Li-Battery SAFETY

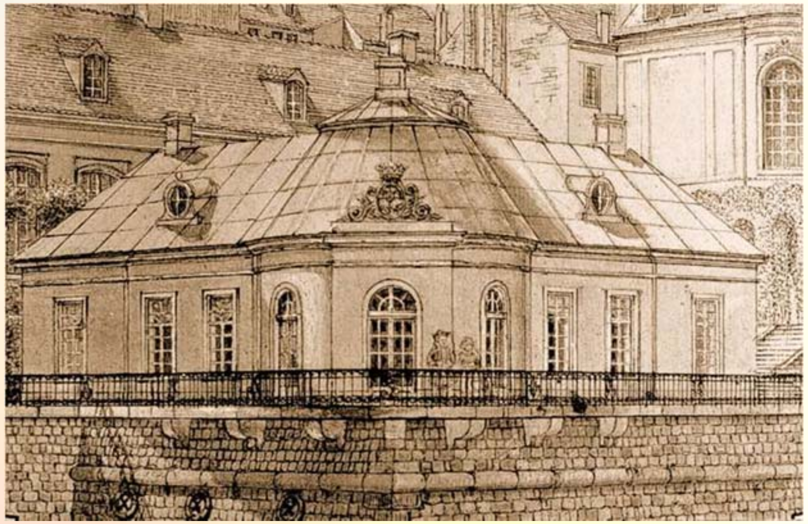
November 2016

TU Dresden

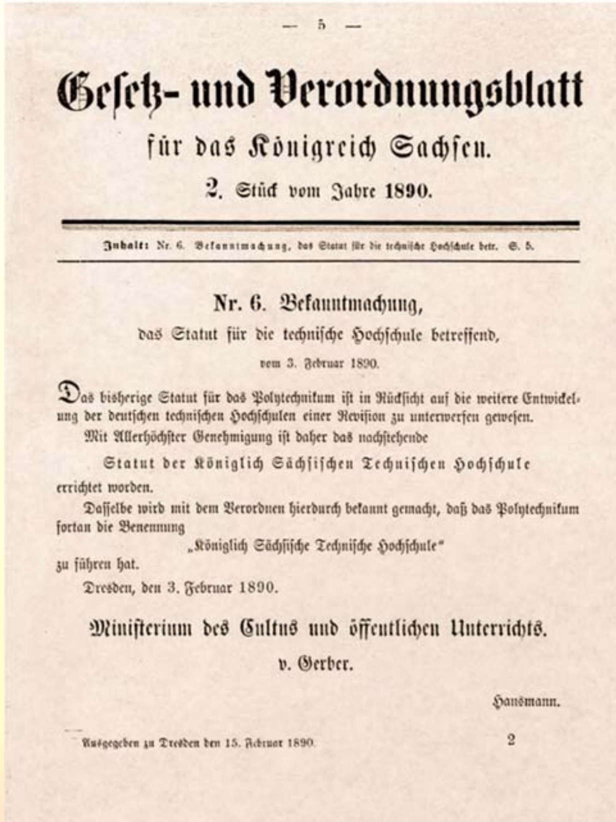
Juergen Garche

www.fcbat.eu

Historischer Rückblick – Elektrochemie



1828 Technische Bildungsanstalt Dresden



— 5 —

Gesetz- und Verordnungsblatt

für das Königreich Sachsen.

2. Stück vom Jahre 1890.

Inhalt: Nr. 6. Bekanntmachung, das Statut für die technische Hochschule betr. S. 5.

Nr. 6. Bekanntmachung,

das Statut für die technische Hochschule betreffend,

vom 3. Februar 1890.

Das bisherige Statut für das Polytechnikum ist in Rücksicht auf die weitere Entwickelung der deutschen technischen Hochschulen einer Revision zu unterwerfen gewesen.

Mit Allerhöchster Genehmigung ist daher das nachstehende

Statut der Königlich Sächsischen Technischen Hochschule

errichtet worden.

Dasselbe wird mit dem Verordnen hierdurch bekannt gemacht, daß das Polytechnikum fortan die Benennung

„Königlich Sächsische Technische Hochschule"

zu führen hat.

Dresden, den 3. Februar 1890.

Ministerium des Cultus und öffentlichen Unterrichts.

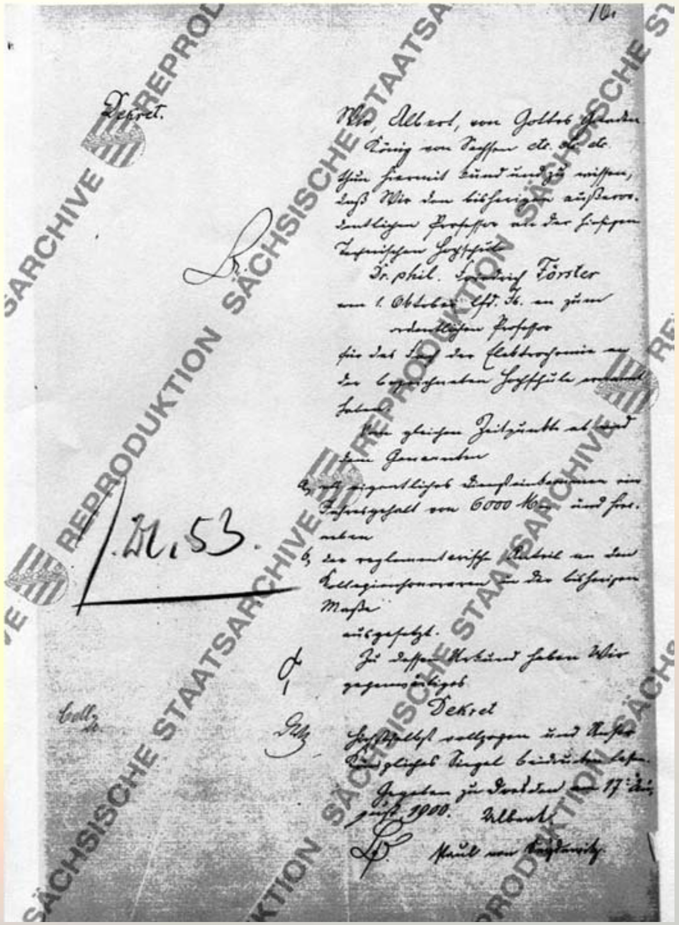
v. Gerber.

Hausmann.

Ausgegeben zu Dresden den 15. Februar 1890. 2

1890 Königlich Sächsische Technische Hochschule

Erstes Elektrochemische Institut Deutschlands
1900 - Prof. Dr. Fritz Förster

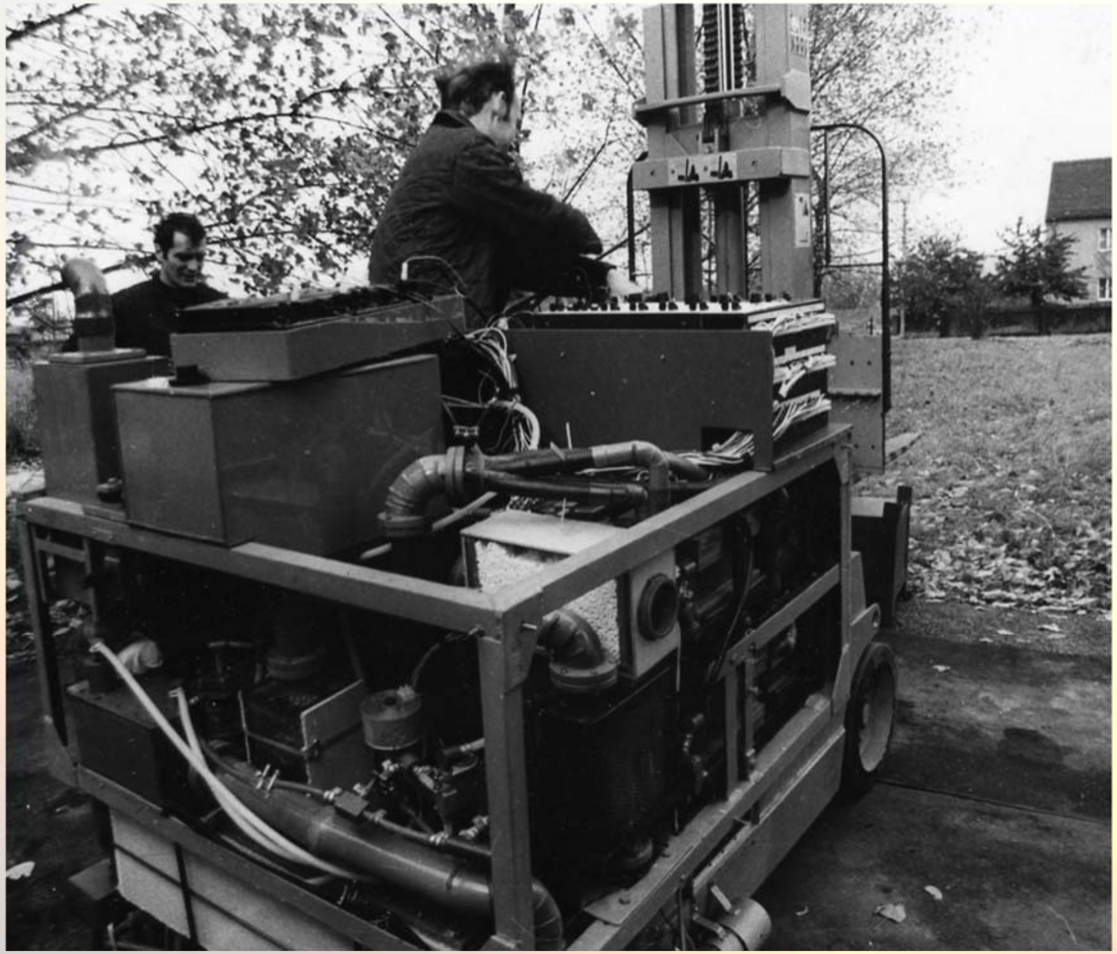


FCBAT

Prof. Dr. Kurt Schwabe (1905 – 1983)

Professor für Physikalische und Elektrochemie, Rektor TU Dresden

FCBAT



1965

5 kW Brennstoffzellen (Hydrazin-Luft) Gabelstapler

TUD - BAE

FCBAT

Li-Primärzellen Fertigung Pirna (Herzschrittmacher)

Start 1980er

LITRONIK

LITRONIK Batterietechnologie GmbH
Birkwitzer Strasse 79
DE-01796 Pirna
Germany

FCBAT

Content

- Introduction Safety Risks
- Li-Battery Systems and their Risks
  - Li-Metalic Systems
  - Li-Ion Systems
- Main Safety Problems (electrical, kinetical, chemical, thermal)

FCBAT

Production and Storage

Fire at HELLA in Bockum-Hövel (Germany) 24.11.2007, 18:47 h

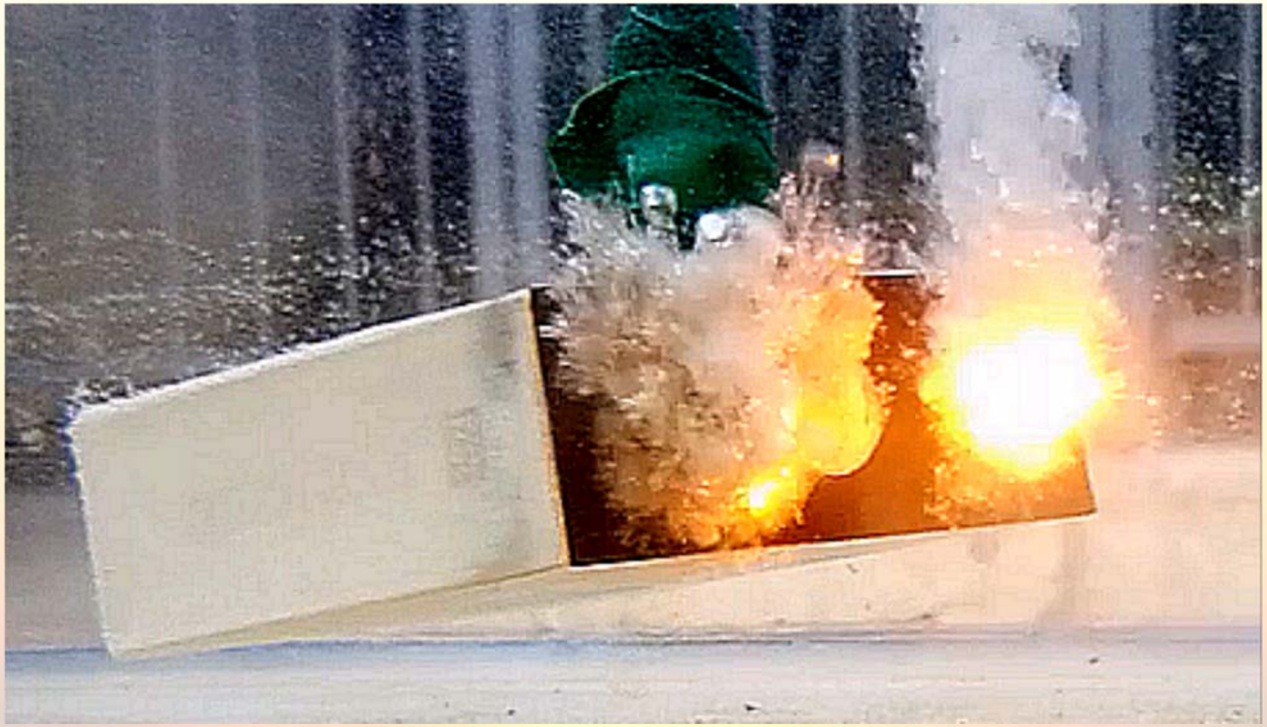
EV-Use - EV under Water (Storm Tide)

More Than A Dozen Fisker Karma Hybrids Caught Fire And Exploded In New Jersey Port After Sandy

Approximately 16 of the $100,000+ Fisker Karma extended-range luxury hybrids were parked in Port Newark, New Jersey last night when water from Hurricane Sandy's storm surge apparently breached the port and submerged the vehicles. As *Jalopnik* has

FCBAT

Fire even under Water



Fire of a 11.5 Ah LFP cell under salt water (3.5. % NaCl)

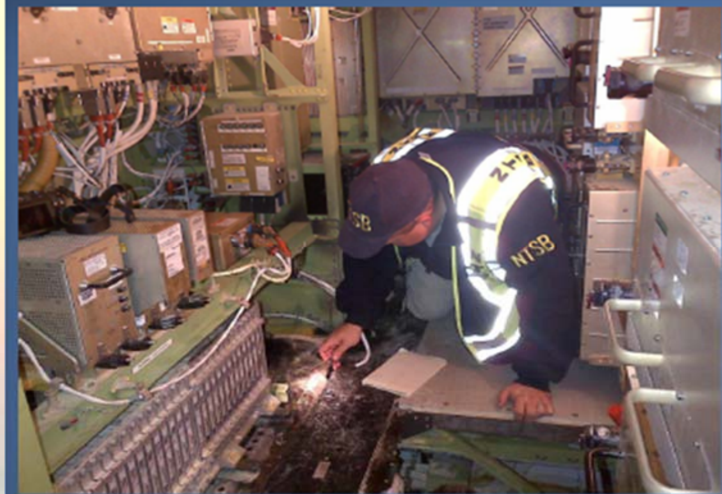
FCBAT

Source: Tsinghua University

Boeing 747-400 Cargo
3rd September 2010
Dubai
Li-Battery overheating

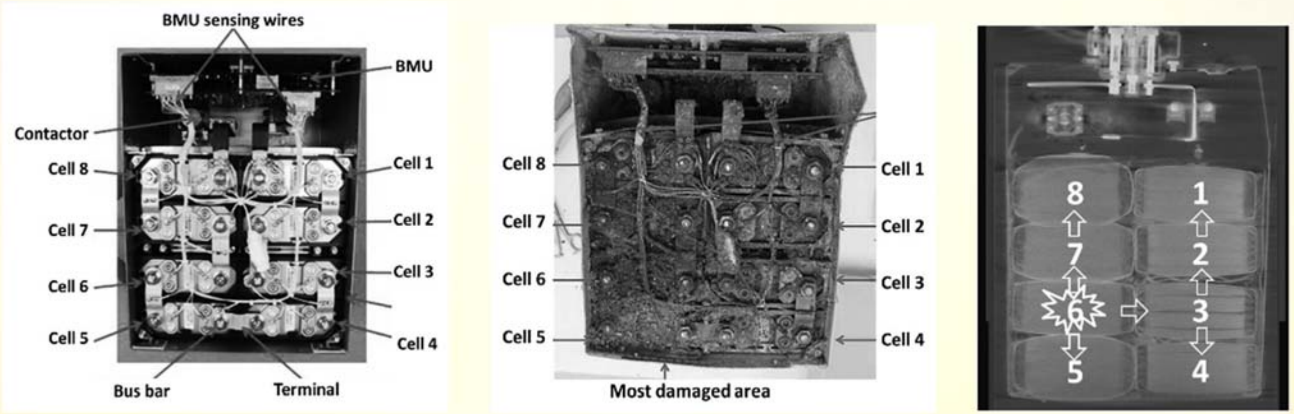
FCBAT

Boeing Dreamliner B 787



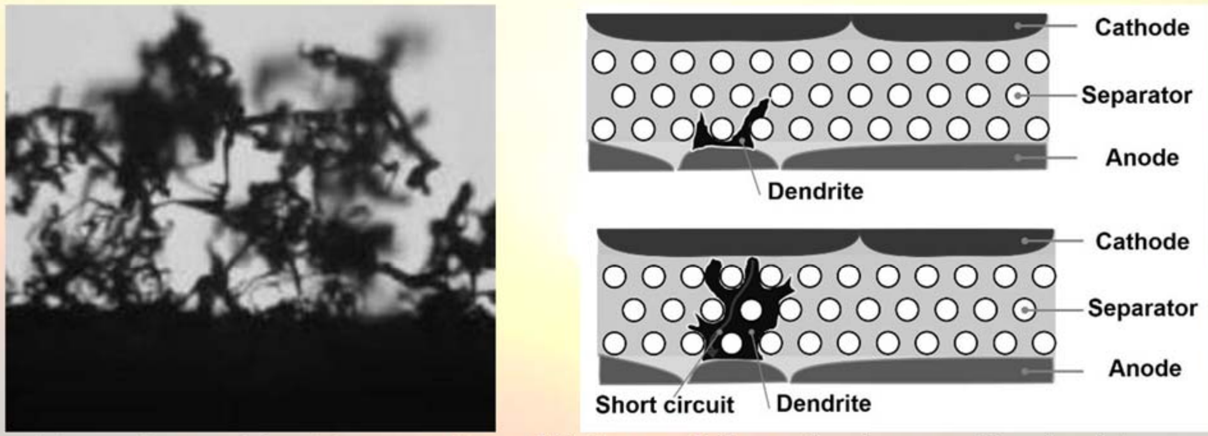
FCBAT

BOEING Dreamliner – Fire Reasons



(a) The battery pack (b) After burning (c) CT result

Thermal propagation



(a) A photo of dendrite growth (b) Internal short circuit caused by dendrite growth

FCBAT

Cell/Battery Recalls

Date	Accident device	Recall scale
Aug. 2006	Sony cell in Dell note PC	4.1 M packs
Aug. 2006	Sony cell in Apple note PC	1.8 M packs
Oct. 2006	Sony cell in Toshiba & Fujitsu note PC	3.7 M packs
Dec. 2006	Sanyo cell in Mitsubishi cellular phone	1.3 M packs
Mar. 2007	Sanyo cell in Lenovo note PC	0.2 M packs
Jun. 2007	NEC-Tokin cell in Welcomm cellular phone	0.13 M packs
Jun. 2007	NEC-Tokin cell in KDDI cellular phone	0.07 M packs
Aug. 2007	Panasonic cell in Nokia cellular phone	46 M packs
Mar. 2008	NEC-Tokin cell in Kyocera cellular phone	0.21 M packs
Jun. 2008	Sony cell in note PC	0.438 M packs
Mar., 2010	HP note PC	-
Jul. 2010	Sony cell in note PC	0.055362M packs

Samsung Expands Recall to All Galaxy Note7 Devices

Updated – Oct. 13 2016

FCBAT

Disposal

https://www.americandisposal.com/blog/lithium-ion-batteries

TESLA-S - e.g. 6th November 2013

FCBAT

Failures

	Failure Trigger	Example	Reference
1	**External heat**	1. Tesla wall plug initiated fire	1. Tesla official Statement 10-01-2014
2	**Over-Charge**	1. US & UK 'Hoverboard' recall	1. Recall notice CPSC 16-218,CTSI press brief
3	**Over-Voltage**	1. US & UK 'Hoverboard' recall	1. Recall notice CPSC 16-218,CTSI press brief
4	**Crush**	1. BYD Taxi crash, 2. Samsung S7 note	1. BYD official statement 05-29-2012 2. Samsung Info-graphic "what we discovered" Samsung, 01-23-2017
5	**Penetration**	1. Tesla Highway debris incident	1. NHTSA investigation:PE13-037
6	**Internal short-circuit**	1. Boeing 787 Dreamliner	1. NTSB incident report NTSB/AIR-14/01 PB2014-108867
7	**Manufacturing Particle**	1. Sony Battery warehouse, 2. Samsung S7 note	1. Lithium-ion Hazards and Use Assessment (Springer Science & Business Media, 2012) 2. Samsung Info-graphic "what we discovered" Samsung, 01-23-2017
8	**Dendrite**	1. Mitsubishi iMiev charging issue 2. Boeing 787 Dreamliner	1. Mitsubishi 'cease charging request' 03-27-2013 2. NTSB incident report NTSB/AIR-14/01 PB2014-108867
9	**Separator misalignment**	1. Samsung S7 note	1. Samsung Info-graphic "what we discovered" Samsung, 01-23-2017
10	**External short-circuit**	1. Chevrolet Volt, 2. Honda civic HEV 3. Fisker Karma Recall	1. NHTSA investigation, Doc. Number: DOT HS 811 573 2. NHTSA Recall Number: 07V034000 3. NHTSA Recall Number: 12V241000

Tesla Fire in France – August 2016

BUT

ICE-Cars

FCBAT

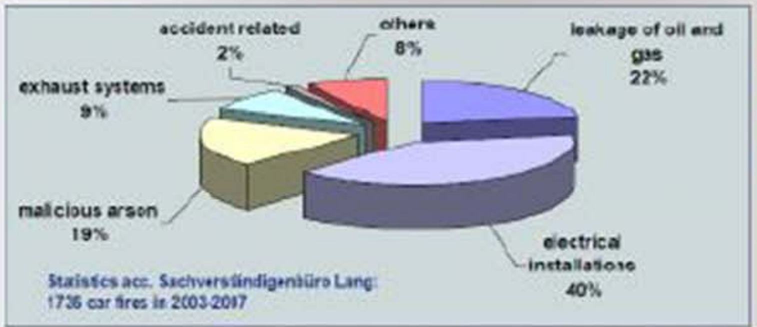
ICE-Vehicle Fire - Germany

Accidents: Burning batteries

ICE Cars in Germany 2007: **25'000 fires of passenger cars per year**

Fire of passenger vehicles

- GDV (Gesamtverband der Versicherungswirtschaft):
  25.000 fires of passenger vehicles per year in Germany (2007)
- Exact statistics of reasons for fires of passenger vehicles is not available



- Electrical installation main reason for car fires (ca. 40 %):
  Heating of electrical connections and parts by high current, short circuit

Dr. Claus Rüdiger, BU Polycarbonates, Bayer MaterialScience AG

Bayer MaterialScience

~40% electrical installations
~20% «malicious arson»
~40% other, ICE-related

~ 70 ICE-car fires per day in Germany

FCBAT

Source: JP Wiaux, Recharge, Amsterdam 13th September 2012

ICE-Vehicle Fire - USA

NFPA Data

VEHICLES

In 2003-2007, U.S. fire departments responded to an average of 287,000 vehicle fires per year. These fires caused an estimated 480 civilian deaths, 1,525 civilian injuries and $1.3 billion in direct property damage annually.

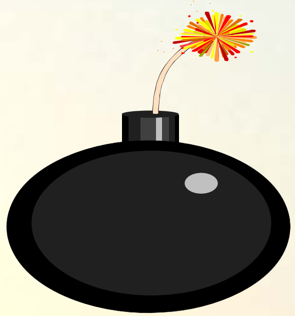
Every 2…3 minutes there is a ICE-car fire – USA

We put more and more energy into a given volume

We put more and more energy into a given volume

- Is the Li-Battery a controlled Bomb?

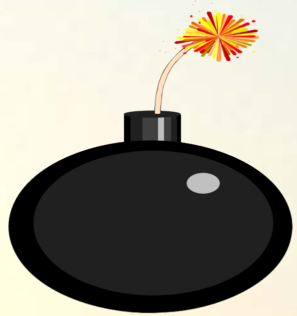
Li-Battery – The controlled bomb?



- **Energy density of TNT**
  6.7 kJ/cm^3

- **Energy density of advanced batteries**
  3.3 kJ/cm^3

Li-Battery – The controled bomb?



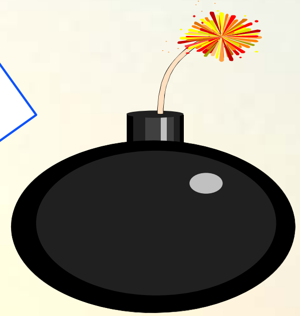
- Energy density of TNT
  6.7 kJ/cm³

- Energy density of advanced batteries
  3.3 kJ/cm³

- Energy density of chocolate
  22 kJ/cm³

Li-Battery – The controled bomb?

- Energy density of TNT
  6.7 kJ/cm^3



- Energy density of advan… …atteries
  3.3 kJ/cm^3

- Energy den… … chocolate
  22 kJ/cm…

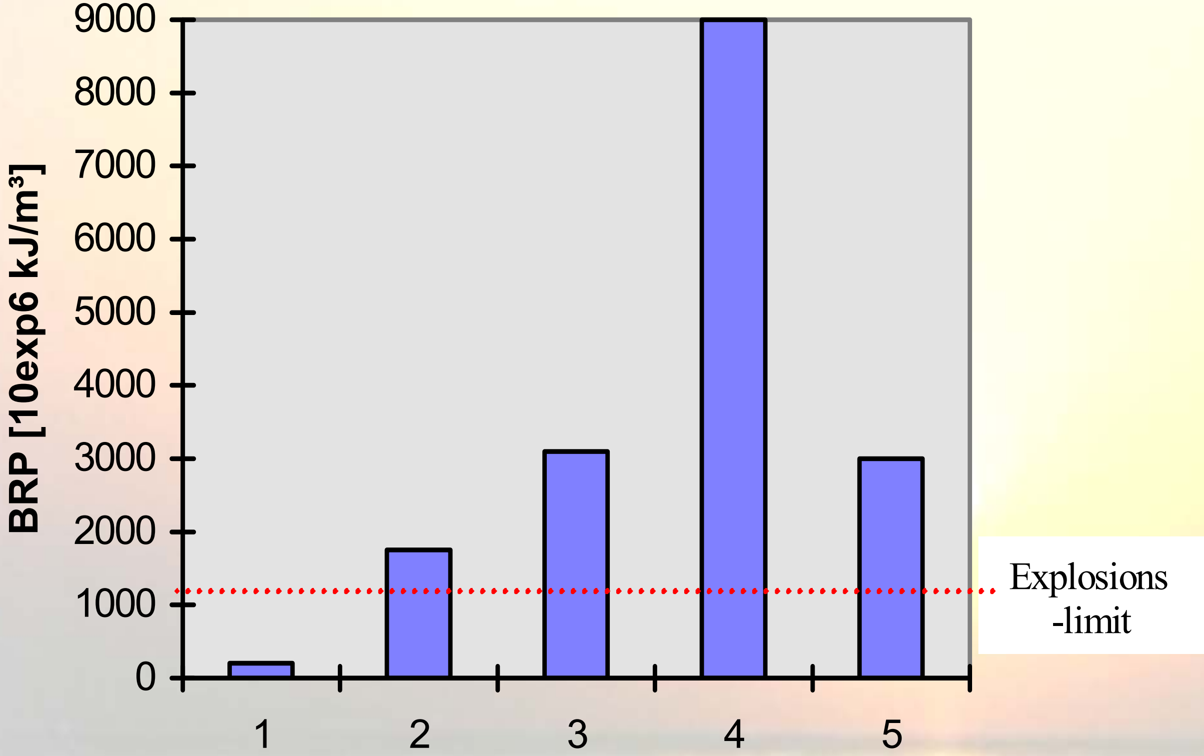
High energy densities pose no inherent risk

FCBAT

High energy densities pose no inherent risk

Explosion risk is given by the Berthelot-Roth Product (BRP)

$$BRP \sim V_{gas\ products} * \Delta H_{reaction}$$



1 : Li / anorg. Elektrolyt / $LiCoO_2$
2 : LiC / org. Elektrolyt / $LiCoO_2$
3 : Li / SO_2/ (C)
4 : Li/ org. Elektrolyt / MnO_2
5 : Schwarzpulver (KNO_3, C, S)

FCBAT

Source: G. Hambitzer, FORTU

Li-Ion Cell Safety

Li-Ion Cells are produced in a quantity of ~ 5 Bill per year (2014)

- *The insident rate is in the low ppm area*

FCBAT

Li-Ion Cell Safety

Li-Ion Cells are produced in a quantity of ~ 5 Bill per year (2014)

- The insident rate is in the low ppm area 1 ppm

BUT

1 Tesla S => 7,200 cells

100 Tesla S => 720,000 cells

139 Tesla S => 1,000,000 cells (1 ppm)

„Each 140th Tesla S will burn"

FCBAT

Li- Battery Systems

FCBAT

Li-Systems

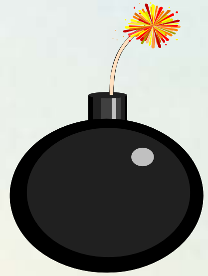
Metallic Lithium

Li reacts with the electrolyte (El) => Protective Layer (SEI) + Heat

Protective Layer

Solid Electrolyte Interphase - SEI

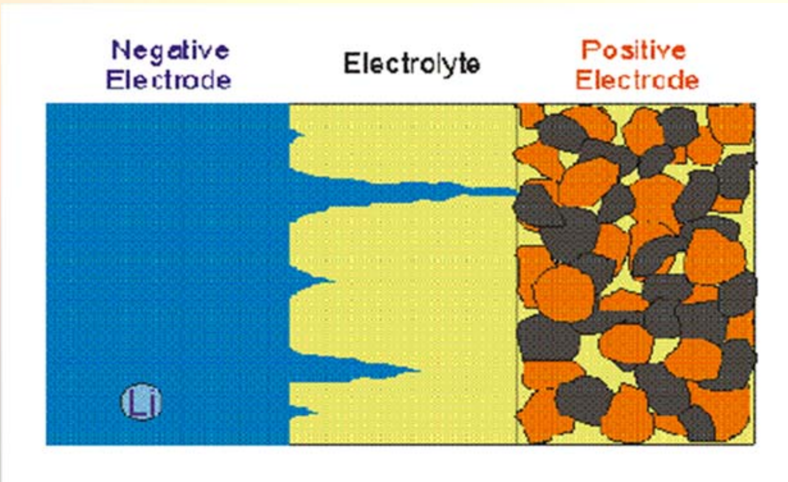
Li-Systems



Metallic Lithium

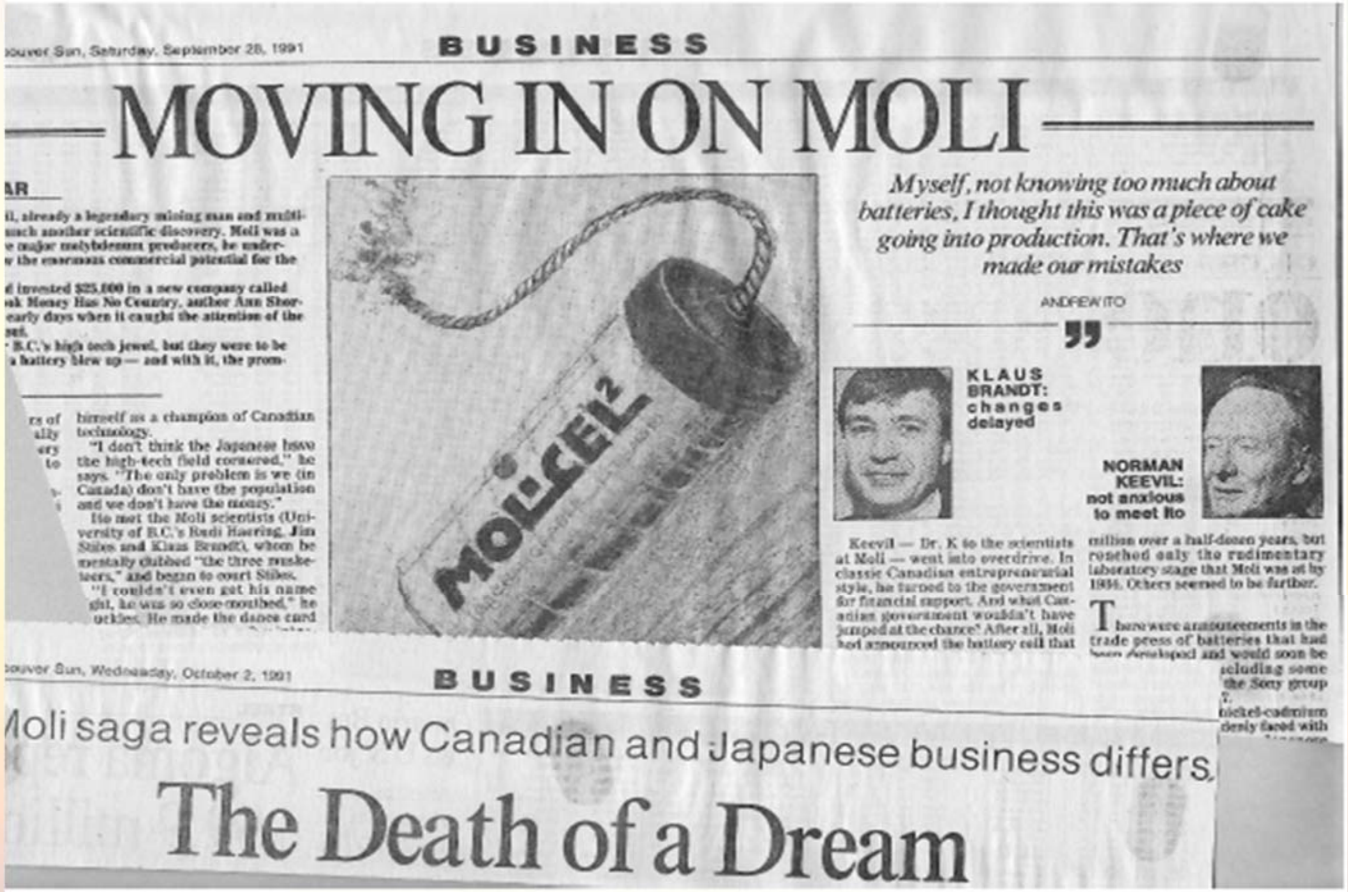
Li reacts with the electrolyte (El) => Protective Layer (SEI) + Heat

Problem: Dendrites growth through the electrolyte



Source: Russ Chianelli -Exxon

First Rechargeable Li-Metall MoO_2 Cell – MOLI 1988



ouver Sun, Saturday, September 28, 1991

BUSINESS

MOVING IN ON MOLI

AR

il, already a legendary mining man and multi- unch another scientific discovery. Moli was a e major molybdenum producers, he under- w the enormous commercial potential for the

d invested $25,000 in a new company called ok Money Has No Country, author Ann Shor- early days when it caught the attention of the ued.

B.C.'s high tech jewel, but they were to be a battery blew up — and with it, the prom-

himself as a champion of Canadian technology.

"I don't think the Japanese have the high-tech field cornered," he says. "The only problem is we (in Canada) don't have the population and we don't have the money."

He met the Moli scientists (University of B.C.'s Rudi Haering, Jim Stiles and Klaus Brandt), whom he mentally dubbed "the three musketeers," and began to court Stiles.

"I couldn't even get his name ght, he was so close-mouthed," he uckles. He made the dance card

Myself, not knowing too much about batteries, I thought this was a piece of cake going into production. That's where we made our mistakes

ANDREW ITO

KLAUS BRANDT: changes delayed

NORMAN KEEVIL: not anxious to meet Ito

Keevil — Dr. K to the scientists at Moli — went into overdrive. In classic Canadian entrepreneurial style, he turned to the government for financial support. And what Canadian government wouldn't have jumped at the chance? After all, Moli had announced the battery cell that

million over a half-dozen years, but reached only the rudimentary laboratory stage that Moli was at by 1984. Others seemed to be further.

There were announcements in the trade press of batteries that had been developed and would soon be ncluding some the Sony group

nickel-cadmium denly faced with

ouver Sun, Wednesday, October 2, 1991

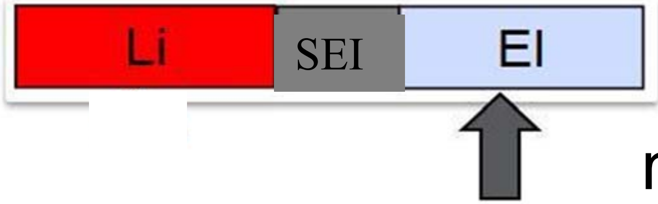
BUSINESS

Moli saga reveals how Canadian and Japanese business differs

The Death of a Dream

MOLI 1979: First functional Li-MoS2 Battery – 6V

MOLI 1988: First commercial Li-MoS2 AA-Cell



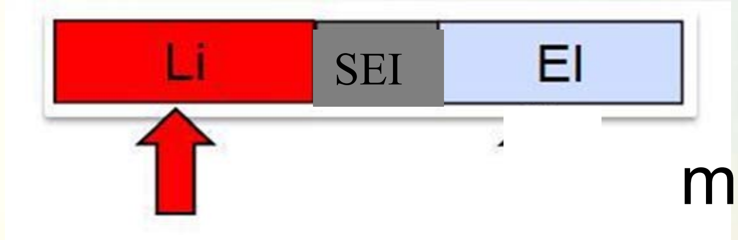
mitigate

- A – Using of more inert electrolytes: **Solid electrolytes**

  ==> Li All-Solid Systems

  A_1 – Solid electrolyte: polymer electrolytes **=> Li-Polymer Systems**

  A_2 – Solid electrolyte: inorganic crystaline materials/glasses



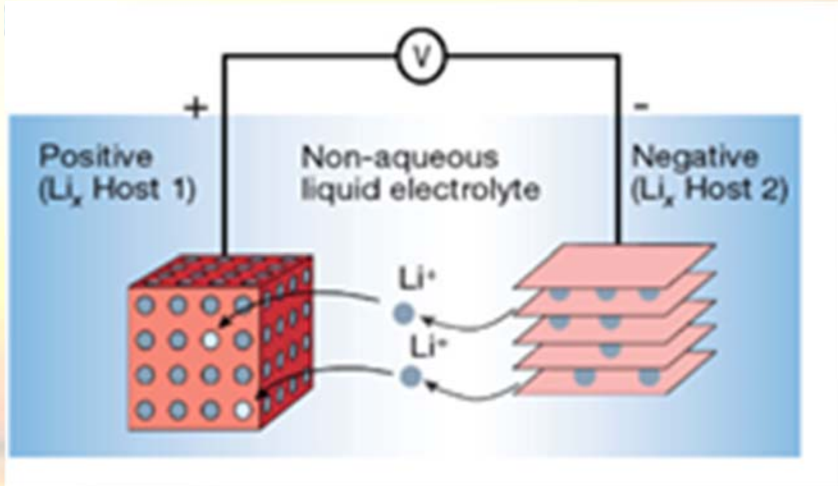
mitigate

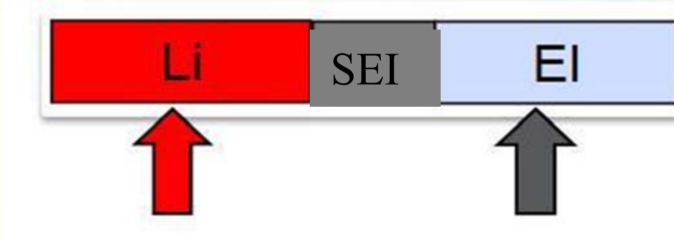
- A – Using of more inert electrolytes: **solid electrolytes**

  ==> Li All-Solid Systems, *Li-Polymer Systems*

- B – Using of more inert Li-electrodes: **Li-intercalation electrodes** (carbon, alloys - $a_{Li} < 1$)

  ==> Li-Ion Systems





mitigate

- A – Using of more inert electrolytes: **solid electrolytes**

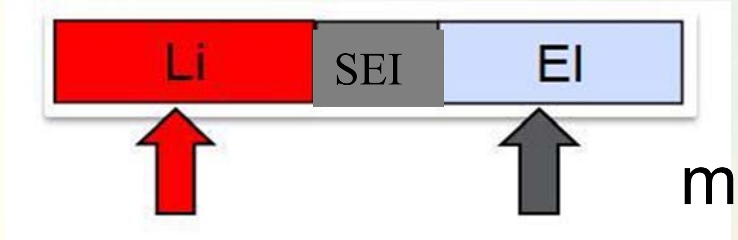
  ==> Li All-Solid Systems, *Li-Polymer Systems*

- B – Using of more inert Li-electrodes: **Non-metallic Li- intercalation electrodes** (carbon, alloys - $a_{Li} < 1$)

  ==> Li-Ion Systems

- C – Using of more inert electrolytes **(Polymer electrolytes)** *and* more inert Li-electrodes (**Li-intercalation electrodes)**

  ==> Li-Ion Polymer Systems



mitigate

- A – Using of more inert electrolytes: **Polymer electrolytes**

  ==> Li-Polymer Systems

SAFETY for ENERGY

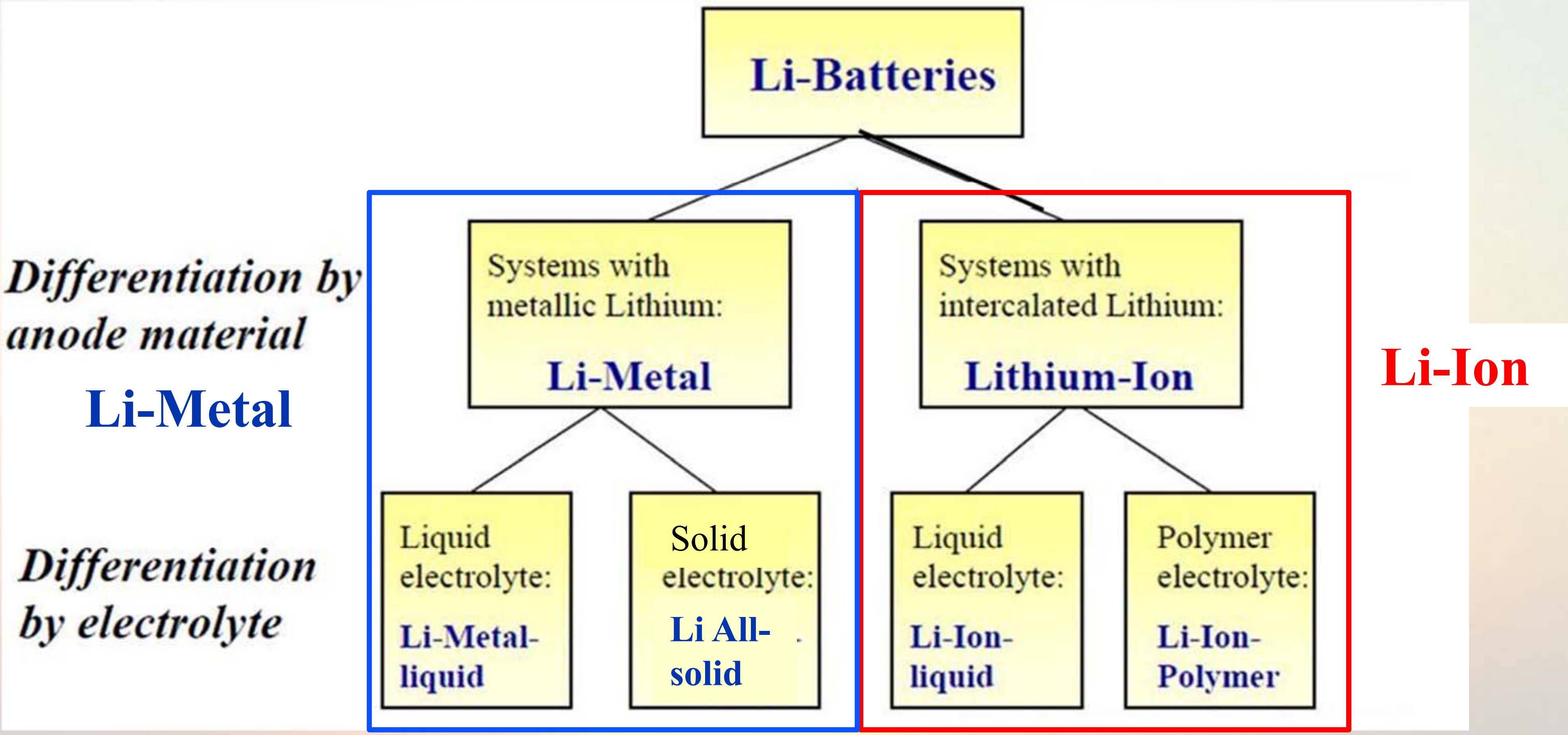
- B – Using of more inert Li-ele **-metallic Li-electrodes** (carbon, alloys - $a_{Li} < 1$)

  ==> Li-Io

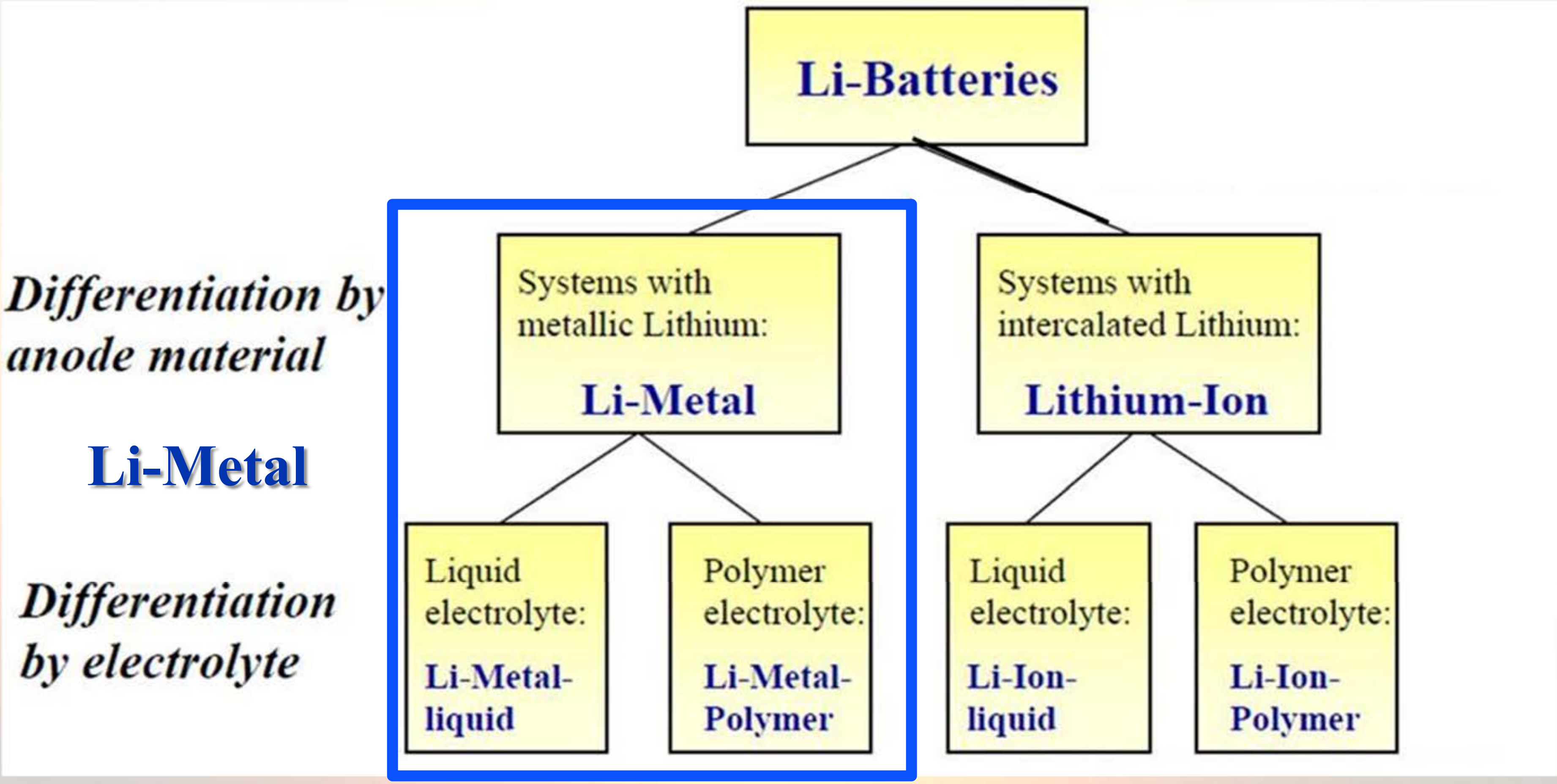
- C – Using more inert electrolytes **(Polymer electrolytes)** and more inert Li-electrodes (**Non-metallic Li-electrodes)**

  ==> Li-Ion Polymer Systems

Li - Battery Systems

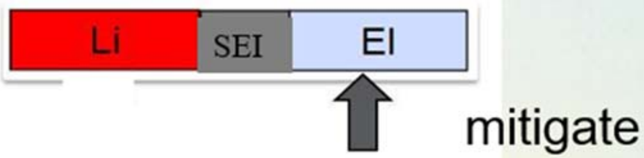


Li – Metal Systems

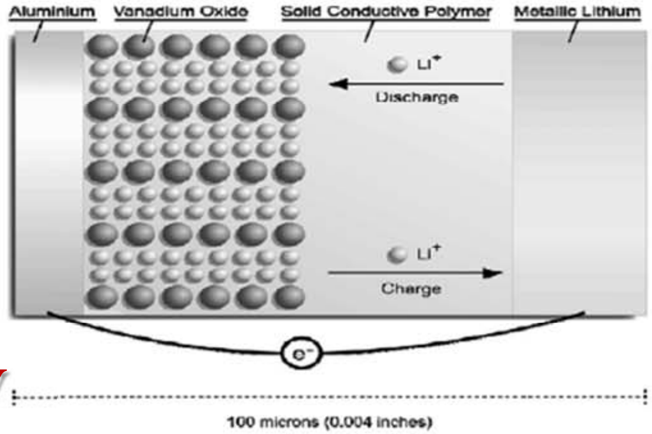


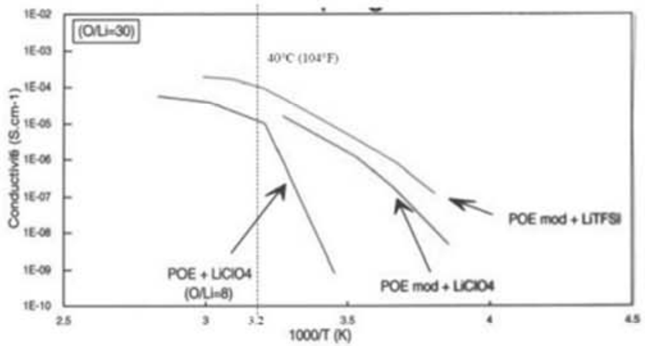
Only few Li Metal system are under development (coin cells, Bolloré)

Li-Metal Polymer System



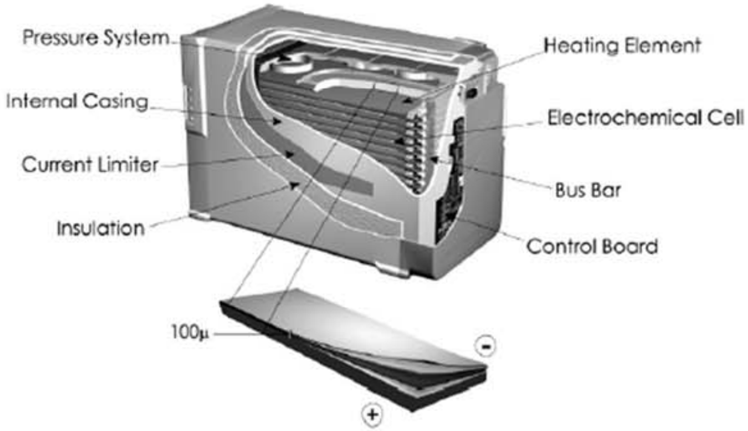
Avestor Technology





80 Ah, 48 V

- Li/V_3O_8 – PEO/LiTFSI polymer electrolyte
- 3 V cathode used due to limit of stability of the PEO
- Heated System to operate above 40°C
- Stack pressure on flat cells to improve lithium cycling



V. Duval et. al., Avestor, 2004

FCBAT

Source: K. Brandt

Lithium Metal Anodes with Solid Polymer Electrolytes

The End of the First Commercial Effort

Avestor Shuts Down

2 November 2006

Avestor, the Canadian developer of Lithium-Metal-Polymer (LMP) battery technology, is shutting down. The company filed with the Office of the Superintendent of Bankruptcy in Montréal with a view to making a Proposal to its creditors on 31 October.

AT&T Begins Massive Battery Replacement

~~After four equipment fires in two years, including a Christmas Day 2007~~ explosion in Wisconsin, AT&T Inc. (NYSE: T) says it is no longer comfortable with the batteries that provide backup power to thousands of its equipment cabinets in neighborhoods all over the U.S.

"Following incidents involving batteries used in AT&T U-verse network cabinets, the company is replacing 17,000 similar batteries, all manufactured by Avestor," writes an AT&T spokesman, in an email to *Light Reading*.

NEWS ANALYSIS
PHIL HARVEY

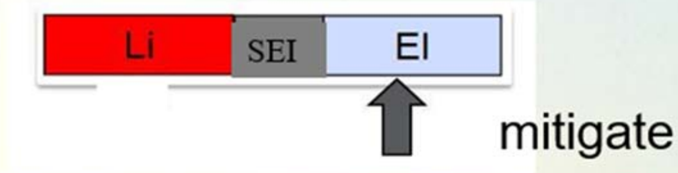
March, 5th 2007

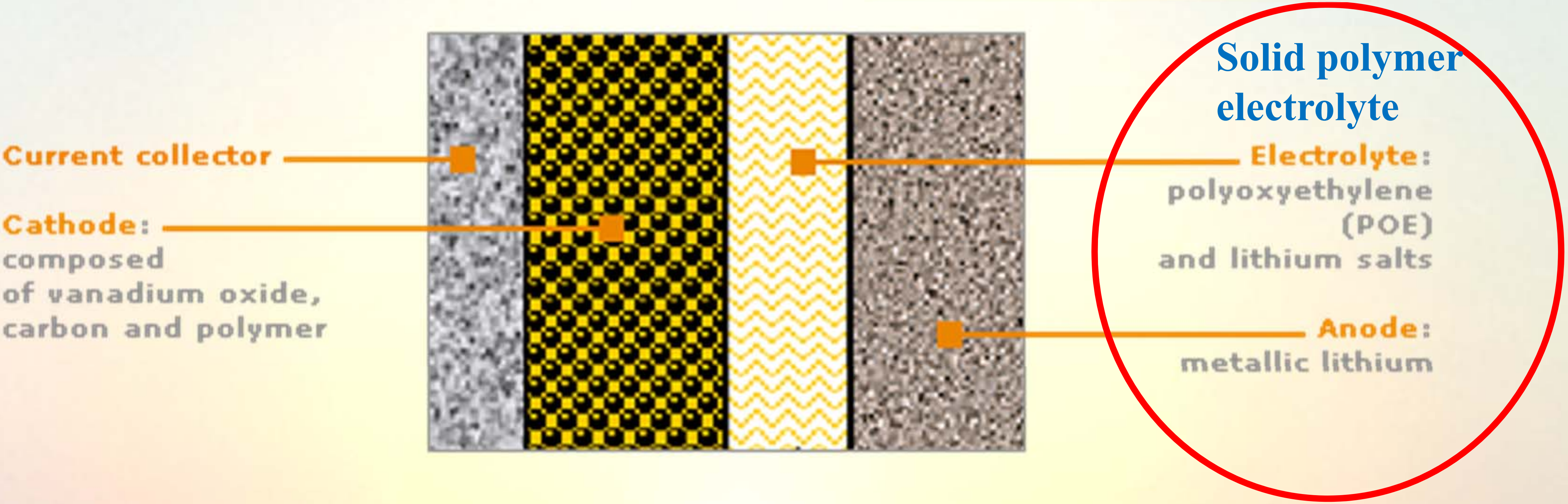
The Bolloré Group acquires the assets of Canadian manufacturer Avestor and strengthens its electric battery production activity

FCBAT

Source: K. Brandt

Li-Metal Polymer System





Bolloré (France)

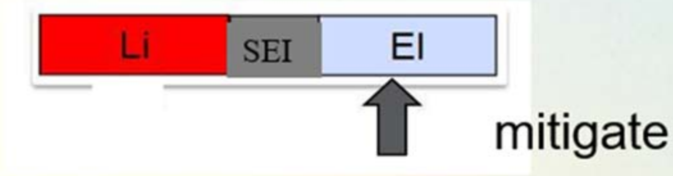
2.8 kWh, 31 V, 25 kg, 25 l,
P_{max}: 8 kW, 110 Wh/kg,

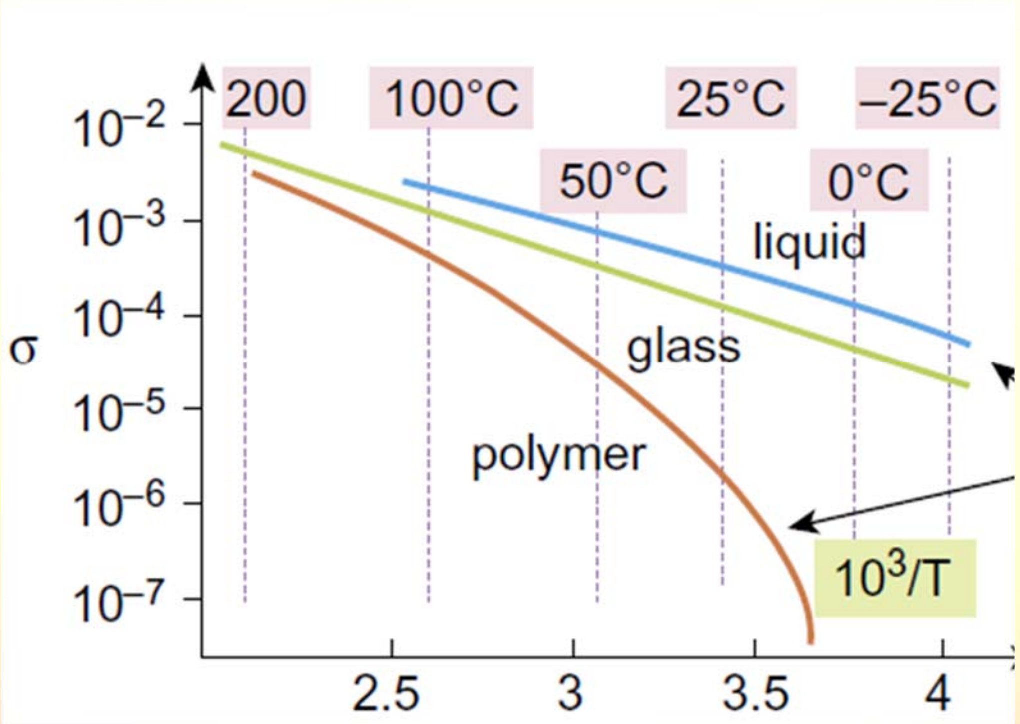
-

Source: M. Armand, Munich, March 2014

FCBAT

Li-Metal Polymer System Operating Temperature





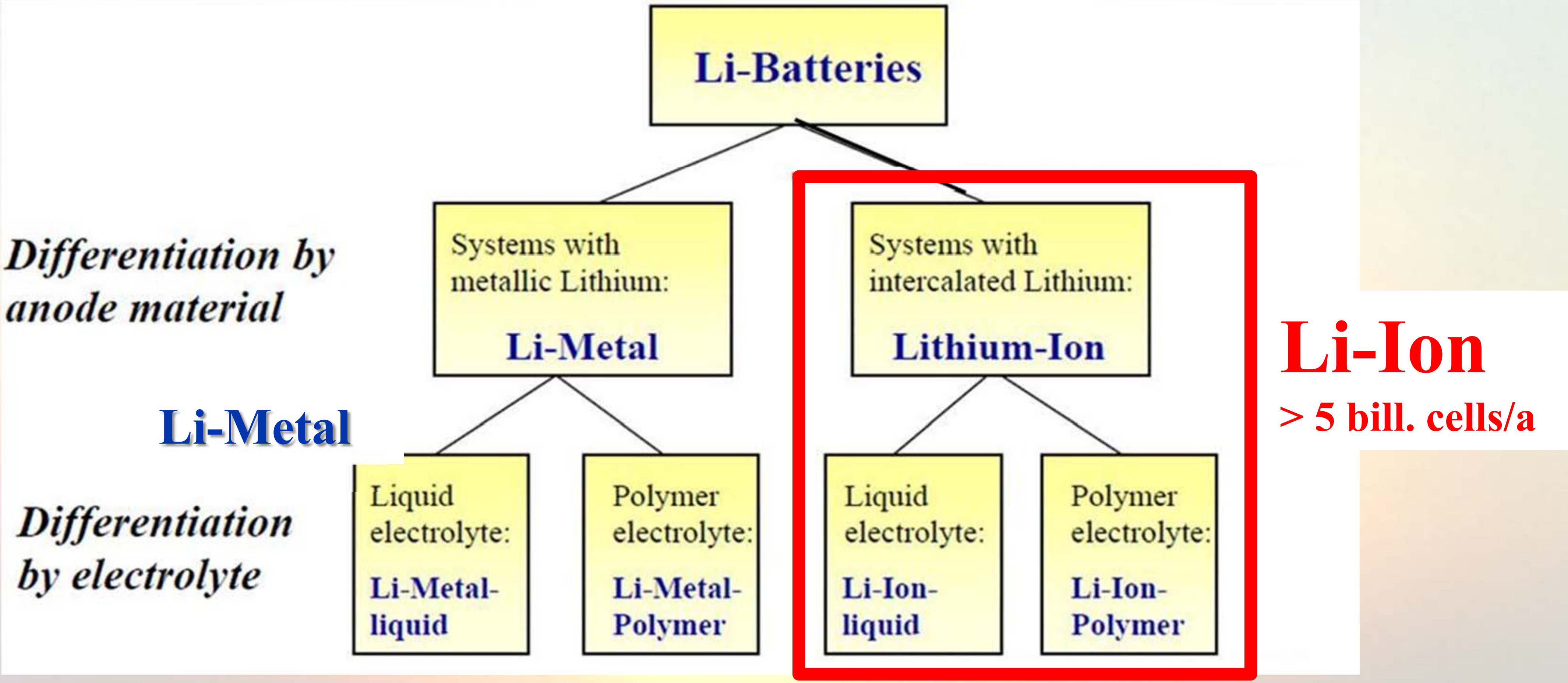
Operating temperature: 80°C

Melting Temperature Li : 180 °C

-

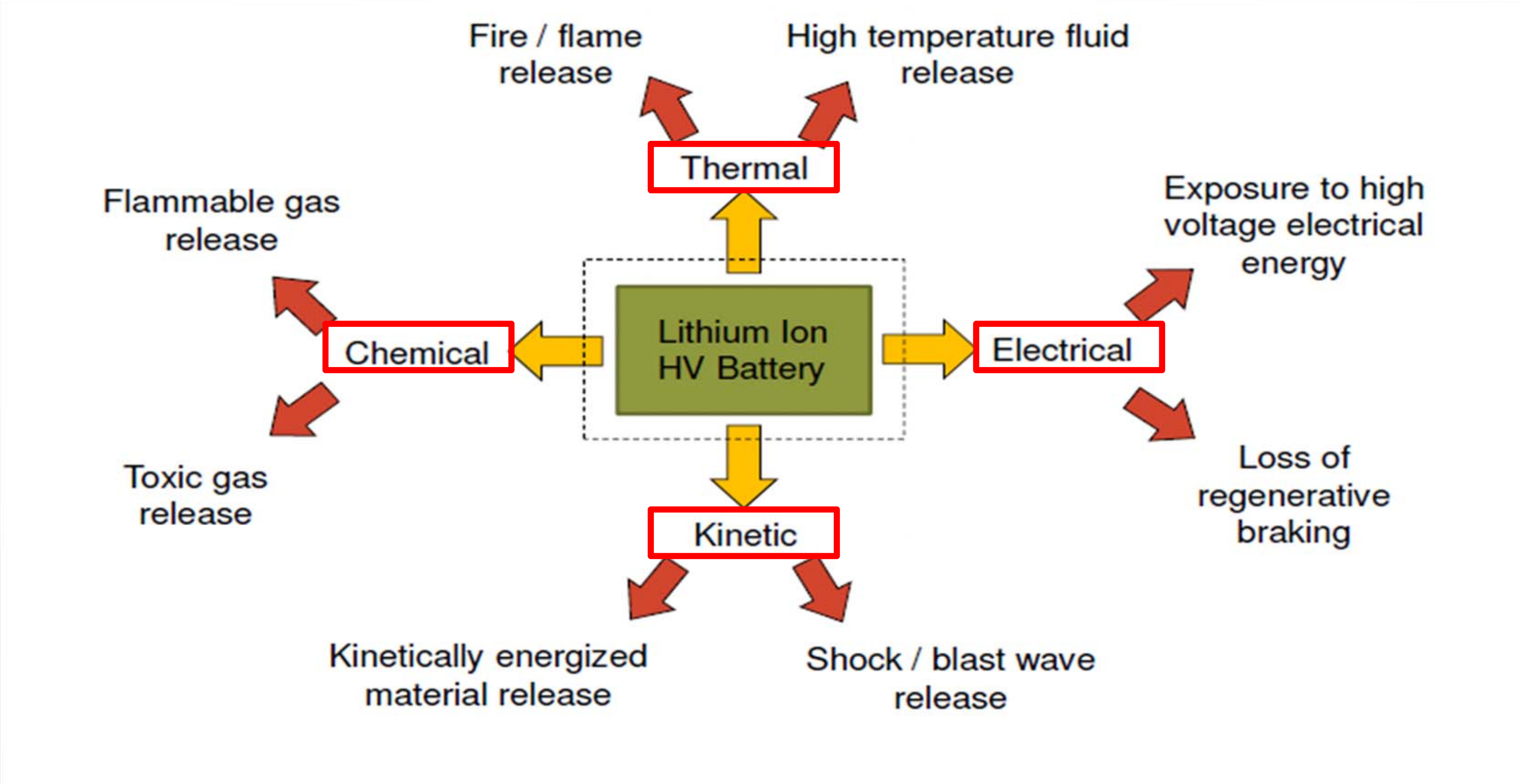
Source: M. Armand, Munich, March 2014

Li - Battery Systems



FCBAT

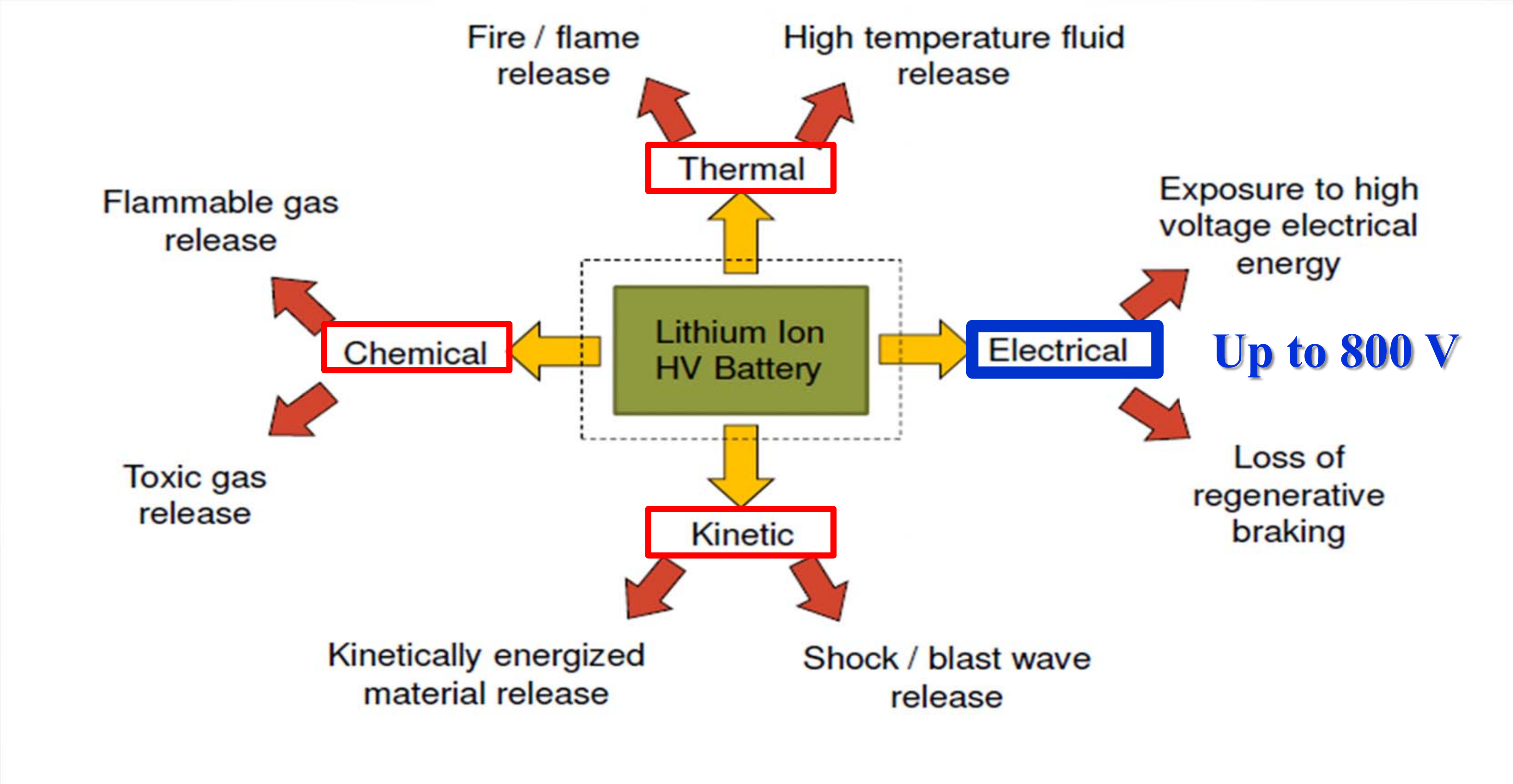
Where are the Main Safety Problems?



Source: Landrover- Jaguar

FCBAT

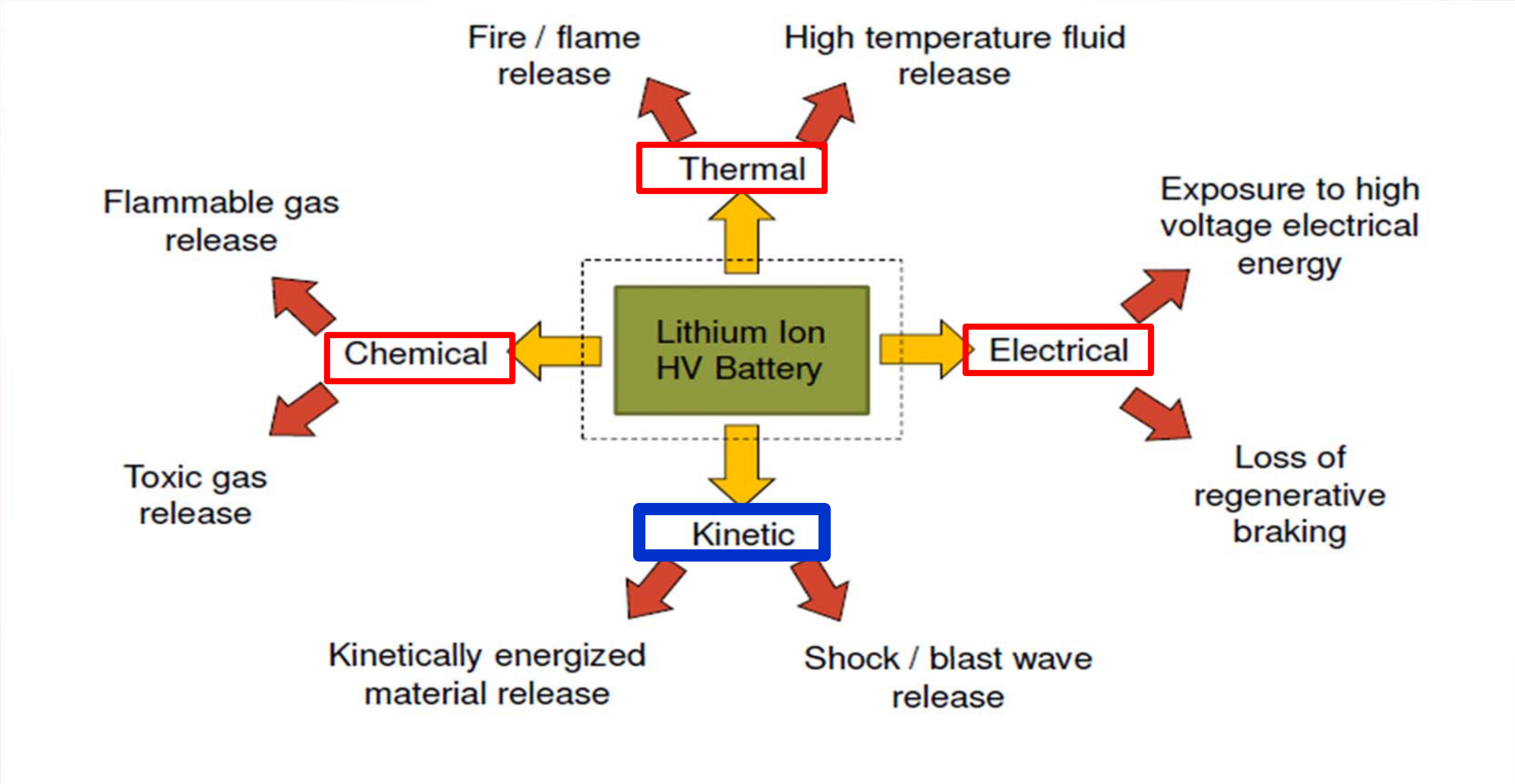
Where are the Main Safety Problems?



Source: Landrover- Jaguar

FCBAT

Where are the Main Safety Problems?



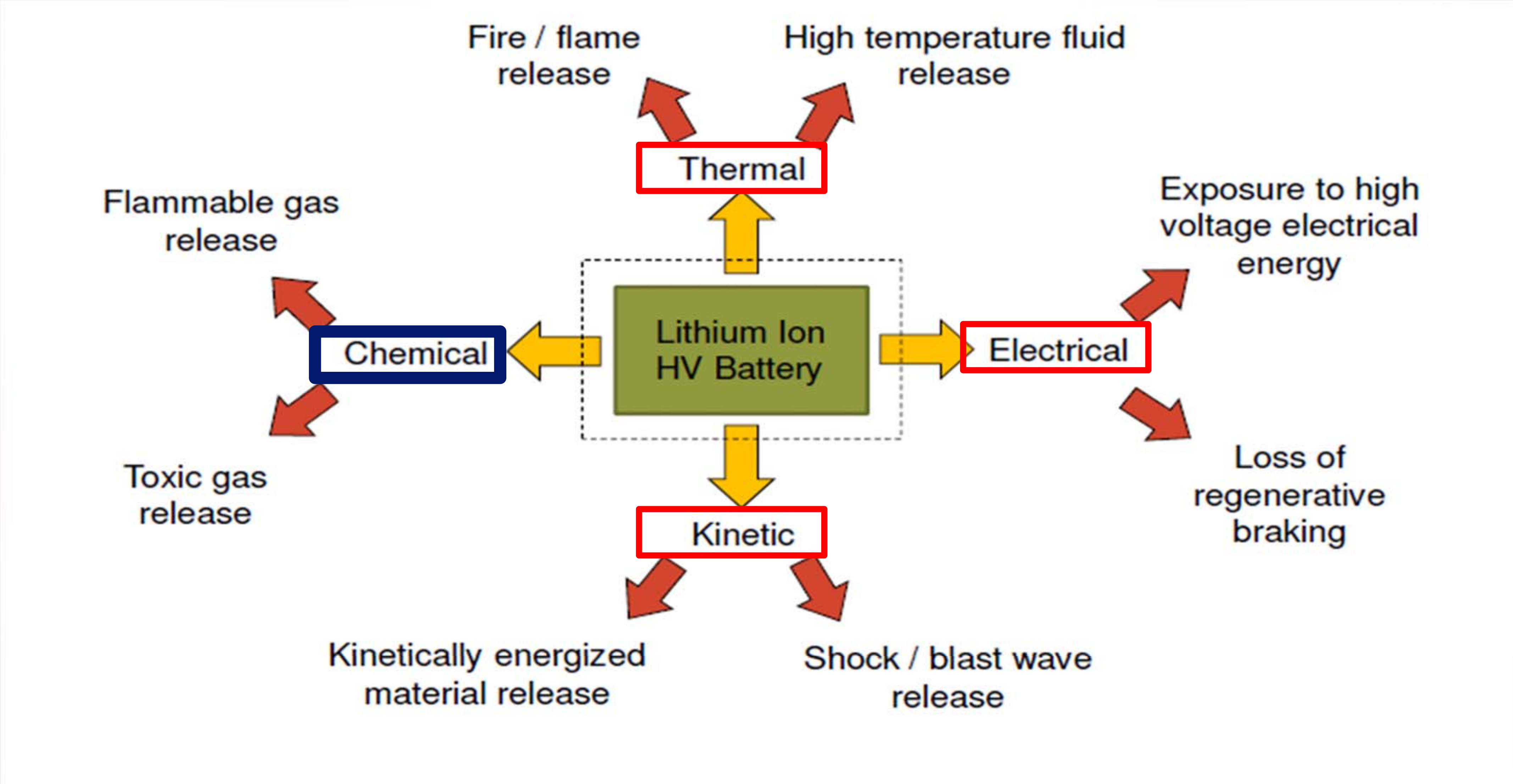
Source: Landrover- Jaguar

FCBAT

NASA Robot October 2016

FCBAT

What are the Main Safety Problems?



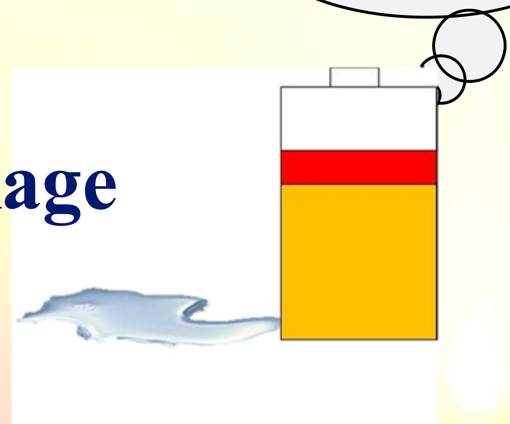
Source: Landrover- Jaguar

Chemical Risk - Main Source: Electrolyte

Gas Development

(Pressure, Flammable, Toxic)

Electrolyte Leakage



Electrolyte

1-1.5 m $LiPF_6$ (Salt) in Polycarbonats (Solvent)

Li-Salt - source of Li^+, $LiPF_6$, $LiPF_6$ => Li^+ + PF_6^-

Solvent - helps to dissociate $LiPF_6$ => Li^+ + PF_6^-
Mixtures of organic polycarbonats as EC, PC, EMC, or DMC

Electrolyte Materials - Safety Significance

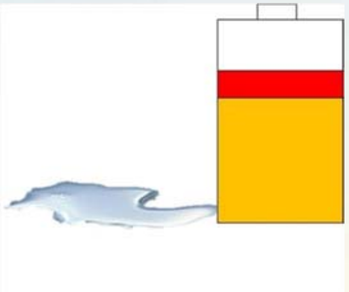
Solvent: Solvent Burning

$LiPF_6$: HF and other Fluorid Compounds Formation

Solvent

substance	abbrev.	boiling [°C]	flash [°C]	self- ignation [°C]
Dimethylcarbonat	DMC	90	16	465
Ethylencarbonat	EC	250	150	465
Propylencarbonat	PC	240	135	510

Flammable gas release: Externally supplied ignition



Electrolyte - Leakage

Li-Salt (**source** of Li^+): 1-1.5 molar solution of $LiPF_6$

$$LiPF_6 \rightarrow LiF + PF_5$$
$$PF_5 + 4H_2O \rightarrow H_3PO_4 + 5HF$$

HF Hazard related to NFPA 704

Flammability

Health (toxic)

Instability/Reactivity

low 0 … high 4

MAK-Wert: 1mg/m³.

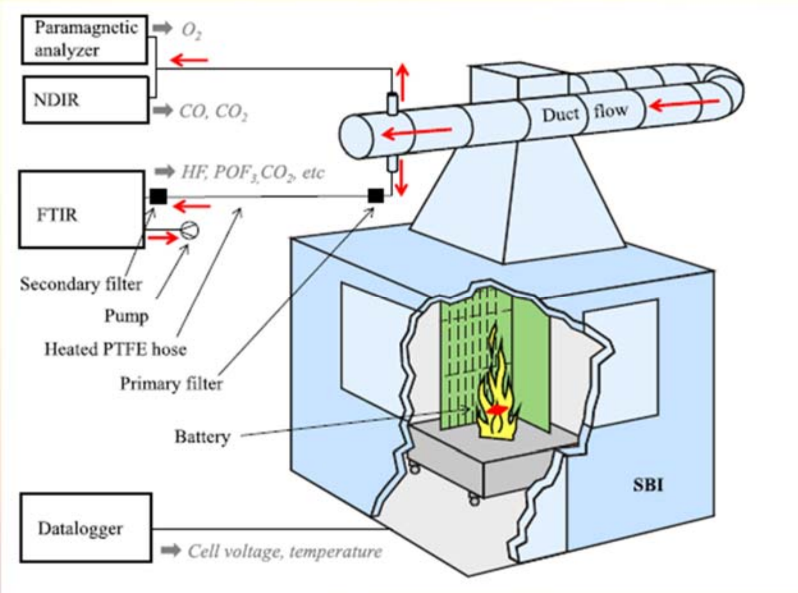
IDLH –Wert 25 mg/m³.

(Immediately Dangerous to Life or Health)

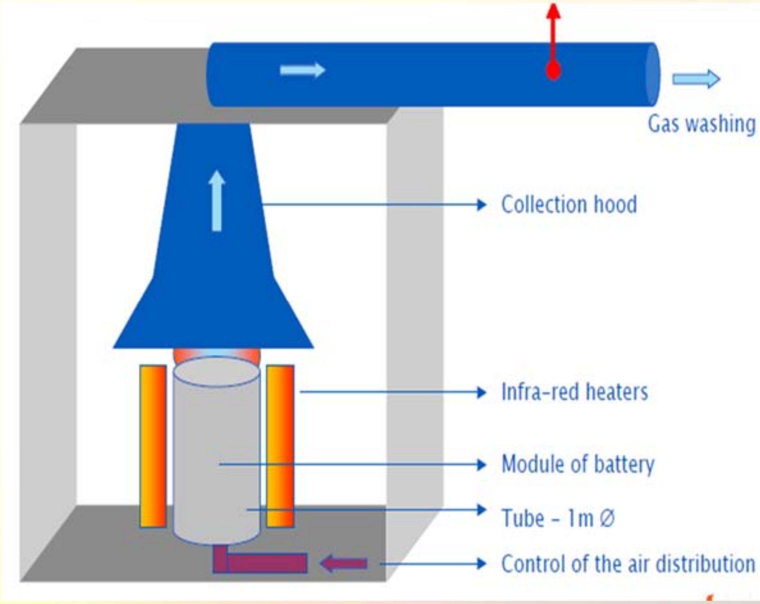
FCBAT

Experimental Measurement of HF under Thermal Runaway Conditions (Fire) - Cells

RESULTS **40 – 90 g HF/kWh** **40 – 120 g HF/kWh**

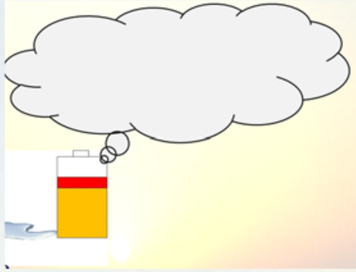


Fire heating *(15 kW burner)*
35 Ah pouch LFP
Source: F. Larsson et al., J. Power Sources 271 (2014) 414

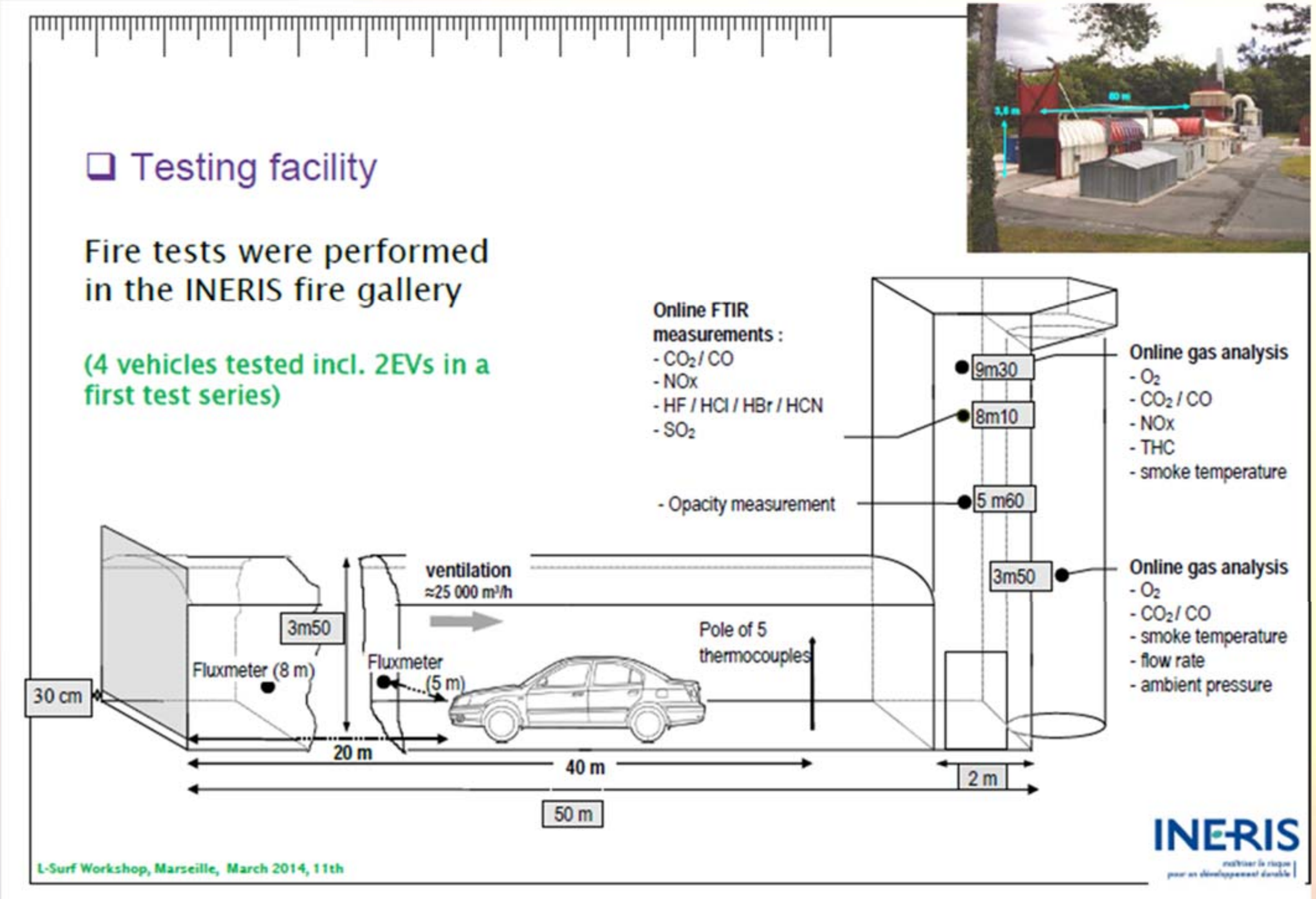


IR heating *(~350 °C)*
2.9 Ah pouch LMO
Source: P. Ribiere et. al. Energy Environ. Sci., 5 (2012) 5271

FCBAT



Experimental Measurement of HF under Thermal Runaway Conditions (Fire) - Cars



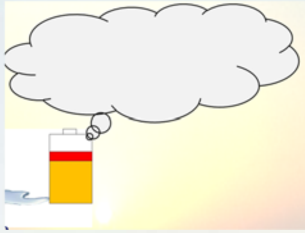
Results

EV with LFP 23.5 kWh
28 g HF/kWh

EV with LFP 16.5 kWh
56 g HF/kWh

$$\mathbf{m\ (HF_{Batt})} = m\ (HF_{EV}) - m\ (HF_{ICE})$$

Source: INERIS



HF-Measurement Results under Thermal Runaway Conditions (Fire)

Cell 1 – LMO 2.9 Ah pouch — **40 – 90 g HF/kWh**

Source: P. Ribiere et. al. Energy Environ. Sci., 5 (2012) 5271

Cell 2 – LFP 35 Ah pouch — **40 – 120 g HF/kWh**

Source: F. Larsson et al., J. Power Sources 271 (2014) 414

EV with Battery 1 — **56 g HF/kWh**

LFP 16.5 kWh

EV with Battery 2 — **28g HF/kWh**

LFP 23.5 kWh

Source: INERIS (http://hal-ineris.ccsd.cnrs.fr/ineris-00973680/document)

=> 28 – 120 g HF/kWh

MAK-Wert: 1mg/m^3.

IDLH –Wert (Immediately Dangerous to Life or Health) 25 mg/m^3.

FCBAT

Incomplete Combustion

Incomplete combustion (in argon)

- HCN, HF and Co concentrations were larger than TLV.

Components	In air Conc.	Ref. In Argon Conc.	Unit	Analytical method
CN^-	< 0.3(※1)	**21**	mg/m^3	Photometric method
F^-	1.6	**20**	mg/m^3	Ion chromatography
PO_4^{3-}	< 2(※1)	< 2(※1)	mg/m^3	Ion chromatography
Li	0.5	1.3	mg/m^3	ICP-OES
P	< 0.3(※1)	6.0	mg/m^3	ICP-OES
pH(gas components absorbed in aq.soln)	6.1	4.5	-	Glass electrode method

TLV of HCN : 5.2mg/m3, HF; 0.4mg/m3

The above result suggests that incomplete combustion may generate highly hazardous gasses of HCN and HF.

東洋システム株式会社
TOYO SYSTEM CO.,LTD.

Japanese Results

No HF!!!

Comparison of Fires in Lithium-ion Battery Vehicles and Gasoline Vehicles

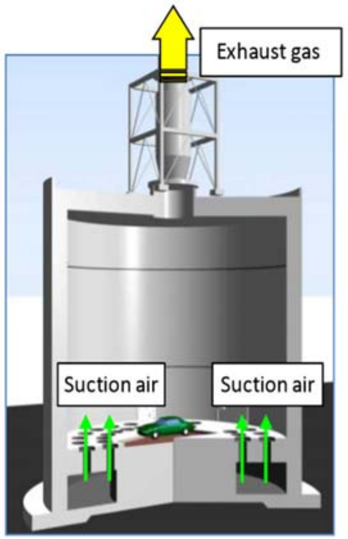
Masashi Takahashi, Masayuki Takeuchi, Kiyotaka Maeda, Shouma Nakagawa
Japan Automobile Research Institute

SAE INTERNATIONAL

JARI

LIB Vehicle-2

Exaust gas and smoke treatment equipment



Graphic model of Explosion resistant fire test cell

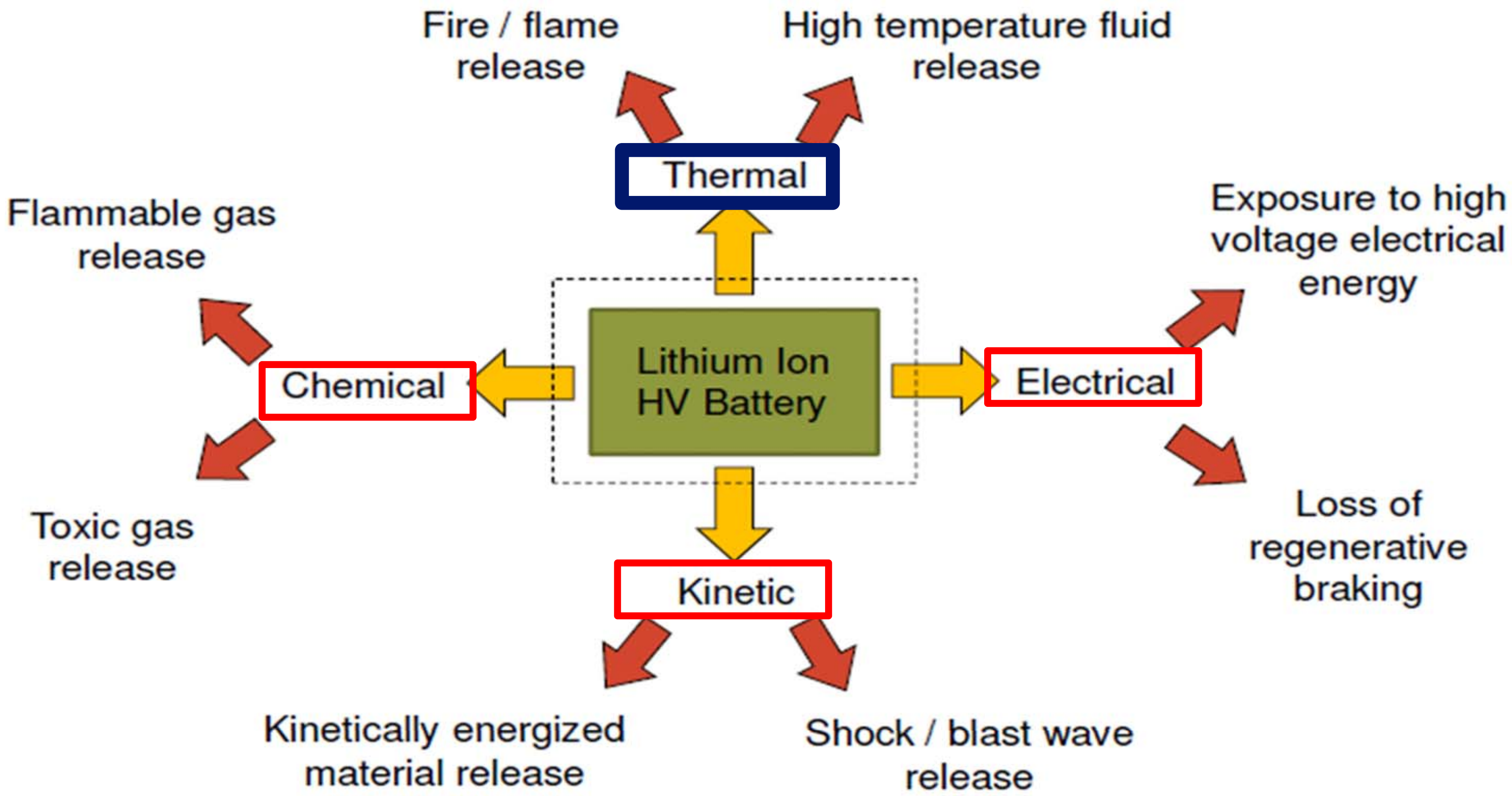
- Indoor tests are not affected by weather, so highly reproducible data can be obtained.
- The test apparatus is cylindrical with a ceiling height of 16 m and a internal diameter of 18 m.
- The air is blown into the apparatus at a rate of 750 m^3/min through a suction hole opened under the floor.
- Combustion gasses generated from the fire test are discharged from the ceiling and then sent to the exhaust gas and smoke treatment equipment.

Results:

HF concentration was below the detection limit at all sampling positions.

CO concentration was at a distance of 1 m from the vehicle, less than 100 ppm

What are the Main Safety Problems?



FCBAT

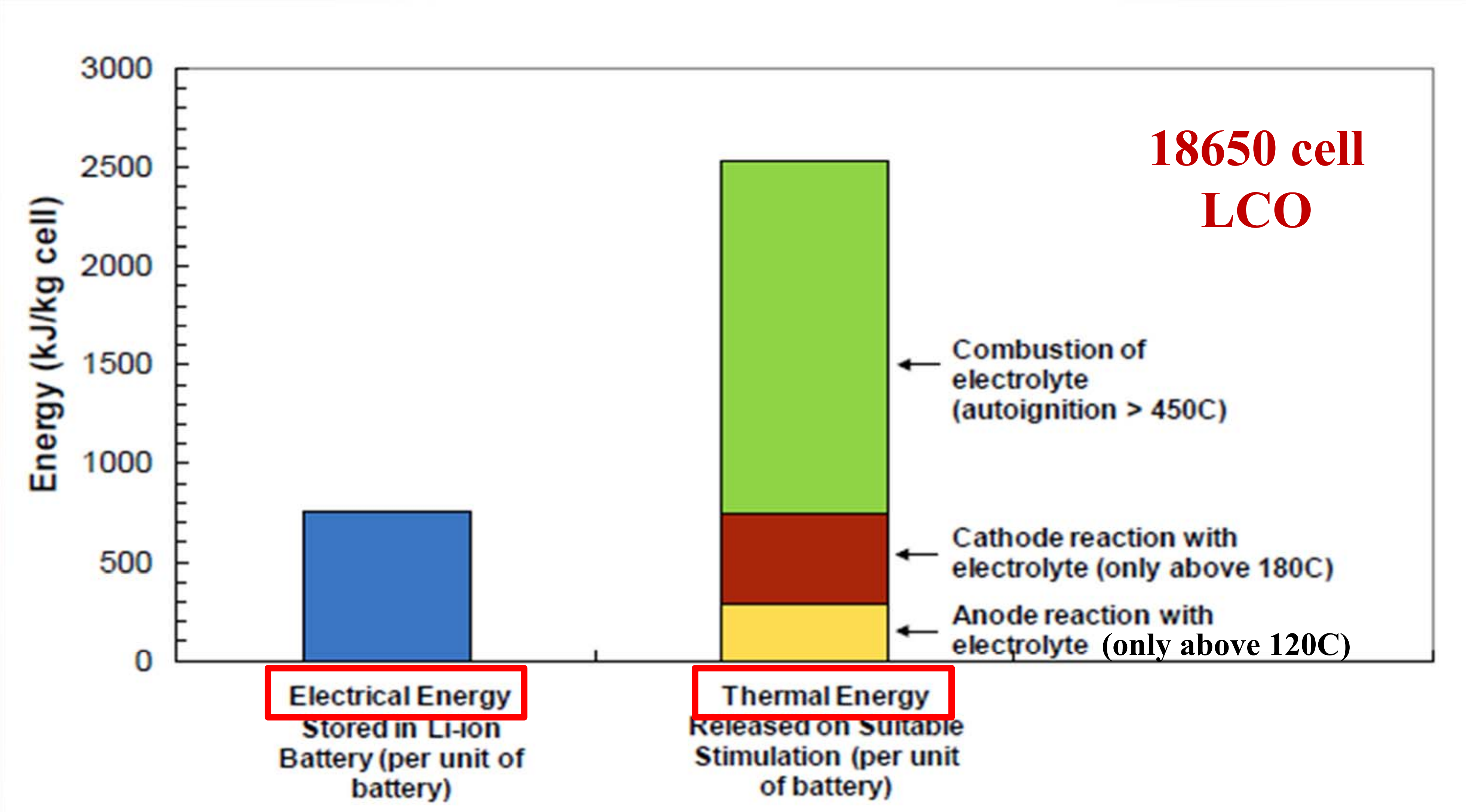
Source: Landrover- Jaguar

What contributs to the Li-Ion Cell Energy (3.3 kJ/kg)?

Energy density of advanced batteries
3.3 kJ/cm^3

FCBAT

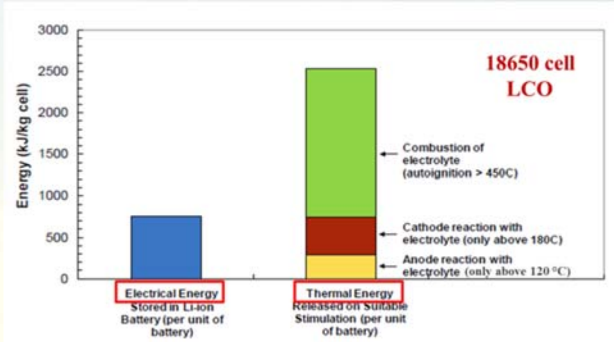
Electrochemical and Thermal Energy



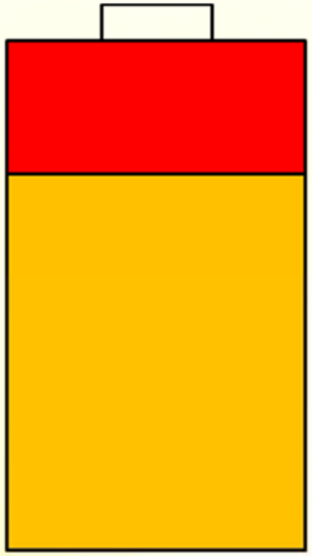
FCBAT

Source: Stringfellow, R.; Ofer, D.; Sriramulu, S.; Barnett, Brian., TIAX Las Vegas, NV, Oct. 12, 2010 (Abstract #582).

18650 LCO Cell



10 Wh — **Electrical Energy**



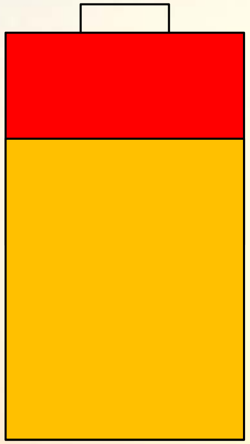
30 Wh — **Thermal Energy**

100 % SOC

FCBAT

Energy of 18650 Cell (LCO)

10 Wh



30 Wh

100 % SOC

„Electro“chemical Energy

(**Active mass** - EC activ)

Source for heating up

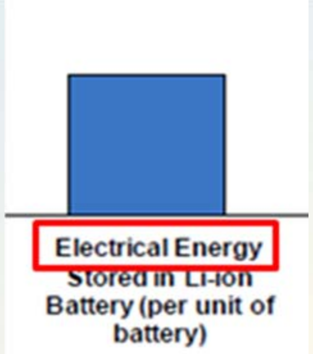
Chemical Energy

(mostly **Electrolyte** –

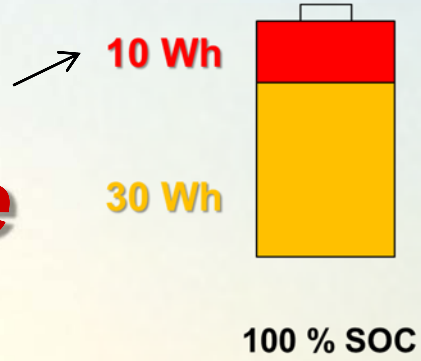
EC non-activ)

Source for burning

FCBAT



Electrochemical Energy
=> *Temperature Increase*



Spec. heat capacity C: ~ 1,000 kJ/kg K
Spec. energy E: ~ 200 Wh/kg

E/C = 720 K

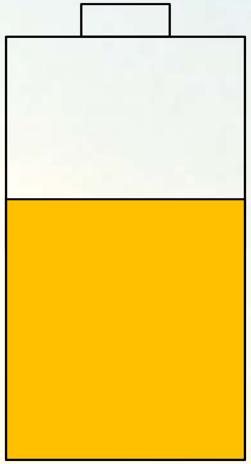
⇒ 1 % SOC increases the cell temperature by 7.2 K *(adiabatic)*

⇒ 100 % DOD increases the cell temperature by 720 K *(adiabatic)*

Source: TUM - EES

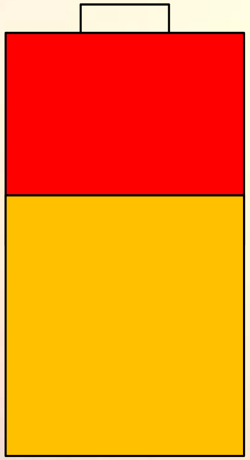
SOC = 0

0 Wh



30 Wh

10 Wh



30 Wh

100 % SOC

The cell should be safe, if SOC = 0 and no outside thermal trigger

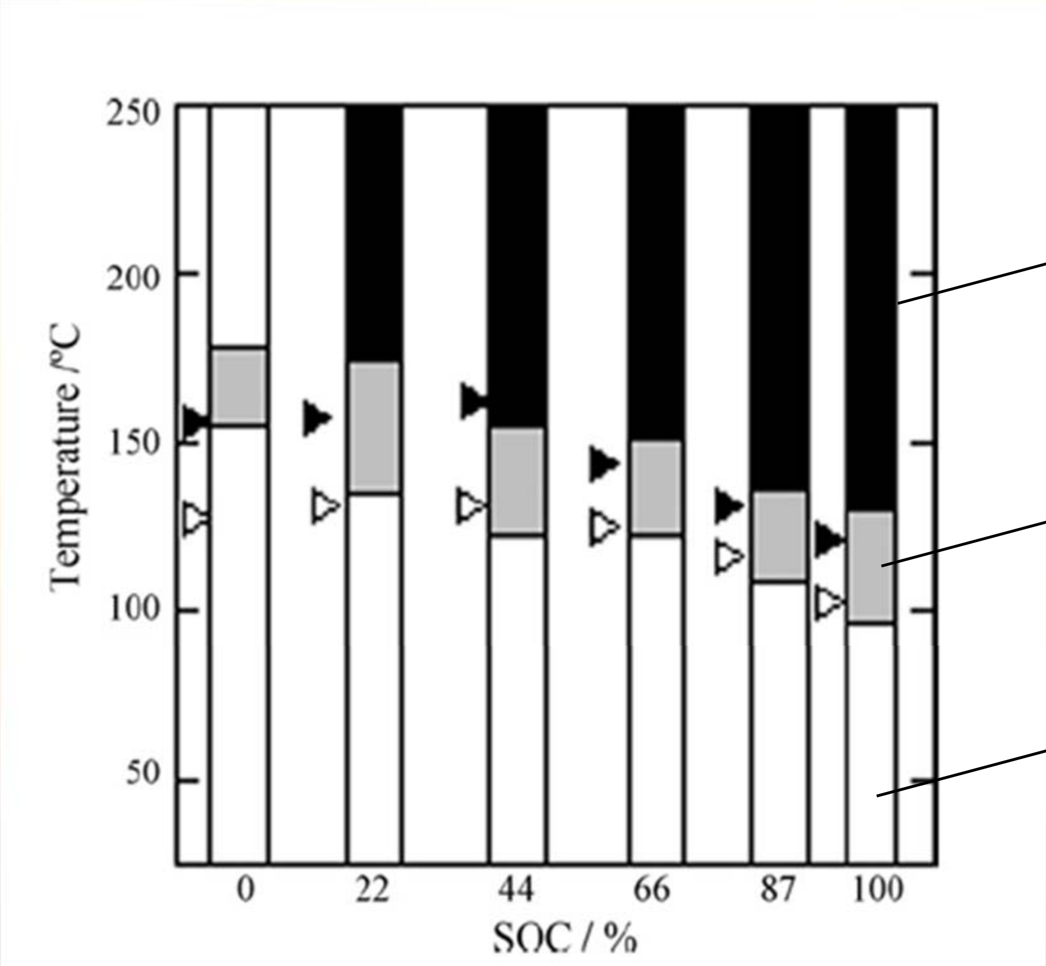
To be safer –

We need incombustible electrolytes

FCBAT

Safety – SOC dependency

LCO 18650 Panasonic



Thermal runaway

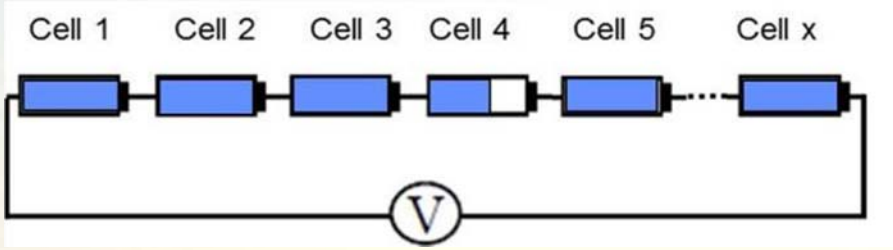
Self-heating area
(>0.05 °C)

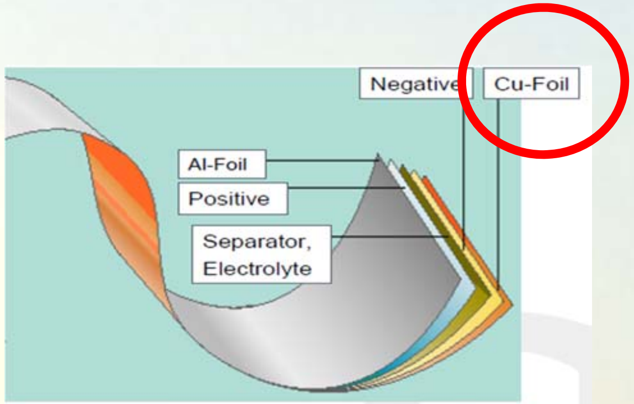
Non-self-heating area
(< 0.05 °C)

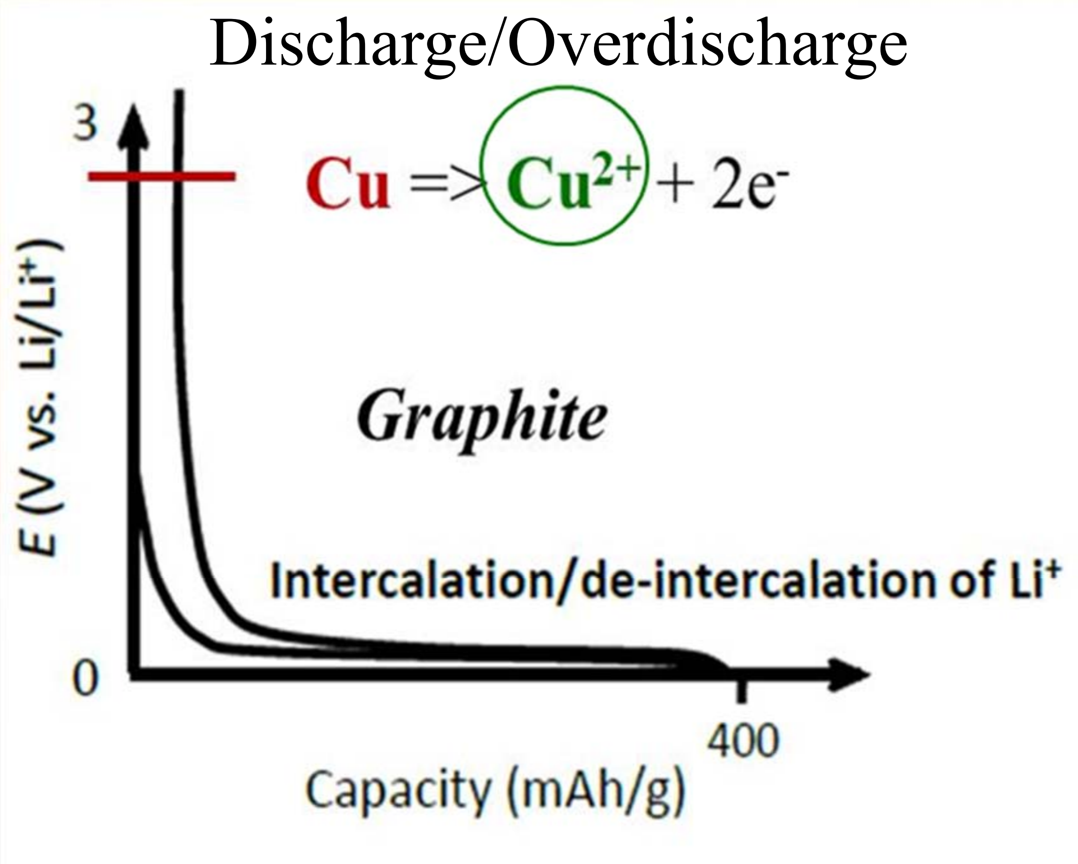
Storage and Transport at SOC=0 ?

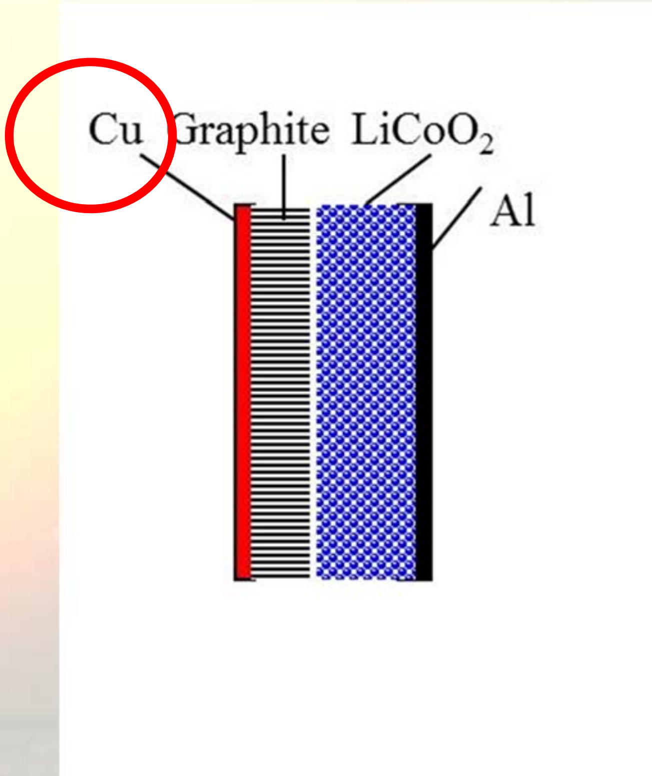
SOC = 0

Overdischarge



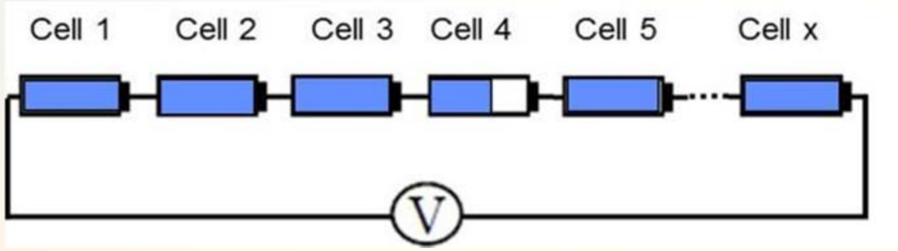


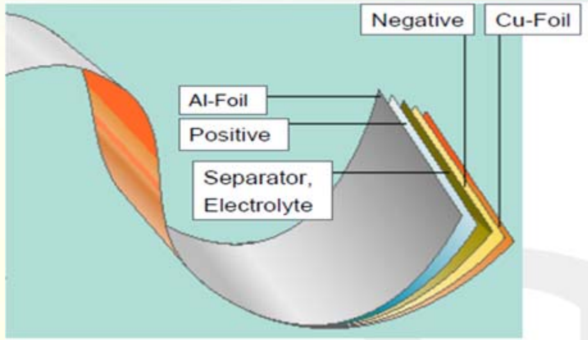


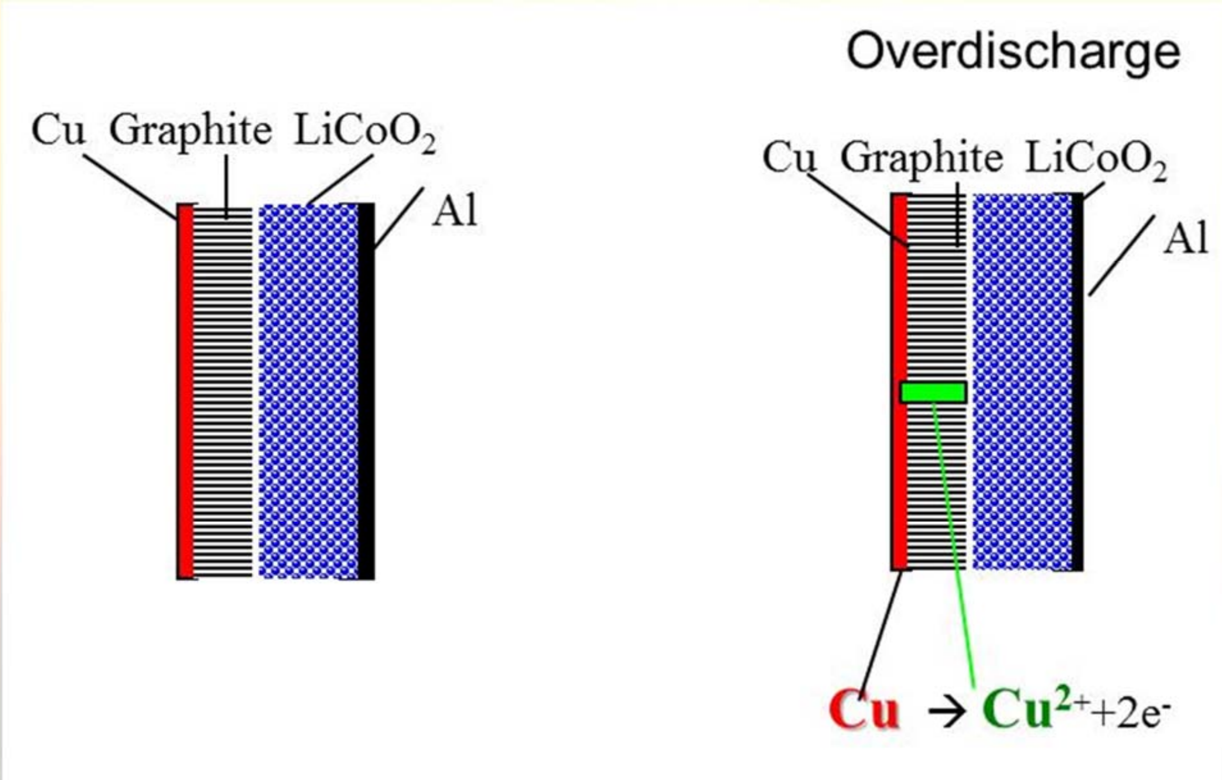


FCBAT

Overdischarge

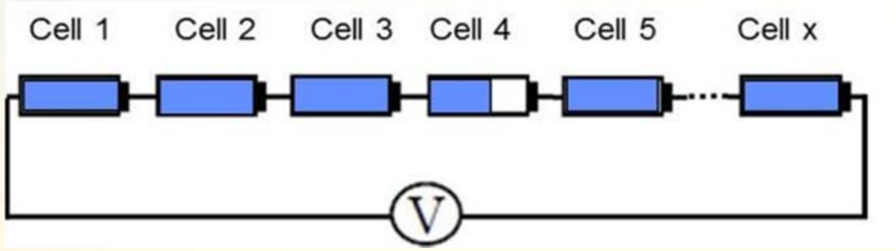


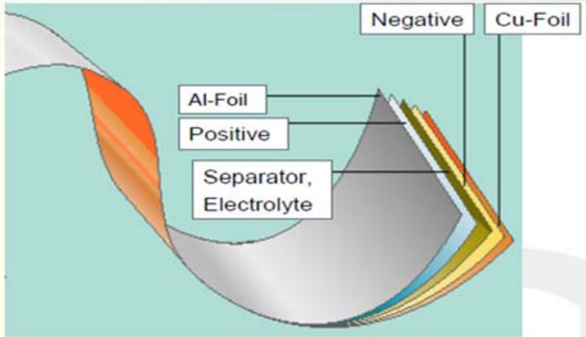


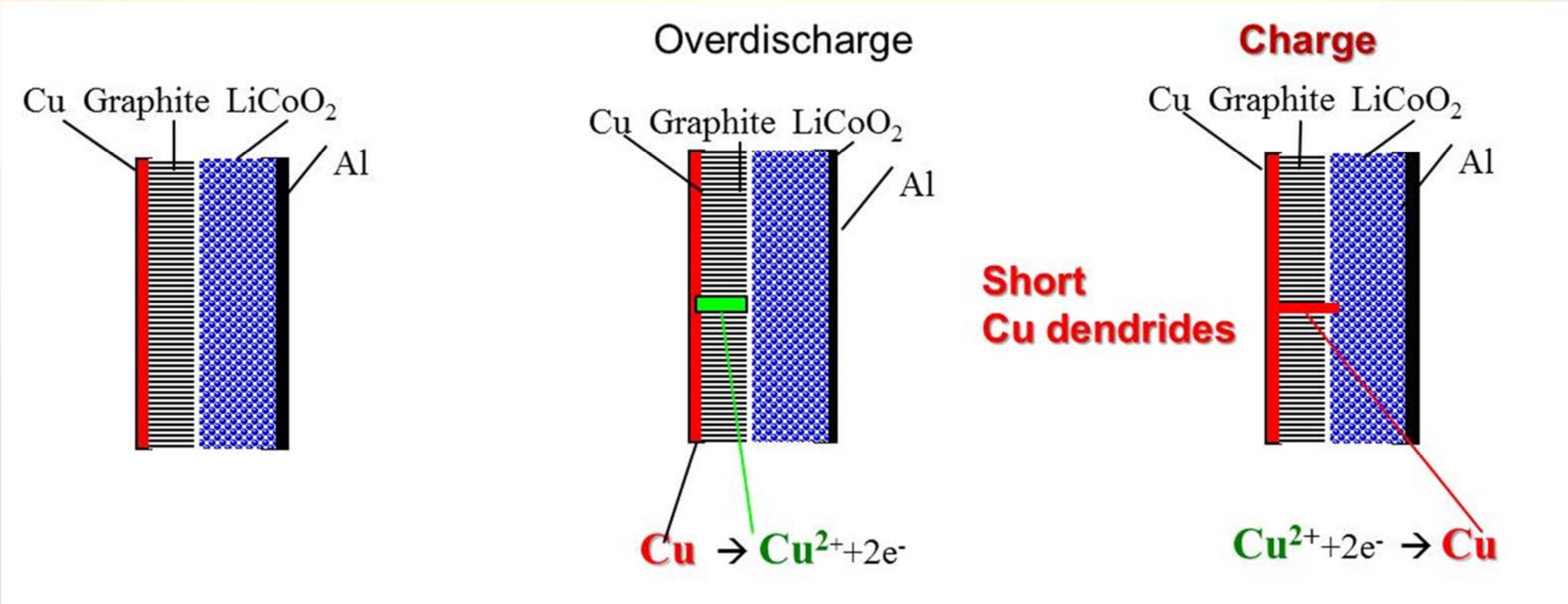


FCBAT

Overdischarge

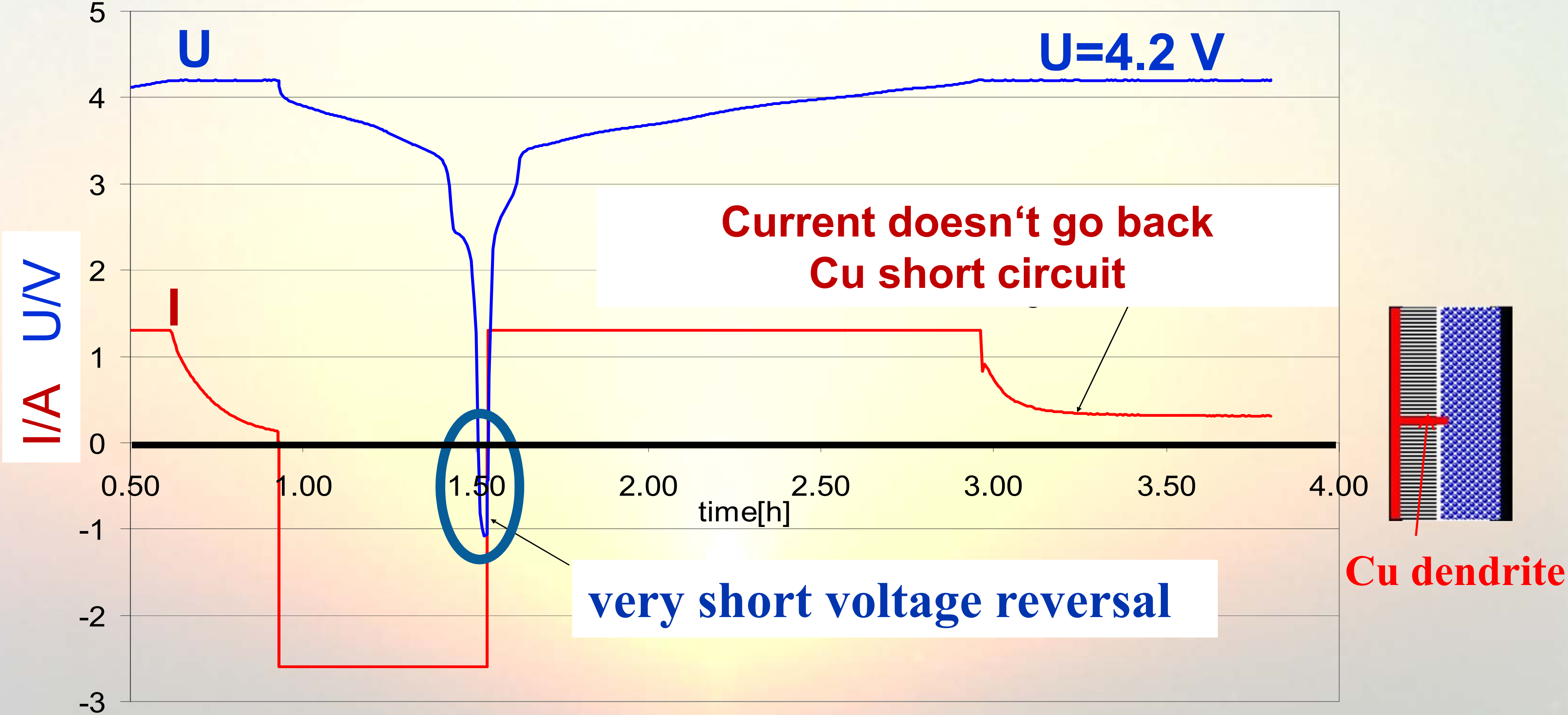






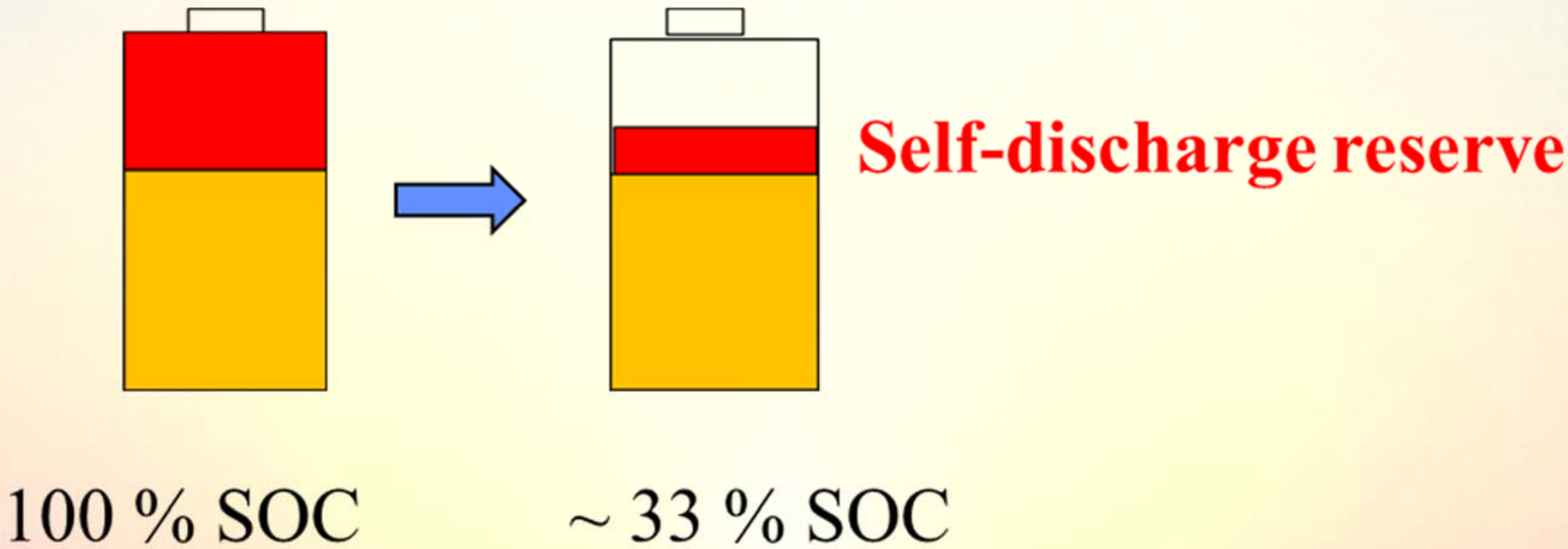
FCBAT

Voltage Reversal

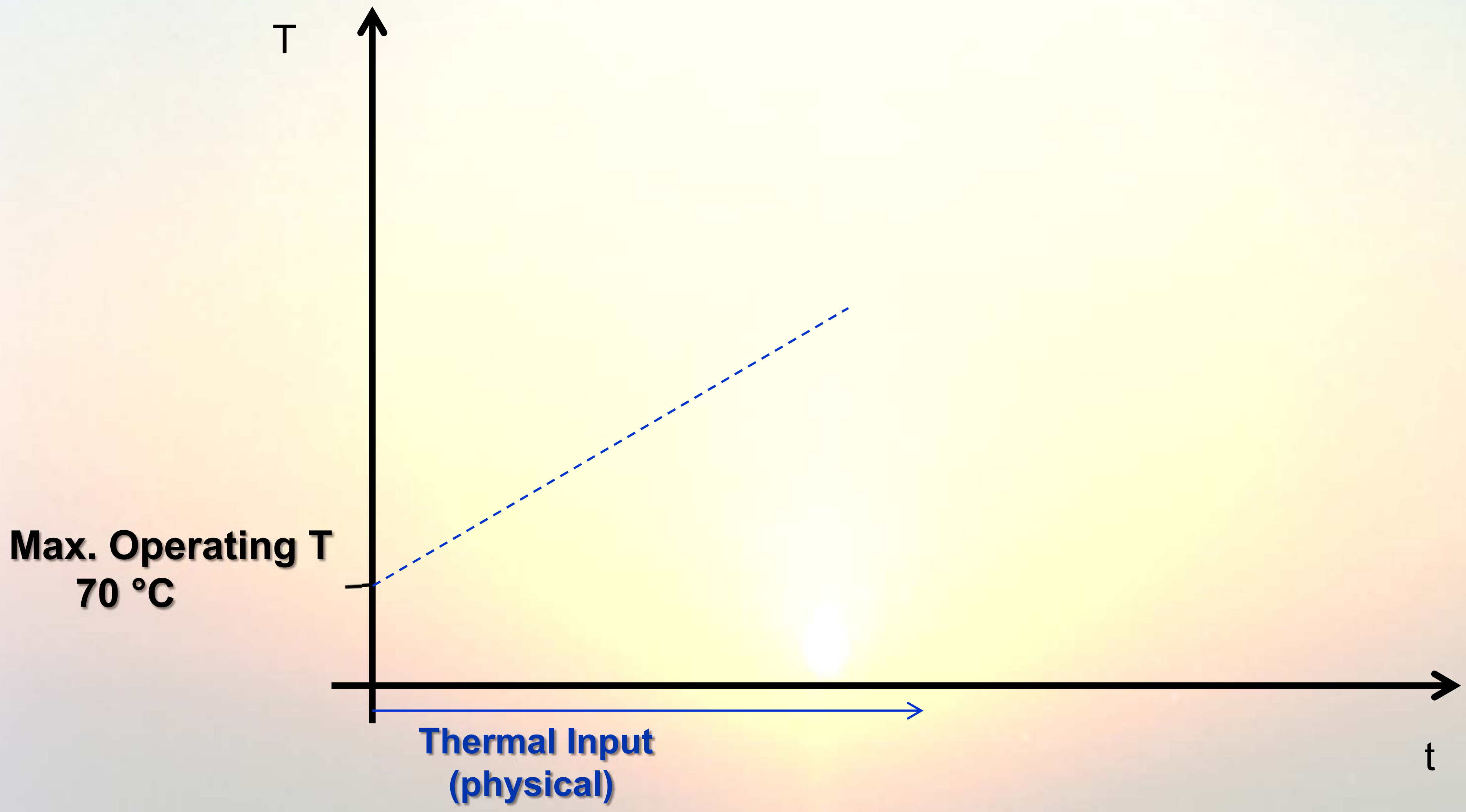


Source: TUM, EES

Storage and Transport at SOC ≈ 33 %

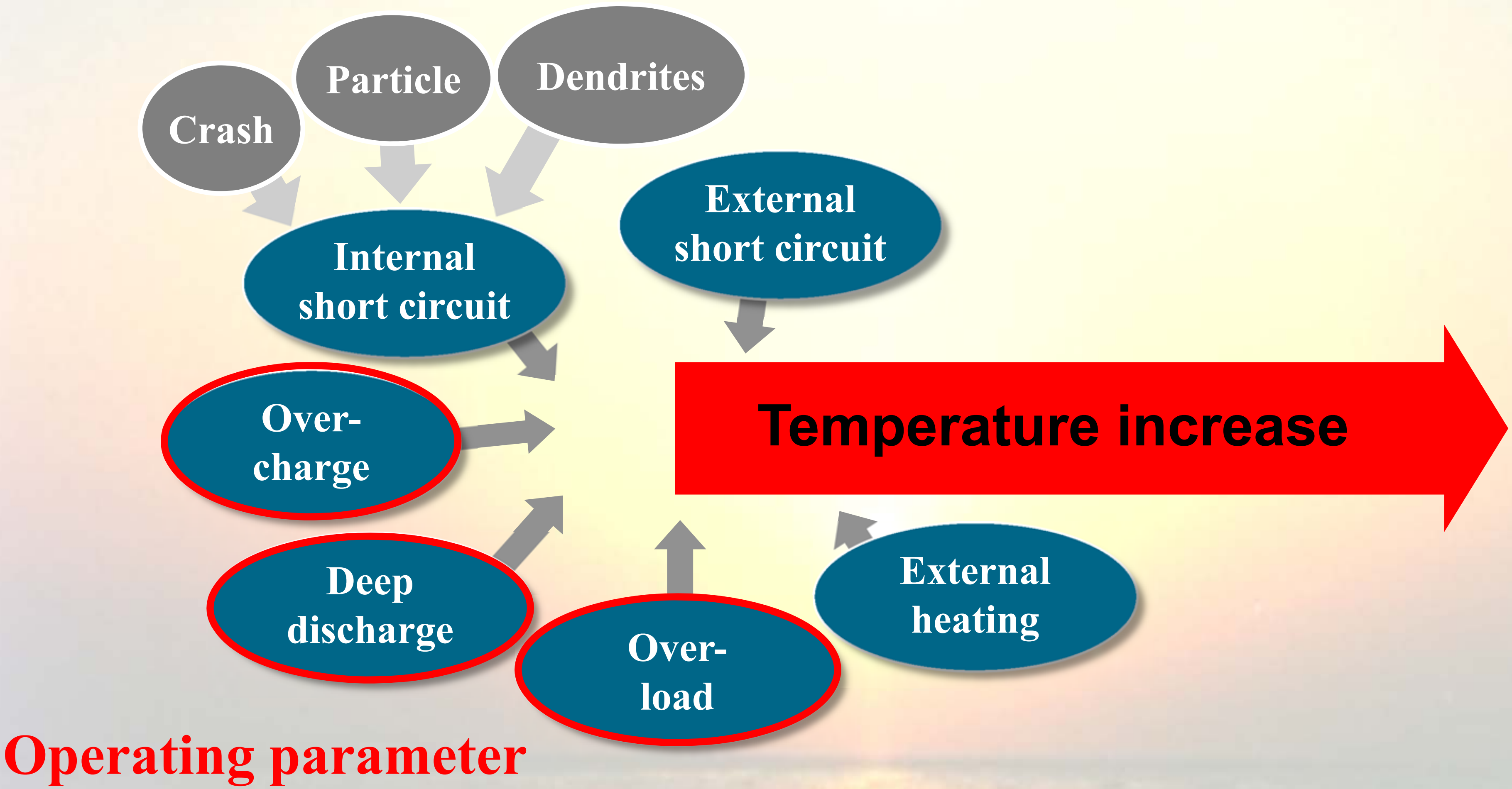


Temperature increase of Cell by Thermal Input

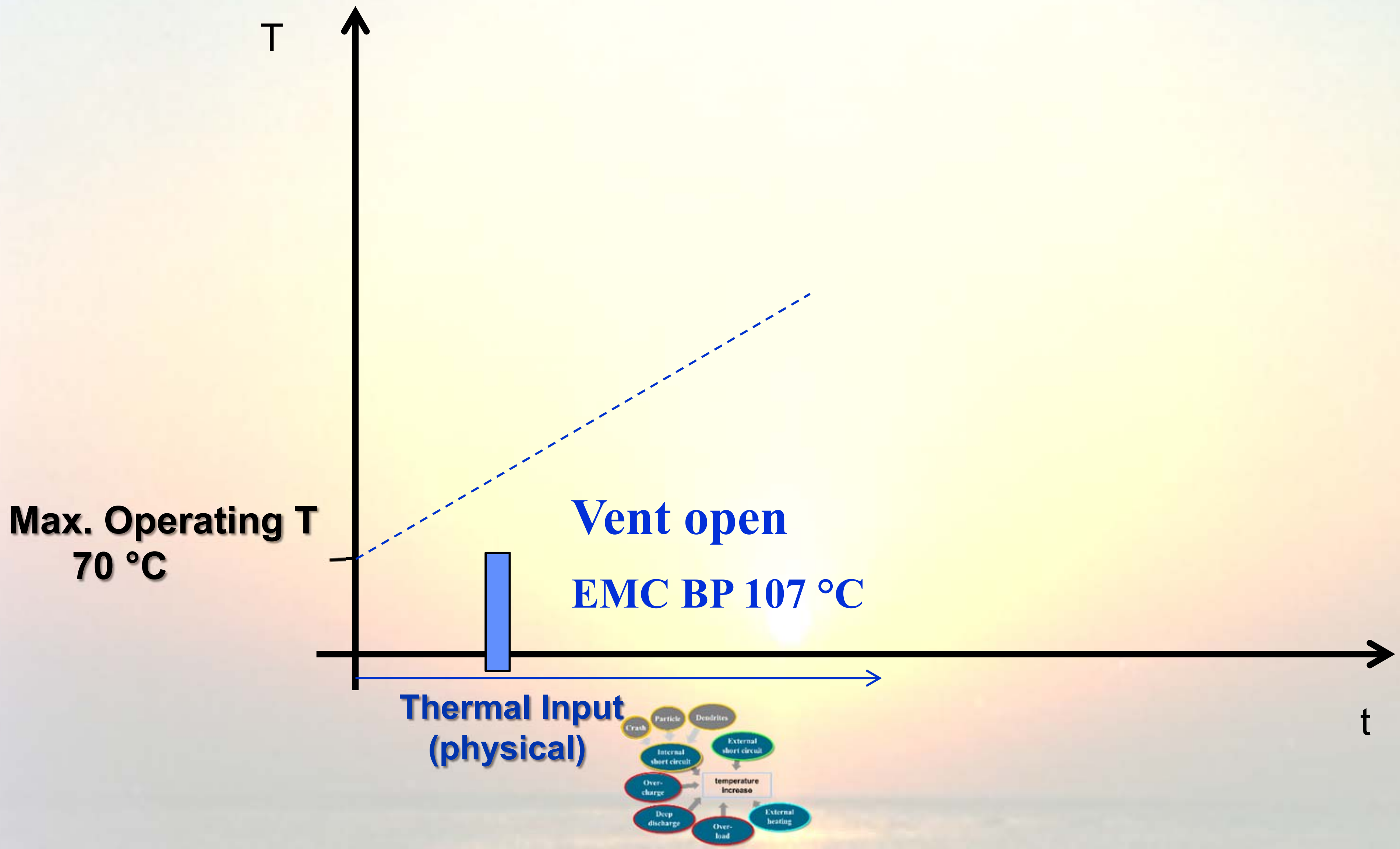


FCBAT

Reasons for Temperature Increase

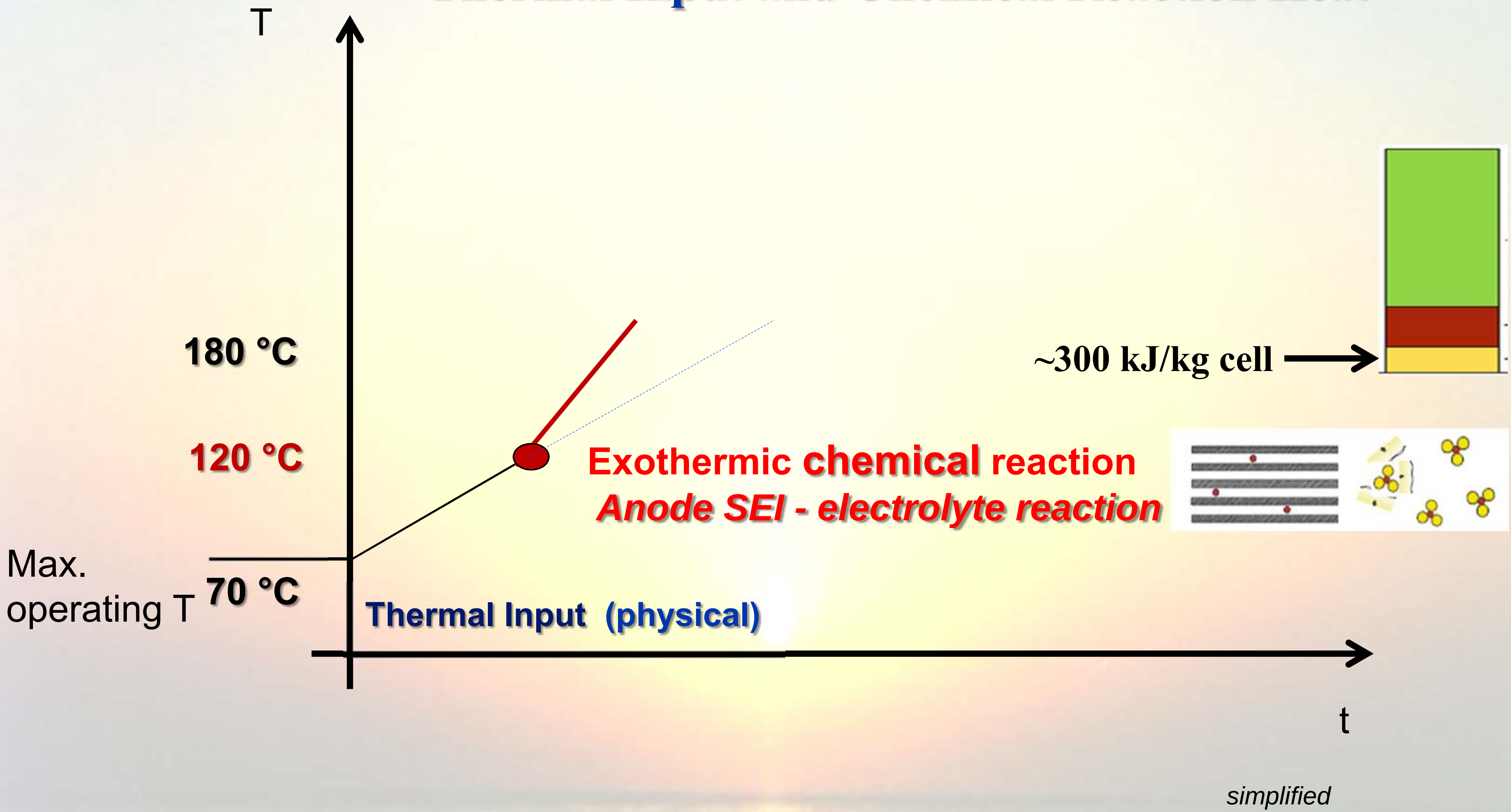


Temperature increase of Cell by Thermal Input



FCBAT

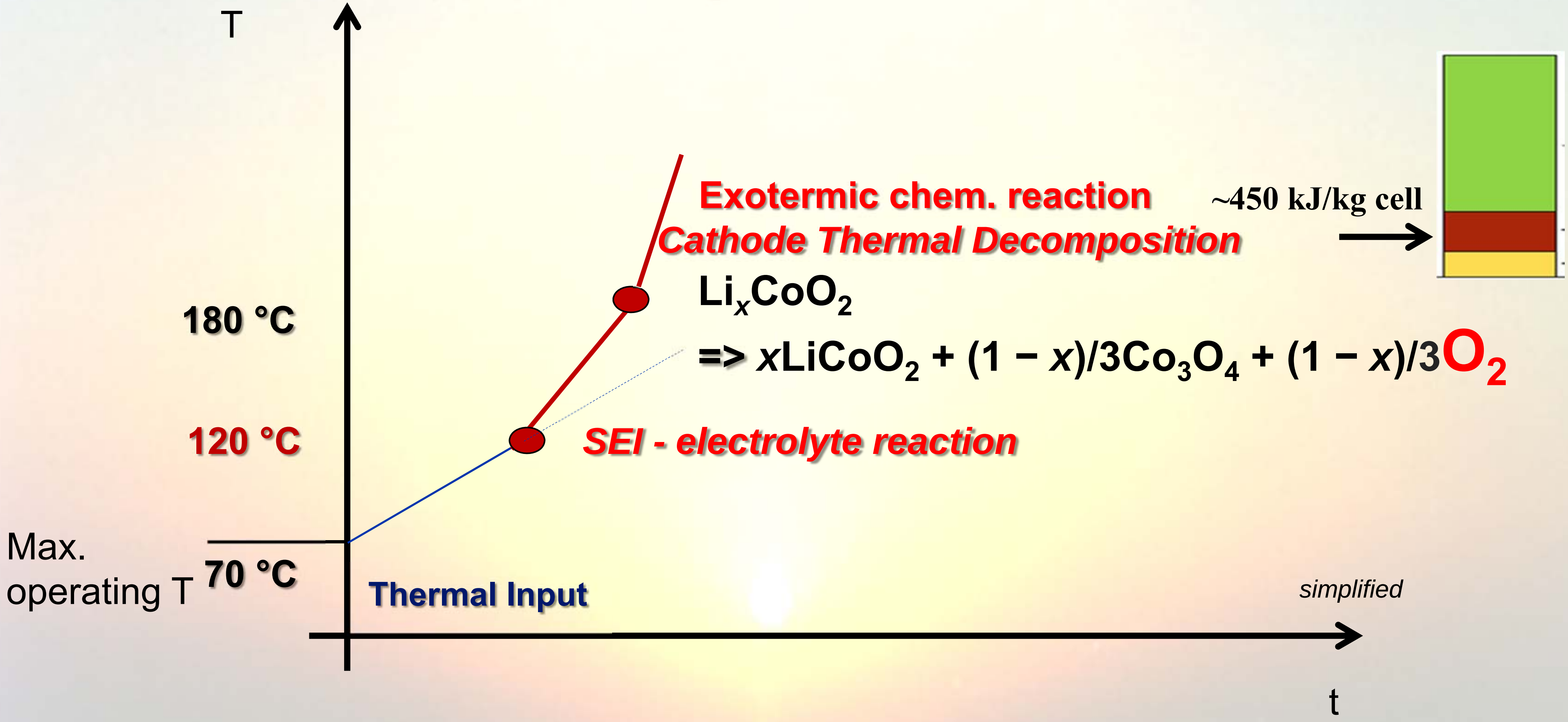
Temperature increase of Cell by Thermal Input and Chemical Reaction Heat



FCBAT

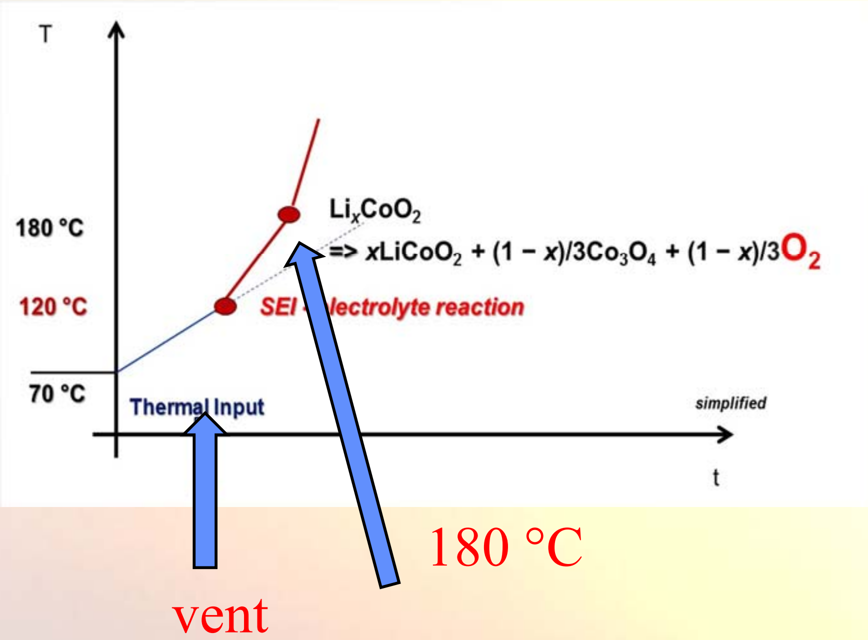
Temperature increase of Cell

by Thermal Input and Chemical Reaction Heat



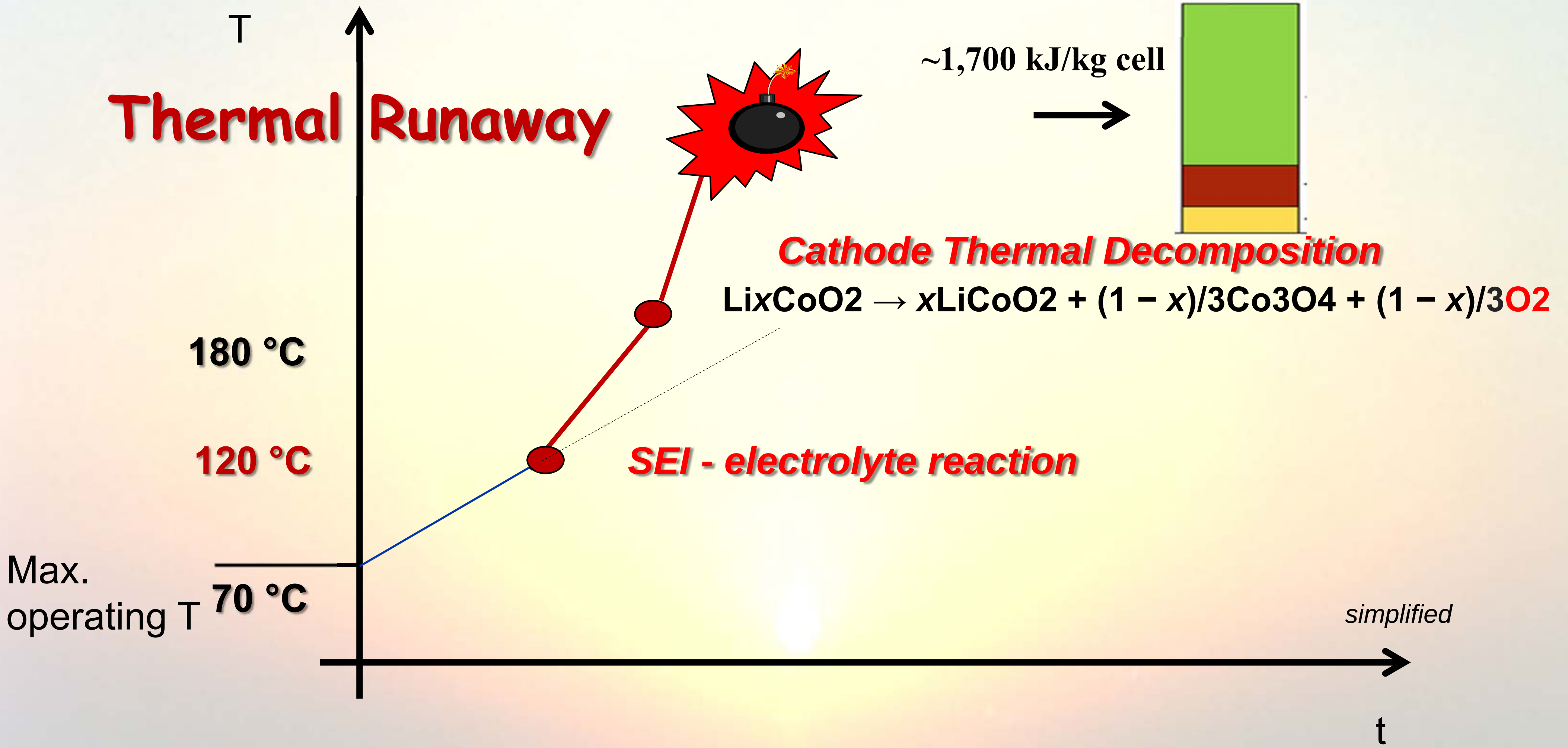
External heating

Temperature increase



$$Li_xCoO_2 \Rightarrow xLiCoO_2 + (1 - x)/3Co_3O_4 + (1 - x)/3O_2$$

Thermal Runaway



FCBAT

What to do ?

A – Chemical Influence (AM, electrolyte)

B – Physical Influence (Active and Passive Safety Devices)

t

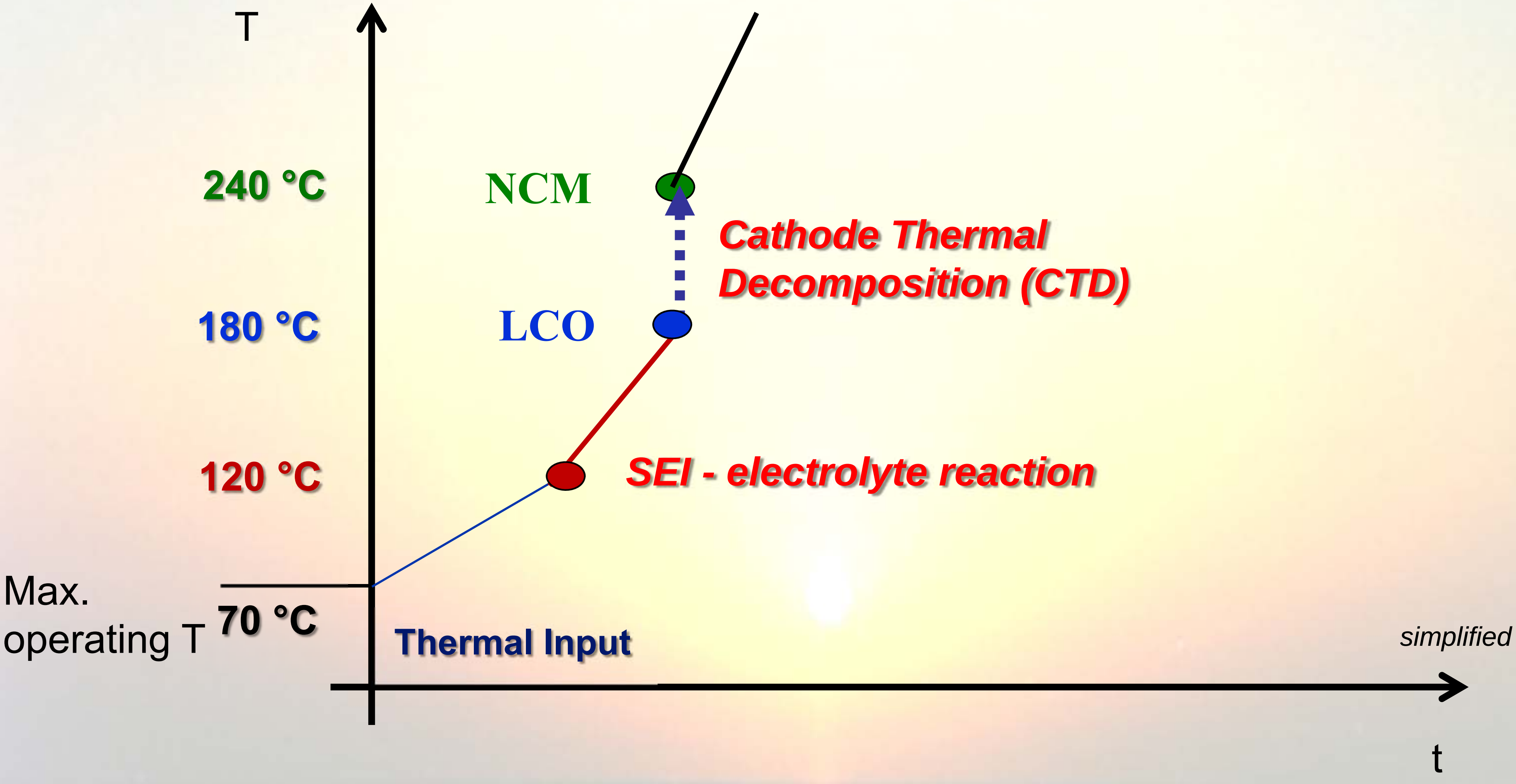
What to do ?

A – Chemical Influence (AM, electrolyte)

B – Physical Influence (Active and Passive Safety Devices)

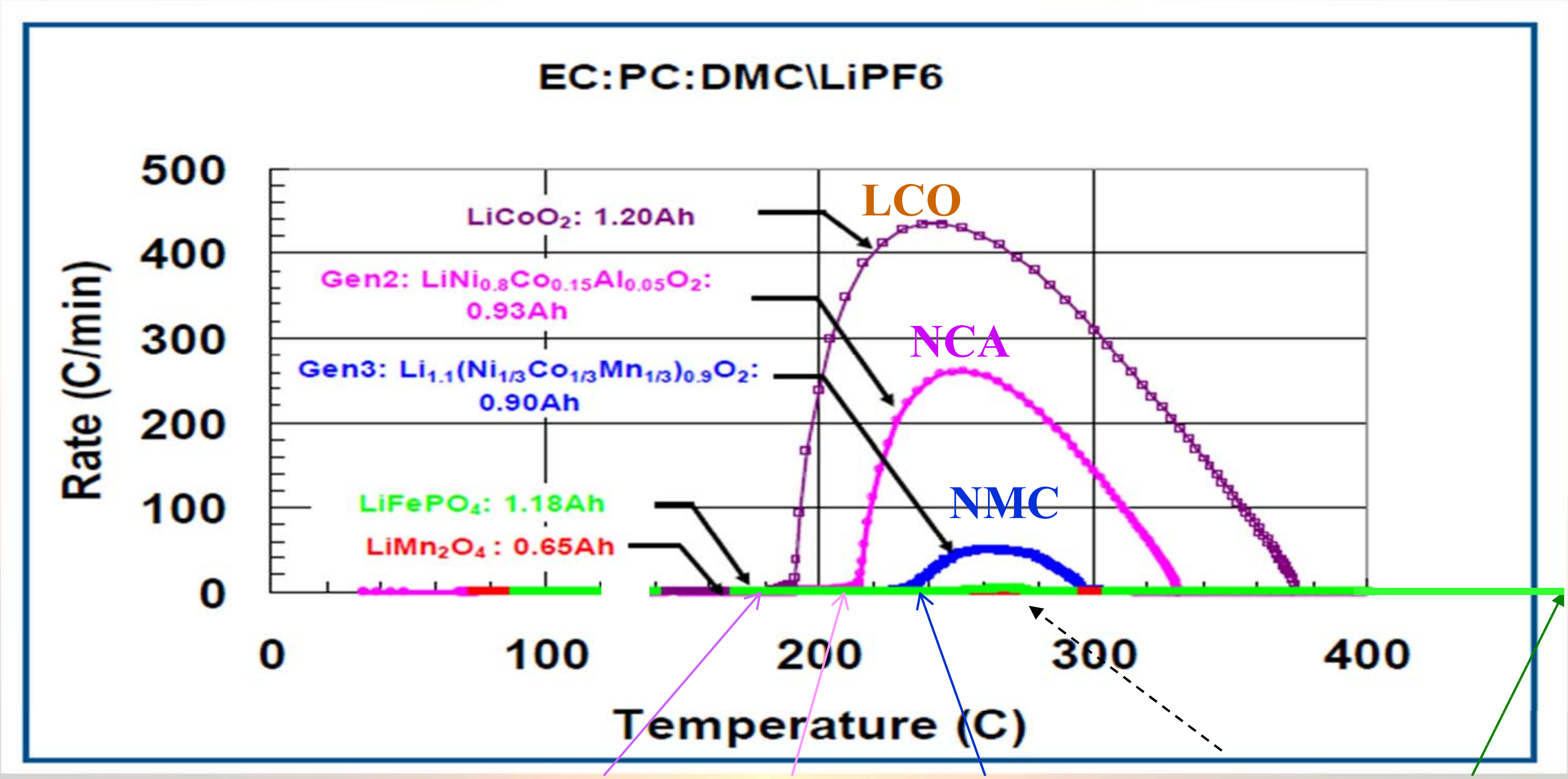
t

What to do ?
Increase CTD-Onset



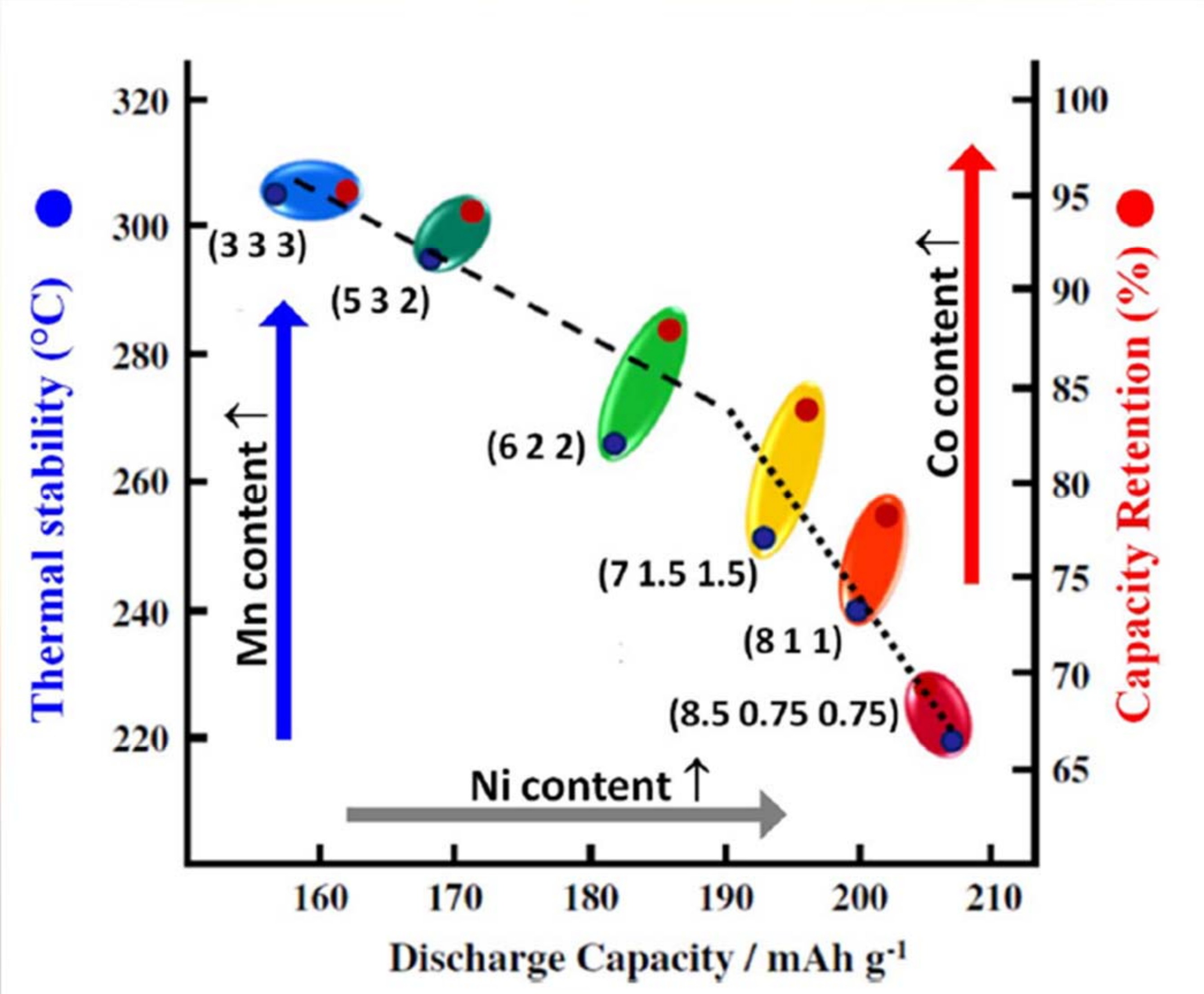
FCBAT

Cathode Thermal Decomposition (CTD) – Onset T



CTD Onset T	LCO	NCA	NMC	LMO	LFP
	~180 °C	~220°C	~240°C	~ 280 °C(?)	~ 350 °C

$LiNi_xCo_yMn_zO_2$ NCM - $N_xC_yM_z$ $(x+y+z = 1)$

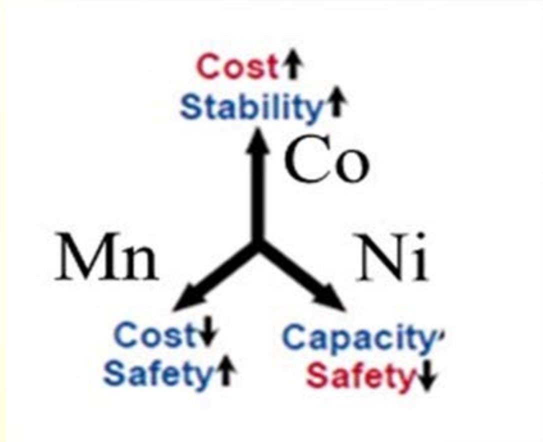


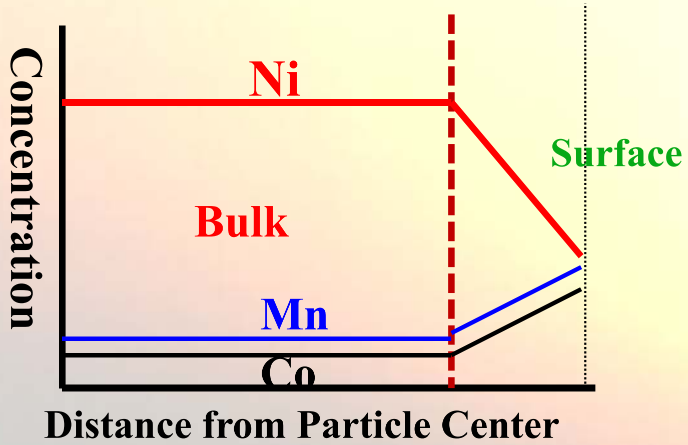
Source: *P. Rozier, JM Tarascon, JES 162 (2015) A2490*

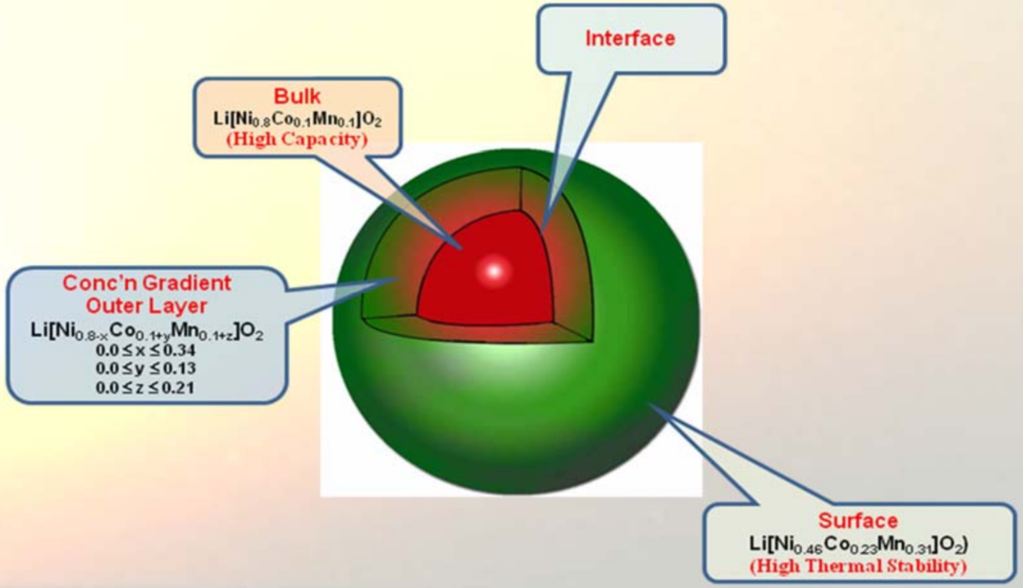
FCBAT

Core-Shell Concept (1/2)

Effect of the metal	
Ni	High capacity, Poor thermal stability & cycling
Co	Structural Stability and conductivity
Mn	Excellent thermal stability & cycling, Low capacity



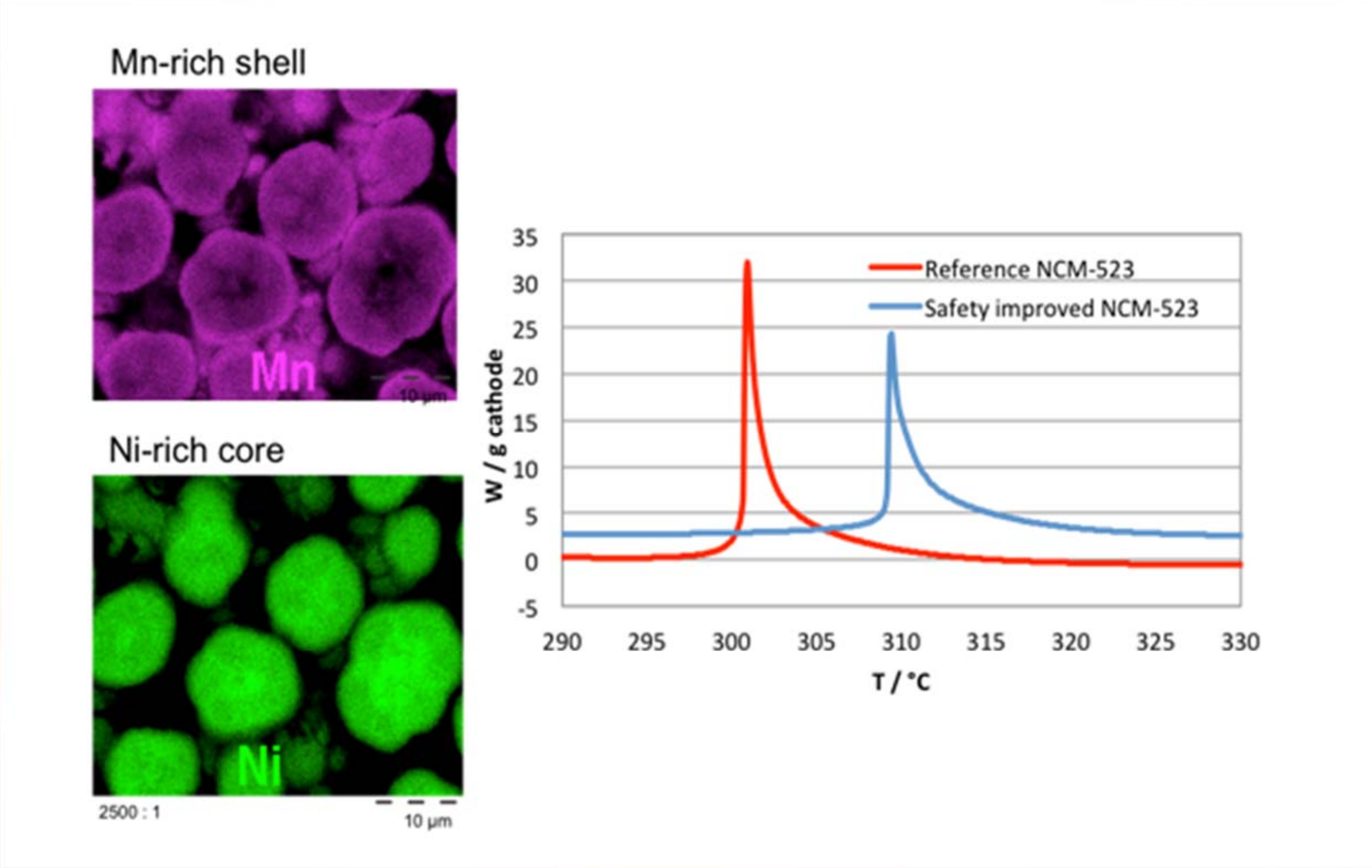




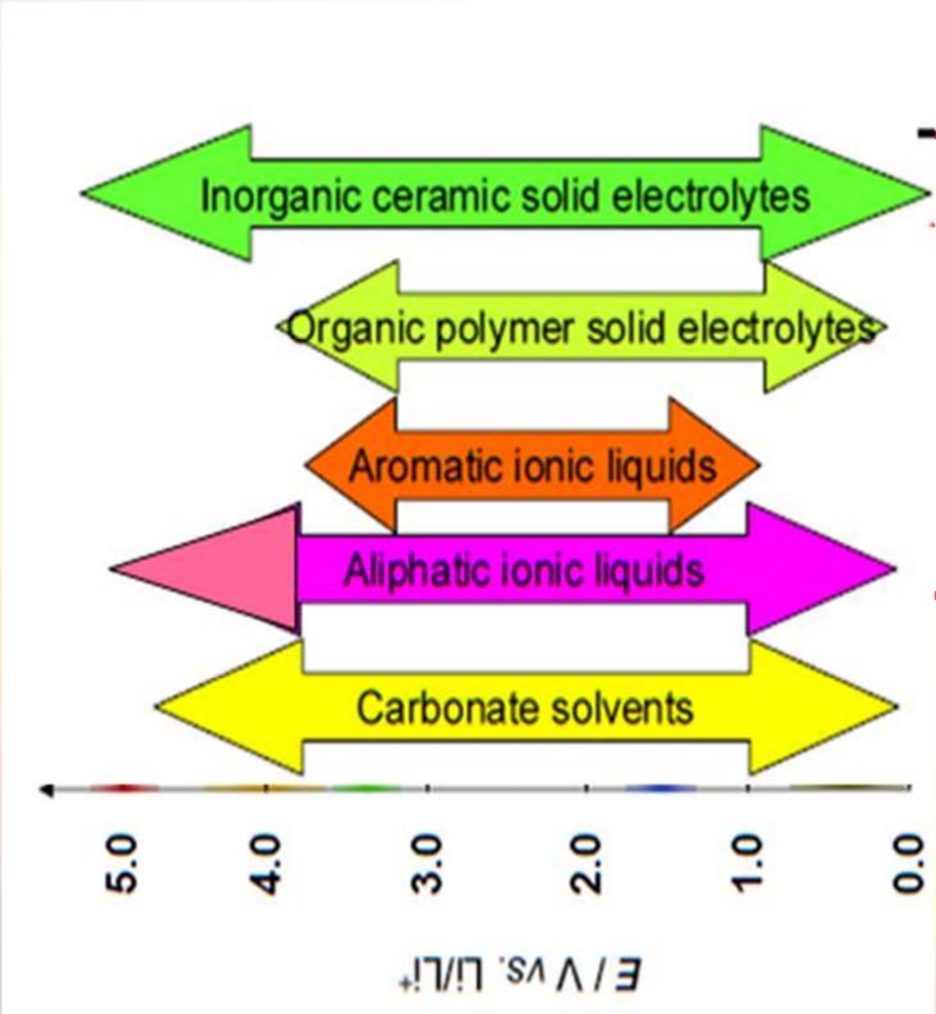
FCBAT

1. Y.-K. Sun, et al., Nat. Mater. 8, 320 (2009). Y.-K. Sun, et al., Adv. Funct. Mater. 20, 485 (2010).

Cathode Core-Shell Materials



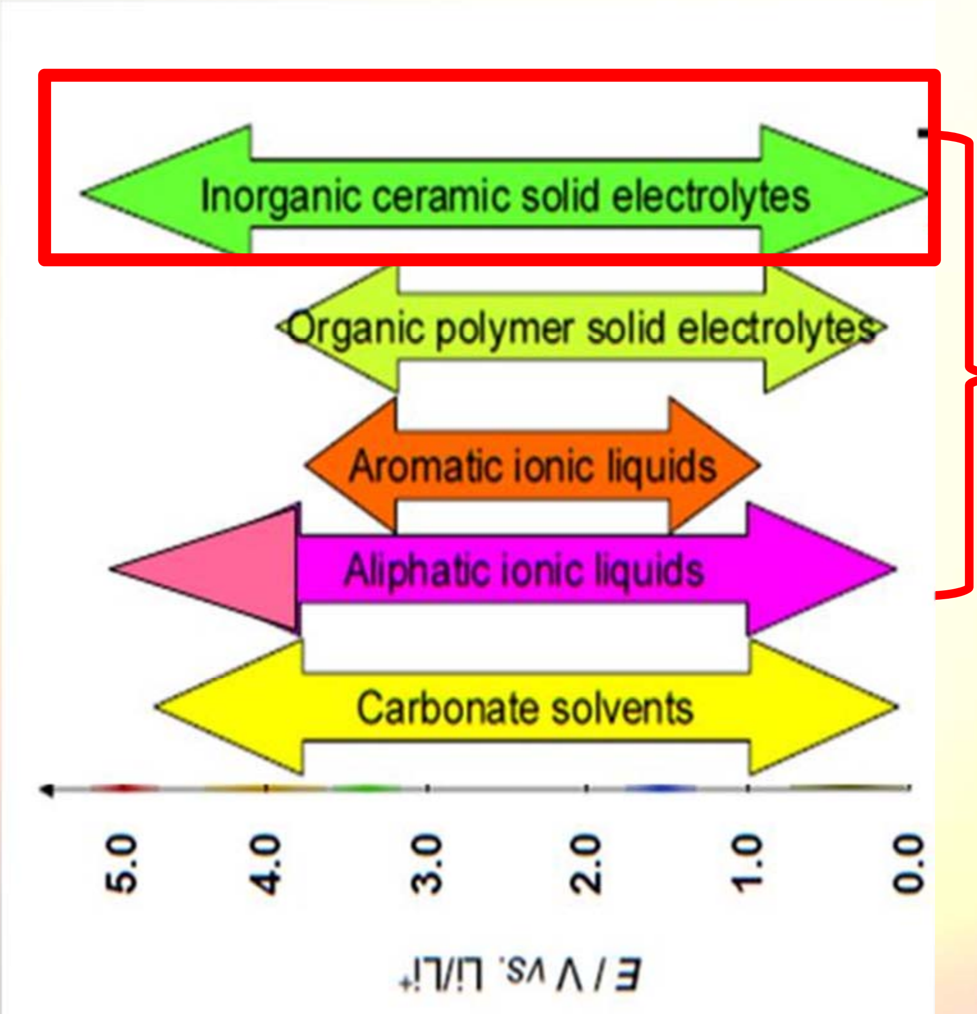
Non-flammable electrolytes



Non-flammable
– but not commercial

(conductivity, stability, costs …)

Non-flammable electrolytes



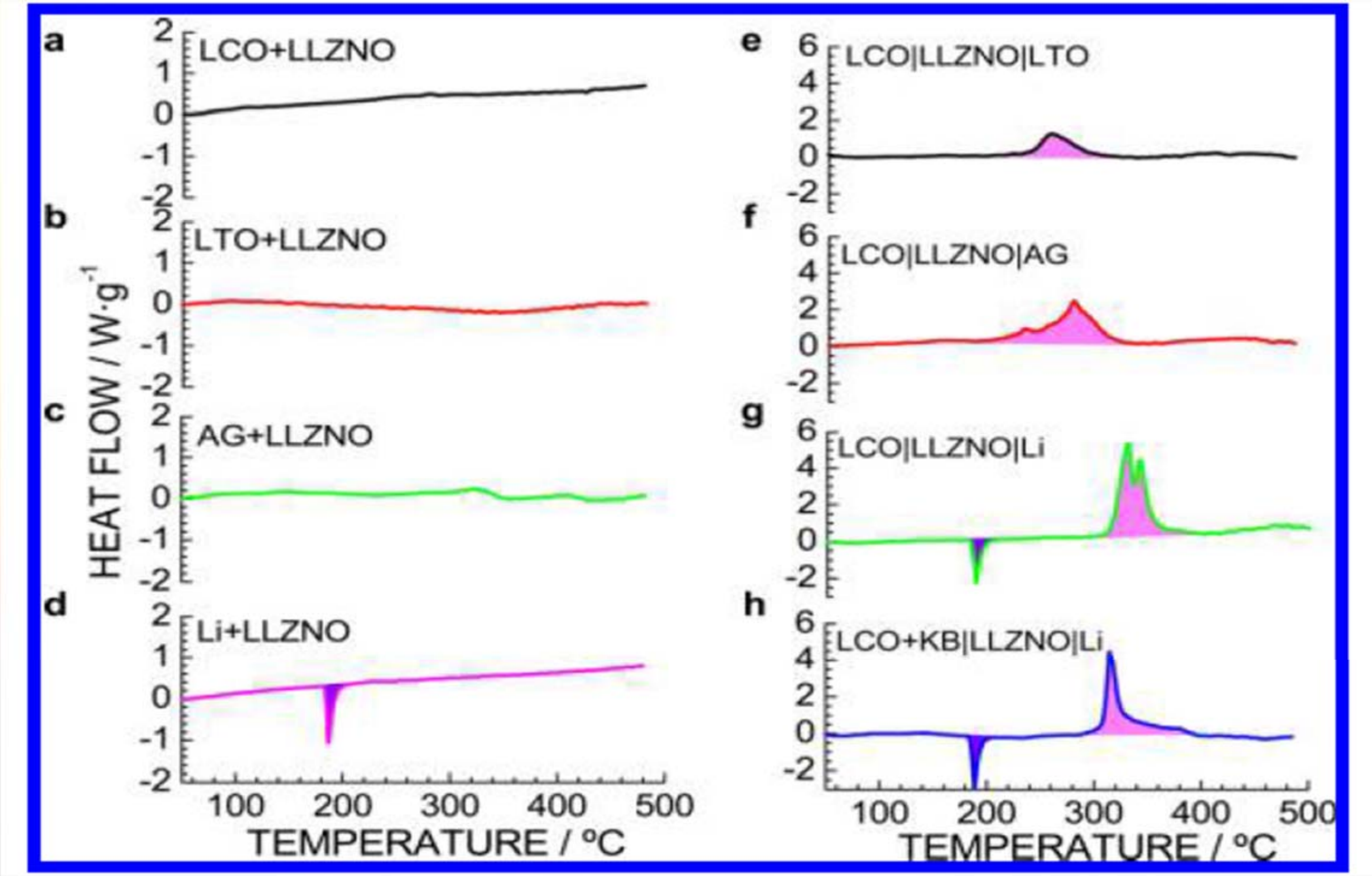
Non-flammable
– but not commercial

(conductivity, stability, costs …)

Ceramic Solid Electrolyte Cells

Li6.75La3Zr1.75Nb0.25O12 (LLZNO)

Material combinations **Full cell**



Anode

LTO

C

Li

Li
(cathode + KB)

FCBAT

T. Inoue, K. Mukai, ACS Appl. Mater. Interfaces 2017, 9, 1507−1515

What to do ?

A – Chemical Influence (AM, electrolyte)

B – Physical Influence (Active and Passive Safety Devices)

t

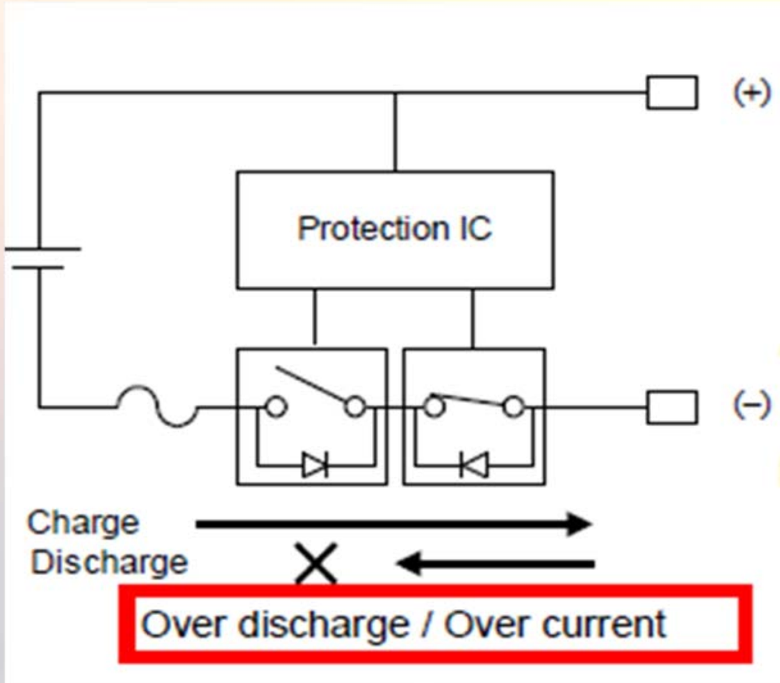
FCBAT

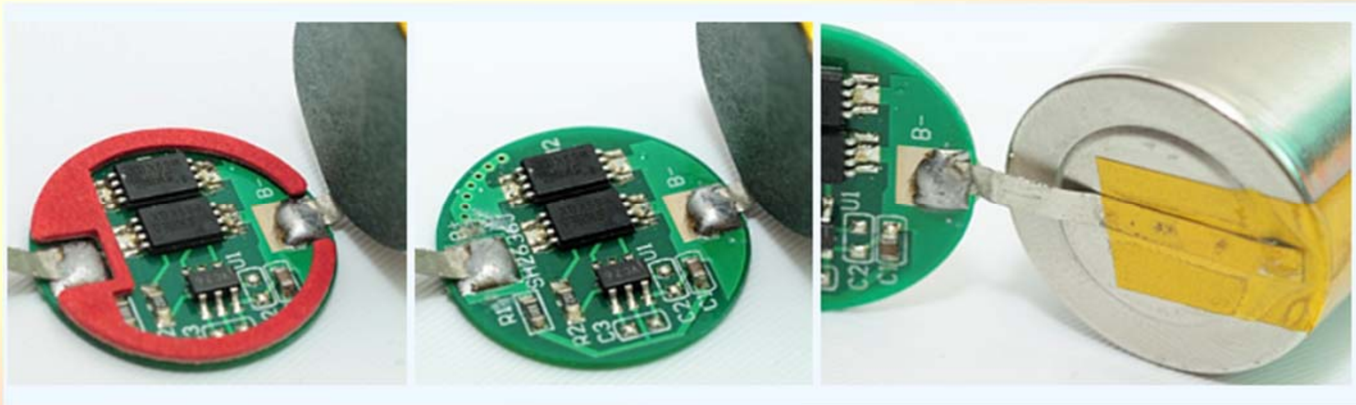
Active and Passive Safety Devices

- Protection Circuit Board – PCB
- Positiv-T-Coefficient resistor (PTC)
- Circuit Interrupt Devices (CID)
- Fuses
- Shutdown separators
- BMS (increase cooling, reduction of current, switch-off, etc.)

FCBAT

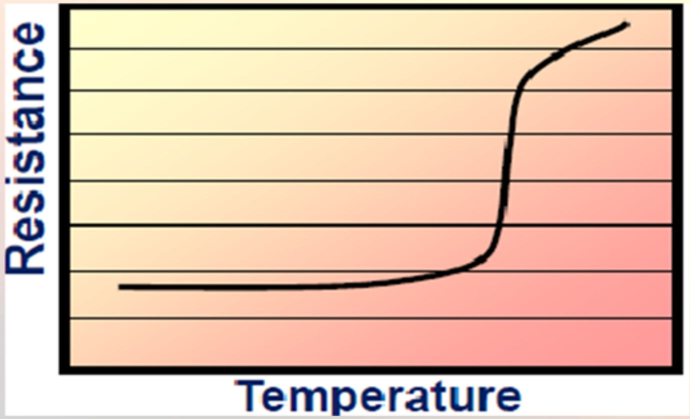
Protection Circuit Board - PCB

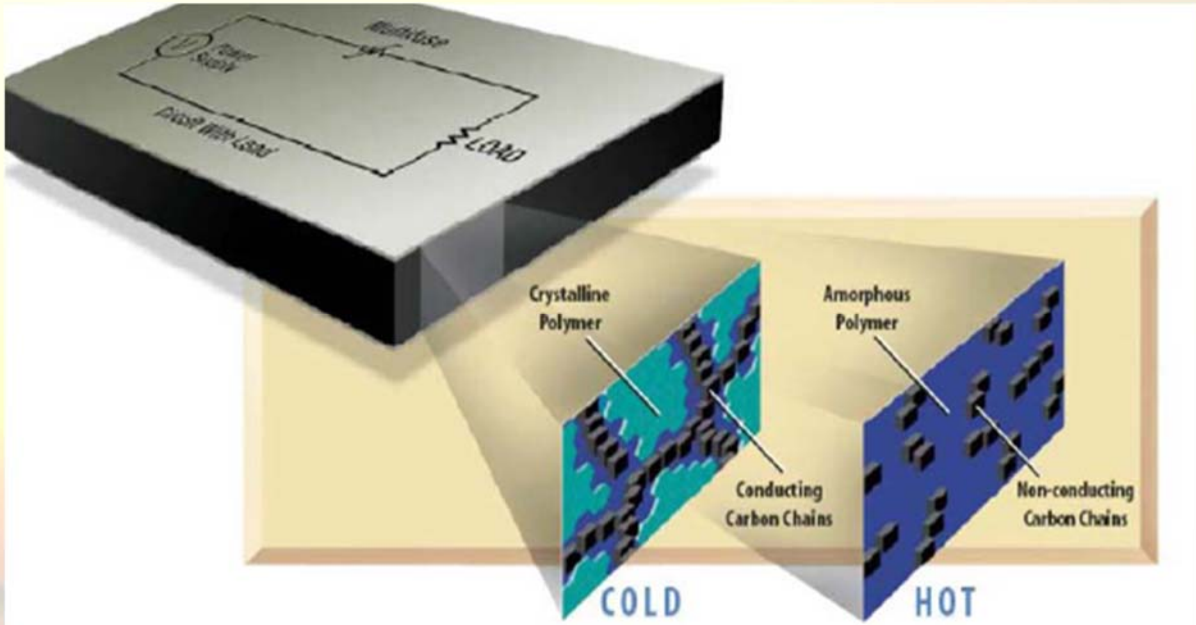




Source: http://www.lygte-info.dk/info/battery%20protection%20UK.html

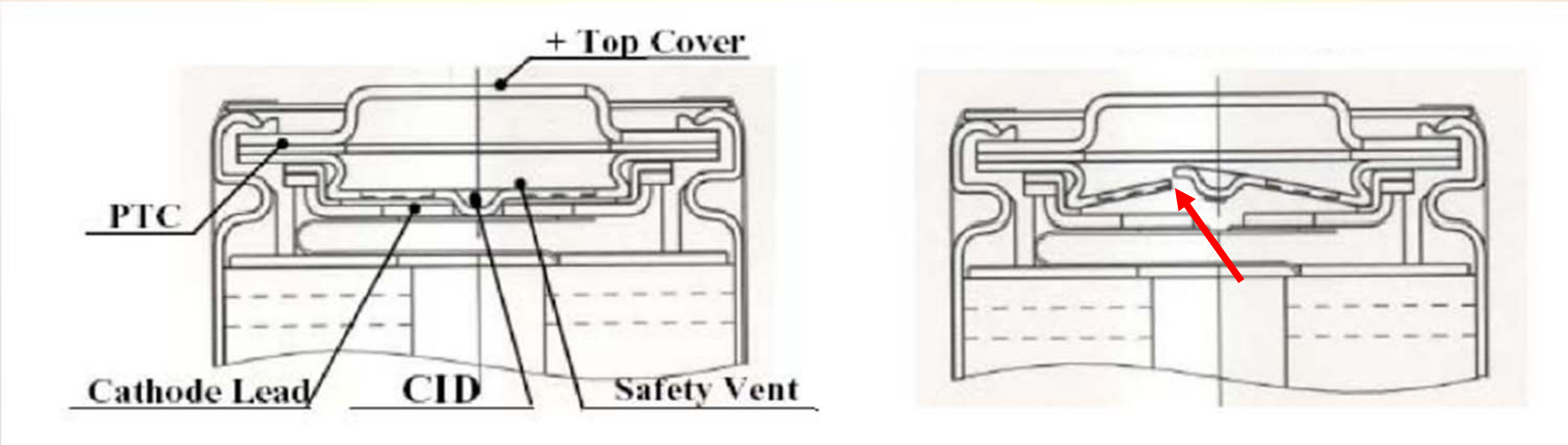
Positive Temperature Coefficient Resistor - PTC





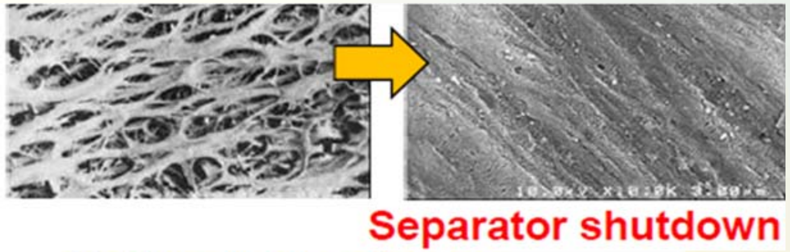
Circuit Interrupt Devices - CID

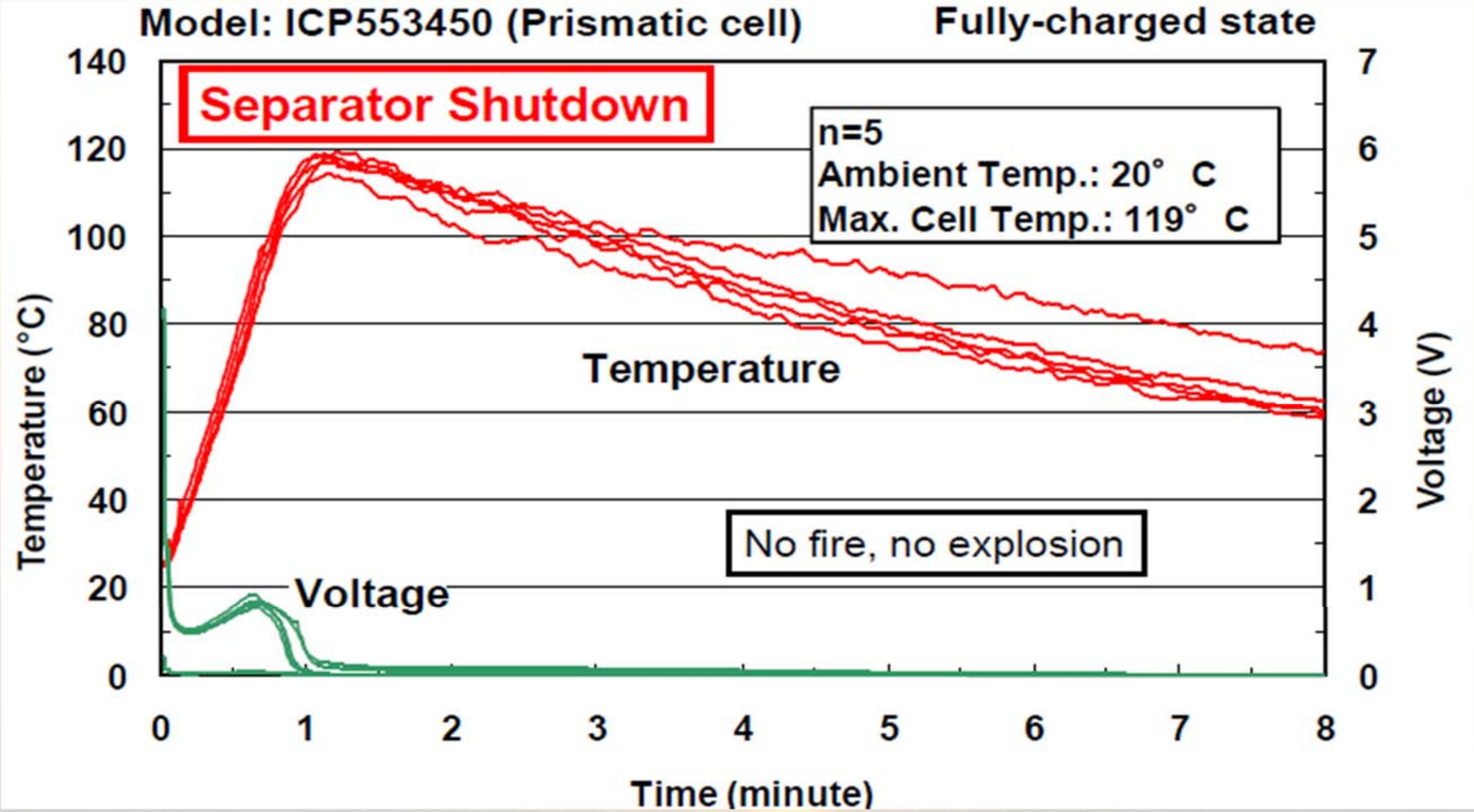
CID closed **CID opened**



FCBAT

Shutdown Separator





Source: BAJ

FCBAT

Active and Passive Devices lead to Safe Systems

Safety is a System Approach

Material | Cell | Module | Pack | Battery

Increasing Number of Safety Devices

Not all materails are thermal stable

burst membrane
internal cell fuse
protection circuit
etc.

mechanical cover
cell voltage +
T-sensor, etc.

fuse
balancer
main switch, etc.

BMS
battery case
cooling, etc.

FCBAT

Source: http://www.eco-aesc-lb.com/en/product/liion_hev/

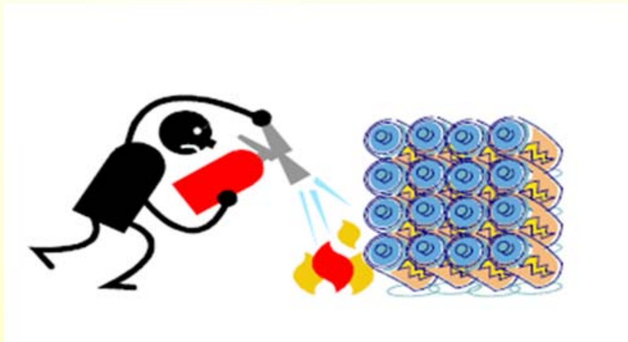
Battery Fire

Fire preconditions

- Combustible material
- Temperature
- Oxygen

Battery Fire

	Primary lithium	Lithium-ion
Fires involving batteries only	Lith-X Class D extinguishing agent, no water	ABC dry chemical extinguisher or water
Fires involving batteries and other materials	ABC dry chemical extinguisher or water	ABC dry chemical extinguisher or water, according to combustible materials involved



For larger fires

Mainly H_2O

- separated air from battery
- cooled down the battery

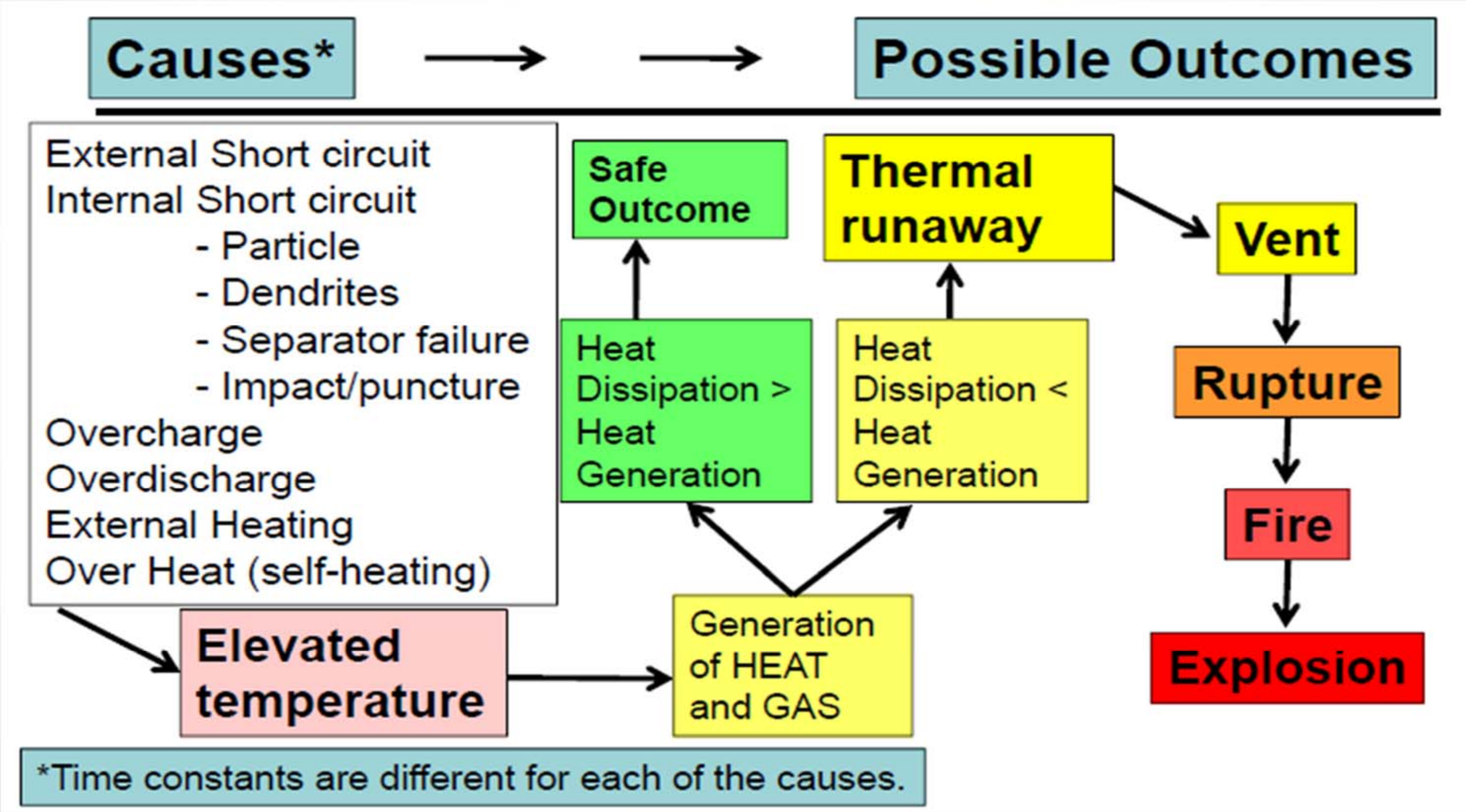
For smaller fires

Mainly ABC Dry Extinguisher

Summary

FCBAT

Anatomy of Cell Failures



Source: NTSB - Doughty, 11 Apr 2013

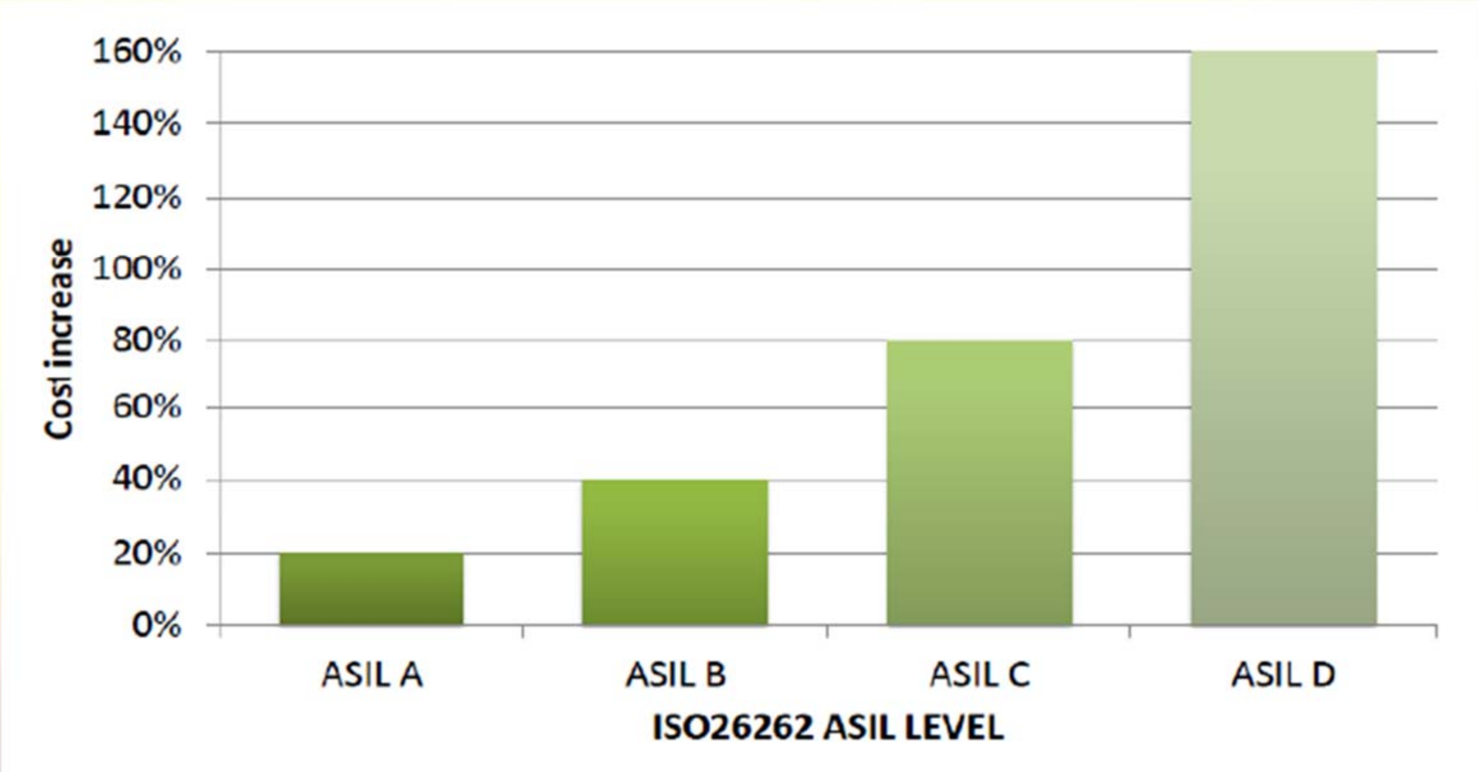
FCBAT

Full Safety is Possible

Full Safety is Possible – but not free of Charge

Automotive Safety Integrity Level – ASIL (ISO 26262)

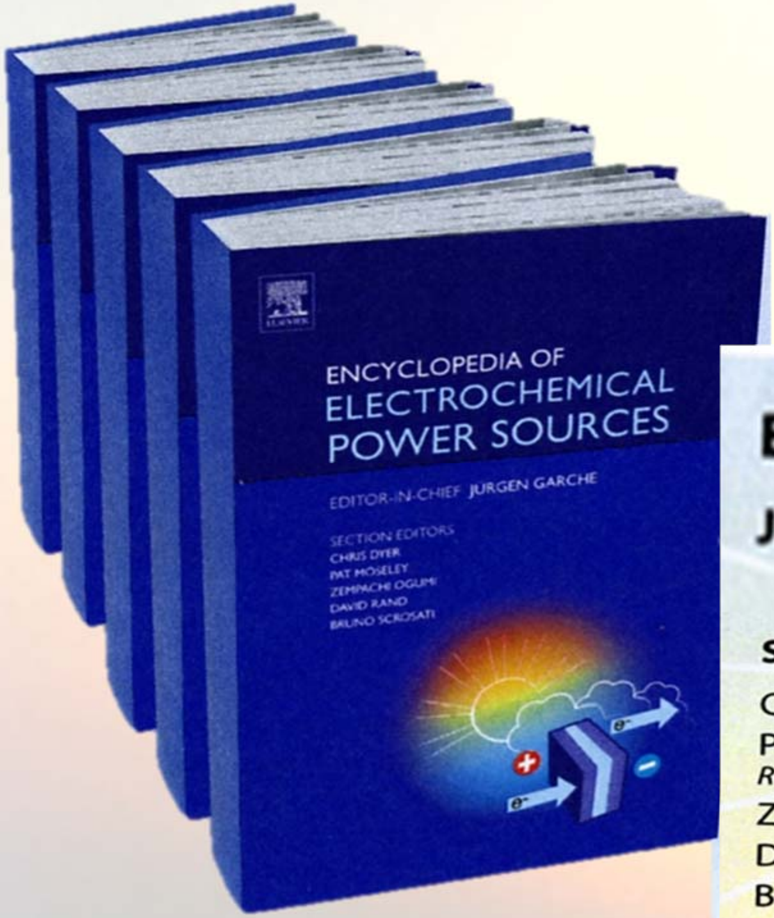
ASIL rating
based on
parameters
- Exposure
- Controllability
- Severity



Increasing Safety Risk

FCBAT

Many information about Safety are to find in:



Editor-in-Chief:

Jürgen Garche, *ZSW Ulm, Germany*

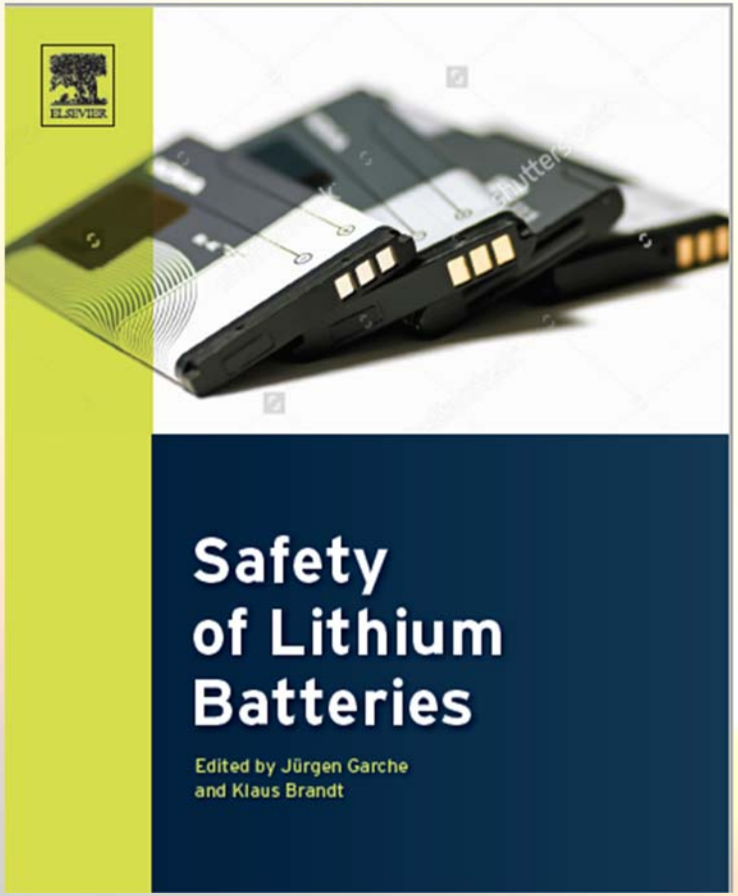
Section Editors:

Chris Dyer, *Lightening Energy, USA*
Pat Moseley, *International Lead Zinc Research Organization Inc.*
Zempachi Ogumi, *Kyoto University*
David Rand, *CSIRO Energy Technology*
Bruno Scrosati, *University of Rome, Sapienza*

5 Volumes
> 350 chapters

Mass: 12 kg
Cost: 100 €/kg

Safety of Lithium Batteries



Elsevier, 2018 (May)

510 pages

FCBAT


Thank you for your Attention
Ulm

Back-up

Fire Extinguishing Agents

LIB

European Fire Class	mate-rial	water	water spray	water foam	BC powder	ABC powder	metal fire powder	CO_2	fate fire exting.
A	solid	good applicable	good applicable	good applicable	not applicable	good applicable	not applicable	not applicable	good applicable
B	liquid	by use hazard	applicable	good applicable	good applicable	good applicable	not applicable	good applicable	applicable
C	gas	not applicable	not applicable	not applicable	good applicable	good applicable	not applicable	not applicable	not applicable
D	metal	by use hazard	by use hazard	by use hazard	not applicable	not applicable	good applicable	by use hazard	by use hazard
F	fat	by use hazard	good applicable	by use hazard	not applicable	not applicable	not applicable	not applicable	good applicable

good applicable	applicable	not applicable	by use hazard

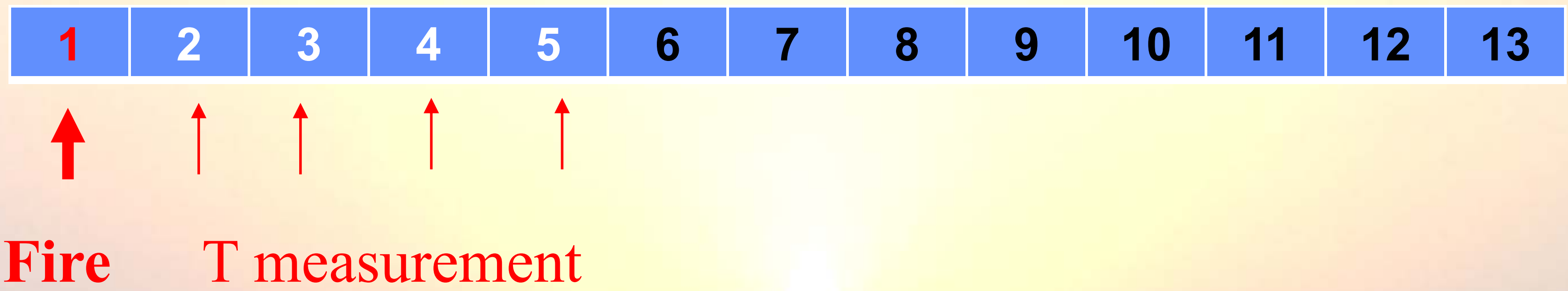
BC powder, preferable for **B** and **C** fires, based mostly on sodium bicarbonate

ABC powder, preferable for **A**, **B** and **C** fires, based mostly on mono-ammonium phosphate and ammonium sulfate

Fire Tests

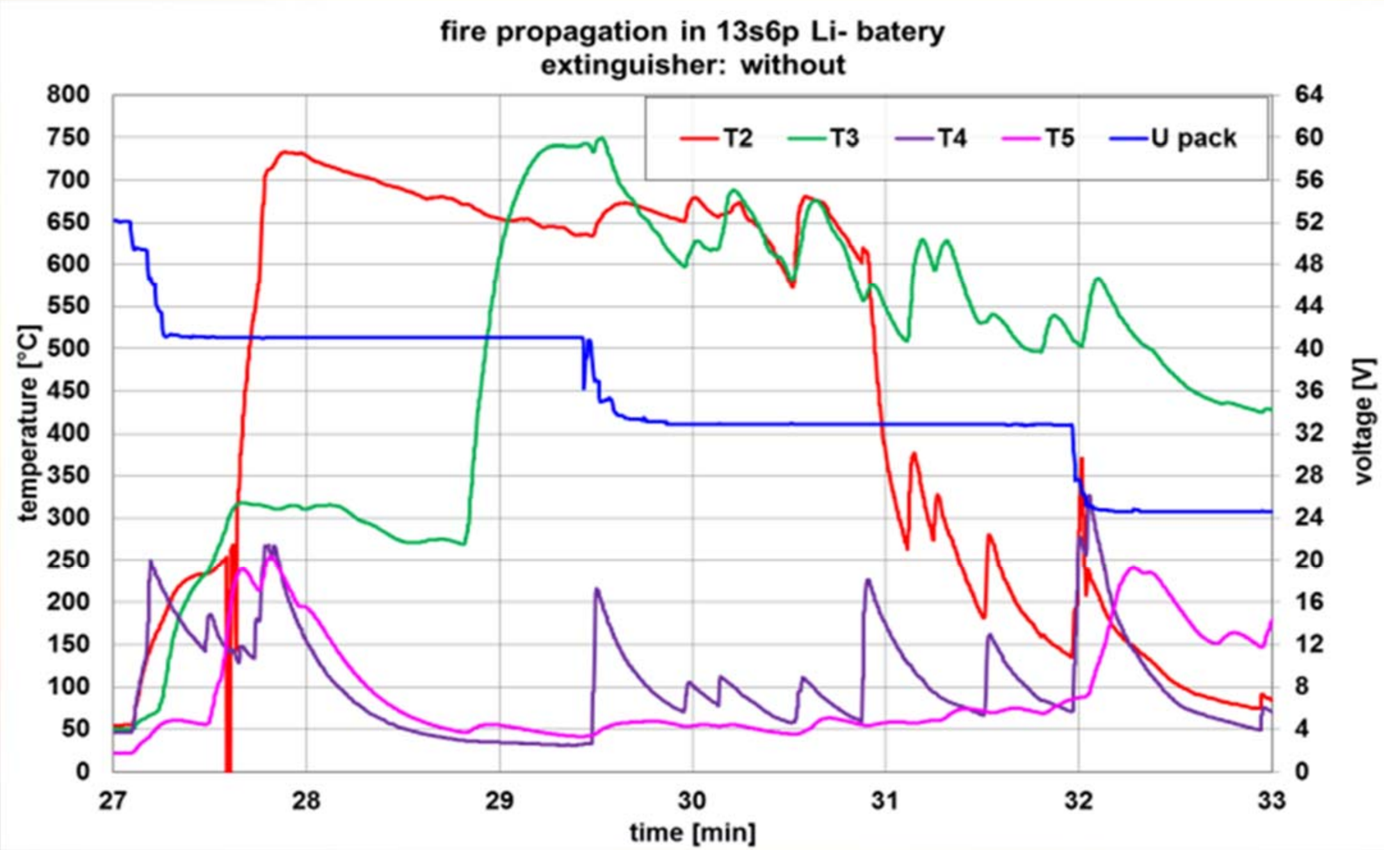
800 Wh NMC battery with 18650 cells in a 13s6p

6p cell cluster was ignited by overheating

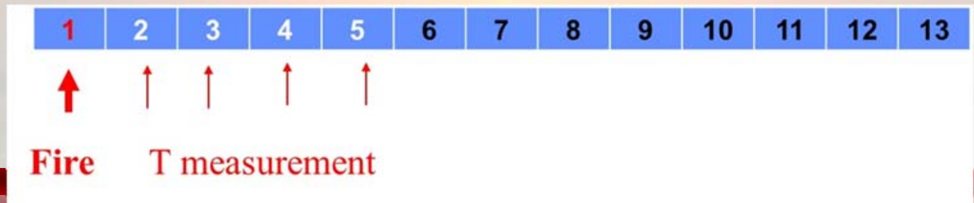


Fire extinguisher: 6-8 litre of liquid, or 200 g powder, or 10 kg CO_2.

No Extinguishing

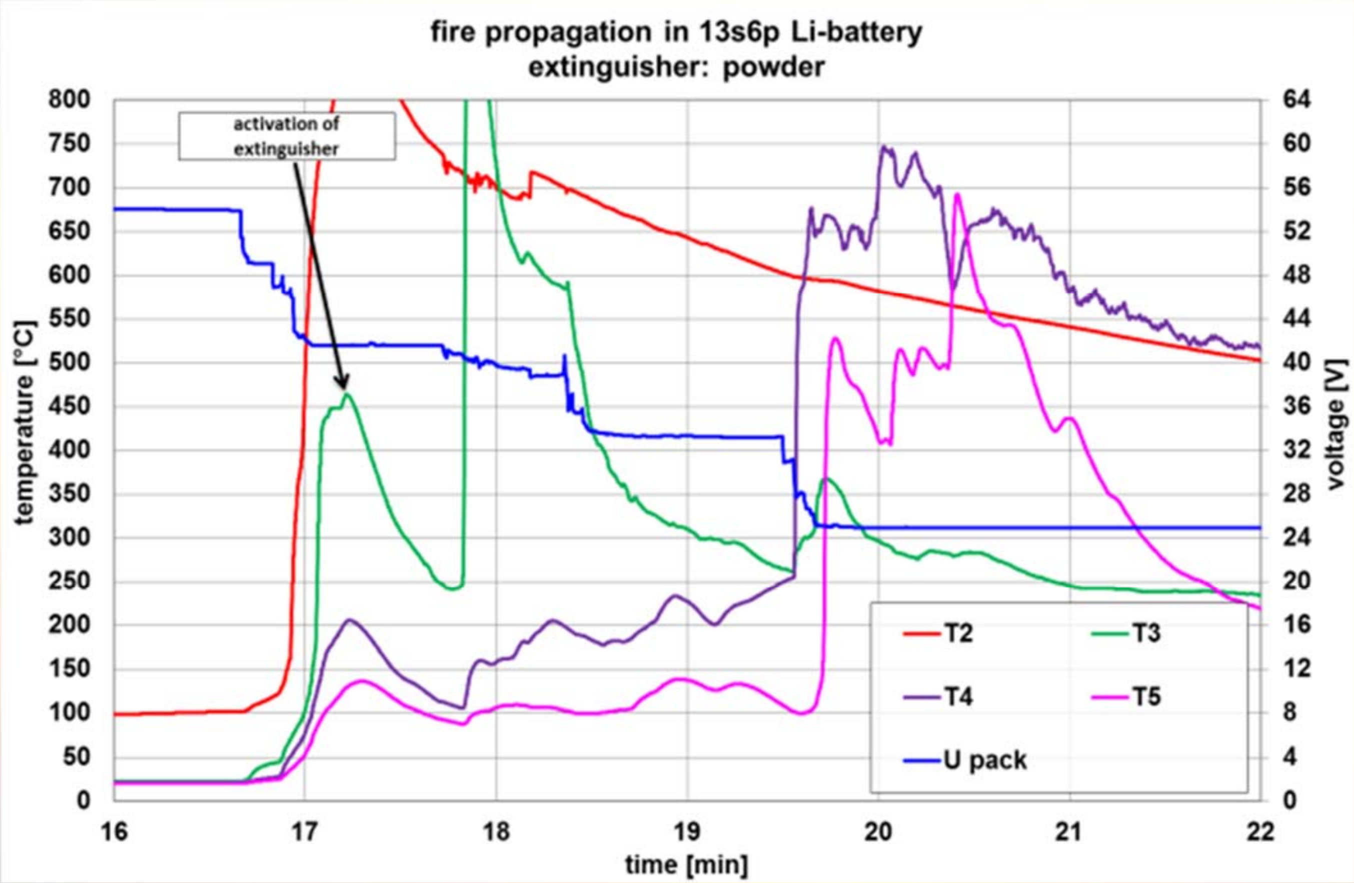


Propagation: **Yes**

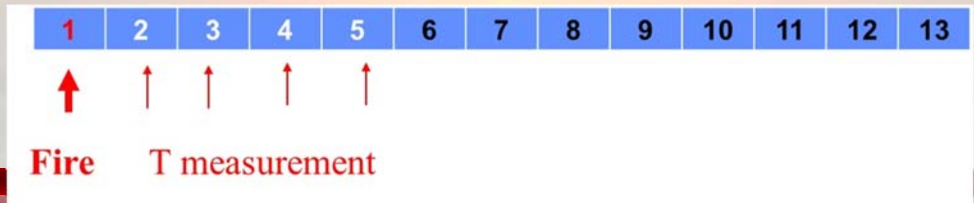


FCBAT

Powder Extinguisher

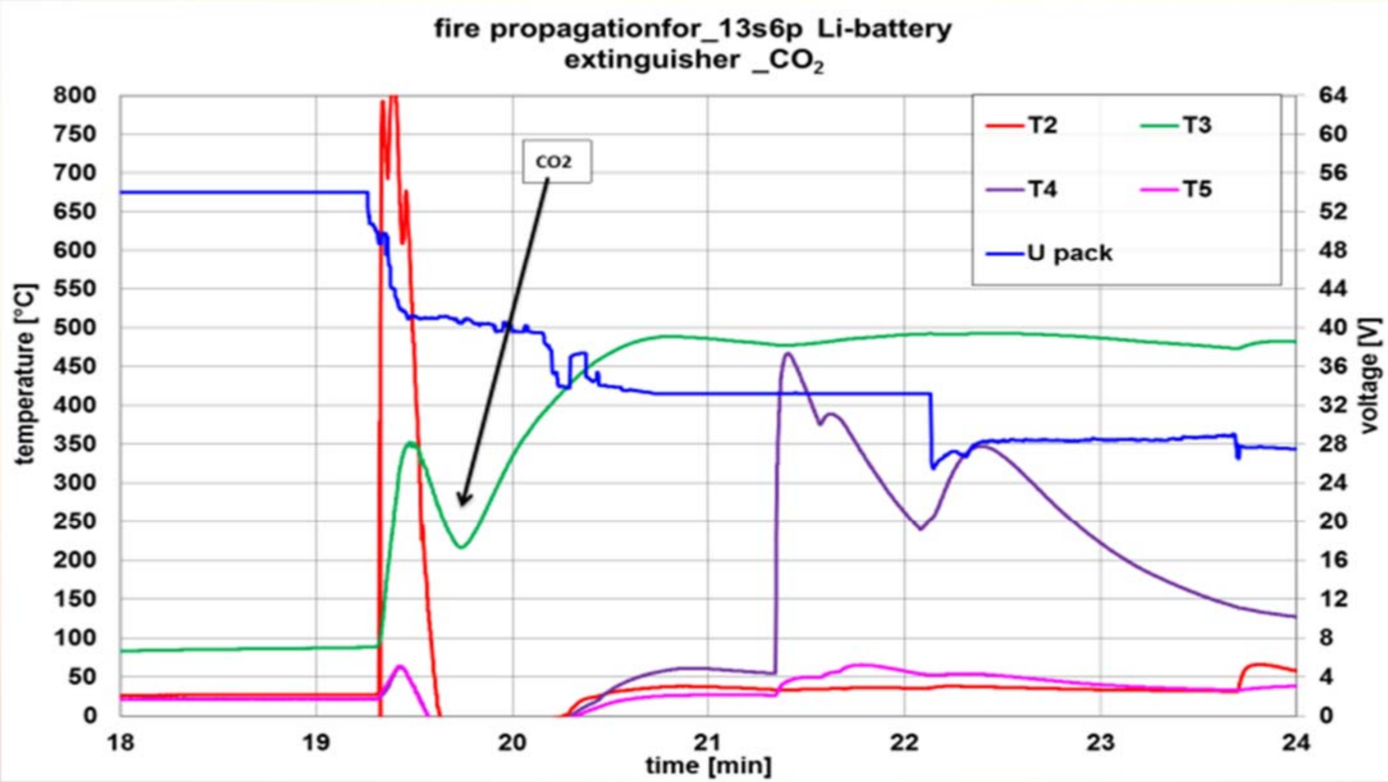


Propagation: **Yes**
Fire Exting. : **Yes**
Re-ignition: **Yes**



FCBAT

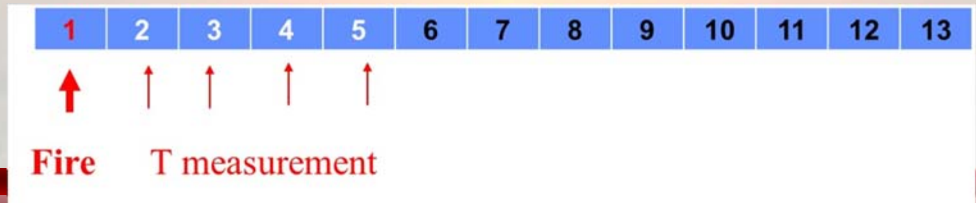
CO_2 Extinguisher



Propagation: **Yes**

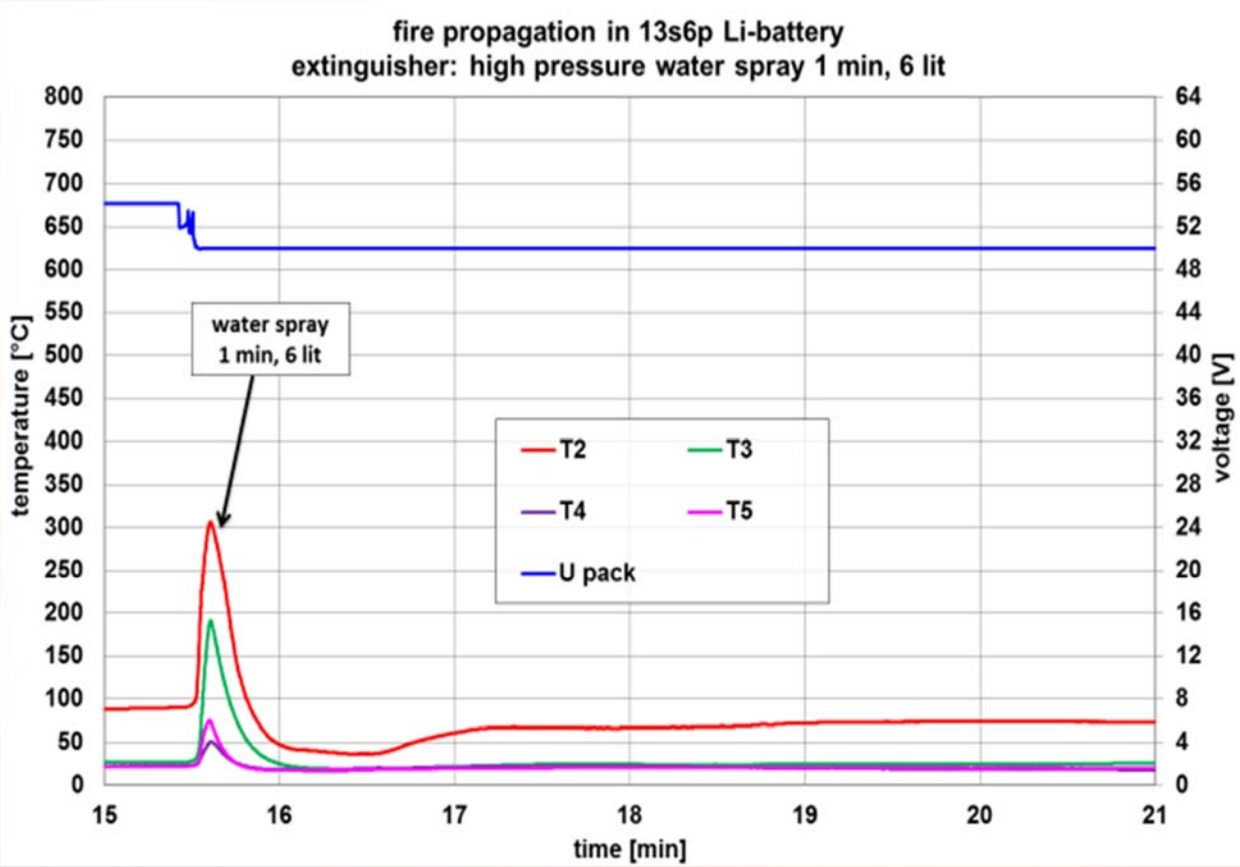
Fire Exting. : **Yes**

Re-ignition: **Yes**



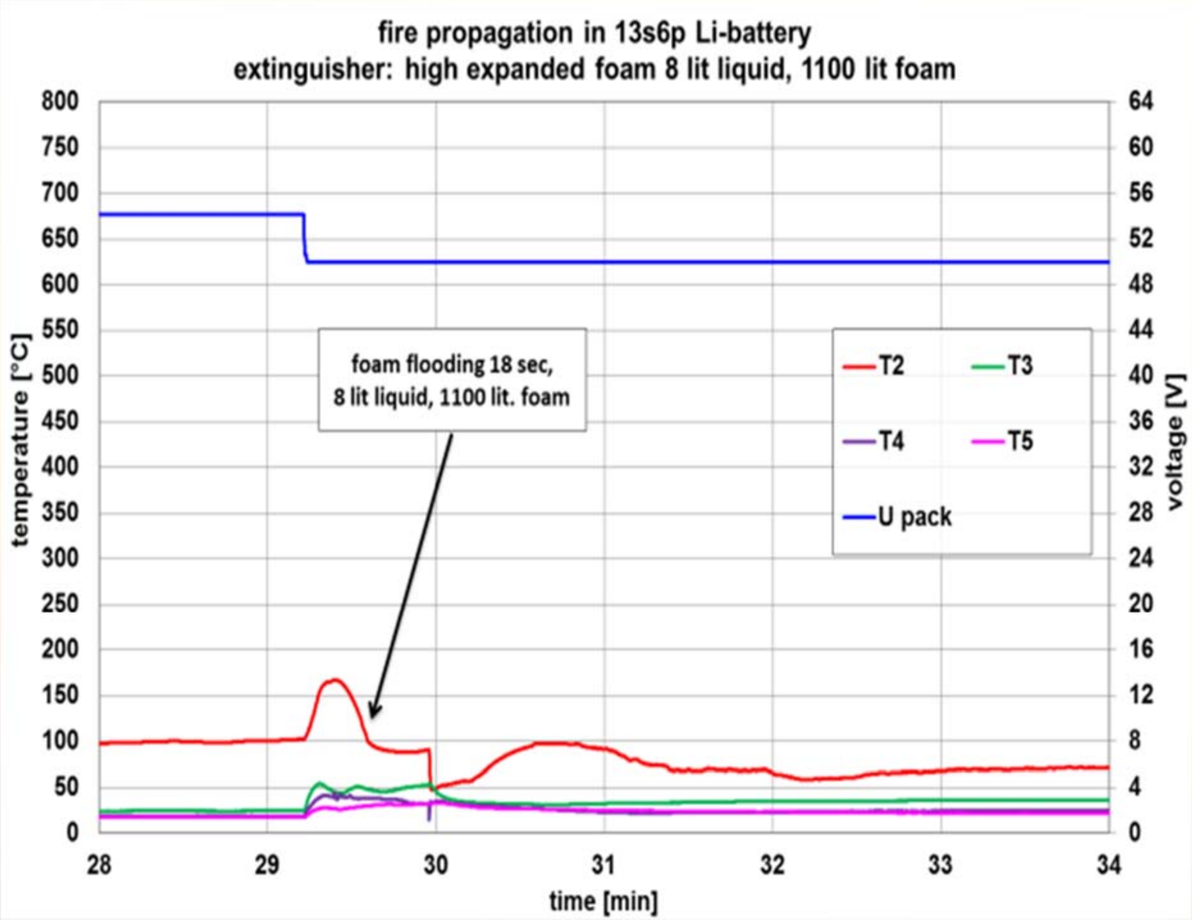
FCBAT

High Pressure Water Extinguisher



Propagation: **No**
Fire Exting. : **Yes**
Re-ignition: **No**

High Expanded Foam Extinguisher



Propagation: **No**
Fire Exting. : **Yes**
Re-ignition: **No**

Fire Extinguising Summary

Water based agents are successful

Gaseous fire extinguishing agents and powders are able to extinguish the flames as well, but re-ignition and failure propagation cannot be avoided.