5 Myths

Jan N. Reimers
Magna E-Car Systems

What is a Myth?

1. A traditional or legendary story, usually concerning some being or hero or event, with or without a determinable basis of fact or a natural explanation, especially one that is concerned with deities or demigods and explains some practice, rite, or phenomenon of nature.
2. Stories or matter of this kind: realm of myth.
3. Any invented story, idea, or concept: His account of the event is pure myth.
4. An imaginary or fictitious thing or person.
5. An unproved or false collective belief that is used to justify a ~~social institution~~ cell technology.

The devil is in the details

- Some of these myths may be converted into correct statements with suitable qualifiers.
- In other words the truth is buried in the fine print.
- Experts tend to qualify their statements accordingly.
- Non experts then propagate the unqualified statement.
- A Myth is born.

#5: Cathode Exotherms above 200^{o}C Determine Cell Safety

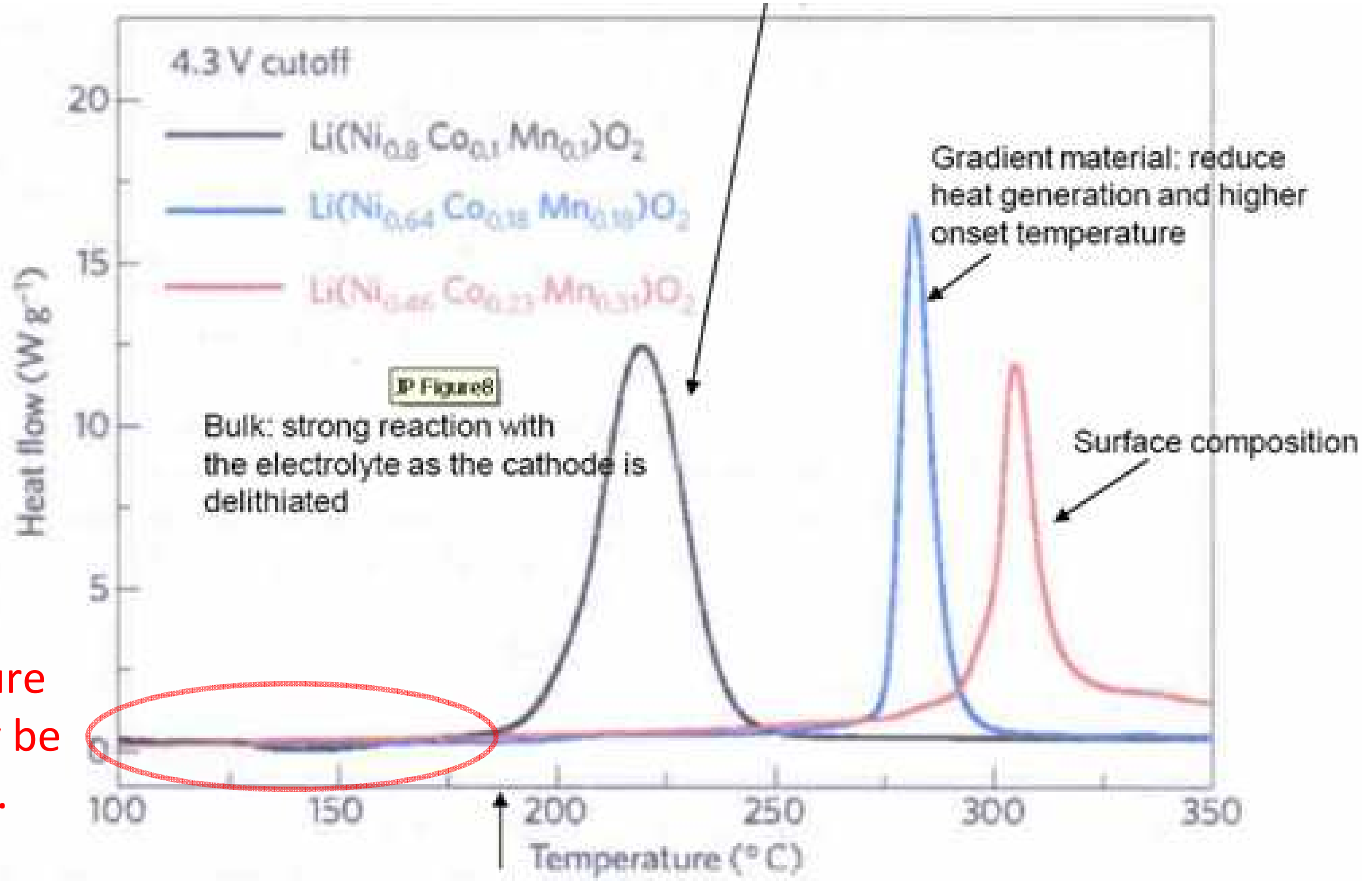
- Test:
  - Charge any cathode
    - $LiCoO_2 \rightarrow Li_{0.5}CoO_2$
    - $Li(NiMnCo)O_2 \rightarrow Li(NiMnCo)O_2$
    - $Li_{1.1}Mn_{1.9}O_4 \rightarrow Li_{0.4}Mn_{1.9}O_4$
    - Etc….
  - Then heat it up in electrolyte.
  - Look for heat evolved from the mixture
  - Big names:
    - Differential Scanning Calorimetry (DSC)
    - Accelerated Rate Calorimetry (ARC)

Probability And Severity

- We need to worry about two orthogonal issues:
  1. The probability of getting a cell into a thermal runaway condition.
  2. The severity of a thermal runaway event. I.e. how much heat is generated.
- We need to consider both of these issues when interpreting data.
- Most literature focuses on severity.

Some Data

Peak Area relates to severity

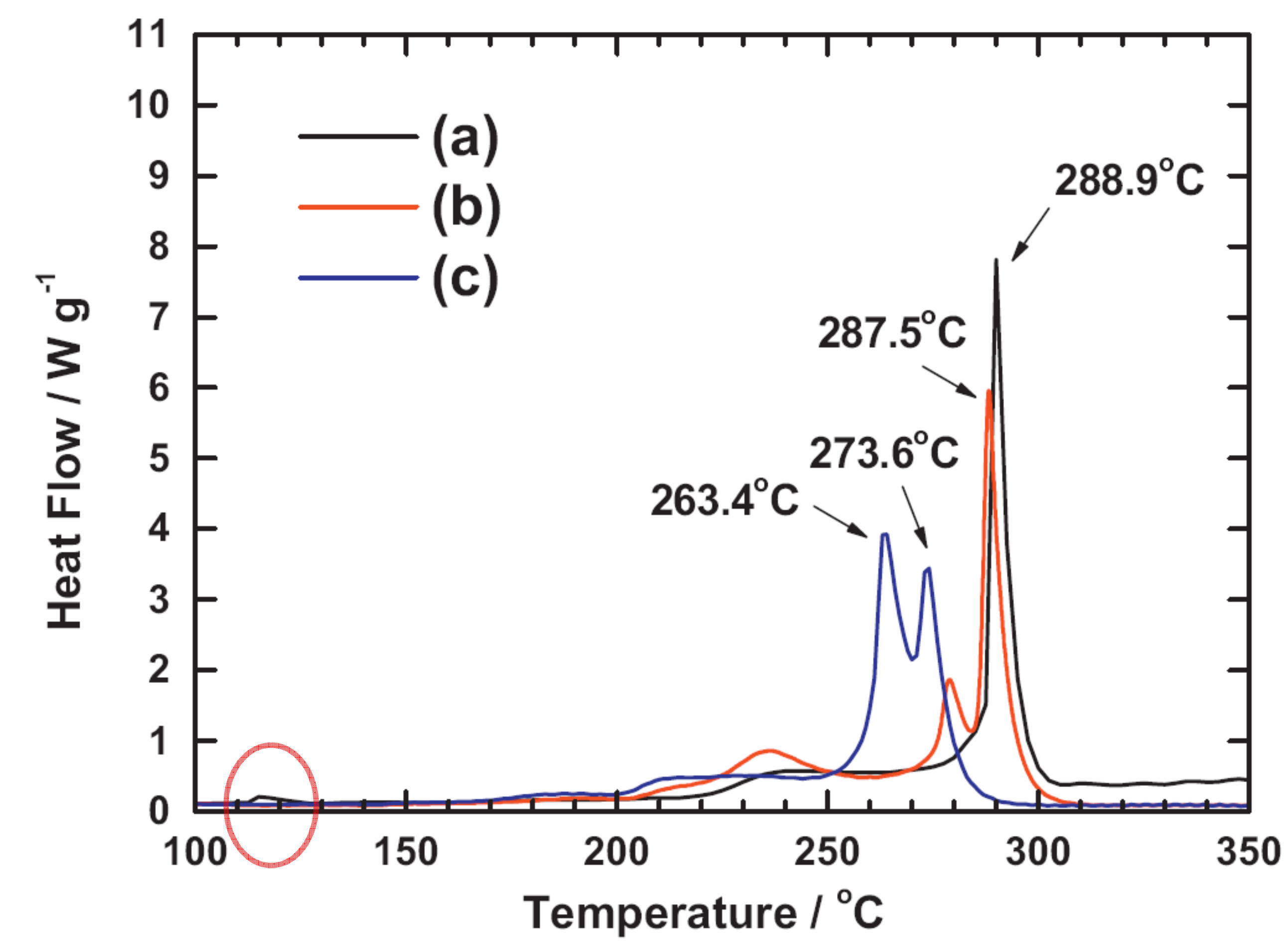


Low Temperature
Exotherms may be
Very important.

Onset temperature of the exothermic reaction occurs at 180 C

Onset relates to Probability

Small peaks below 200°C



#4: Flammable Solvents are the cause of Li-ion safety problems.

- *If only the electrolyte solvents were non-flammable there would be no safety problems*.
- We need to look at all the combustibles in the cell.
  - Graphite
  - Al
  - Li
  - Binder
  - Separator
  - Solvents
- In order for combustibles to burn we need oxygen.

Conventions

- Quantitative examples will be based on a 2.5Ah 18650 Li-ion cell.
- I will assume an NMC cathode and a graphite anode.
- NMC = Li(NiMnCo)O2. Various ratios Ni:Mn:Co exist on the market.
- Cell composition:

NMC	16g
Graphite	8g
Electrolyte	5g
Separator	1g
Al	3g
Mobile Li	0.7g

How much oxygen is available?

- NMC example
  - $Li_{0.5}(NiMnCo)O_2 \rightarrow \frac{1}{4} Li_2O + (NiMnCo)O + {}^{3}/_{8}\, O_2$
  - Translates to 0.06 moles of O_2
- $LiFePO_4$ example
  - No O_2 released !

What can we burn with 0.06mols of O_2?

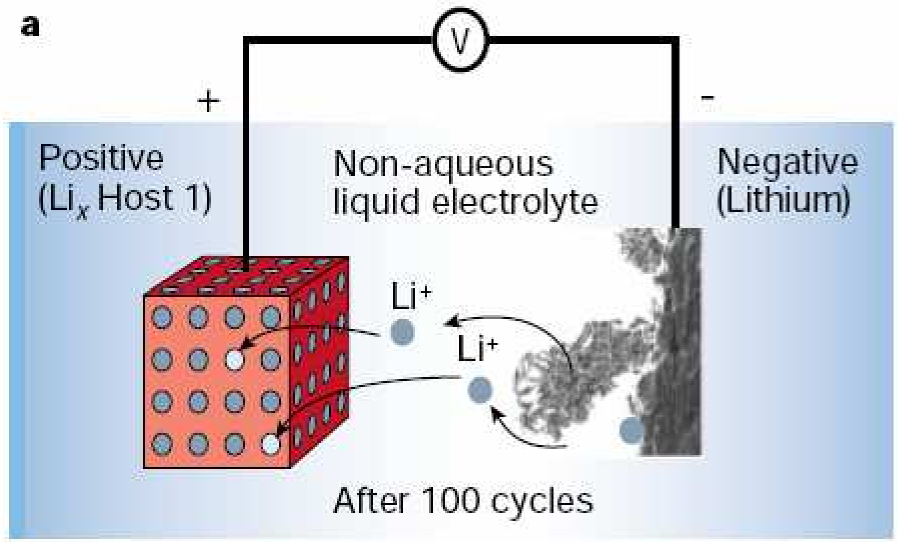
Component	Mass (g)	KJ	Ox required (moles)
DEC	2	45.4	0.102
EC	1	13.24	0.028
PC	1	17.82	0.039
Al	3	93.11	0.083
C	8	2624	0.667
Li	0.7	1.4	0.050
PVDF	0.4	0.09	0.013
PE	1	44	0.107

#3: A lithium dendrite can hard short a cell and send it into thermal runaway

- Before 1991 all commercial Li cells had a Li metal anode.
- Li ion cells replace the metal anode with an intercalation compound. Usually graphite.
- By design Li metal anode cells plate large amounts of Li on every cycle.
- Li-ion cells only plate Li when charged at high rates at low temperature. Relatively small amounts of Li plates in this case.

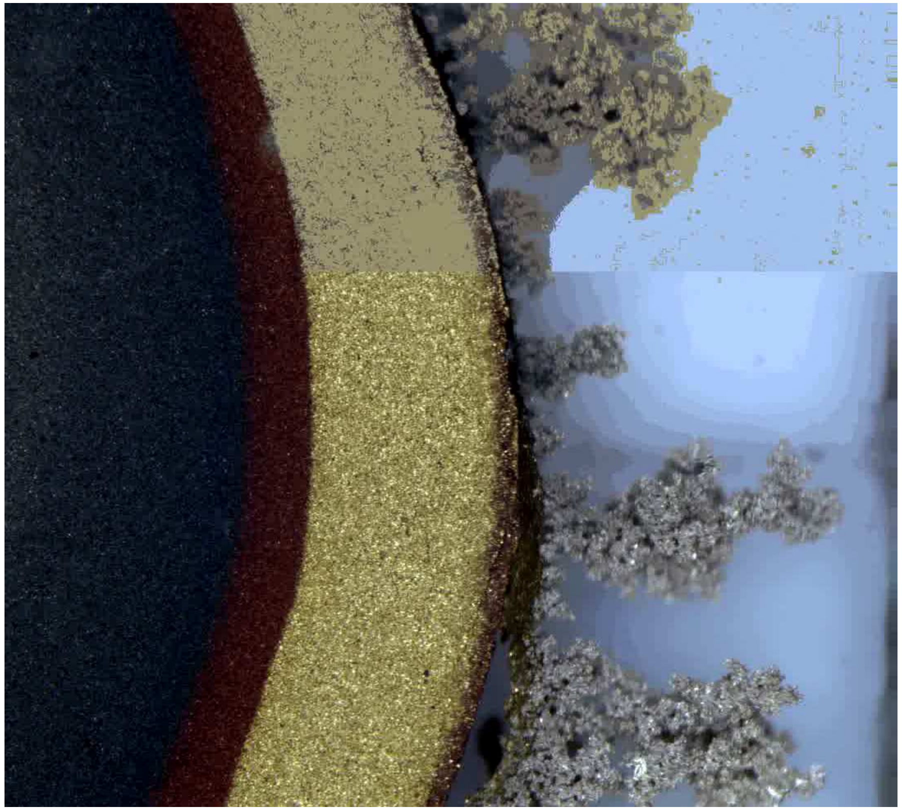
Li Dendrites

- They look like moss
- Very high surface area



J.-M. Tarascon & M. Armand NATURE, VOL 414, 15 NOVEMBER 2001

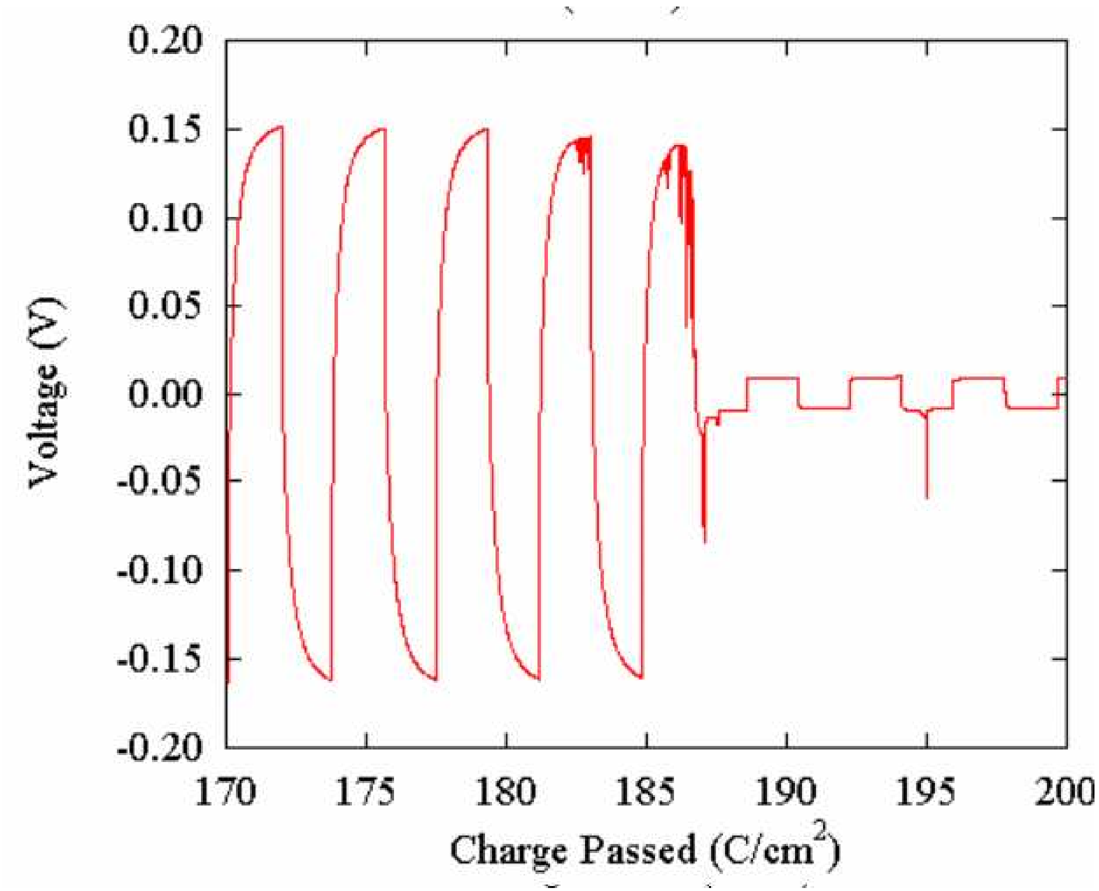
Dendrites in action



Li Electrode is over here

Stephen J. Harris
Li Ion Battery Aging, Degradation, and Failure
http://lithiumbatteryresearch.com/Dendrites-and-Fracture.php
Chemical Physics Letters 485 (2010) 265–274

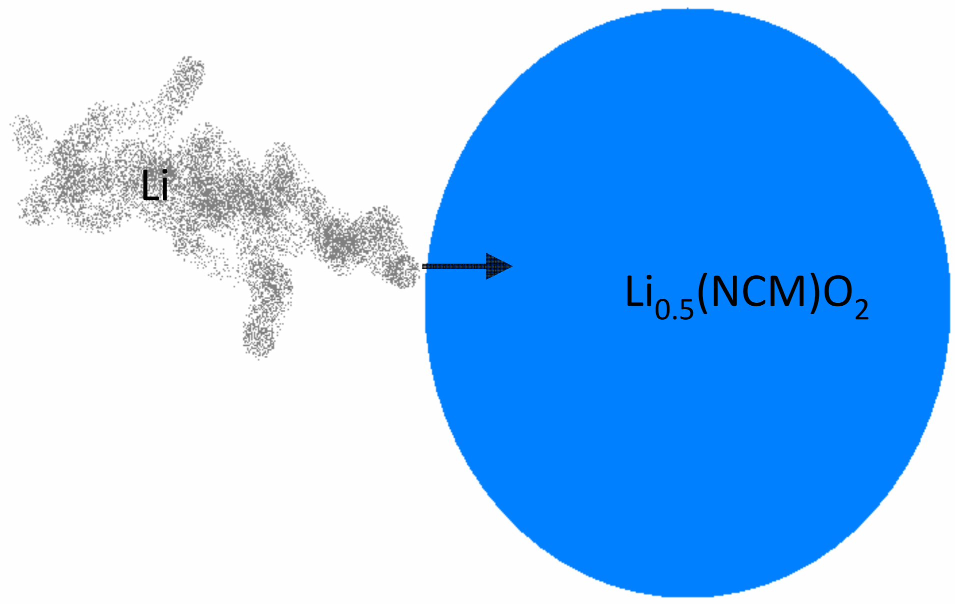
Effect on cell voltage



Scott Mullin (EERE), Greg Stone (BES), Nitash Balsa
University of California, Berkeley
Lawrence Berkeley National Laboratory
https://www.ornl.gov/ccsd_registrations/battery/presentations/Session7-1100-Balsara.pdf

What happens when Li touches the cathode?

- As soon as Li metal touches the cathode it will intercalate
- 4eV is a huge force
- kT is 0.025eV !



When do cells fail (thermal event)?

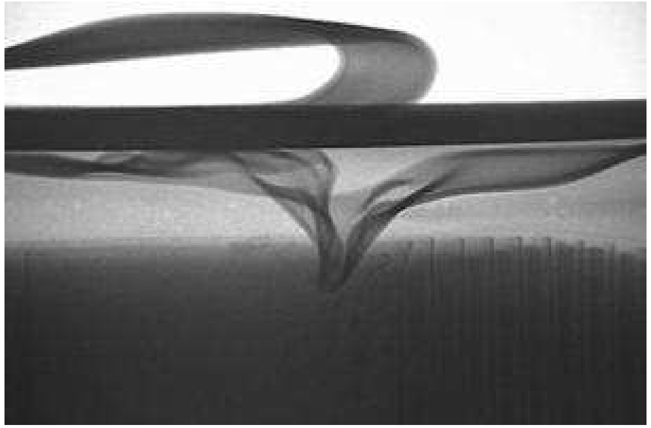
- Typically you need to cycle 100s or 1000s of cycles beyond the first signs.
- By that time there might be 10^6 Li shorts throughout the cell
- A local group of shorts will heat up enough to initiate a thermal event.
- Commercial Li-ion cells simply don't plate enough Li to do this.

#2 The purpose of the nail test is to make sure cell can survive a nail gun.

- Nail Penetration Test: UL, IEC, JEC, SAE J2464 etc.
- Purpose is to: *simulate an internal short*

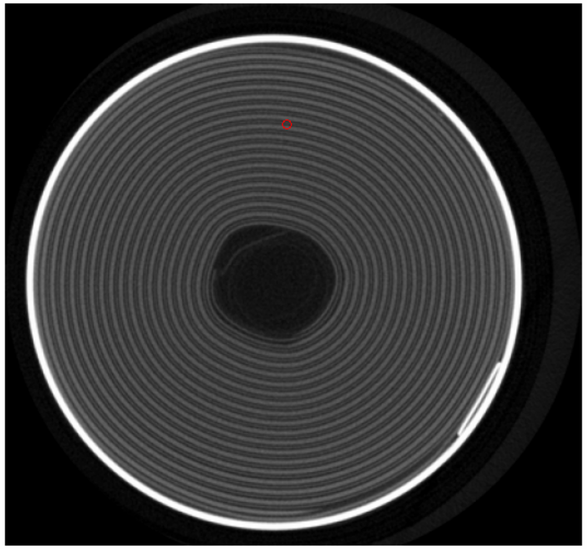
Spontaneous Internal Short

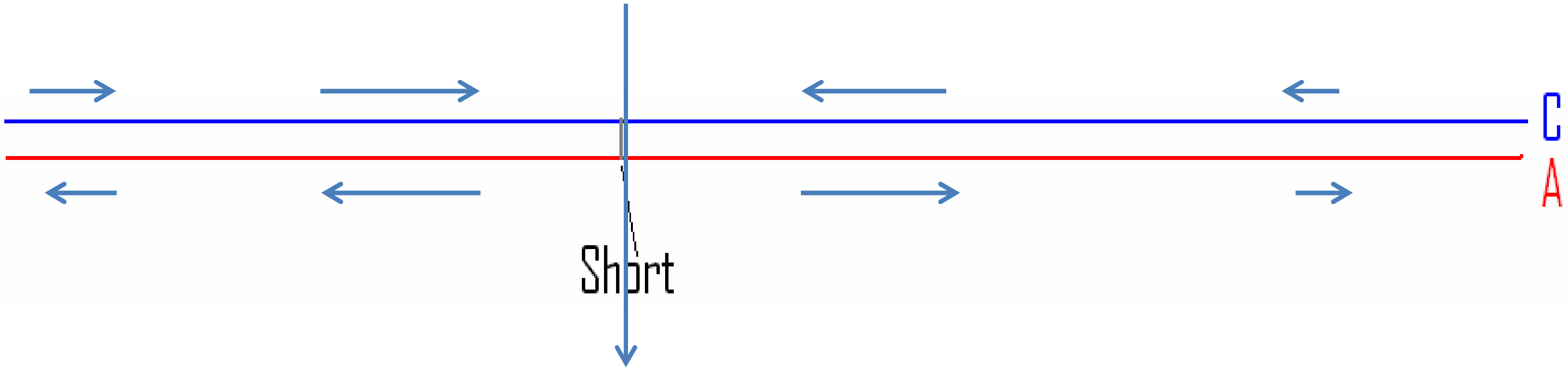
- Caused by mechanical flaws in the cell
  - Included particles
  - Sharp edges, Burrs
  - Folded corners
  - Improper tab folding/bending
  - Core collapse
- No fix at the system level.
- Requires Cell design and process controls.



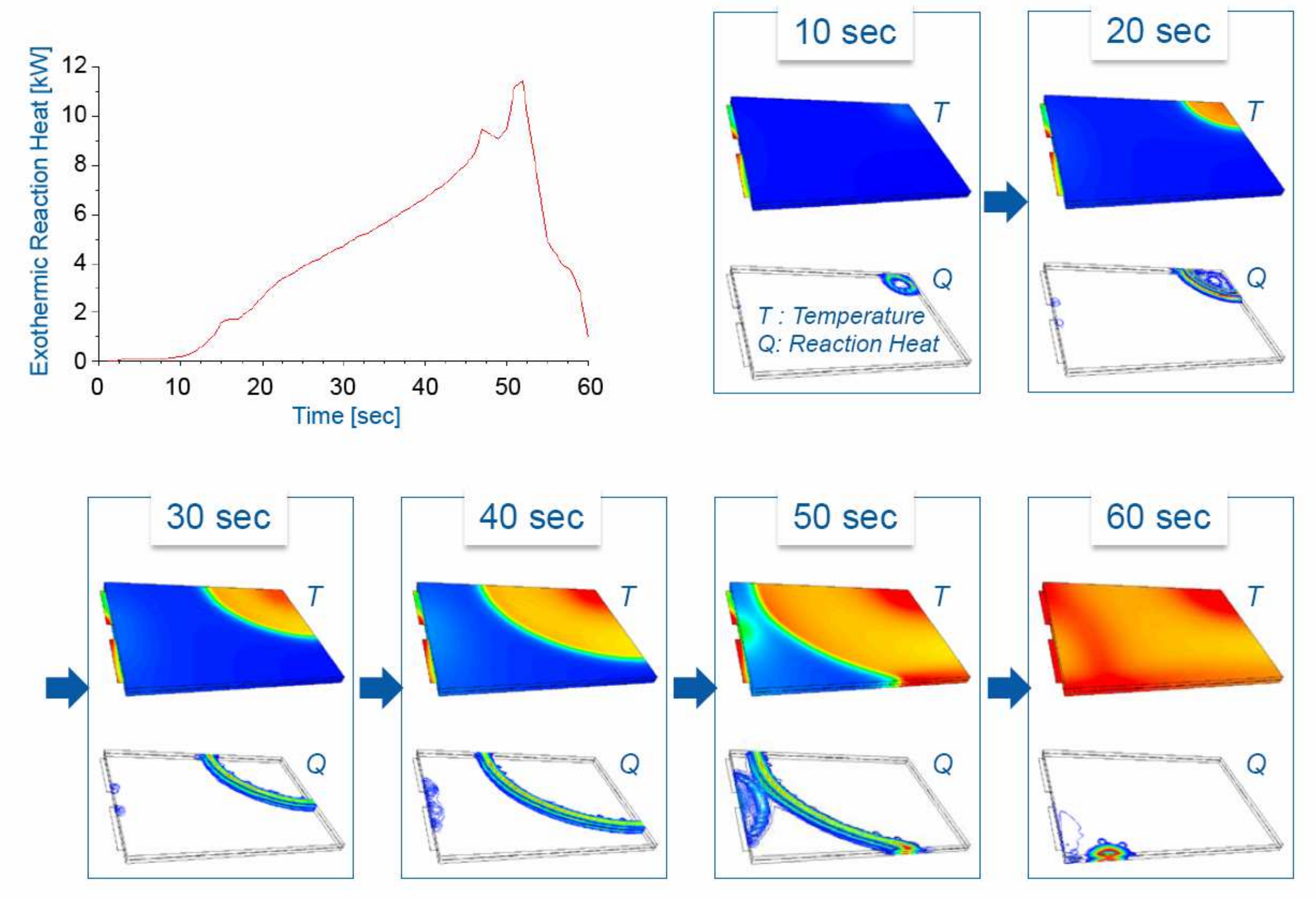
Spontaneous Internal Short

- Current accumulates along the electrode
- Maximum current at short site
- A/cm^2 gets very high
- I^2R_s heating, very local
- Worst case $R_s = R_{cell}$





Thermal Runaway Reaction

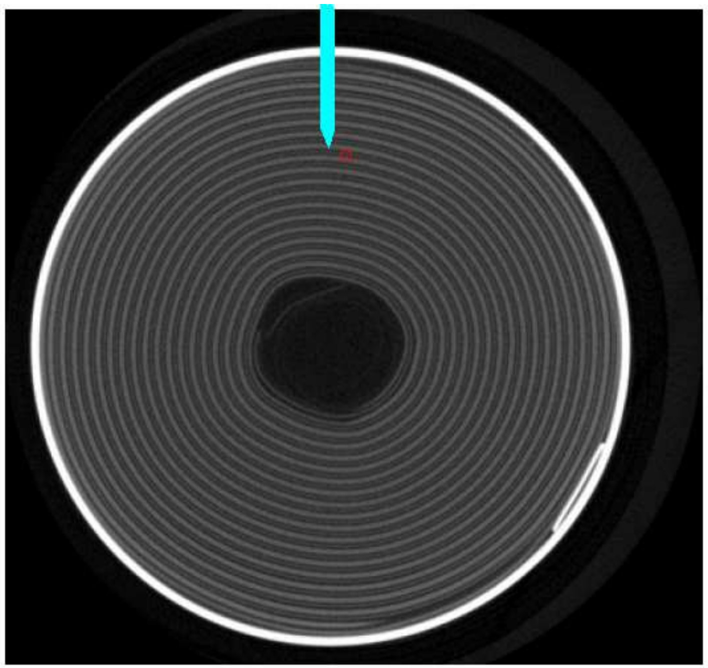


Gi-Heon Kim, Kandler Smith, Ahmad Pesaran

Lithium-Ion Battery Safety Study Using Multi-Physics *Internal Short-Circuit Model*

The 5th Intl. Symposium on Large Lithium-Ion Battery Technology and Application June 9-10, 2009, Long Beach,

Nail test



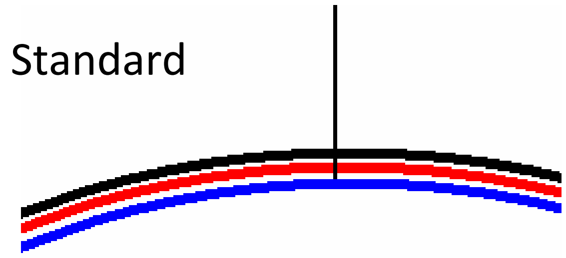
- Nail will short the cell … many times!
- Rs will vary wildly
  - From layer to layer
  - From test to test
- Every detail matters:
  - Nail size
  - Tip shape
  - Nail speed
  - Nail temperature
  - Nail surface
  - Nail E&T isolated?
- Very different from spontaneous internal short.

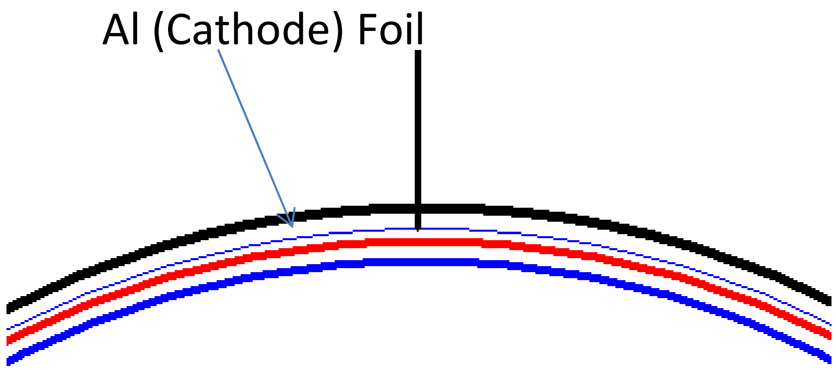
#1 Passing a nail test means your chemistry is robust under internal short conditions.

- Statistically meaningful sample size is required.
- Cell must short inside
- Cell designers can trick the test!

Nasty Cell Design Trick #1

- Separator not shown in figures
- Extra wrap of cathode foil on outside
- Metal-Metal short
- Defeats purpose of regulatory nail test!





Thank You