31. PV-Symposium
Staffelstein
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Performance und Sicherheit von PV-Li-Speicherbatterien

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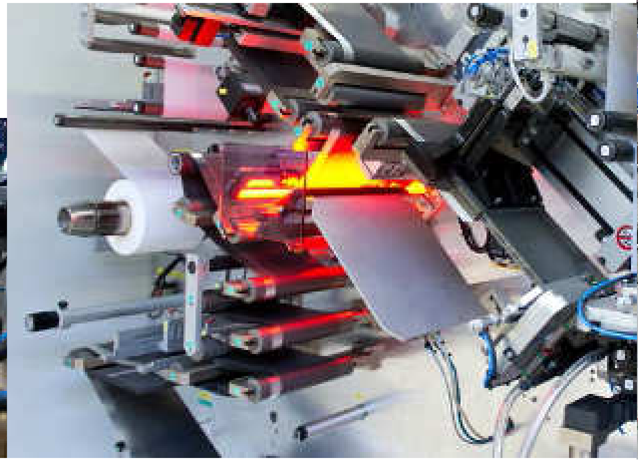
Battery Research at ZSW
Materials Research – Cell Design – Post Mortem Analysis

- Synthesis and characterization of new electrode materials
- Materials development including beyond lithium
- Process development for electrode and cell preparation
- Validation of new cell chemistries in reference cells
- Ageing mechanisms and post mortem analysis

Battery Research at ZSW
FPL - Research Platform for Production of large Lithium Ion Cells

- Fully automatic slurry preparation 60 l batches
- Double side electrode coating (500 mm width, 20 m/min)
- Fully automatic winding, assembling, electrolyte filling
- Formation 240 cycling and
  1.920 storage places



Battery Research at ZSW
Performance Test – Safety Test – BMS

Test field for cells, modules and battery systems

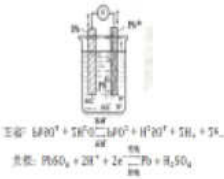
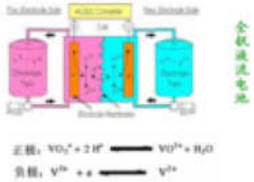
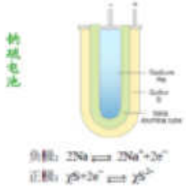
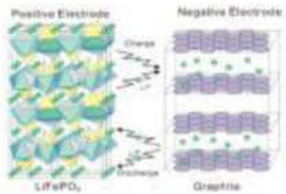
•Lifetime and performance testing

•Safety (abuse) test centre

•Battery management system and monitoring technologies

•Mathematical modelling and system engineering

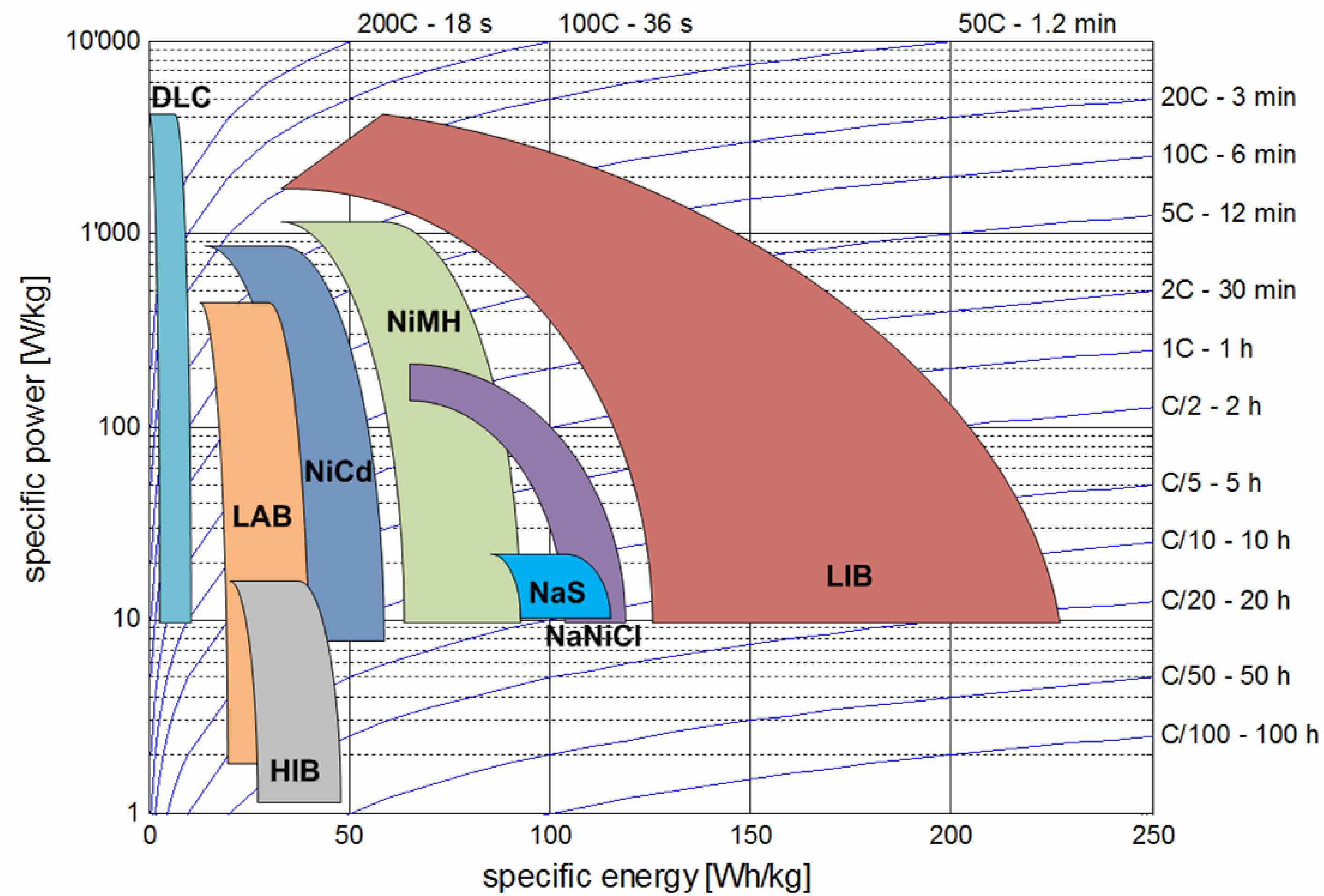
Performance different storage systems

	Pumped Hydro	Lead-Acid	VRB	Na-S	BYD LFP
Principle					
Response time	10s (10% load)	100ms level	100ms level	100ms level (during running)	100ms level
Energy Density (Wh/kg)	/	35	10	170	100~130
Round-trip Eff.	70~80%	65~70% (battery 75%)	70~75% (battery 80%)	85% (during running)	85~92% (battery 97%)
Temperature (℃)	No icing	-15~40	10~50	310~350	-20~60
Cycle Life	50 years	1,000(75%DOD)	10,000(75%DOD)	3,000(75%DOD)	10,000(75%DOD) 6,000 (100%DOD)
Investment ($/kWh)	200*	250*	/	700*	500 (Battery 400)

Quelle: Vortrag BYD

Performance different batteries RAGONE

DLC	Doppelschichtkondensator	NiMH	Nickel-Metallhydrid-Batterie
LAB	Blei-Säure-Batterie	NaS	Natrium-Schwefel-Batterie
HIB	Hybrid-Ionen-Batterie (Aquion)	NaNiCl	Natrium-Nickel-Chlorid-Batterie (ZEBRA)
NiCd	Nickel-Cadmium-Batterie	LIB	Lithium-Ionen-Batterie



Performance different batteries

Technology	Advantage	Disadvantage
pumped hydro power station	established technology low cost, long life	Long construction time, large space, large invest, requires special topography
Lead acid	Low cost, easy recycling good discharge ability, robust, wide spread production facilities, safety	Low energy density, short cycle life, poor low SOC performance, gas emission requires special rooms
Redox flow (V)	simple design High safety	Complex system, low energy/power density, leakage problems, high cost,
NaS, Na/$NiCl_2$	Good energy density,	Permanent high temperature (losses), Complex BMS
Li - Ion	High power and energy density	Safety, complex BMS

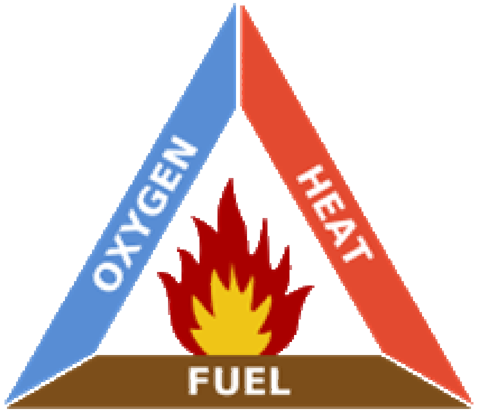
Performance Lead Acid vs. Li-Ion

	Lead acid	Li-ion
Power ability	+	++
specific energy Wh/kg	0	++
energy density Wh/lit	+	++
efficiency/self discharge	+	++
Cycle life	0	+ (+)
cost	++	0
BMS	++	-
Operation temperature	+	+
Installation environment	0 (+)	++
Safety/failure tolerance	++	- -
recycling	++	-

The Safety Hazard of Li-Ion Batteries

Oxidant

Delithiated Cathode:
•High oxidation potential
•Heat generation and gas formation
•linked with O_2 release



Fuel

Electrolyte:
- low flashpoints of the solvent (DMC= 25°C, EC= 160°C)
- exothermic decomposition

Lithiated Anode:
- high reduction potential,
- decomposition reactions (>100°C)
- heat and gas formation (CO, H2)

Internal triggers (short circuit):
- cell balance, converting (Li-plating)
- depth discharge (Cu-plating)
- manufacturing defected separator

•Separator: melting
- deformation/ shock/ vibration

Trigger

External triggers:
- overcharge
- external heat
- external short circuit

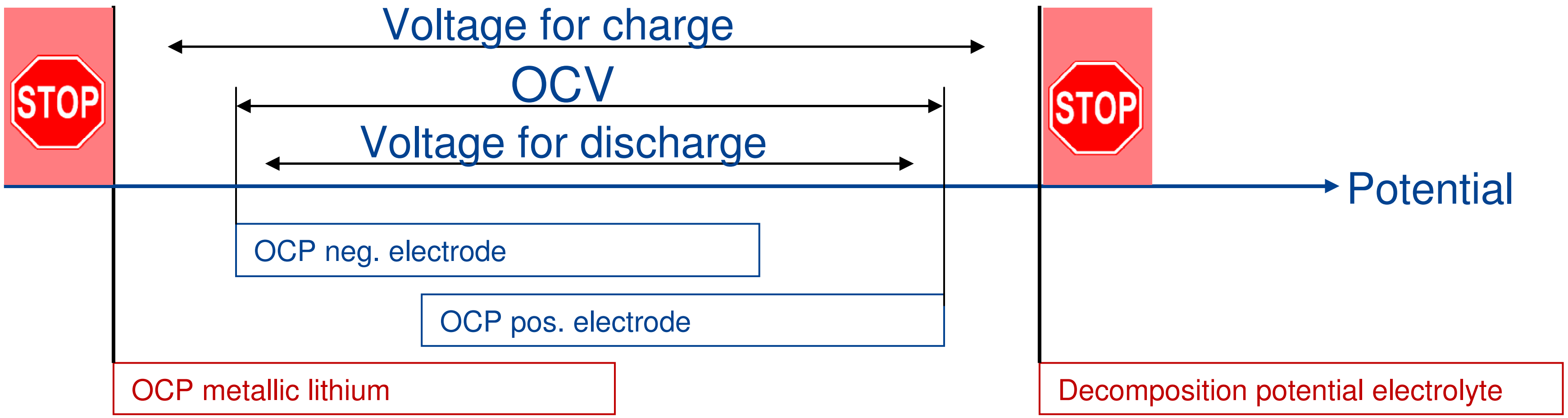
Gas Formation

Electrolyte- Oxidation and Reduction

Heat Formation

Exothermic Decomposition

Operation limits for Li-Ion- batteries



- Limitation of the operation voltage window and limitation of the current (in particular charge current)
- No tolerance against overcharge and over discharge (deep discharge)

Temperature limits

- Comfortable range 10 – 30 °C
- Usual operation window 0 – 50 °C
- Higher temperatures: accelerated ageing, safety
- Lower temperatures risk for Li plating while charging

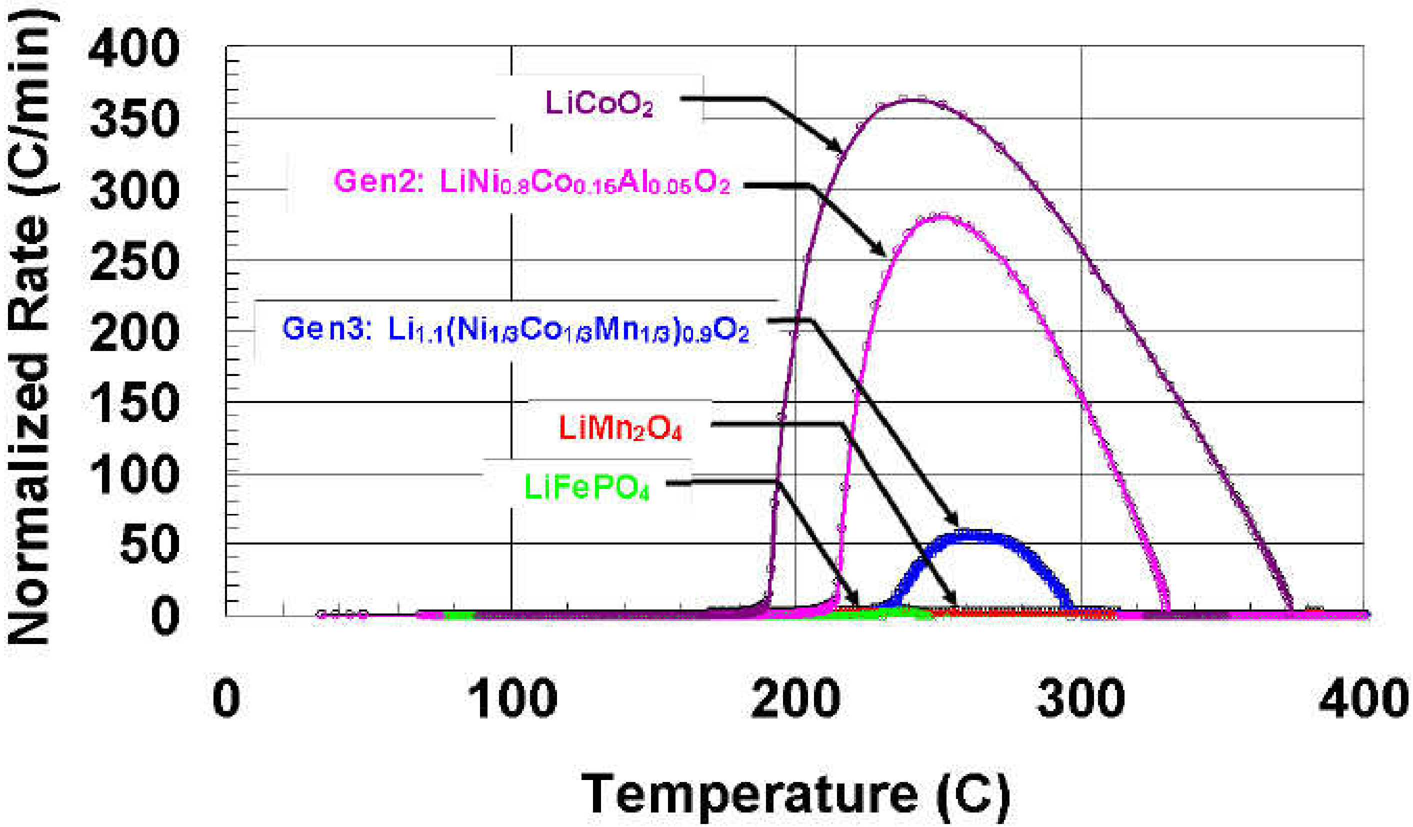
Overcharge

Delay in ignition of the emitted gases might lead to explosion

Safety issues of materials

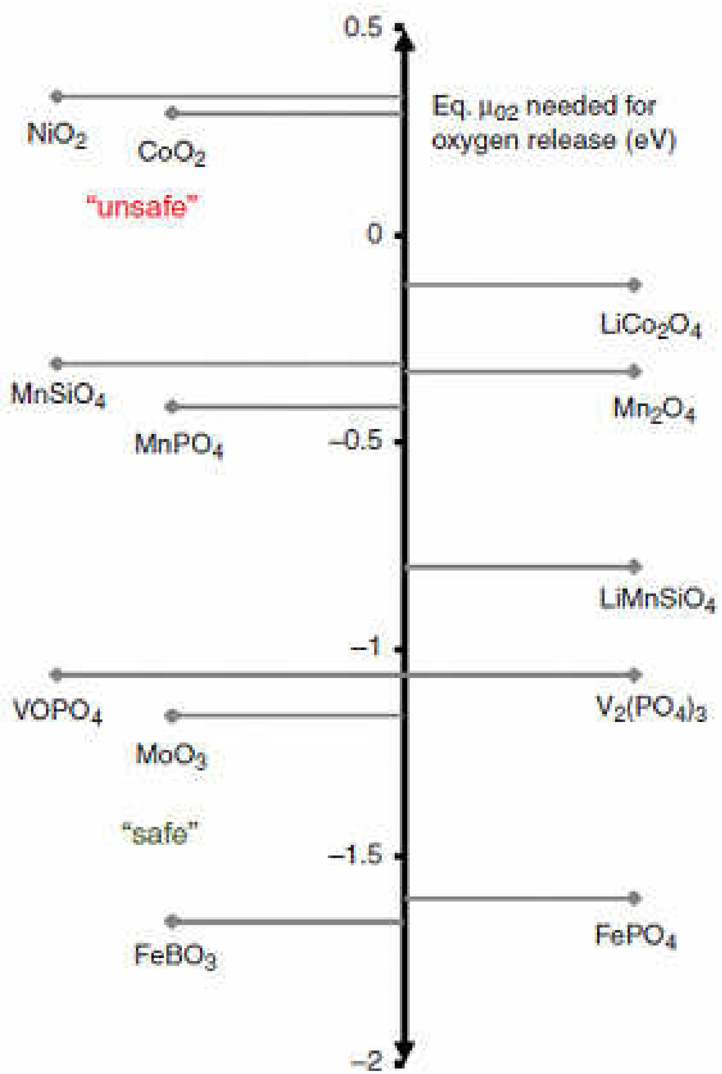
Cathode

•source of heat formation
•different onset and amount of heat generation
•oxygen formation



Roth at al., Pacific Power Sources Symposium 2009

Classification of Cathode Materials by their Oxygen Chemical Potential



[Cider, MRS Bulletin 35 (2010) 693]

thermal instable

$Li_{1-x}(M)O_2 \rightarrow$ MO-type + O_2

$Li_{1-x}(M)O_2$ + EC → 2MnO + CO_2 + H_2O

thermal instable at > 500°C
$Li_xFePO_4 \rightarrow Fe_7(PO_4)_6 + Li_3Fe_2(PO_4)_3$

the probability of oxygen formation decreases the safety

increasing thermal stability:

$LiCoO_2 < LiNi_{0,8}Co_{0,15}Al_{0,05}O_2 < LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 < LiMn_2O_4 < LiFePO_4$

Safety issues of electrolyte

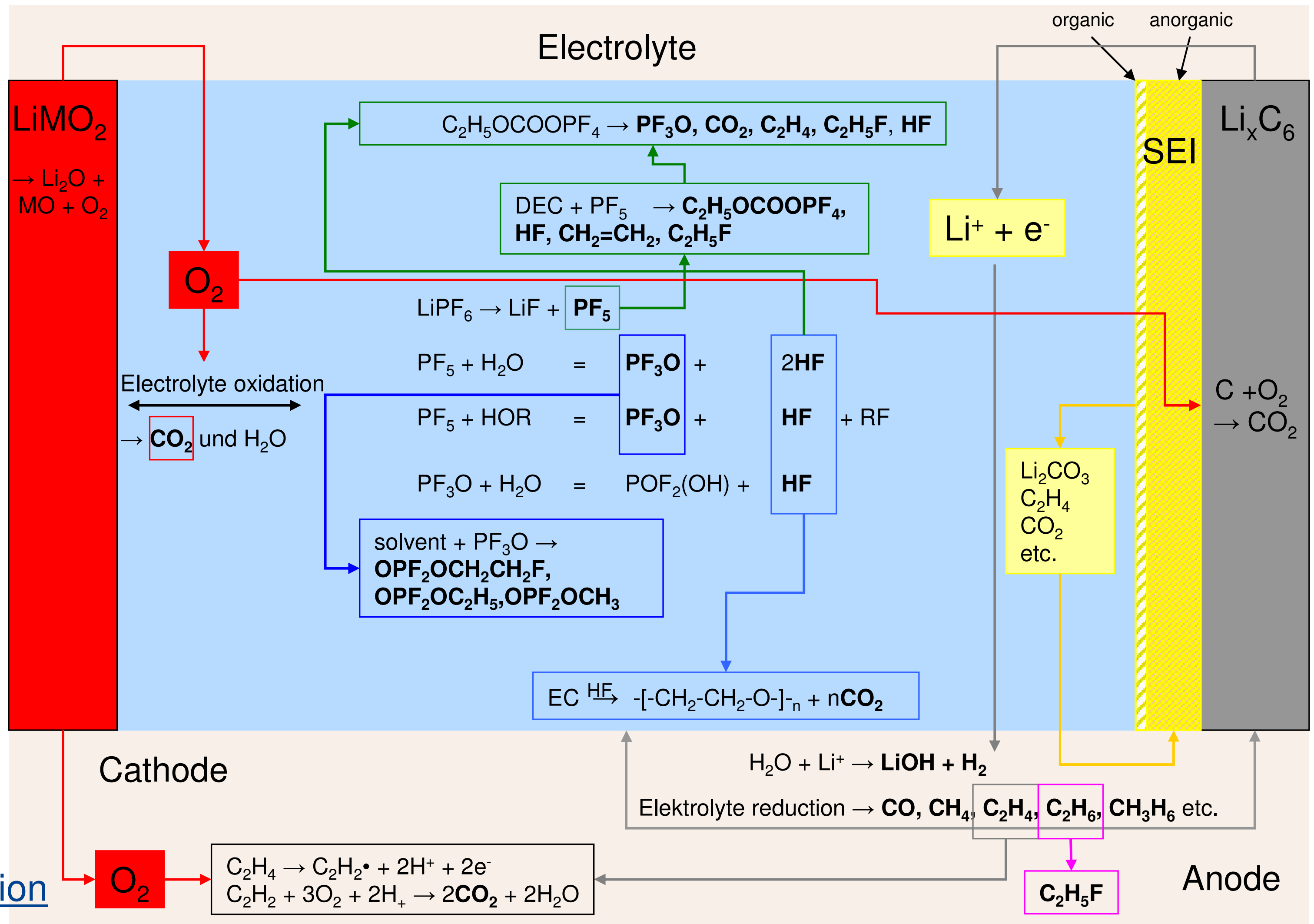
- Liquid electrolytes, organic solvents
- Polymer electrolytes
- Solid electrolytes

Flammable electrolytes, solvents

Name	Techn. Abkürzung	Siede-temperatur °C	Flammpunkt °C
Ethylencarbonat	EC	248	160
Propylencarbonat	PC	242	135
Dimethylcarbonat	DMC	90	15
Diethylcarbonat	DEC	127	33
Ethylmethylcarbonat	EMC	108	23

self ignition @ around 450 °C

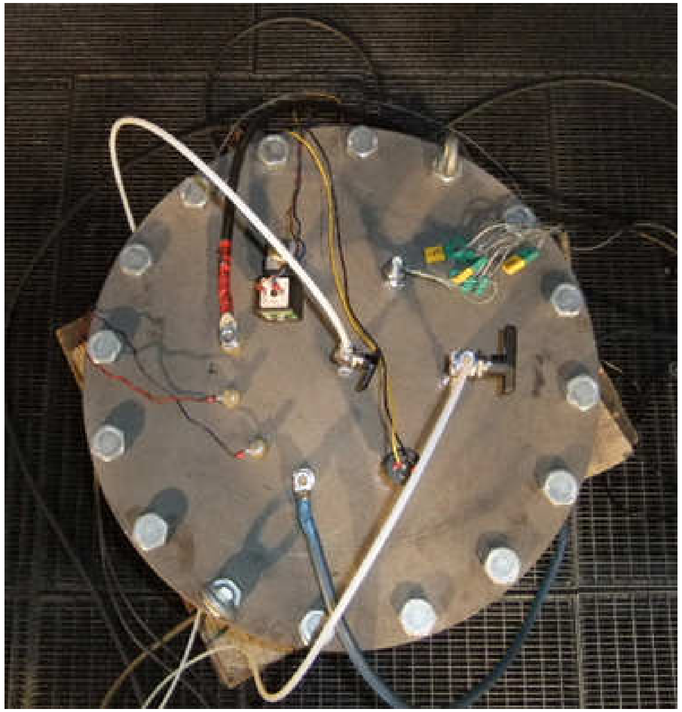
Decomposition Reactions and Gas Formation of Battery Components



HF-Formation

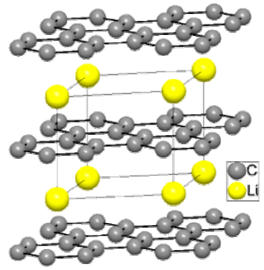
For 18650 size: $LiPF_6$ and PVDF:max.1.1lit HF but $C_2H_5OCOOPF_4$ + HF $\rightarrow$ PF_3O + CO_2 + C_2H_5F reduced amount of HF!

Gas composition after overcharge different scenarios



		Beispiel für die Gaszusammensetzung bzw. Stoffemission nach einem "Event" bei 1C Überladung für eine 50Ah Zelle	
	Einheit	Zelle öffnet bei ca. 100°C ohne thermal runaway	thermal runaway T ca. 600°C
emittierte Gasmenge	lit	11	140
Fluorid angenommen aus HF	mg	10.1	500.6
O2	lit	9.2	0.7
N2	lit	36.0	28.9
H2	lit	<0.05	52.4
CO2	lit	3.28	51.5
CO	lit	<0.05	14.4
Phosphin	µg	1.3	530
Formaldehyd	µg	90	<20
Acetaldehyd	µg	2000	15000
Propionaldehyd	µg	170	6000
Butyraldehyd	µg	20	3800
Valeraldehyd	µg	<10	400
Methan	ml	230	2
Ethan	ml	-	1
Ethen	ml	150	8400
Propan	ml	10	1200
Propen	ml	<1	2700

Anodes



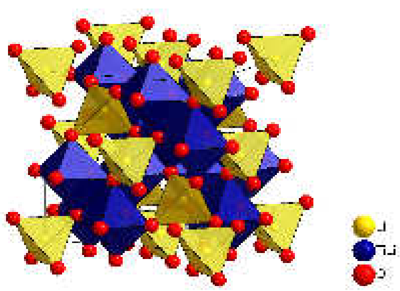
C-based Anode

•source of heat
•Heat generation already at low temperatures

•High stability of the SEI is the key to a stable anode
•exfoliation > 250° C (in the presence of electrolyte)

•Stability influenced by:

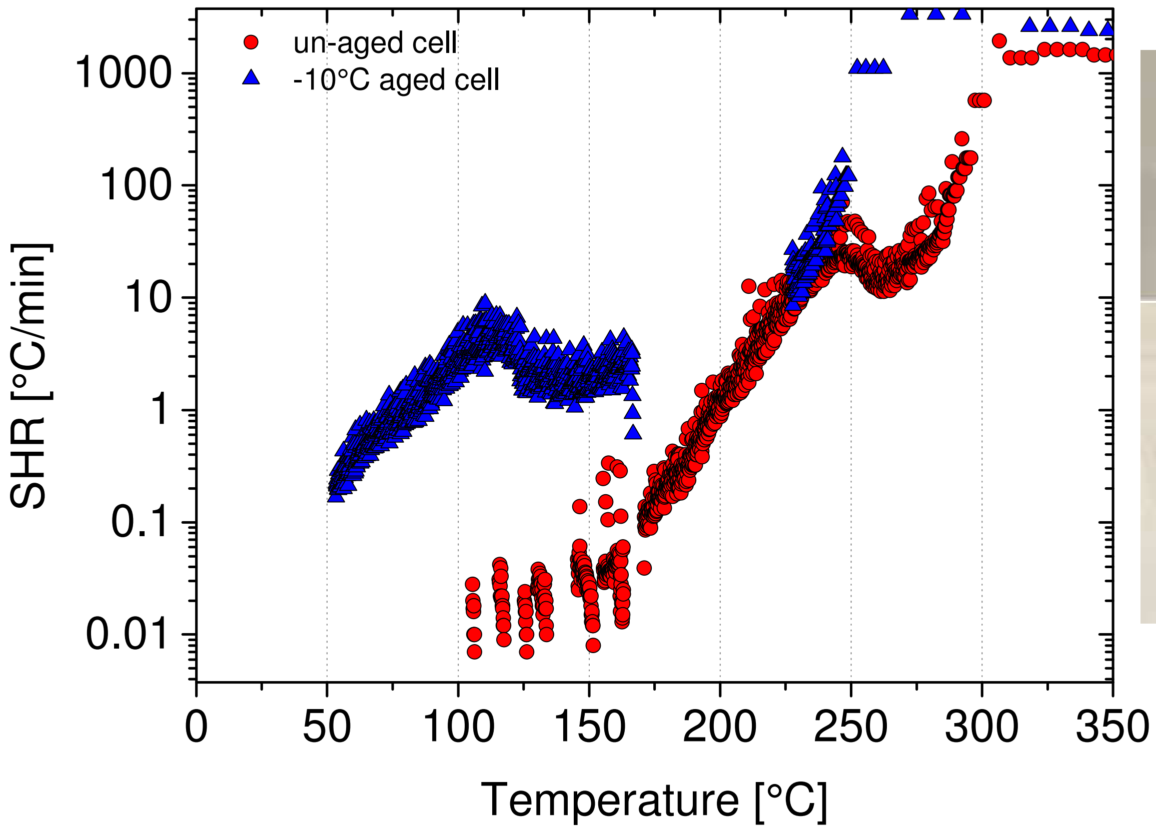
– particle shape and size
– chemistry of the electrolyte

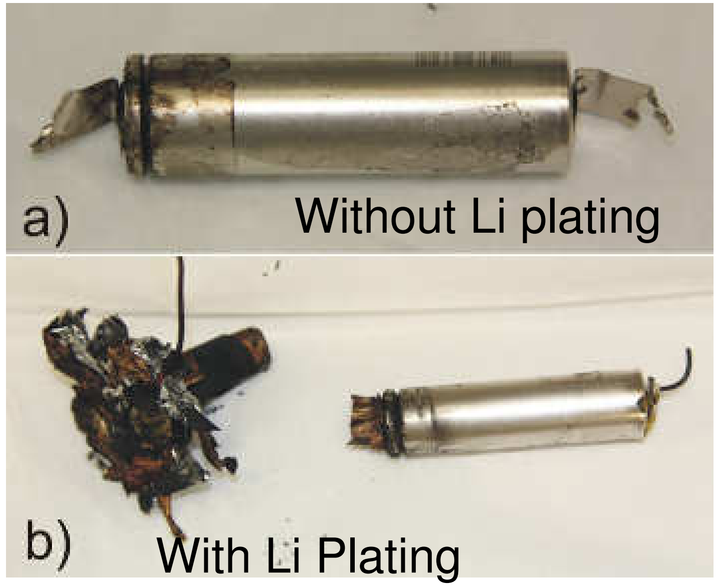


Alternative: Titanate (more positive potential, lower cell voltage)
high thermal stability (~1000°C)

$Li_4Ti_5O_{12} \rightarrow Li_2Ti_3O_7$

Lithium plating: a real safety issue!
ARC run of LMO/NMC-Blend Graphite 18650 Cells





violent decomposition

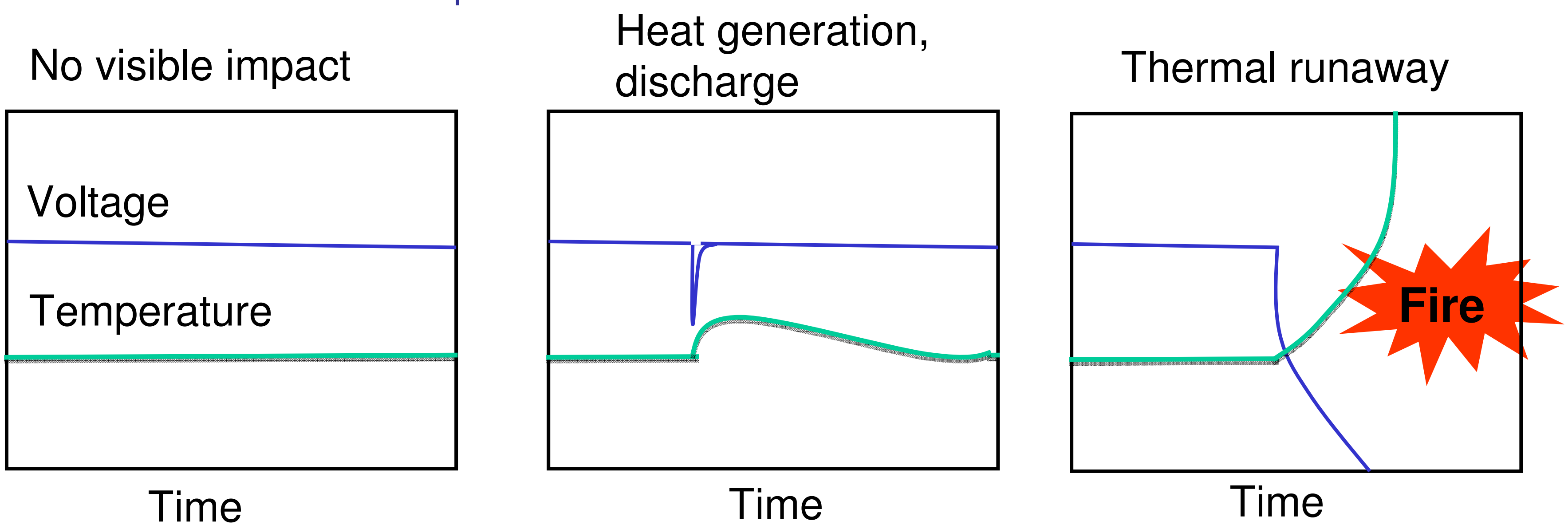
Li-plated cells: heat formation is shifted to lower temperatures and higher SHR

M. Fleischhammer, T. Waldmann, G. Bisle, B.-I. Hogg, M. Wohlfahrt-Mehrens, J. Power Sources. 274 (2015) 432–

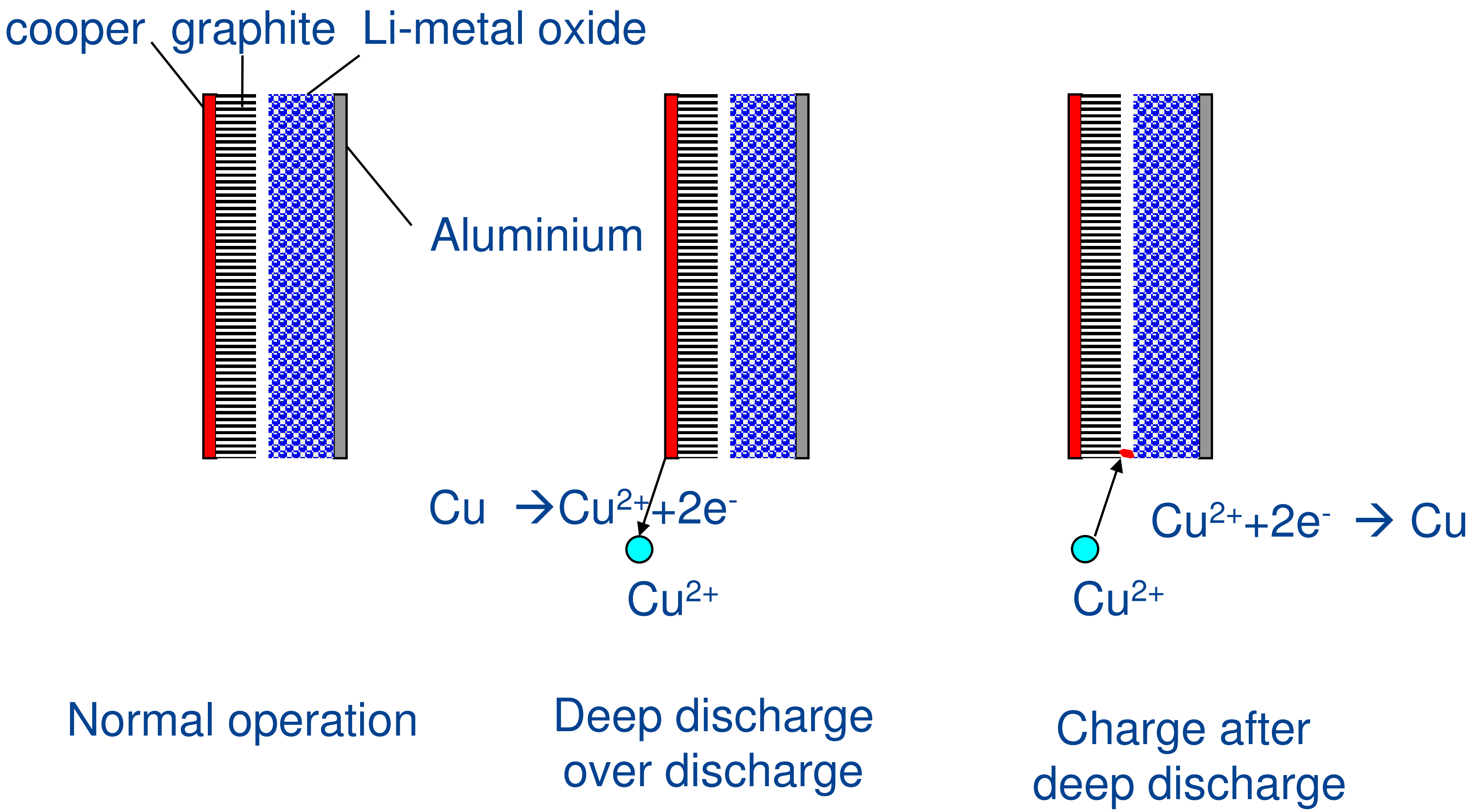
Internal short circuit is one of failure modes of Li-ion cells that is not externally controllable

They might have different sources:

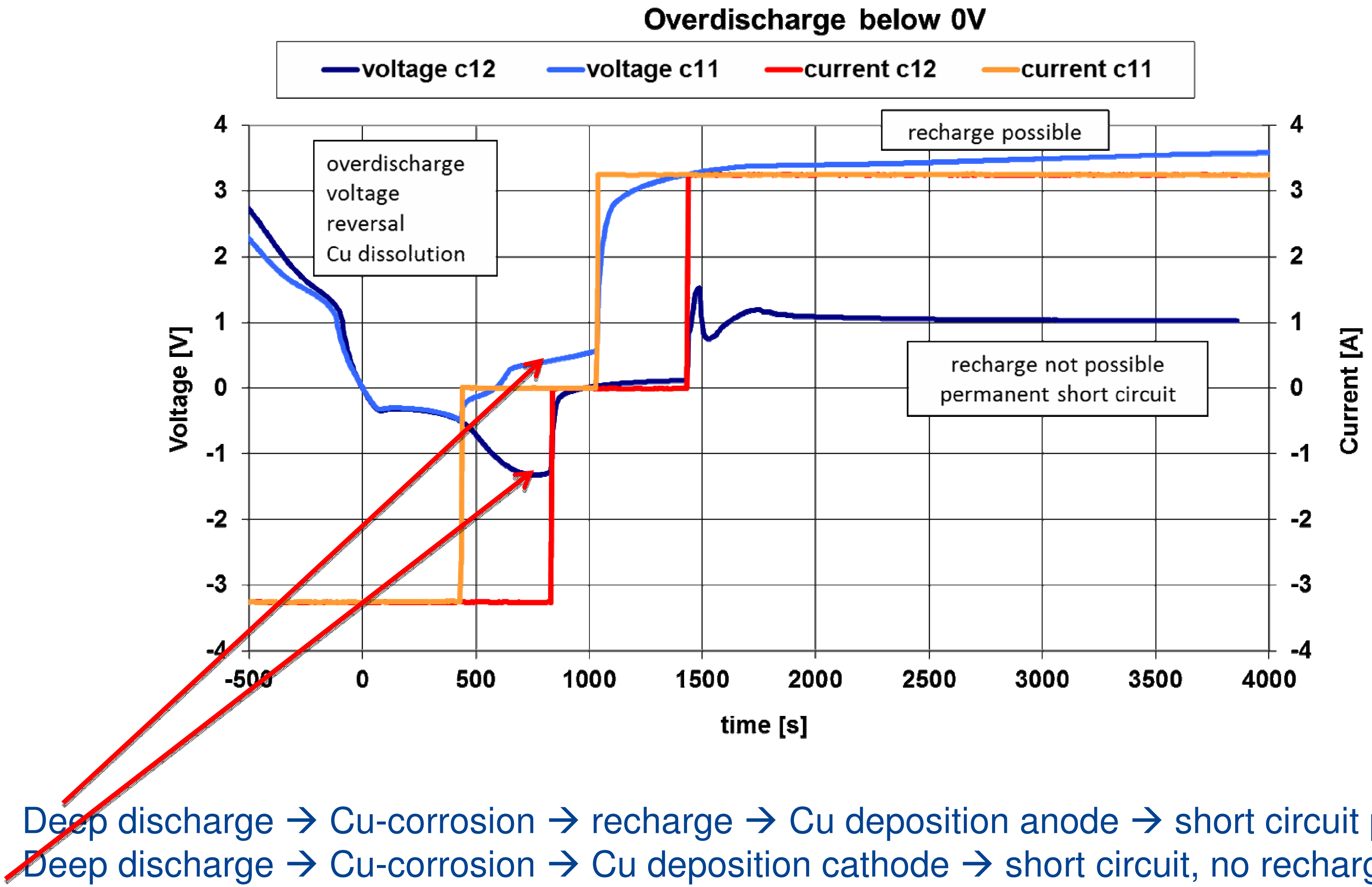
- formation of Li or Cu dendrites
- mechanical failures like crack or pin holes in the separator
- penetration by particles
- mechanical impacts and others



Over-discharge dissolution of Cu followed by formation of Cu dendrites



Cu dendrites in result of deep discharge Cu dissolution and deposition



Deep discharge → Cu-corrosion → recharge → Cu deposition anode → short circuit possible
Deep discharge → Cu-corrosion → Cu deposition cathode → short circuit, no recharge possible

Nail penetration / Puncture

SANDIA/(SAEJ 2464):
cell: Ø 3 mm, mild steel (conductive), perpendicular to electrode plates, through cell, 80mm/sec (<250 mm/s)
module: Ø 20 mm, trough 3 cells or 100 mm

QCT 743: high-temperature resistant, steel spike of Ø 3 mm ~ Ø 8 mm through cell, at the rate of 10 mm/s ~ 40 mm/s (with the spike retained in the cell)
module: trough 3 cells

Additional influenced by:
tip shape, surface of the nail, alloy composition, ……

Very strong impact
- leaves space for variation of test conditions
- limits reproducibility

Therefore nail penetration test is disliked, but still the test carried out most frequently.

Nail penetration

Nail ST37 cell without plates → hazard level 6 (fire, rupture)

Failure Propagation

- Single cell suffered from severe failure (thermal runaway)
- Cell generate heat
- Heat transferred to the neighboring cells by heat conductivity, flames, hot gases, …
- High probability of failure transfer to the neighboring cells causing thermal runaway of the neighbors /complete pack

How to prevent propagation

- Safety distance between cells
- Thermal barriers between cells
- Heat sinks extracting/consuming the heat energy

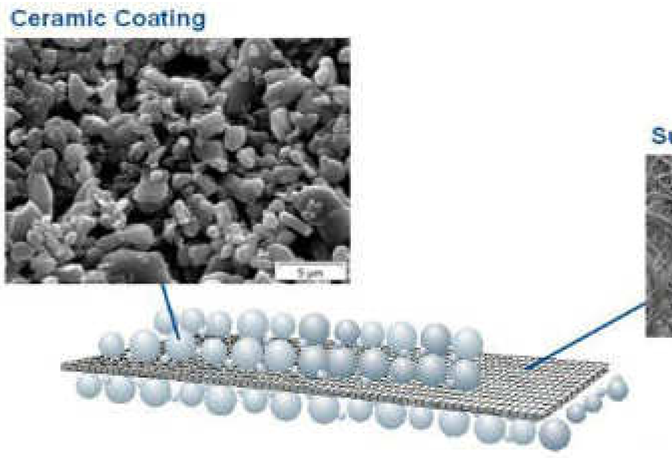
Hersman, NTSB, Investigative Update of Battery Fire Japan Airlines B-787 - Jan 7, 2013

Safety enhancing components

Separator

Ceramic coated Separator

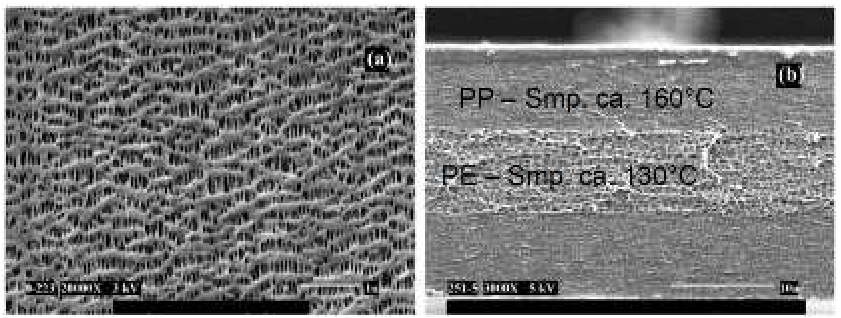
- Ceramic coating still separate the electrode even if the carrier meted away, extreme thermal stable
- Conventional polyolefin separator, melting shrinkage direct contact of the electrodes possible



Quelle: Evonik Separion

Shut-down-Separator (3 layer)

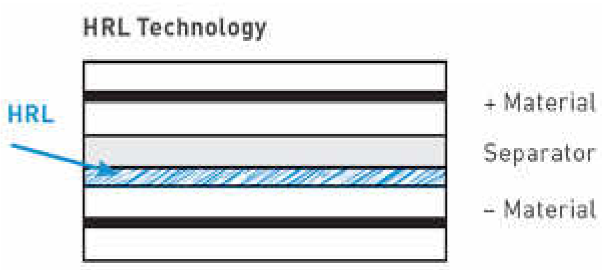
- Inner layer melting, closed pores,
- Lost Ionic conductivity
- Current path way interrupted

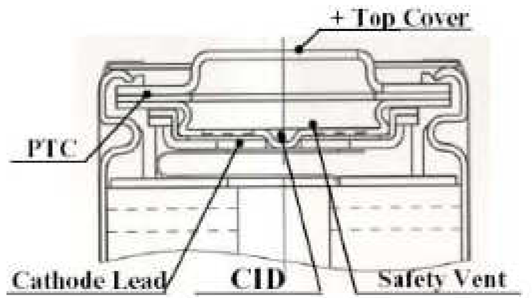


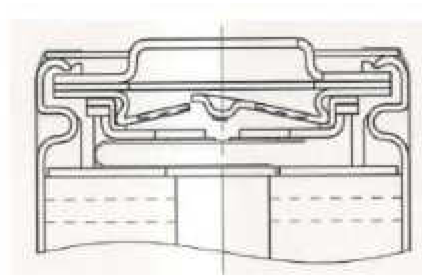
Quelle: Battery Separators. P Arora, ZJ Zhang, Celgard.Chem. Rev. 2004, 104, 4419-4462

Safety enhancing components

- Heat Resistive Layer, HRL, reduce interaction of material-electrolyte
- Burst membrane release accumulated gases before cell case rupture
- Current Interruption Device (CID)
- Overcharge safety device (pressure activated, internal fuse interruption)
- Over current protection Positive Temperature Coefficient Device (PTC)

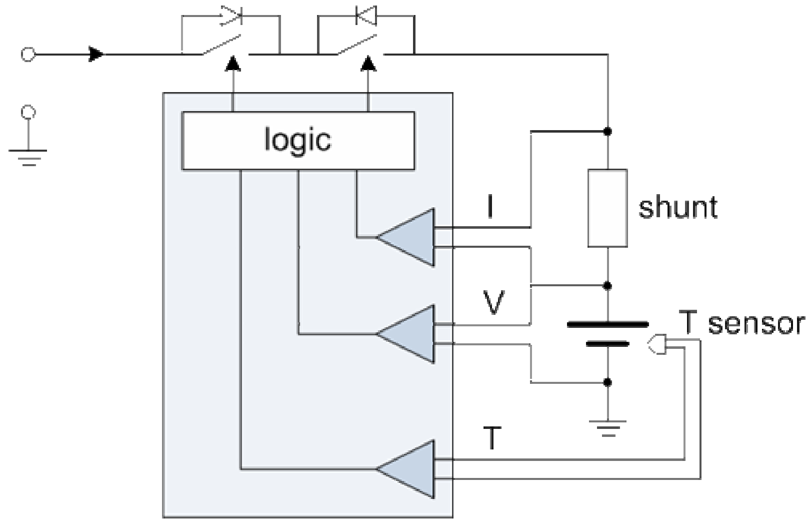






BMS

- Monitoring
- Current/power control or interruption
- Balancing
- Thermal management
- Isolation resistance
- SOC, SOH, SOF



Preventing/Limitation

- Overcharge
- Deep discharge/ over discharge
- Short circuit
- Overcurrent/ overpower
- Over temperatures

Critical parameters: redundancy

- E.g. cell voltage-module voltage-cell voltage monitoring and control independent voltage comparator

Fazit

Lithium-Ion-Technology

- available technology
- no intrinsic safe cell technology
- suitable controllable by BMS
- Safe by
  - Selecting suitable materials and additives
  - Use of safety and protection components
  - Design of cell and module
  - suitable control by BMS
  - Monitoring and control of current, voltage, temperature
  - Redundancy for critical parameters
  - Protection against re-initializing after failure
  - Suitable housing/hosting of the battery

Thank you
for your Attention !

Acknowledgement:

Thanks to my colleagues and co-workers of the battery group and the material group of ZSW-Ulm

- **SPEISI: Sicherheit und Zuverlässigkeit von PV-Anlagen mit Speichersystemen unter besonderer Berücksichtigung von Brandrisiken und Löschstrategien**
  FKZ: 41V6971

Bundesministerium
für Umwelt, Naturschutz
und Reaktorsicherheit

- **Sicherheit und Netzdienlichkeit von elektrischen Heimspeichersystemen mit Lithium-Ionen-Batterien**
  FKZ: 03ET6055C

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