Supporting the deployment of safe Li-ion stationary batteries for large-scale grid applications

Advanced sensors

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CEA

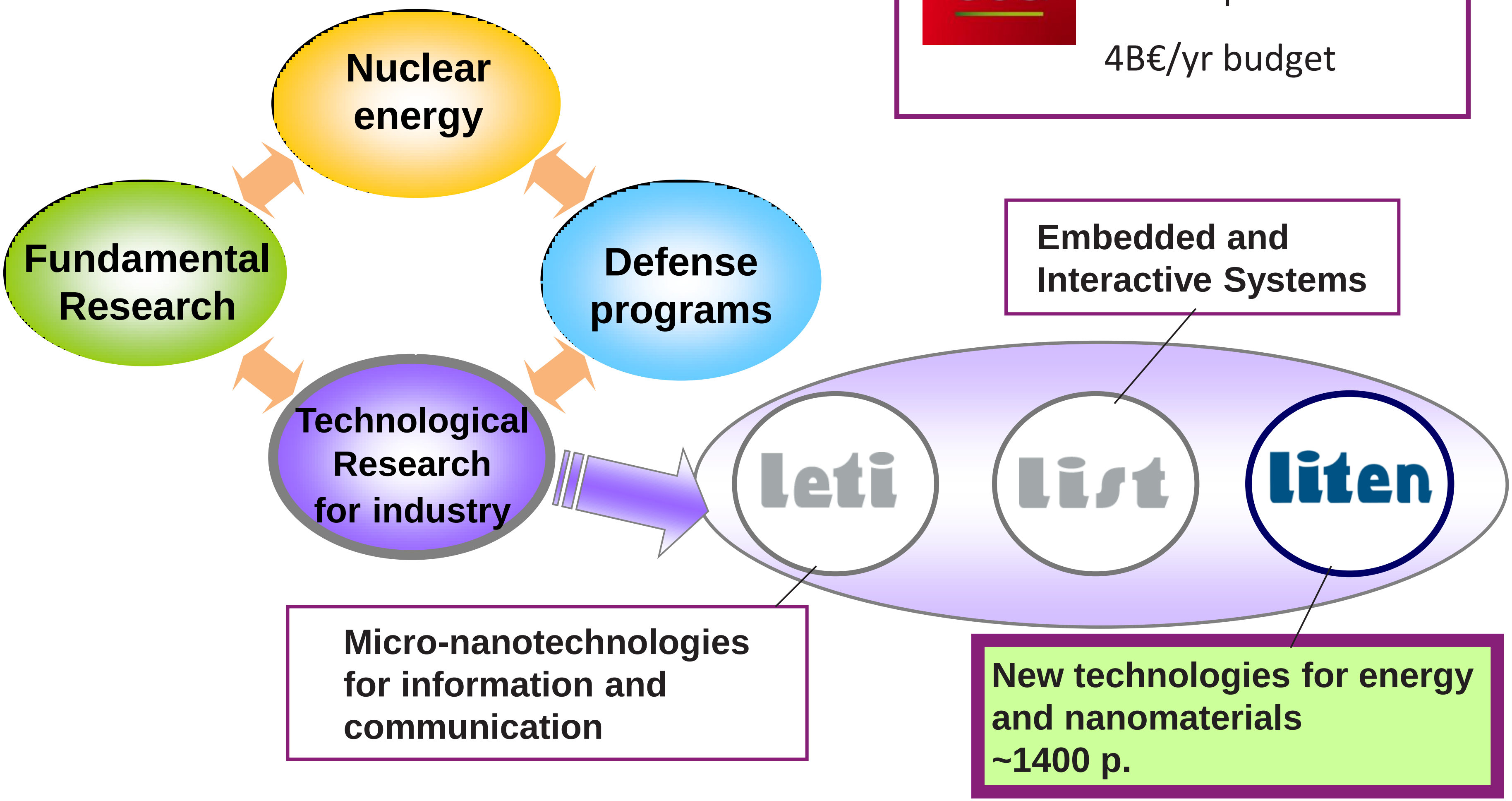
Düsseldorf, 10 March 2015

CEA in a few words

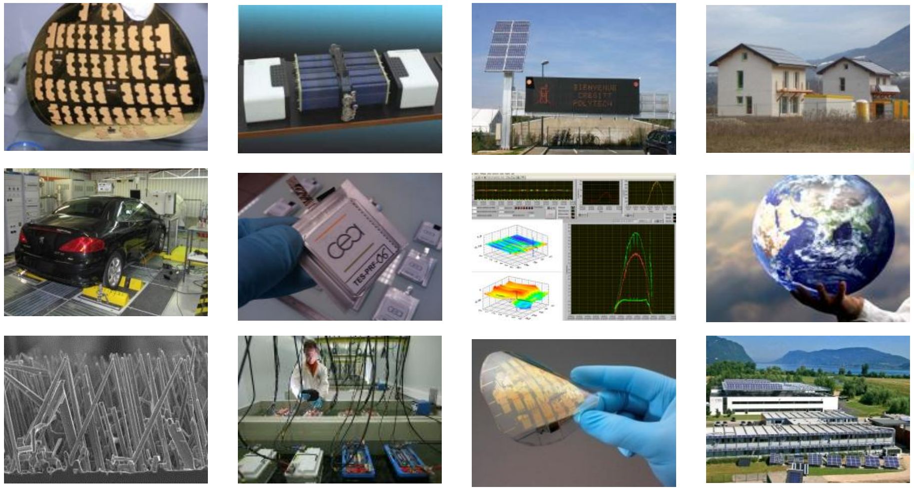
10 research centers

16 000 p.

4B€/yr budget



CEA-LITEN institute: New technologies for Energy



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ines
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Solar/building/smart grids

Electromobility

Thermal/biomass/H_2

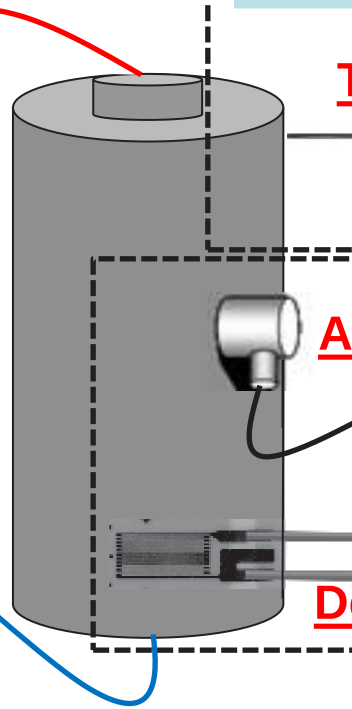
Nanomaterials

The sensors used

Electrochemistry

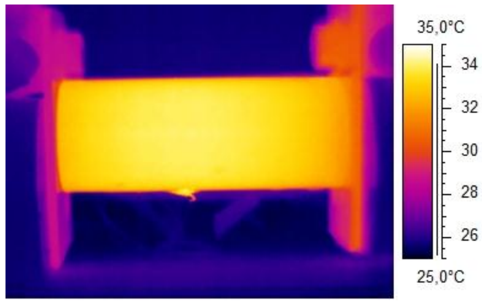
- Current
- Voltage
- Impedance

Determination of battery state by electrical measurements



Impact of battery state and electrical solicitation on temperature

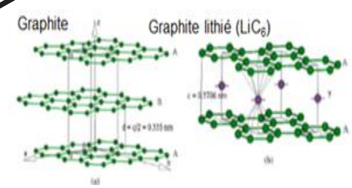
Temperature



After discharge at 3C

Acoustic emission

Li-ion batteries generate sounds during their activity



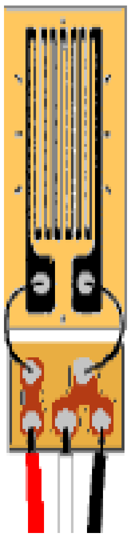
Deformation gauges

- Thermal expansion
- Li insertion
- Gas evolution

The sensors used: deformation gauge

Principle

- ✓ Small resistive circuit made of several coils which extend under the influence of a local deformation of the structure on which it is closely attached.

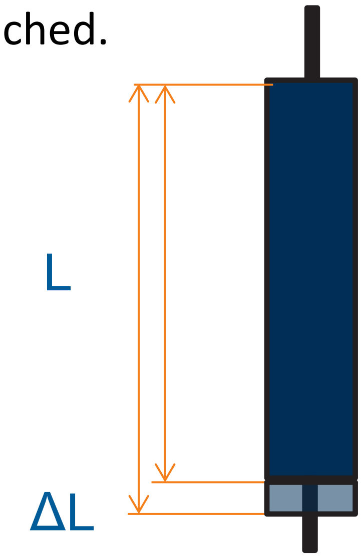


Resistance
$R = \rho \, L/S$

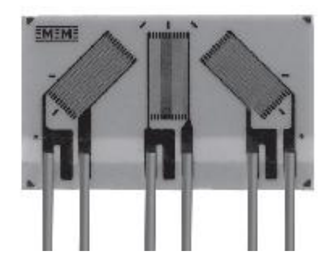
$$\frac{\Delta R}{R} = K \frac{\Delta L}{L} = K\varepsilon$$

ρ = resistivity
L = length
S = cross-section

ΔR = resistance variation
R = resistance of the gauge
K = gauge factor
ε = strain



- ✓ Gauge resistance proportional to the extension of the measuring point
- ✓ Measurement with Wheatstone bridge to increase precision: resolution **1 µm/m**
- ✓ Use of rosette gauge to measure deformation in several directions

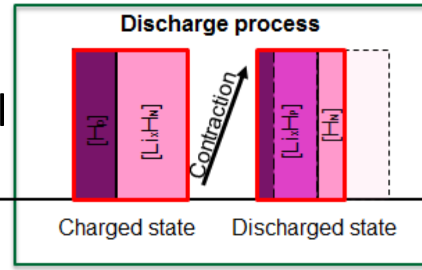


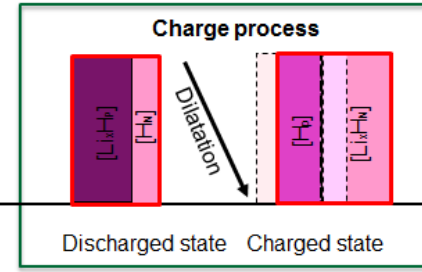
The sensors used: deformation gauge

Application to Li-ion batteries

- **Electrochemical "breathing"**

✓ Depends on the nature of the active material
✓ Amplitudes linked to the internal design (winding, mandrel)



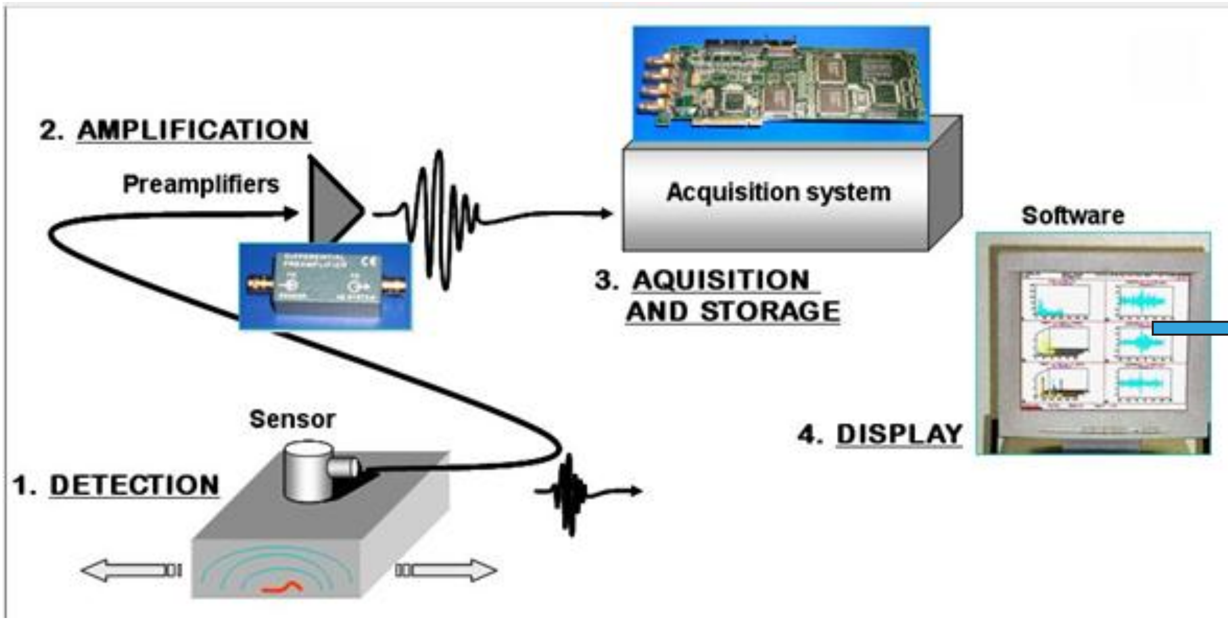


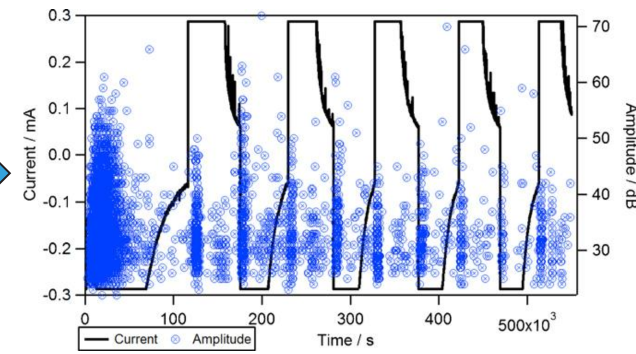
Electrode	Positive		Negative	Global volume variation
Active material	$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	Li_xFePO_4	Li_xC_6	
Volume variation	-3,8%	-6,5%	+11	
Technology	x		x	+ 7,2%
Technology		x	x	+ 4,5%

- **Swelling due to the increase of the internal pressure (gas emission)**

✓ Dependent on the volume of gas (solvents, potential windows)
✓ Continuous dilation expected during aging

The sensors used: acoustic emission

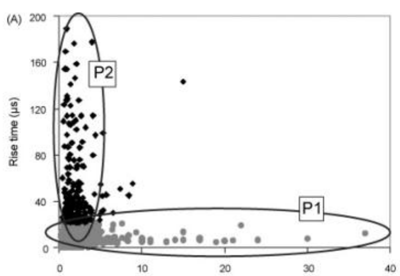




→ Types of phenomena that can be recorded:

H2 Bubbles

NiMH

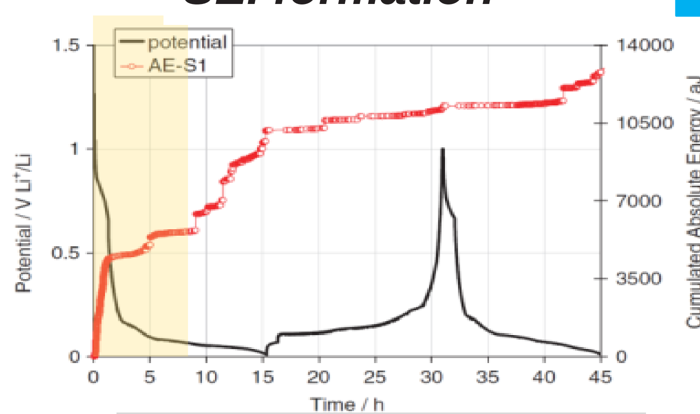


Cracking MH particules

S. Didier-Laurent, and al. , JPS, Vol179, 1, (2008), 412–416

SEI formation

Li-ion



N. Kircheva and Al.J.E.S, **159** (1) A18-A25 (2012)

Tests performed

» Different cell chemistries and designs

Pouch, LTO/NCO
15 Ah

Pouch, LTO/LFP
22 Ah

Cylindrical, C/LFP
15Ah

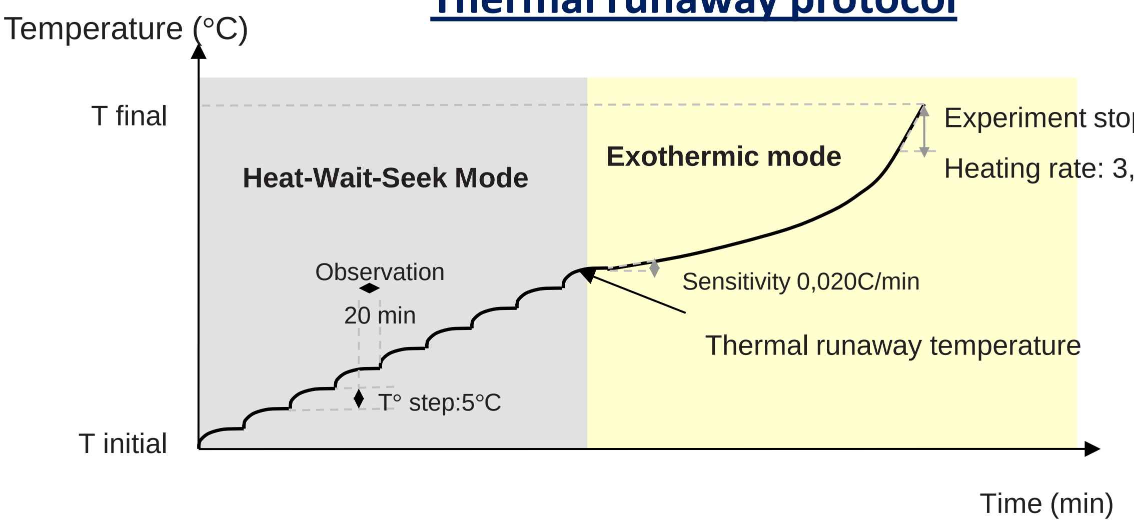
Prismatic, C/LFP
40 Ah

» Electrical tests *(not presented here)*
  » Optimisation of sensor attachment and position on the cell
  » Evaluation of SOC / SOH indication by sensors
» Safety tests in ARC
  » Thermal stability: overheating up to thermal runaway
  » Overcharge in adiabatic condition (worst case)

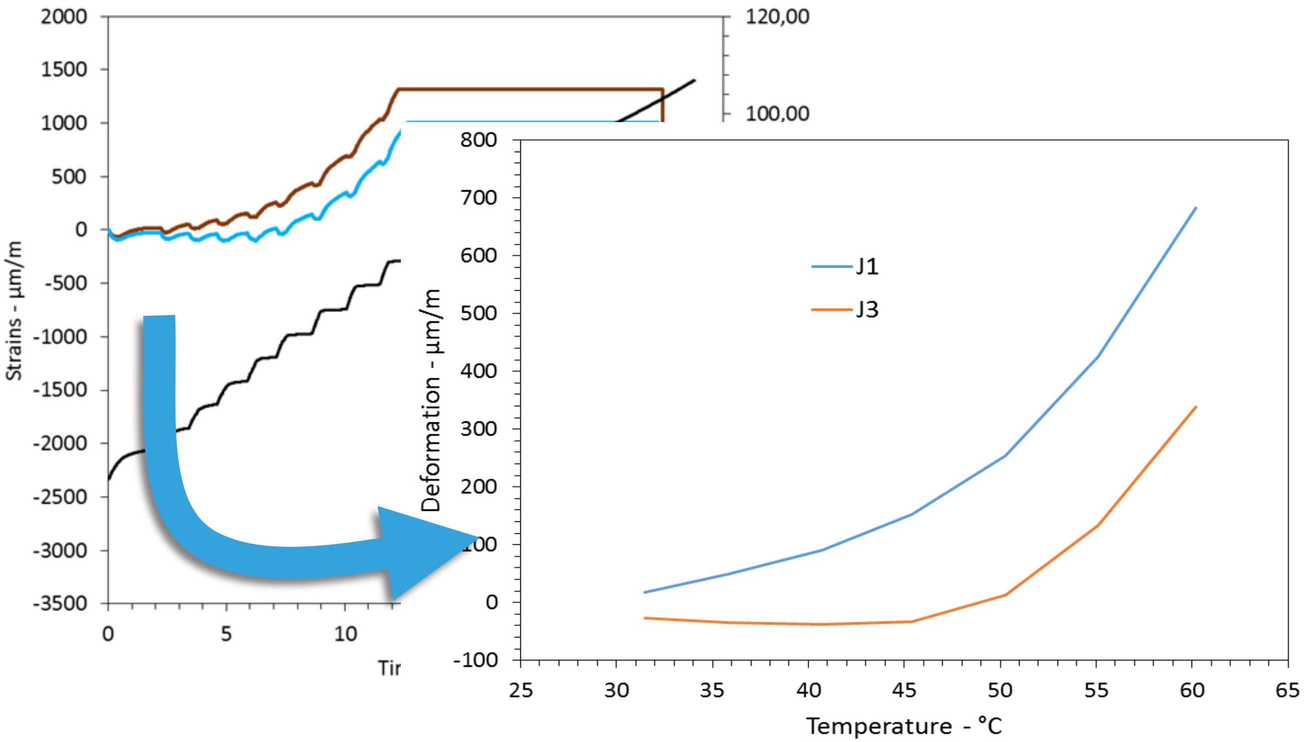
Thermal stability tests

- Performed in an Accelerated Rate Calorimeter (ARC)
- Overheating up to thermal runaway

Thermal runaway protocol



Thermal stability tests / Deformation gauge

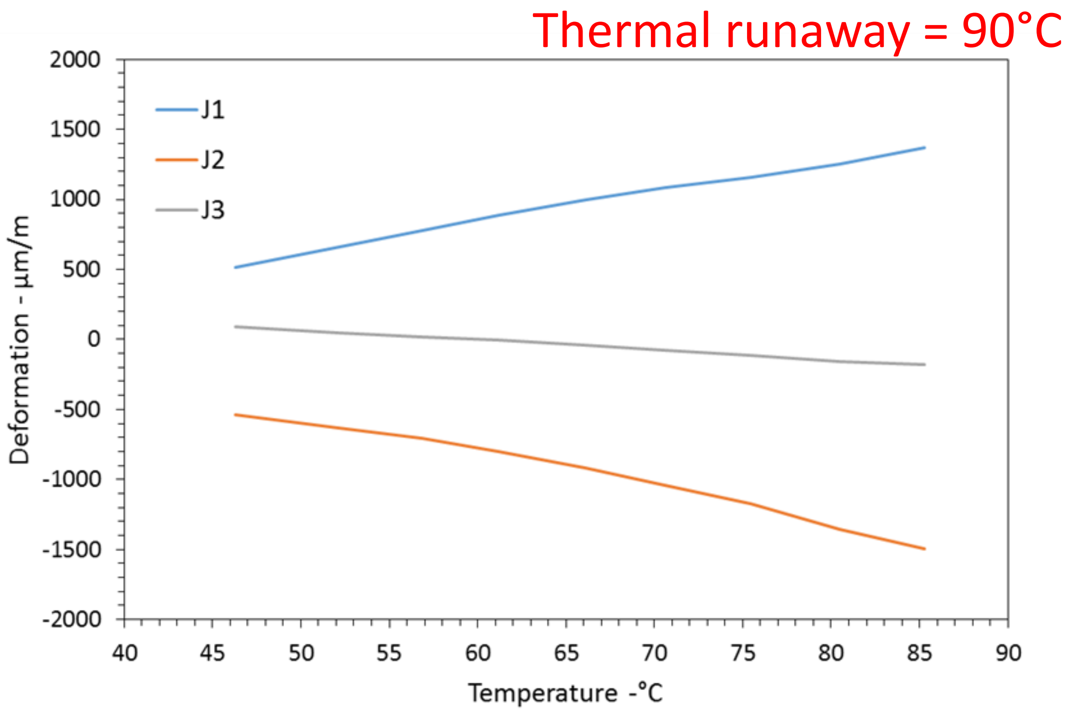


Prismatic, C/LFP

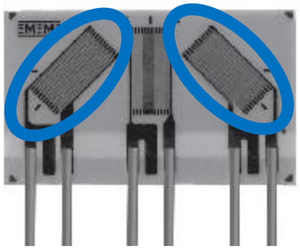
» Very strong deformation: signal saturation
» Deformation begins around 45°C/ thermal runaway 90°C

→ signal different enough from normal operation to be used by BMS

Thermal stability tests / Deformation gauge



Pouch, LTO/NCO

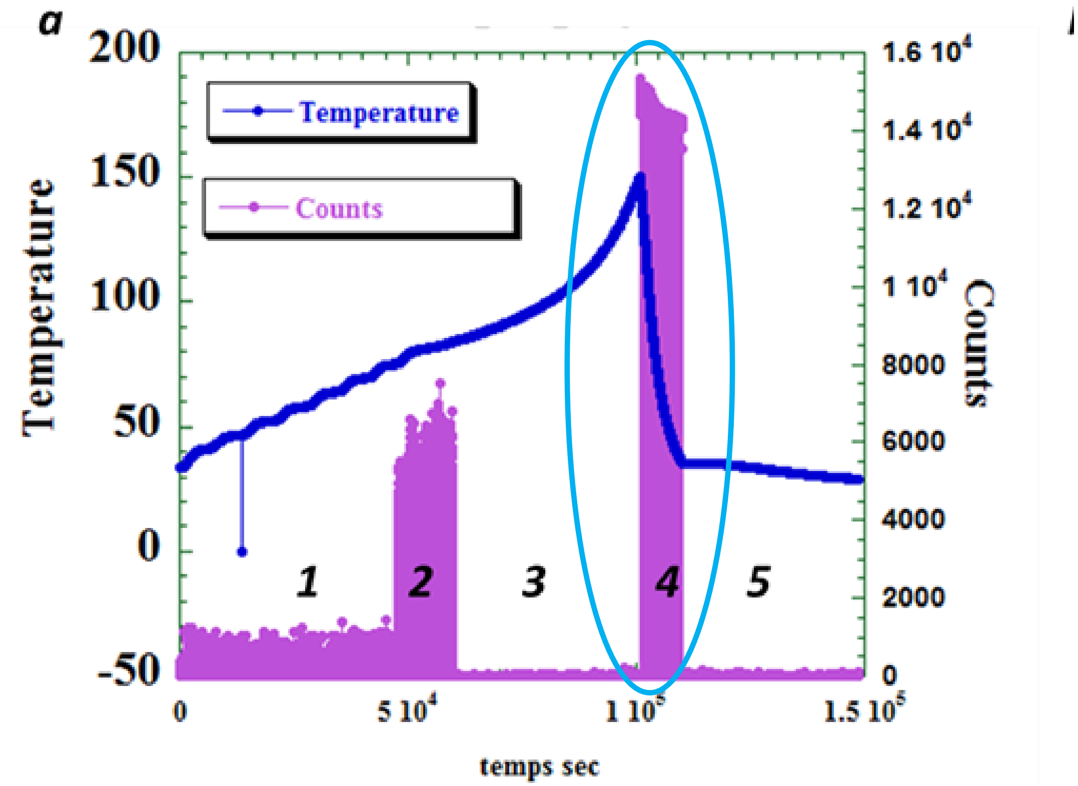


- Large deformation measured
  → Swelling of the pouch
- No explanation about the opposite behavior of J1 and J3 (yet symmetric)
  → Pouch deformation too random

Thermal stability tests / Acoustic emission

Cylindrical, C/LFP

→ ARC is highly a “polluted” environment: noise in terms of mechanical waves (ventilation/electromagnetic)



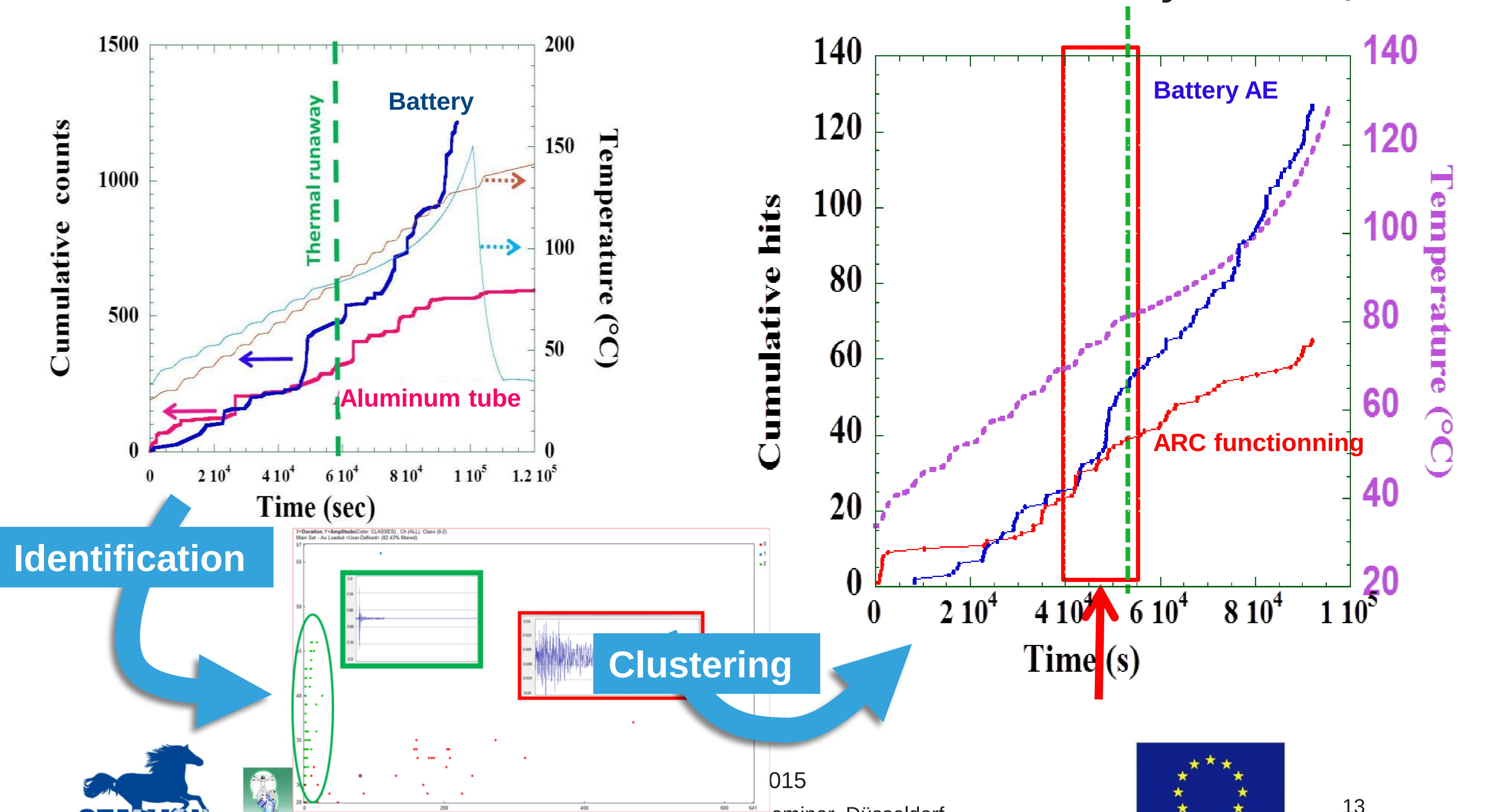
1: Thermal runaway seeking
2: Beginning of Thermal runaway
3: Background AE
4: Triggering of ventilation
5: Background AE

- → Suppress ventilation noise
- → Post-treatment required
- → Blank test with aluminum tube

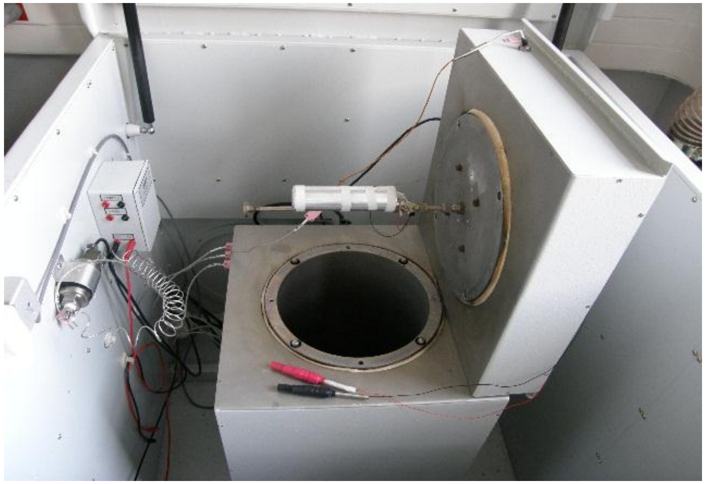
Thermal stability tests / Acoustic emission

- » Removal of background noise from the ARC

Cylindrical, C/LFP

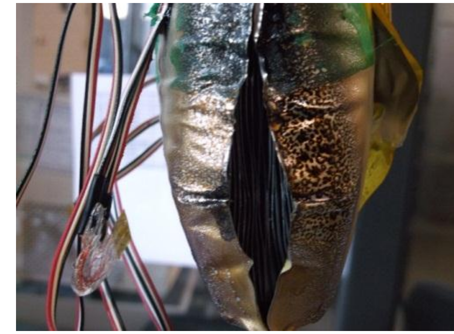


Overcharge tests

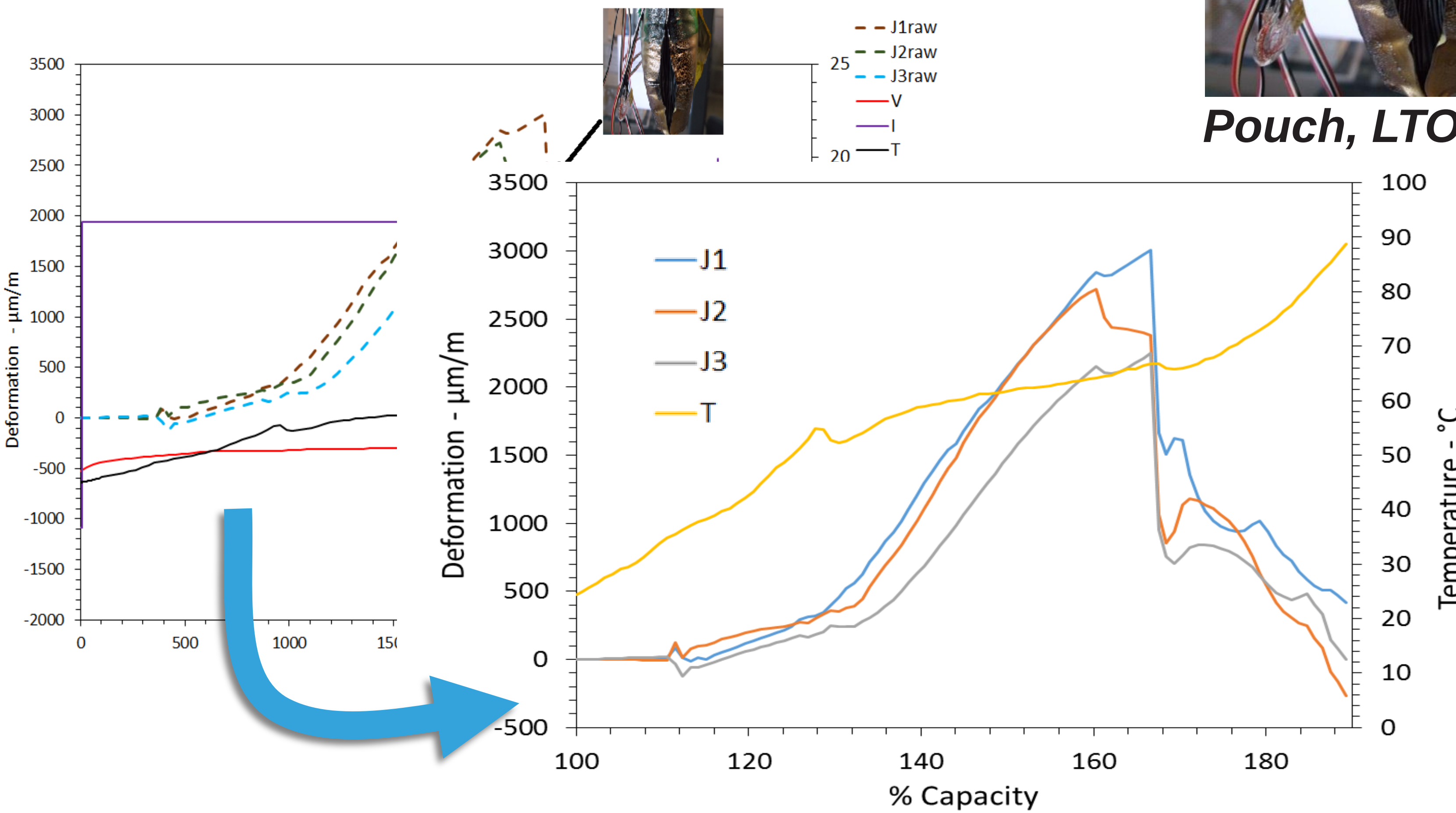


- » Initial standard charge @C/2
- » Overcharge @1C with floating 2 x Vmax
  - » Target 200% overcharge
  - » Stop if temperature increase >10°C/min
- » Tests done in ARC for thermal and safety aspect
  - » ARC blast box as a container
  - » Adiabatic calorimeter: worst case (no heat dissipation)

Overcharge tests / Deformation gauge



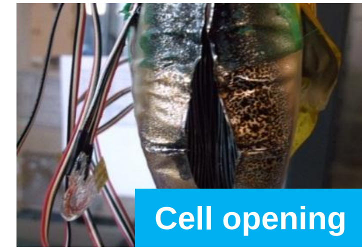
Pouch, LTO/NCO



» Simultaneous increase of deformation and temperature

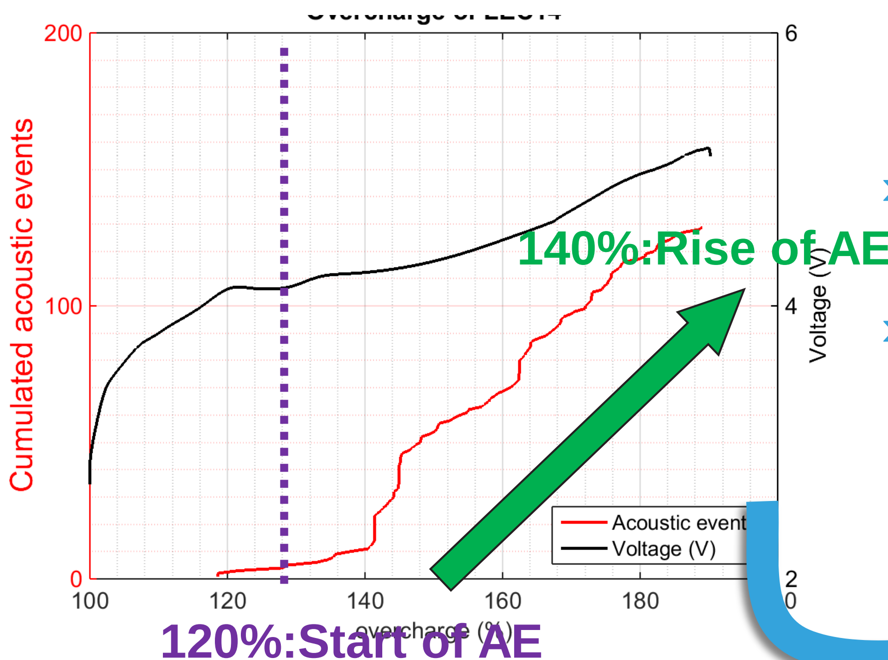
» Large deformation recorded on pouch cell

Overcharge tests / Acoustic emission

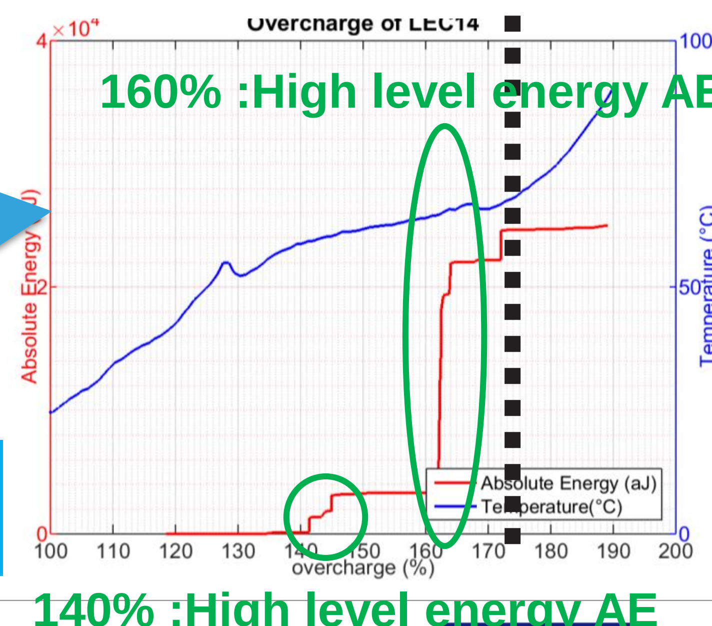


Pouch, LTO/NCO

15 Ah



- Rise of EA at 4.1V (55°C) _140% overcharge
- 160% of overcharge : large high level energy

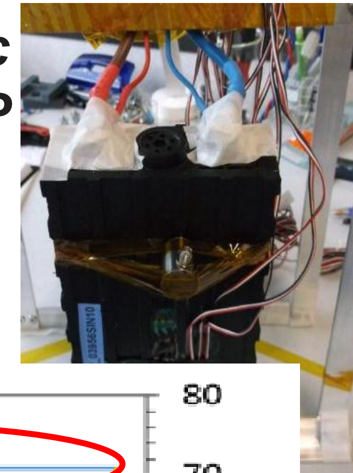


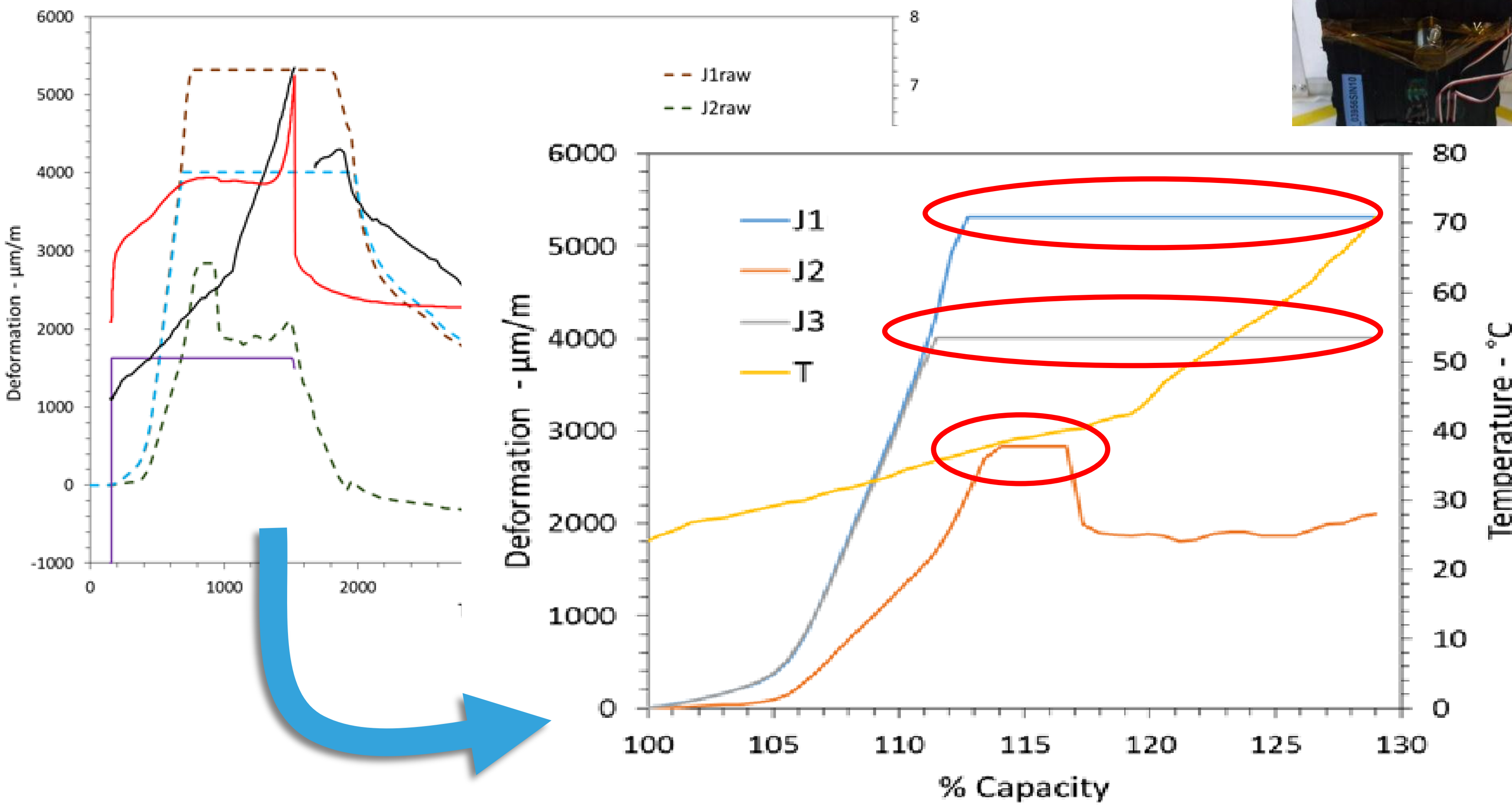
- Predictive detection of degradation mechanism

Interest of acoustic emission to have BMS with overcharge detection

Overcharge tests / Deformation gauge

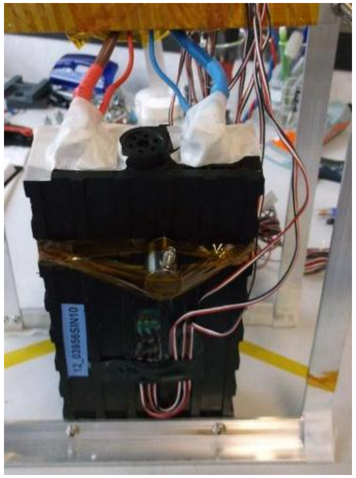
Prismatic C/LFP



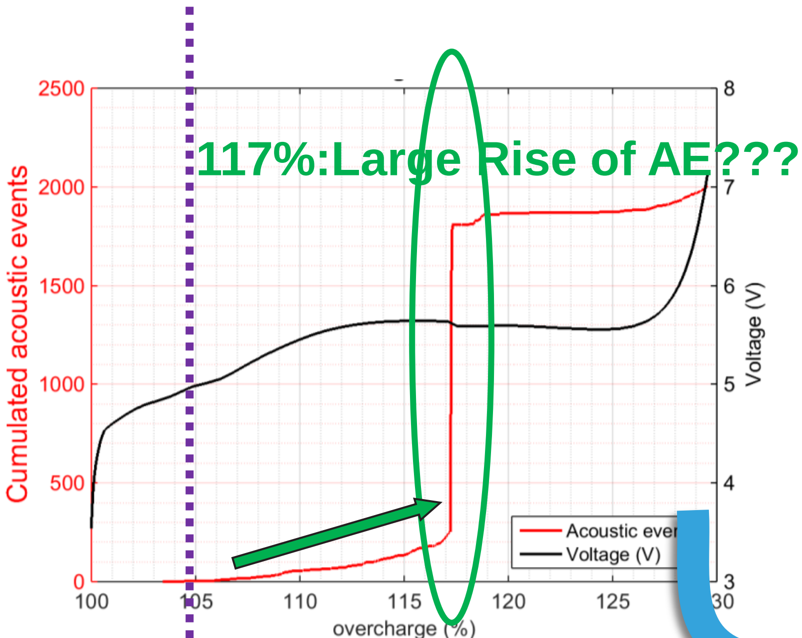


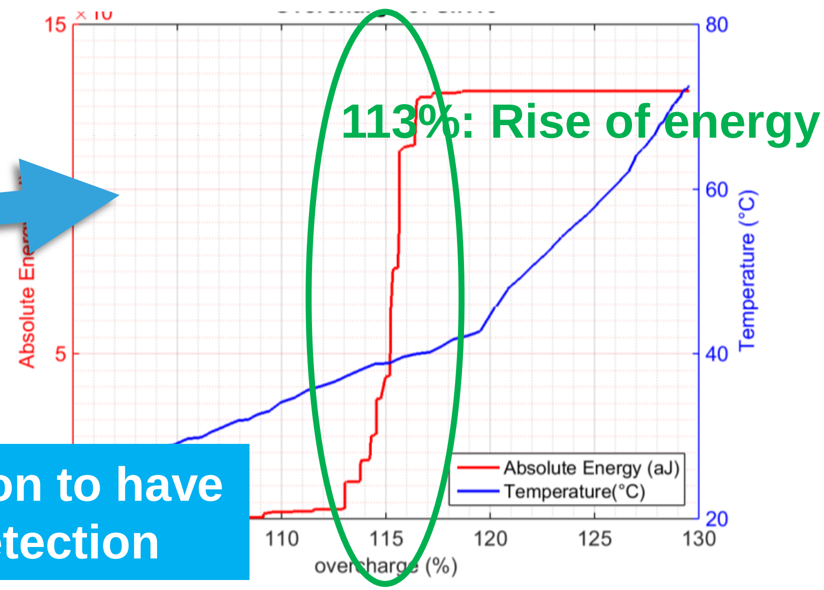
- » Earlier detection than with temperature sensor
- » Signal saturation due to wide deformations

Overcharge tests / Acoustic emission



Prismatic, C/LFP

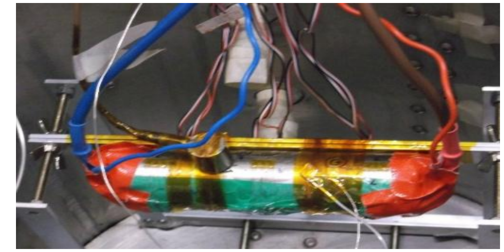




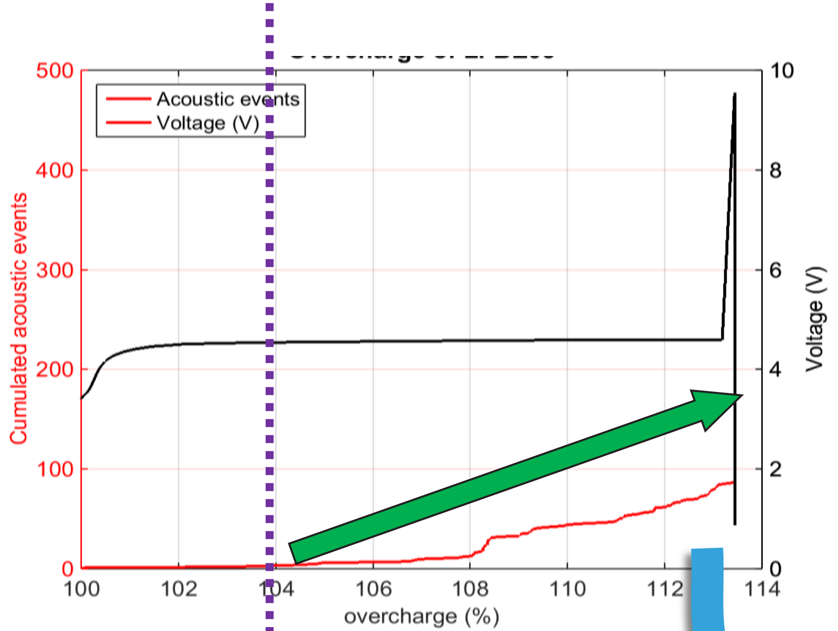
- Rise of EA at 5.6V (40°C)
- Predictive detection of degrad

Interest of acoustic emission to have BMS with overcharge detection

Overcharge tests / Acoustic emission

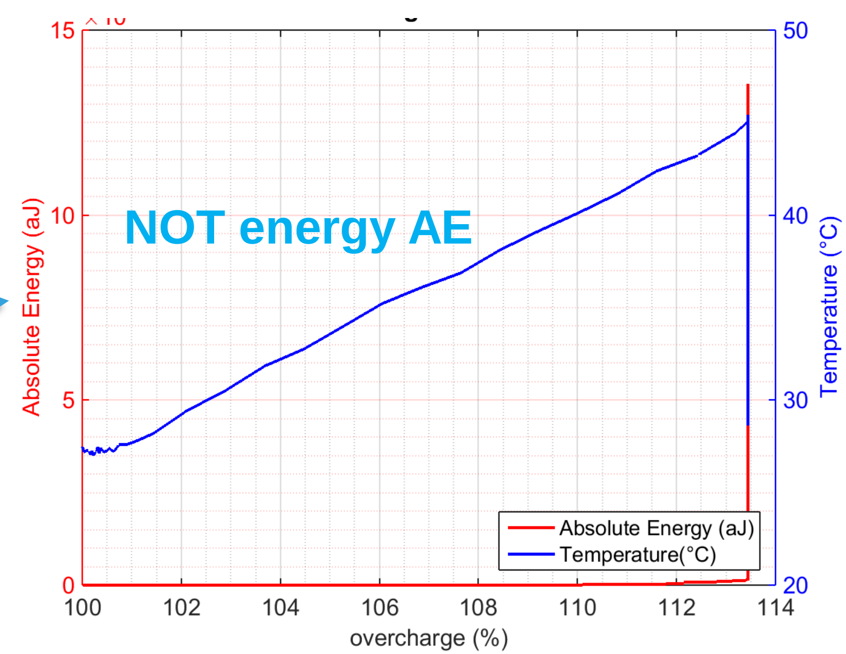


Cylindrical, C/LFP



104%: Start of AE

» Plateau at 4.5V: Electrochemical behavior different from the prismatic C/LFP cell

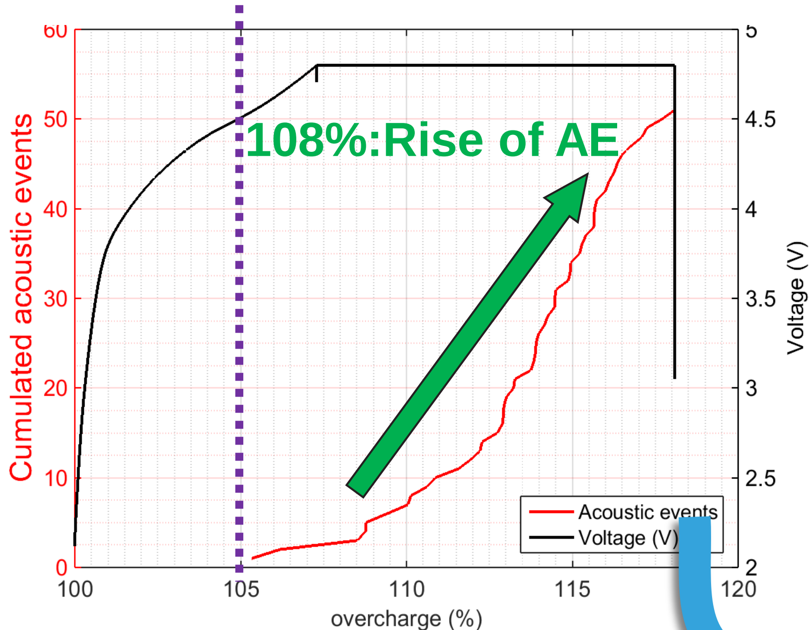


» Rise of EA at 104% overcharge with no high level energy AE

» Cell showed electrolyte leakage

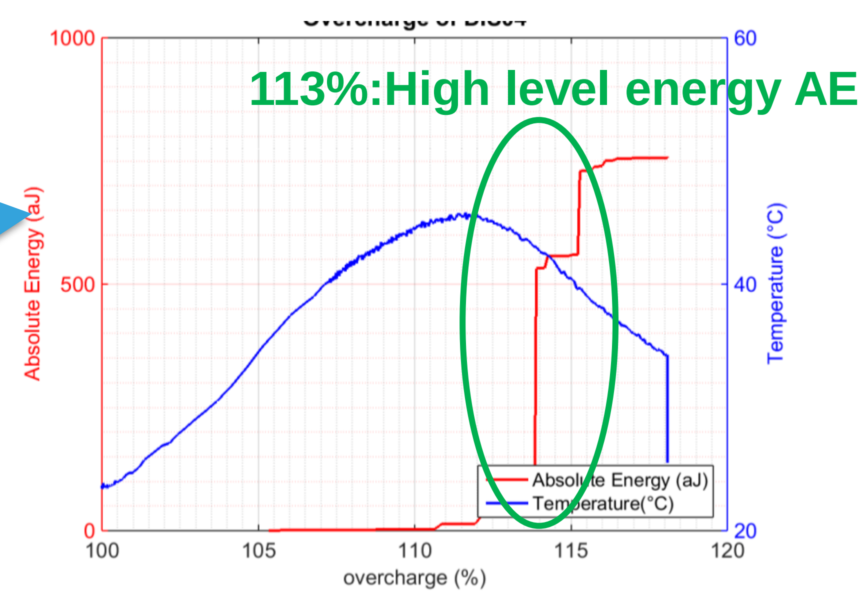
Overcharge tests / Acoustic emission

Pouch, LTO/LFP



105%: Start of AE

- 107%: Rise of acoustic hits at plateau of 4.7V
- 113% (42°C): High energy ??



- Strong signal measured <u>after</u> temperature decrease
- No opening of the cell

Conclusions: sensors for SOS indication

	Thermal stability	Overcharge
Acoustic emission sensors	Early detection Data treatment and calibration required	Early detection Absolute energy as parameter
Deformation gauges	Large temperature variation alters measurement reliability	Strong signal Simultaneous or before temperature rise

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Thank you!
Advanced sensors

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