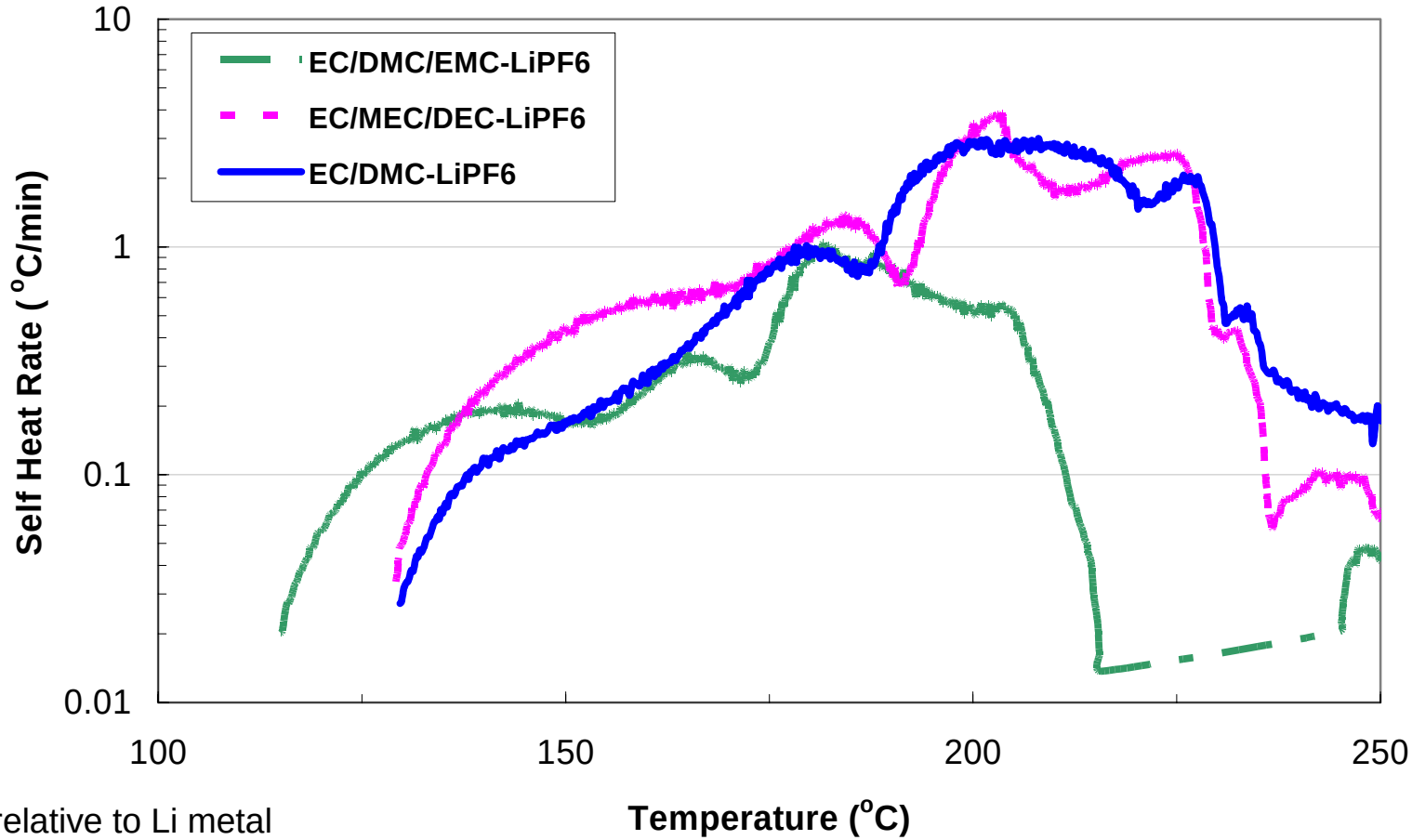
Exothermic reactions of the anode and cathode active materials with the electrolyte, and the electrolyte self-reaction can contribute to thermal runaway.



* Energy per gram of materials. Actual energy release in a cell will be different for each component

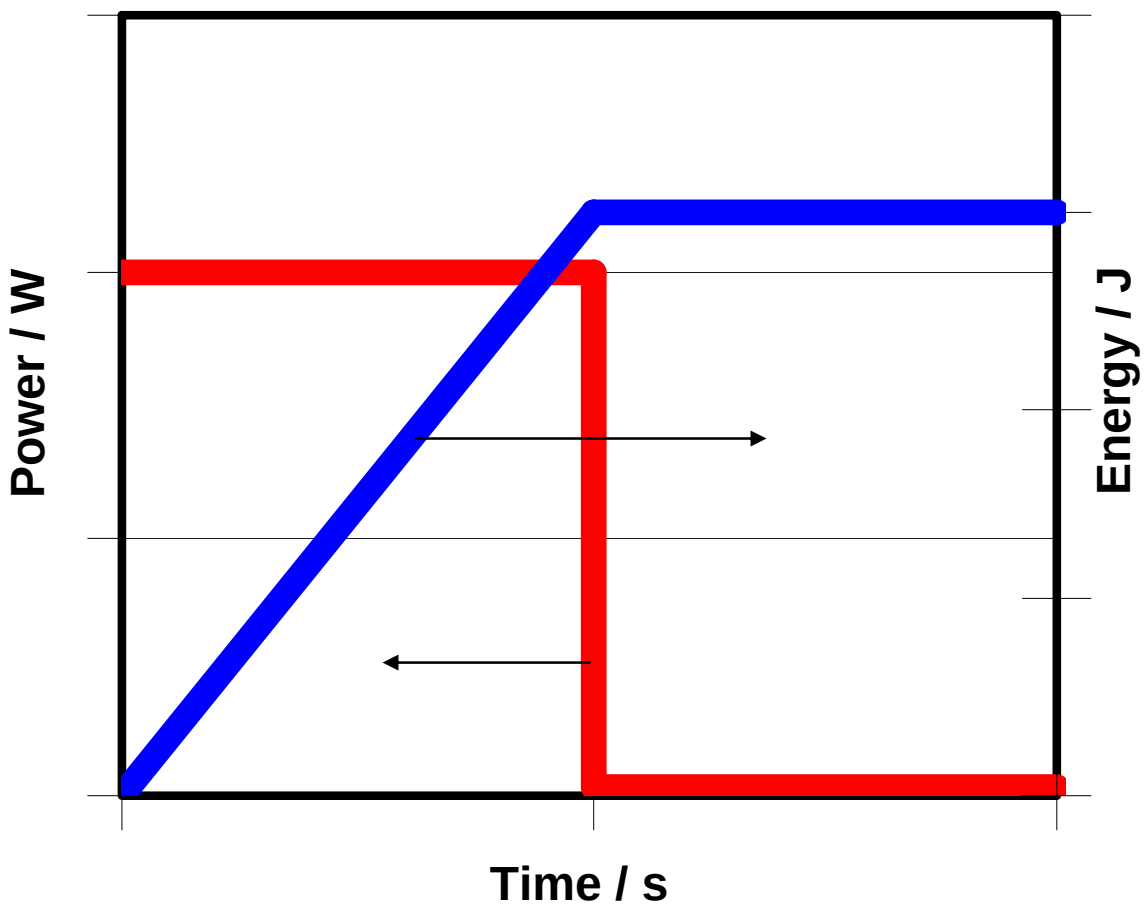
We routinely use the Accelerating Rate Calorimetry (ARC) to assess the heat release kinetics of the active materials in contact with electrolyte.

ARC measurements of the Effect of solvent (with 1 M $LiPF_6$) composition on the heat release kinetics from reaction with charged LCO*



* 4.3 V relative to Li metal

We characterize the short by two parameters: the power dissipated in the short and the energy dissipated in the short.

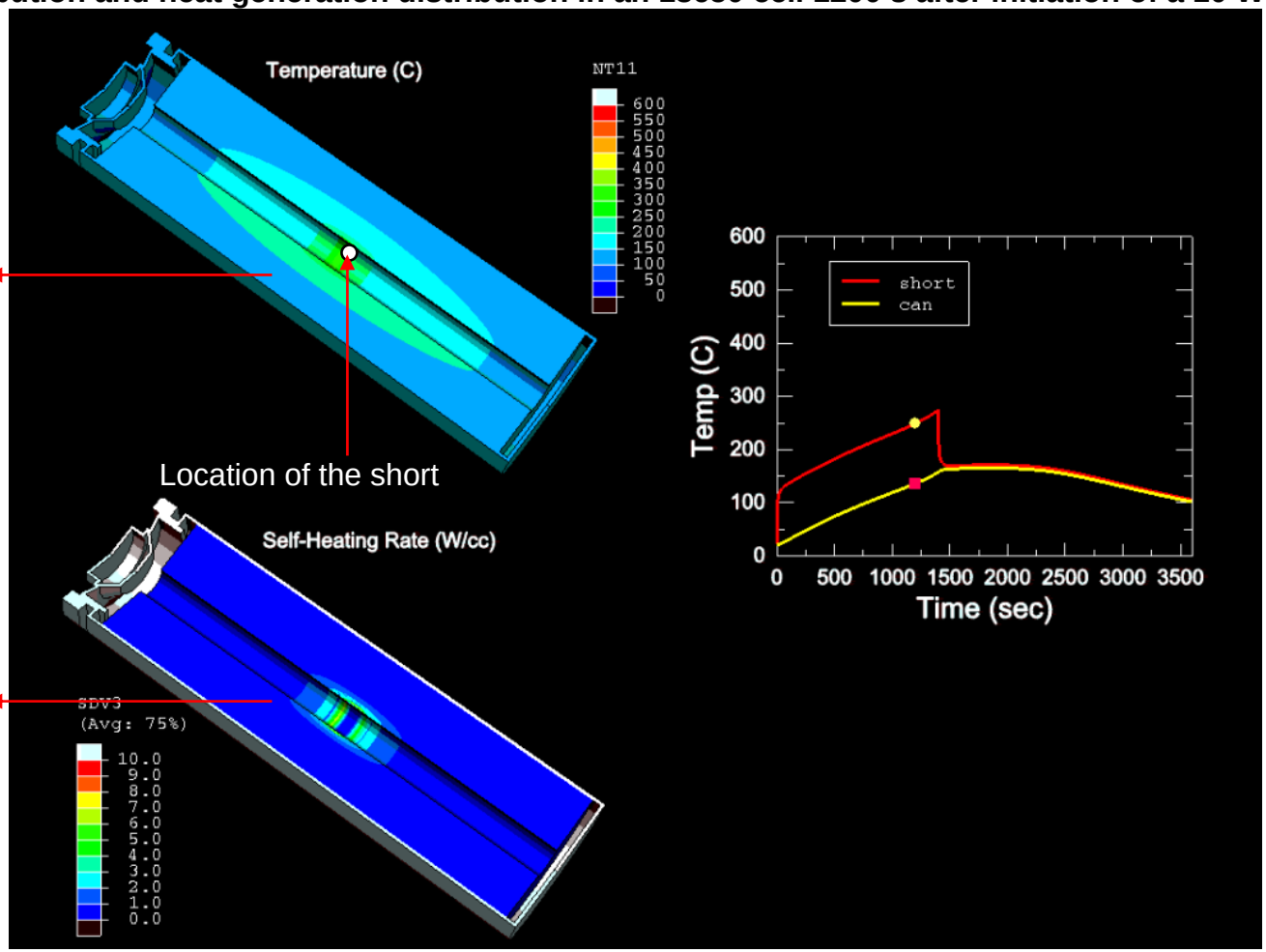


FEA simulations show the temperature distribution and heat release profile when an internal short does not result in a thermal runaway (CASE B).

Temperature distribution and heat generation distribution in an 18650 cell 1200 s after initiation of a 10 W short circuit

Temperature distribution

Distribution of heat generation from thermal decomposition reactions

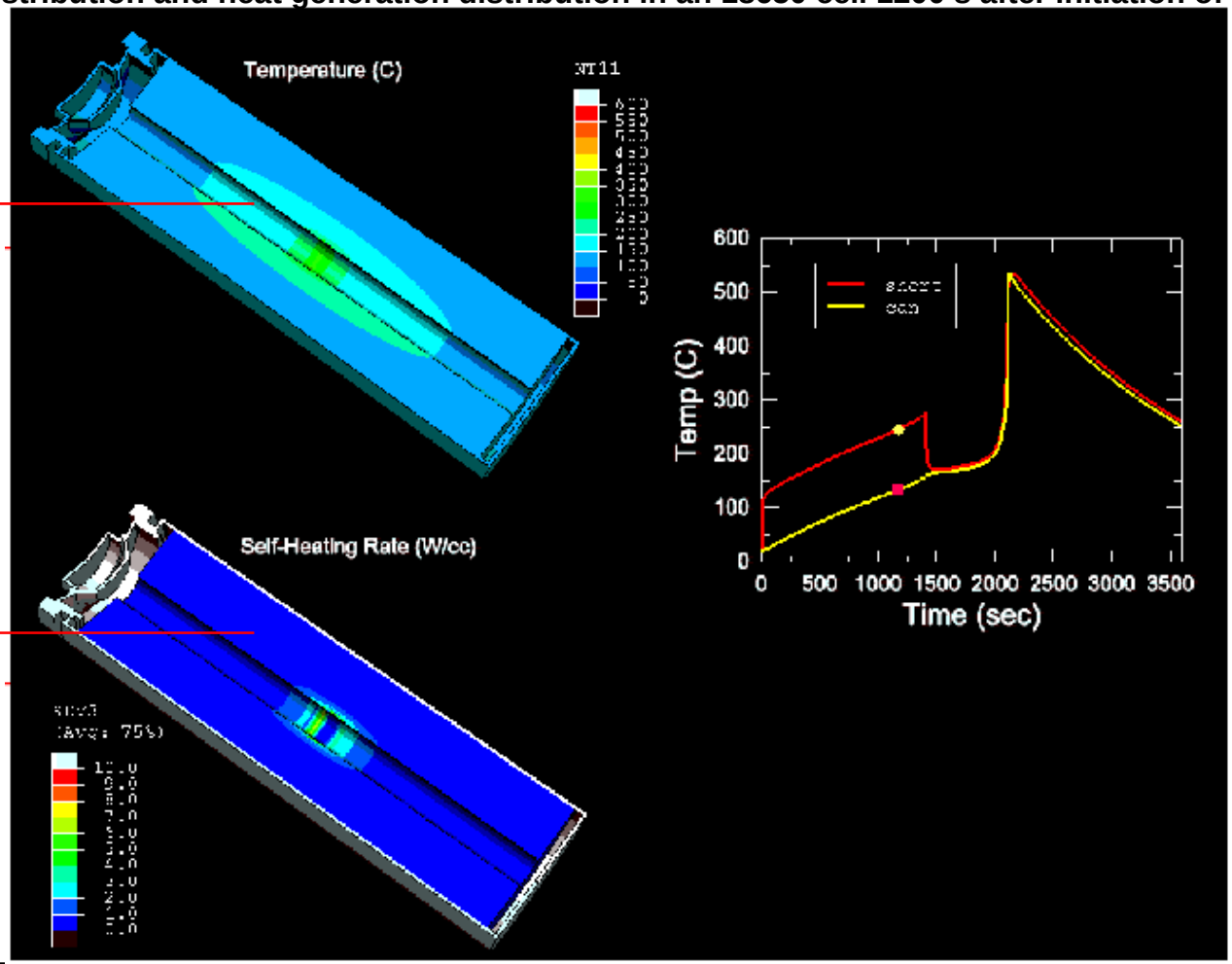


FEA simulations show the temperature evolution and heat release profiles when an internal short results in a thermal runaway (CASE B').

Temperature distribution and heat generation distribution in an 18650 cell 1200 s after initiation of a 10 W short circuit

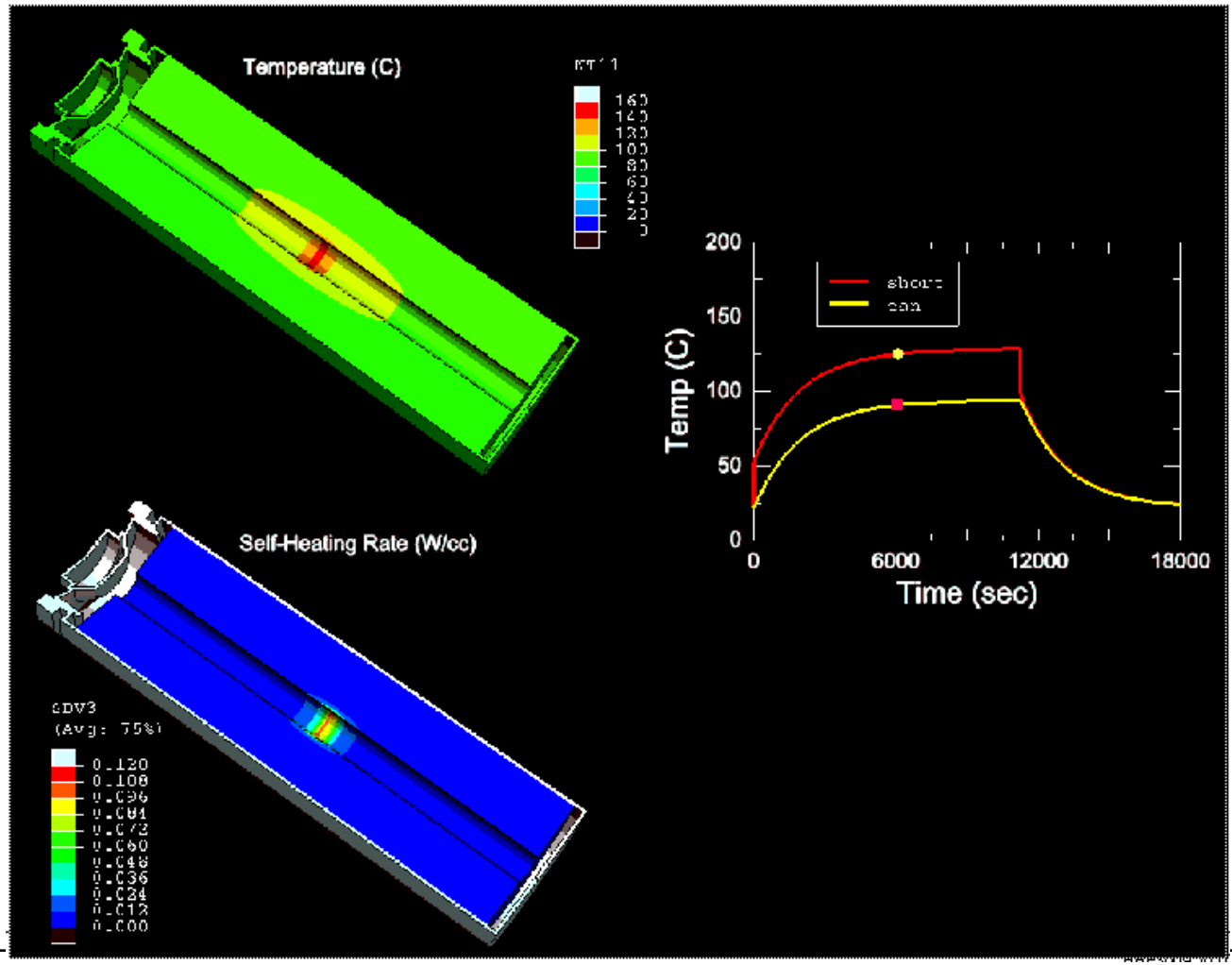
Temperature distribution

Distribution of heat generation from thermal decomposition reactions



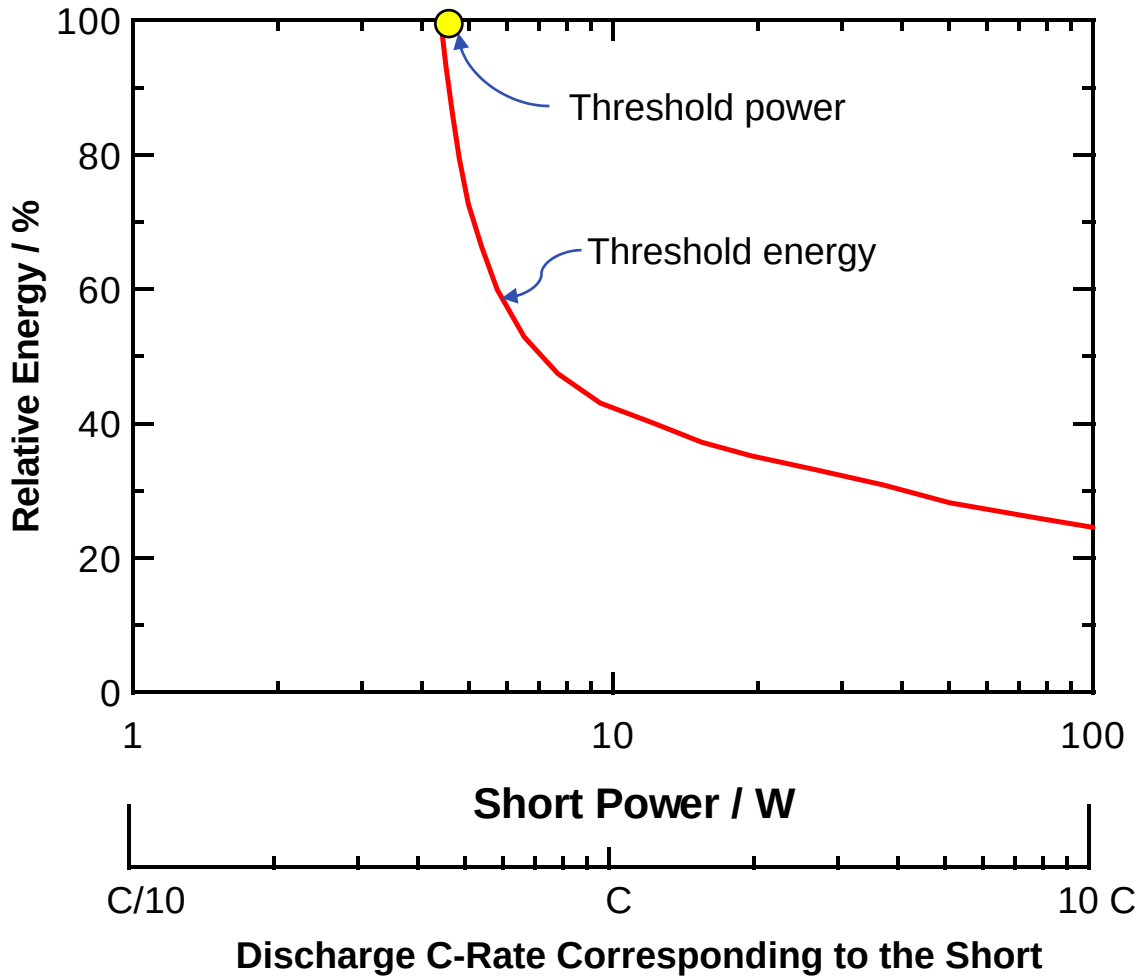
A “mild” short will use the energy of the cell to raise temperature, but not necessarily lead to thermal runaway (CASE A).

Temperature distribution and heat generation distribution in an 18650 cell 6000 s after initiation of a 3.8 W short



Our simulations show that *both* a threshold power and threshold energy must be exceeded for thermal runaway to occur.

Definition of threshold power and threshold energy



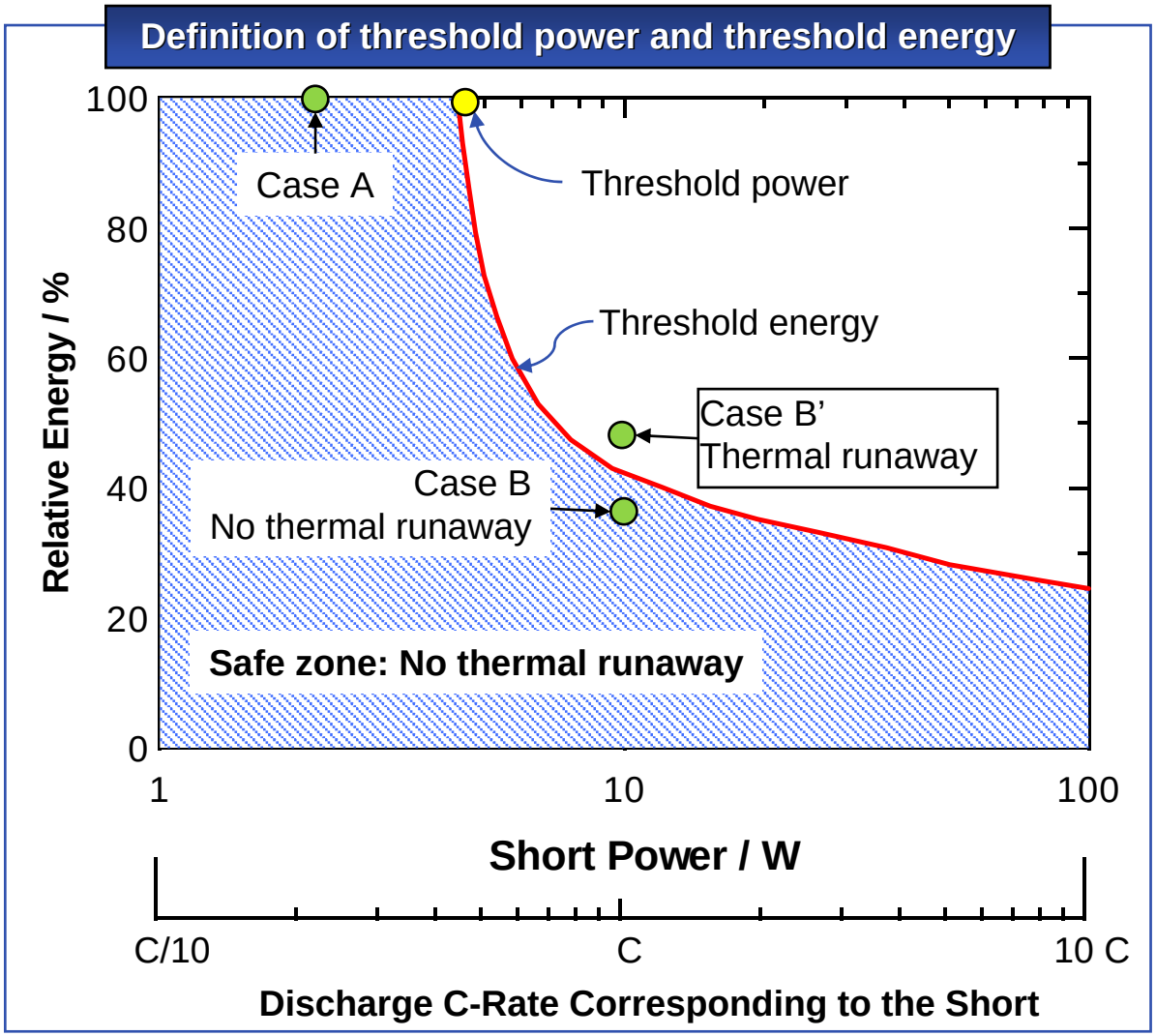
$$RE = \frac{E_s}{E_e}$$

RE: Relative Energy

E_s: Energy dissipated in the short

E_e: Electrical energy stored in the battery

For either power or energy levels lower than the threshold values, thermal runaway will not occur.



$$RE = \frac{E_s}{E_e}$$

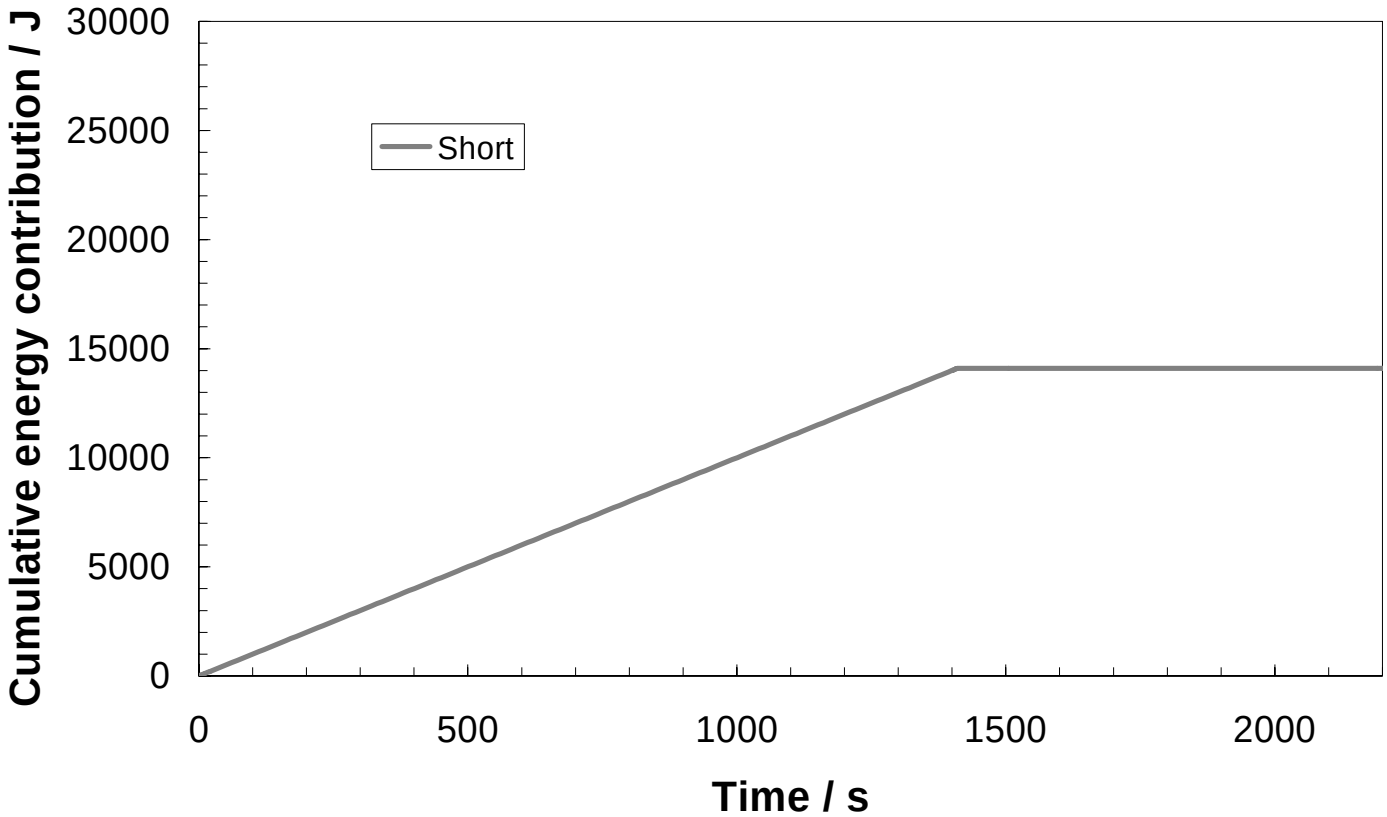
RE: Relative Energy

E_s: Energy dissipated in the short

E_e: Electrical energy stored in the battery

The energy dissipated in the short is primarily responsible for raising the cell temperature – anode and cathode contributions up to 1410 s are negligible.

Cumulative heat generation contributions in an 18650 cell with a 10 W short that is active for 1410 s



The values shown on this plot are integrated over the cell area and cell volume

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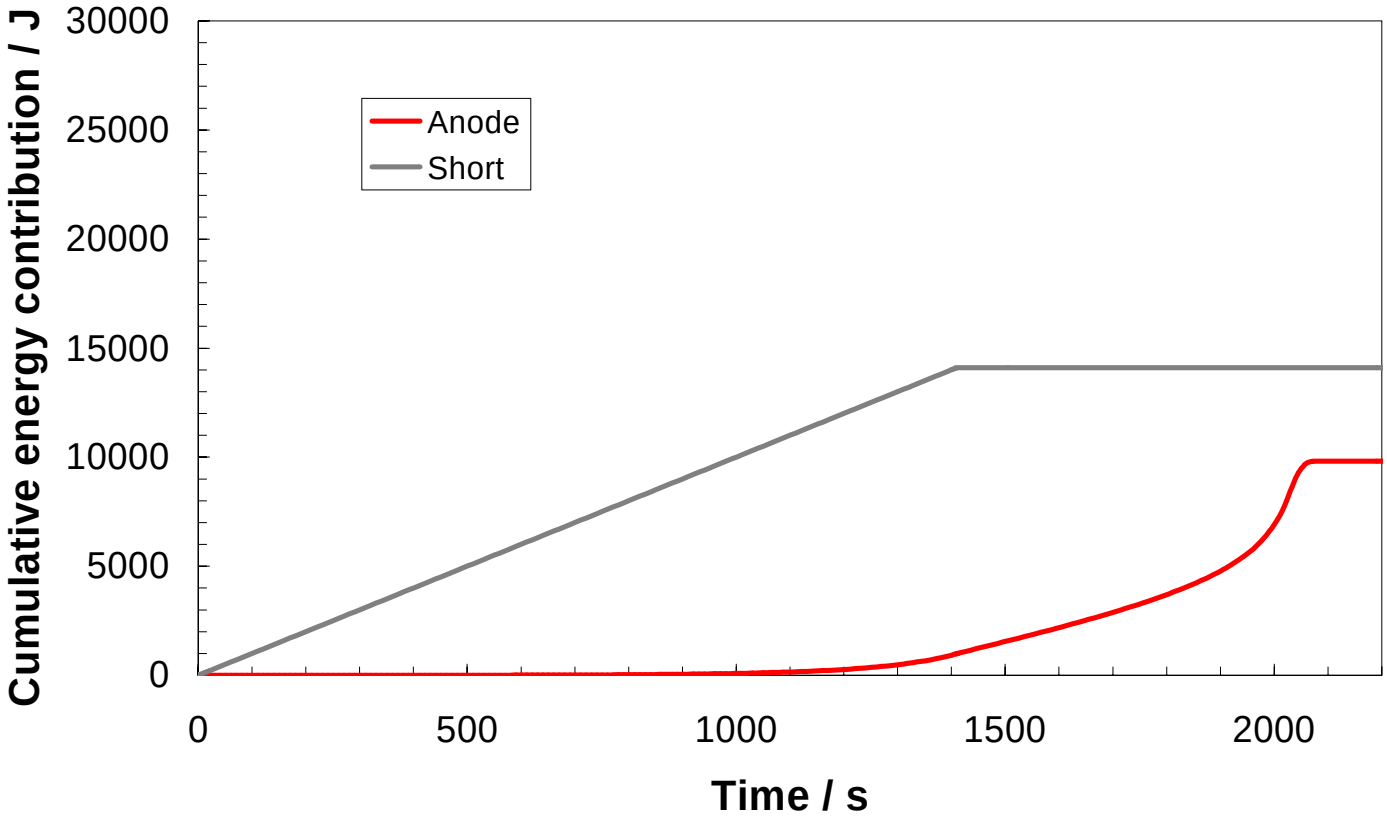

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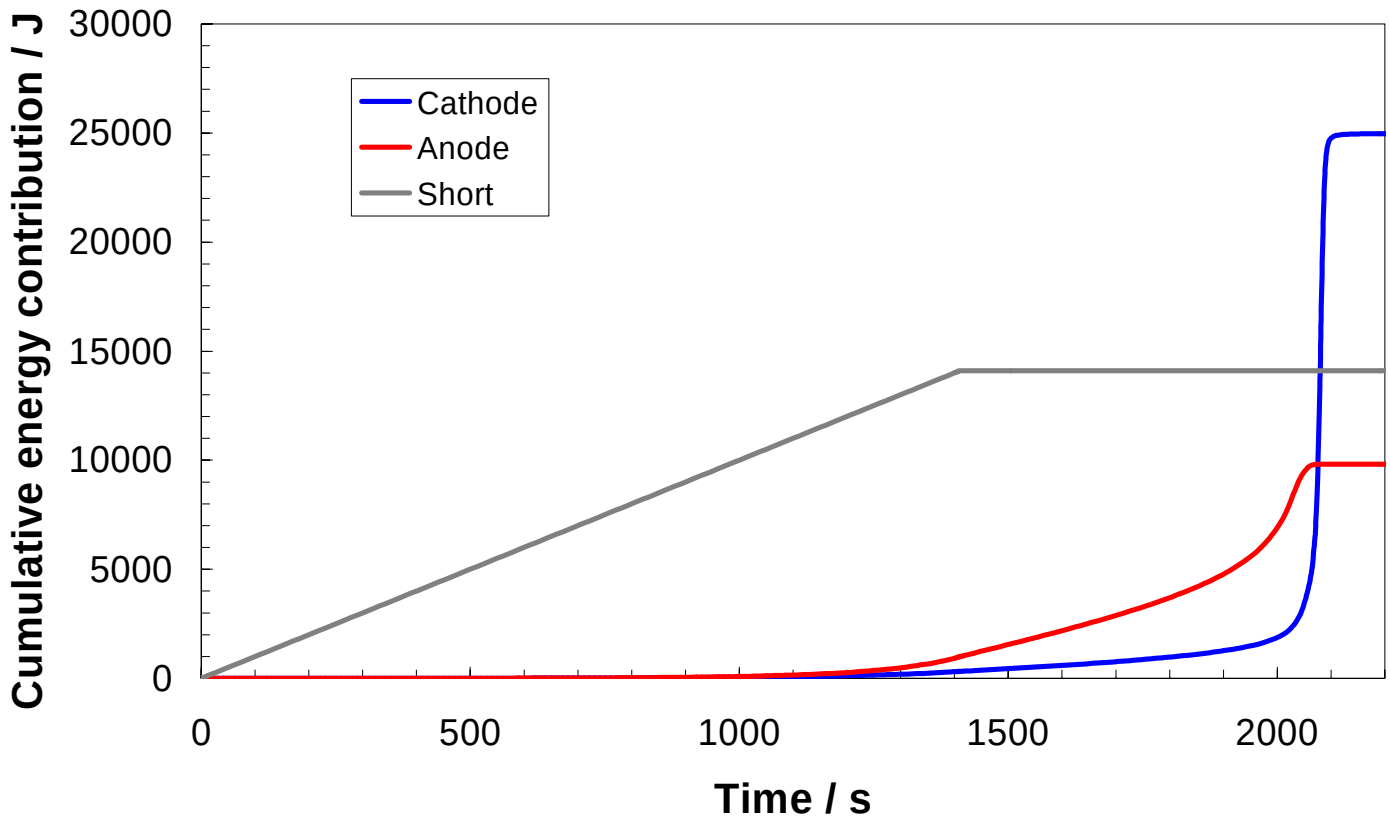
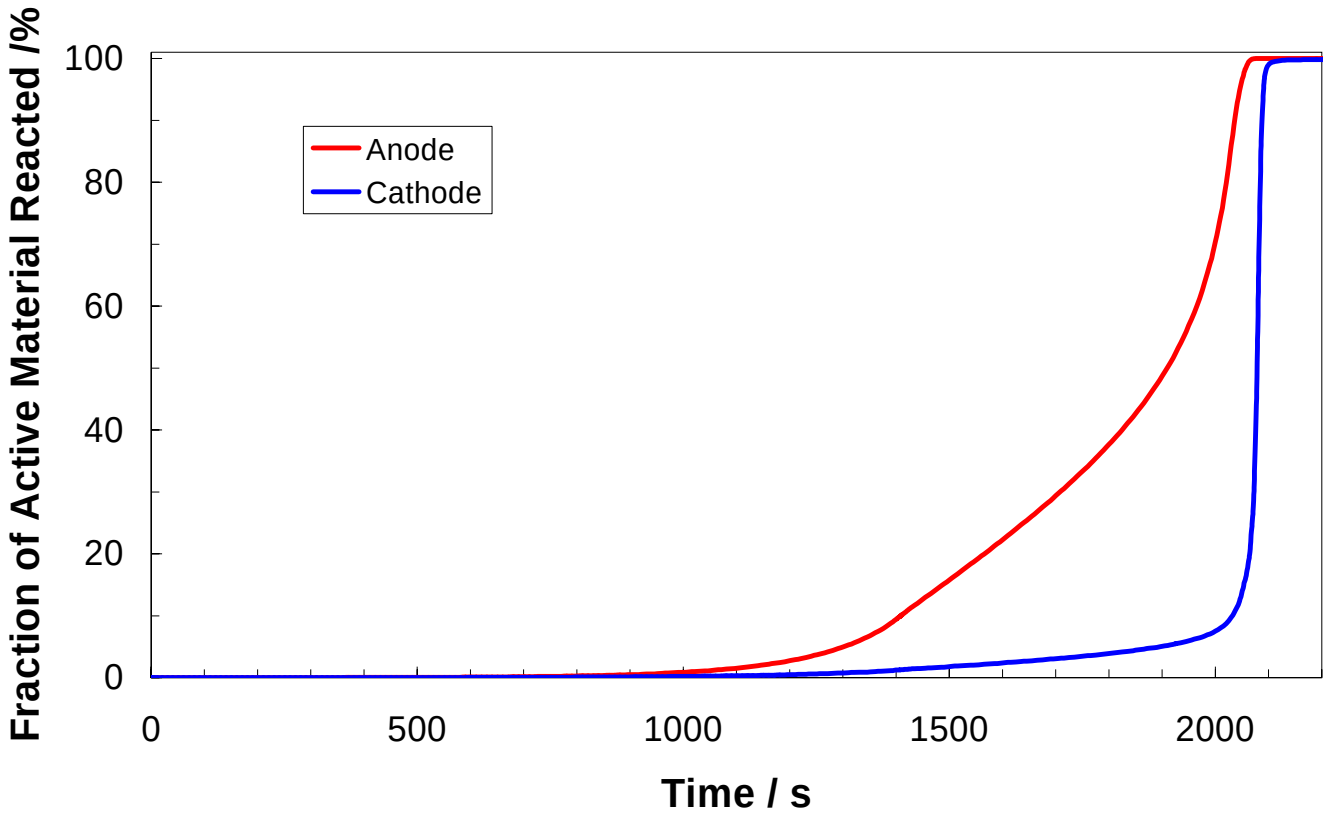


The values shown on this plot are integrated over the cell area and cell volume

At 1410 s, only a small fraction of the anode or cathode active materials have reacted.

Fraction of the anode and cathode active materials reacted in an 18650 cell with 10 W internal short that is active for 1410 s



The values shown on this plot are integrated over the cell area and cell volume

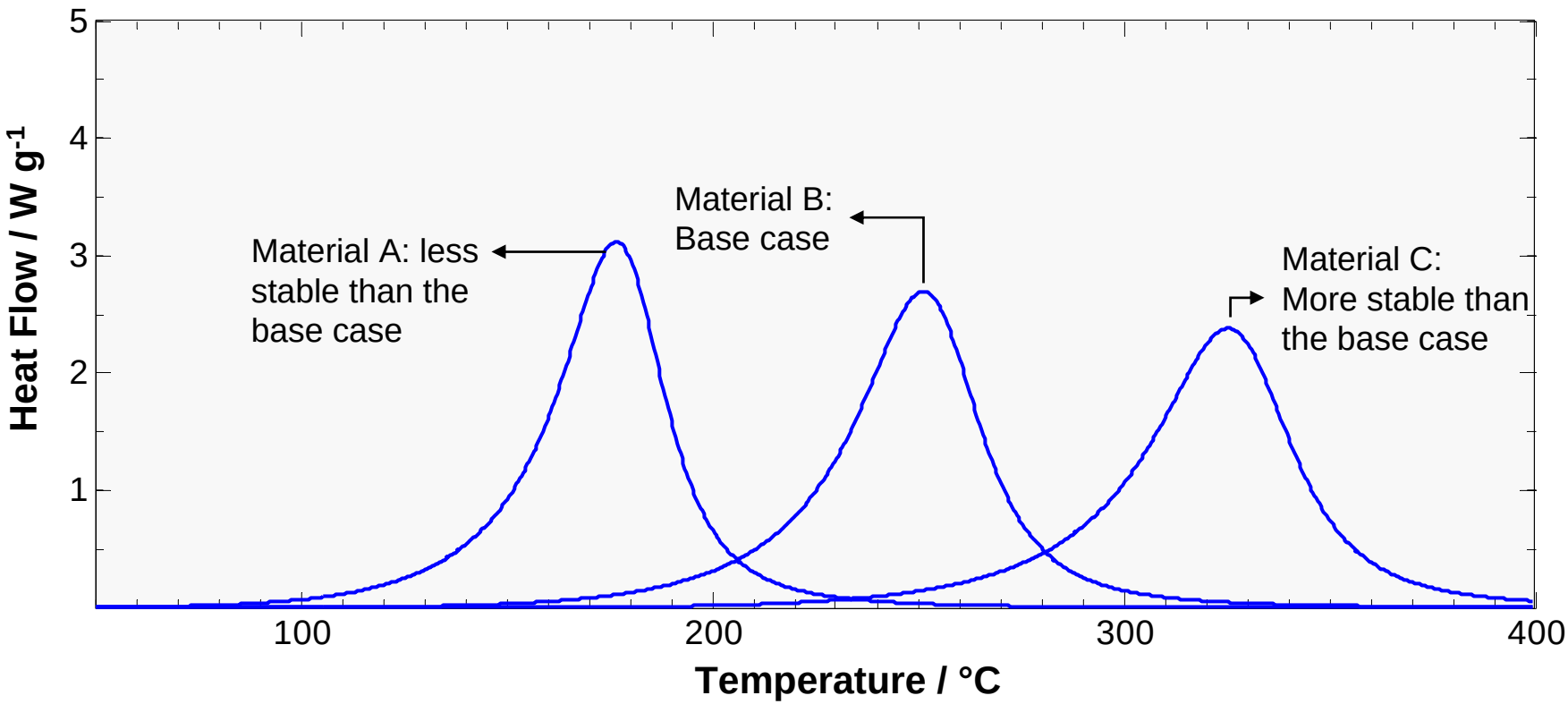
THE ROLE OF CATHODE MATERIAL …

As an example, here we show how the model can help understand whether 'safer' cathodes can eliminate field-failures as is often claimed in the literature.

- The amount of heat and the rate of heat release from metal-oxide cathodes exceeds that from the anode in a typical cell;
- For this reason, developers have been focused on developing 'safer' cathodes in an attempt to influence the outcome following an internal short circuit;
- In fact, there are several developers who claim that field-failures can be eliminated by the use of 'safer' (low thermal release) cathodes such as $LiFePO_4$ or $LiMn_2O_4$
- However, the influence of cathode heat release kinetics on the propensity for field-failure is not adequately understood;
- We simulate the thermal behavior of a wide range of cathodes by adjusting the activation energy in our model;
  - We use $LiCoO_2$ as our base case;
  - Lower activation energy => less stable, more reactive than $LiCoO_2$;
  - Higher activation energy => more stable, less reactive than $LiCoO_2$;

We adjusted the activation energy to cover the range of heat release kinetics observed in commercial cathodes.

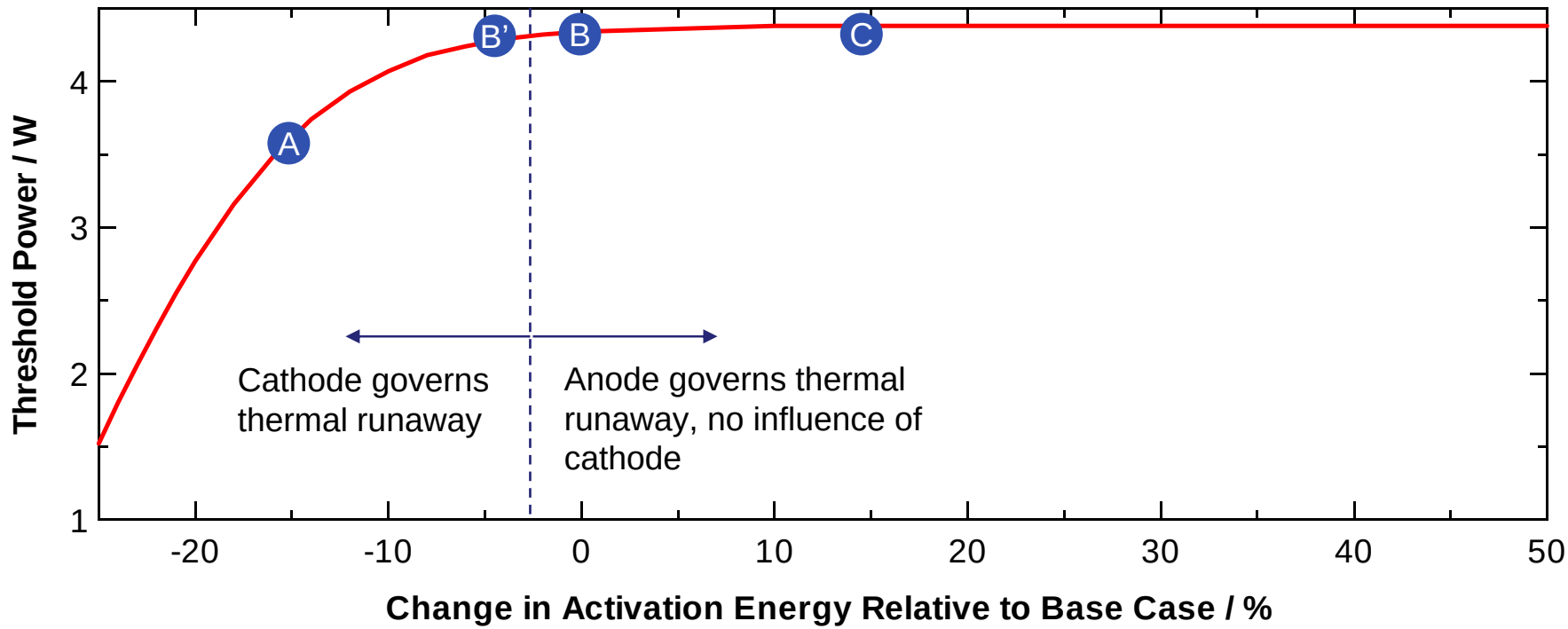
Examples of Simulated DSC curves for the cathode and experimental data for select commercially available cathodes



* LCO: $LiCoO_2$, NCM: $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

Once a cathode material satisfies a certain minimum requirement for kinetics of heat release, further improvement does not affect the threshold power for thermal runaway.

Simulation results: Effect of cathode activation energy on the threshold power

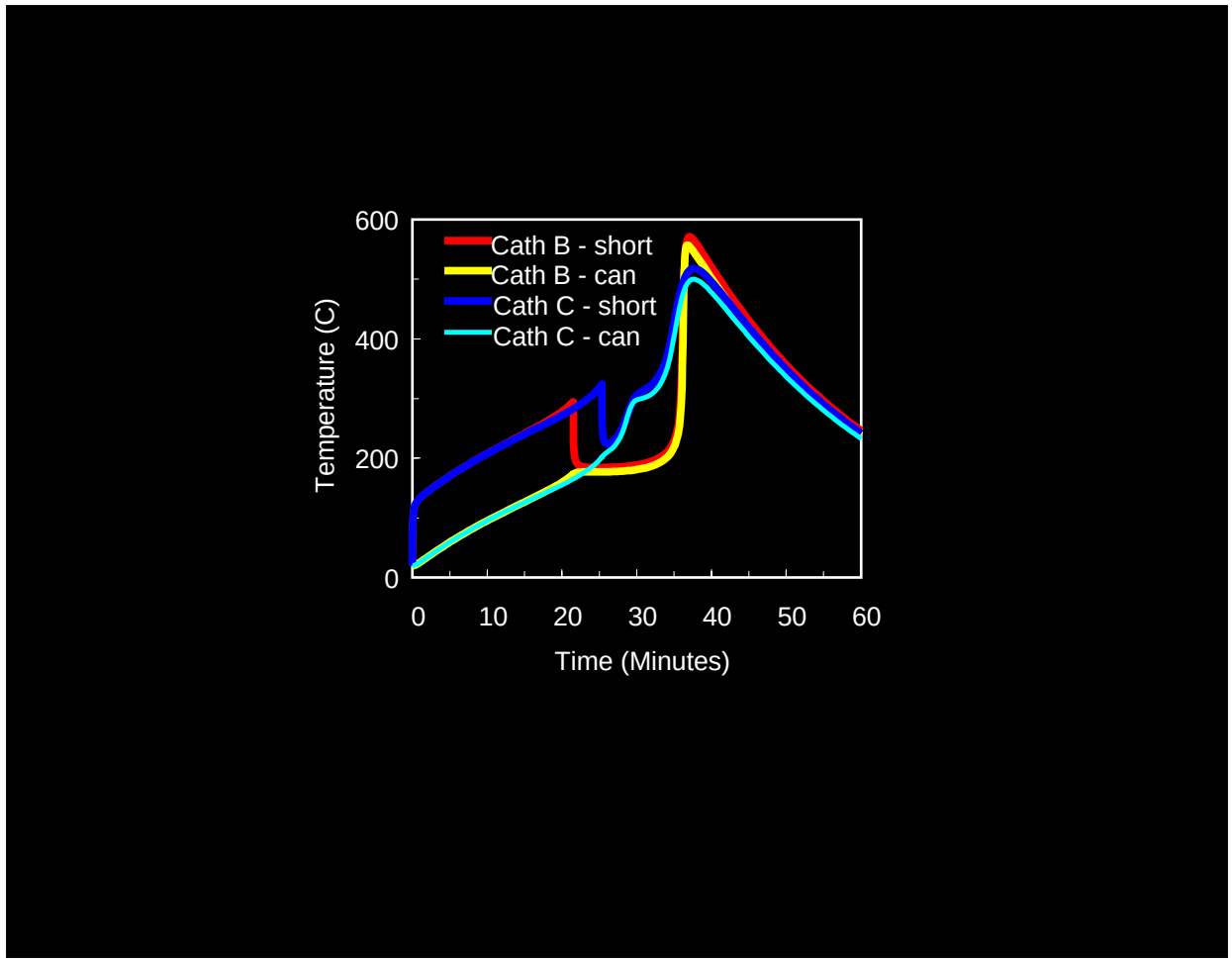


- A: Highly reactive cathode
- B, B': Similar to commercial $LiCoO_2$
- C: Metal-oxide cathode with improved stability

WHAT DIFFERENCE DOES THE CATHODE MATERIAL HAVE ON THERMAL RUNAWAY ?

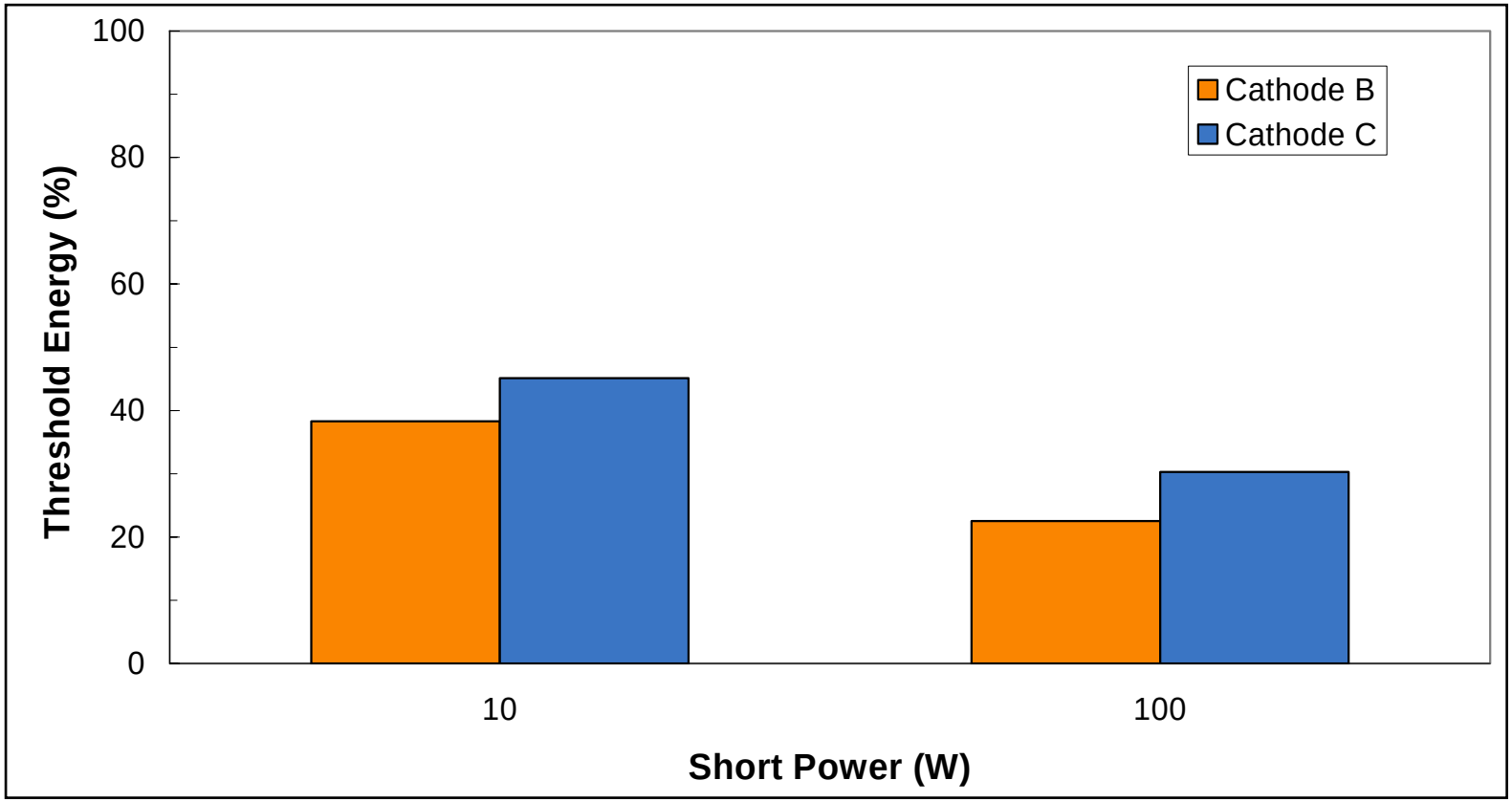
ANSWER: IT CHANGES THE TIME TO RUNAWAY…

However, at the threshold energy input for each cathode, the use of cathode C delayed thermal runaway only by 4 min. compared to cathode B.



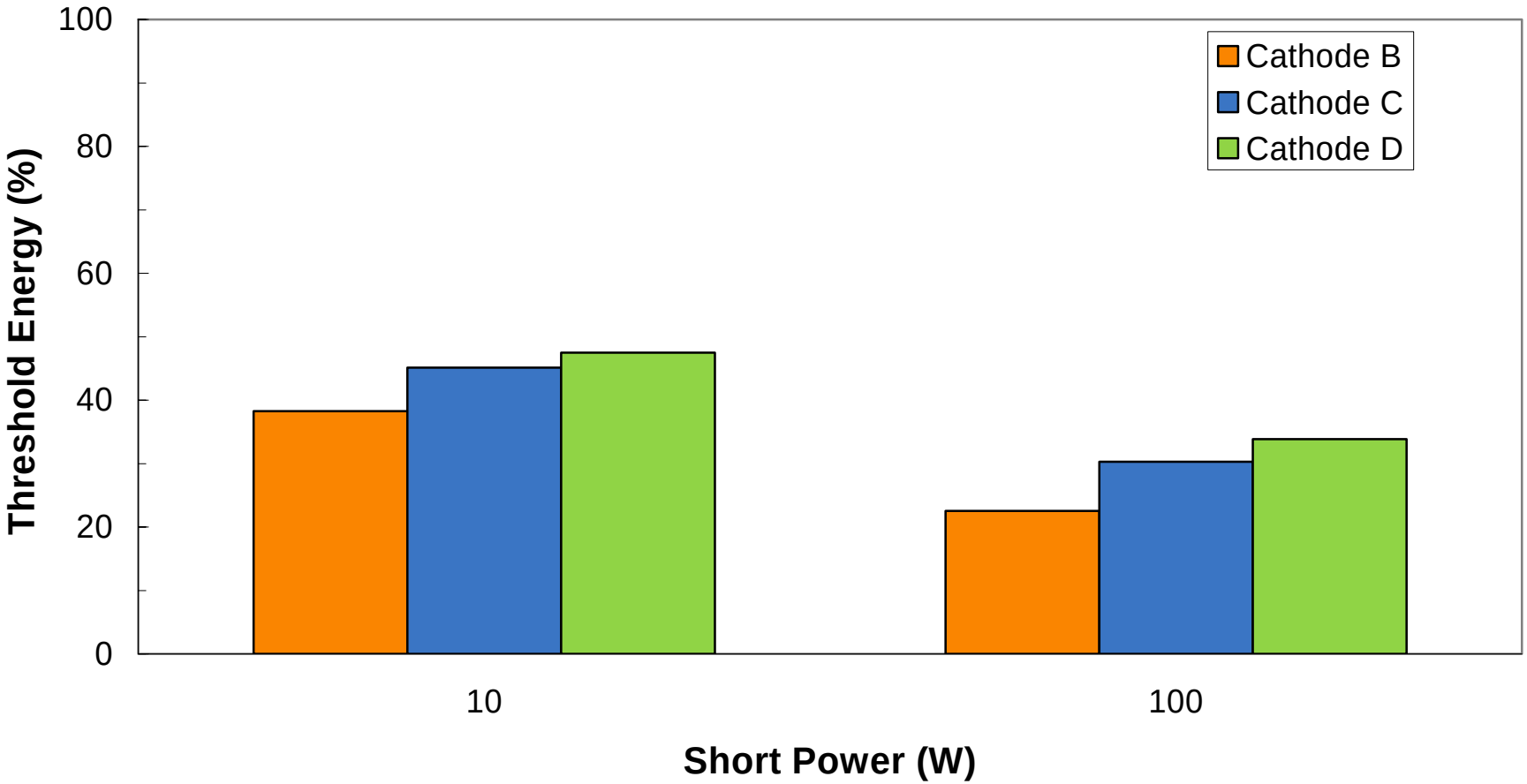
- B: Similar to commercial $LiCoO_2$
- C: Metal-oxide cathode with improved stability, , such as NCM/NMC

The threshold energy increases slightly with increasing stabilization of the cathode.



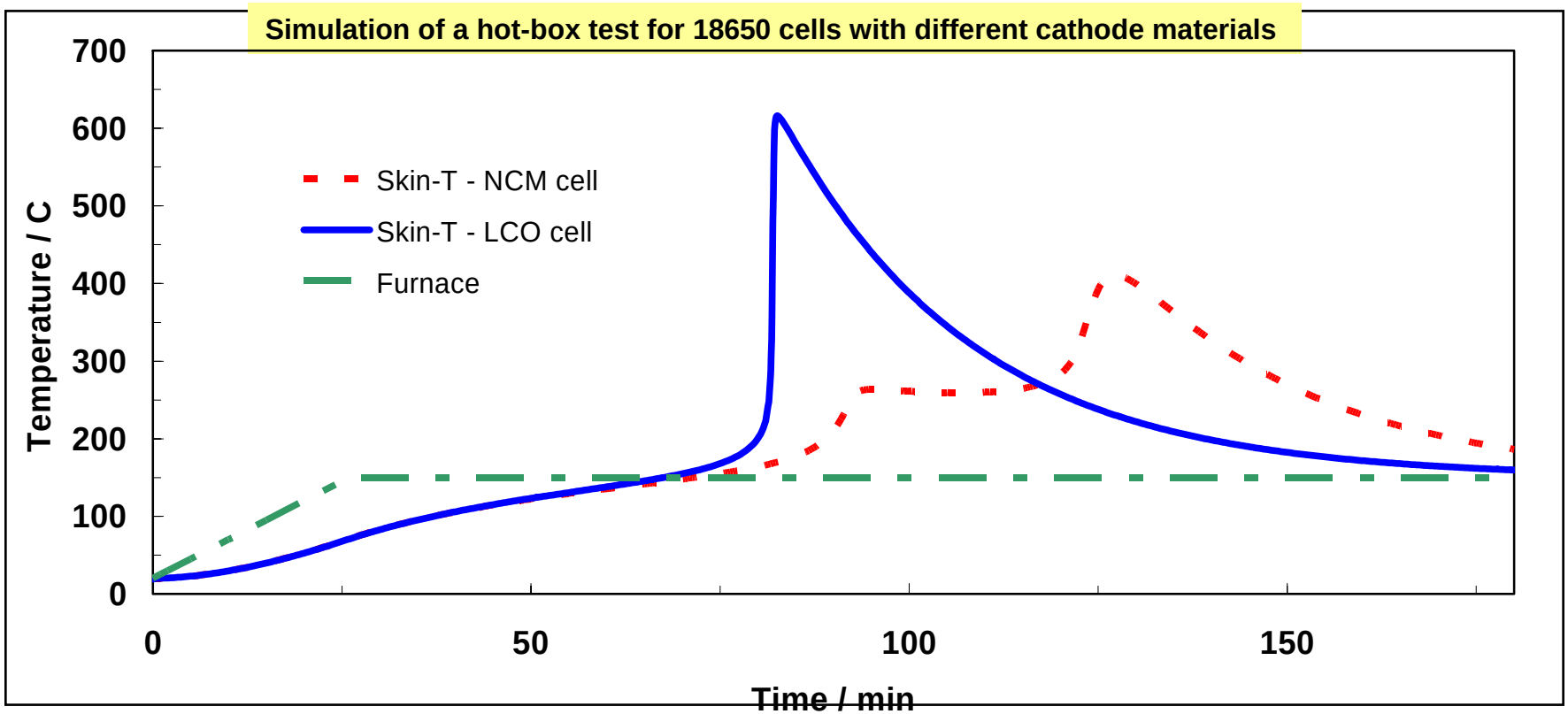
- B: Similar to commercial $LiCoO_2$
- C: Metal-oxide cathode with improved stability, such as NCM
- Threshold energy is the minimum relative energy needed for thermal runaway to occur

The threshold energy increases only slightly even if the heat release from the cathode (shown as cathode D) were zero.



- B: Similar to commercial $LiCoO_2$
- C: Metal-oxide cathode with improved stability, such as NCM
- D: Cathode with zero heat release, but in this case the electrolyte-self reaction heat release was taken into account
- Threshold energy is the minimum relative energy needed for thermal runaway to occur

In a hot box abuse test, where the cell is heated slowly, the maximum skin temperature from thermal runaway *does* depend on the cathode reaction kinetics, as has been observed experimentally.



However, this result cannot be extrapolated to field-failures. Essentially, whether or not thermal runaway occurs following an internal short is determined by heat balance in the vicinity of the short circuit, which is not at all reflected in an abuse test.

SOME CONCLUSIONS ...

Major effort is required to improve the ways we address safety in lithium-ion batteries.

- Standard abuse tests used across the industry have very little relevance to the actual safety incidents that occur.
- FEA models, supported with key thermal data, can provide real insight to help develop safer cells and batteries.
- There are threshold values for both short circuit power and energy below which a safety incident does not occur.
- Safety is a system issue that cannot be judged based solely on measurement of a property of single component in a cell.
- New strategies/technologies for mitigation of incidents are required.