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Ultrasound interrogation, an operando technique for the monitoring of battery materials

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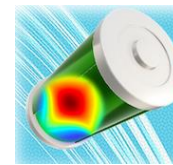
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ULTRASOUND INTERROGATION, AN OPERANDO TECHNIQUE FOR THE MONITORING OF BATTERY MATERIALS

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b) Univ Grenoble Alpes, Université Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, Grenoble, F-38000, France

Dr Nicolas Guillet (CEA/Liten)

- **CV**

- *Chemistry / electrochemistry (Univ. Grenoble, INP Grenoble)*
- *PhD Material process & engineering (Mining school St Etienne, France) 1998 – 2001: « Potentiometric gas sensors for automotive application »*
- *Post-doctoral (INRS – Varennes, Canada) 2002 – 2004: « Non noble catalysts for electrochemical reduction of oxygen and H₂O₂ electrosynthesis »*
- *Since 2005: research engineer at CEA/Liten; Senior expert on electrochemical storage*



- **knowledge and expertise**

- *Electrochemistry / electrocatalysis*
- *Fuel cells (catalyst synthesis, electrodes fabrication, tests and characterization)*
- *Hydrogen production devices (PEM / Alkaline electrolyzers)*
- *Electrochemical device for energy conversion*

Contact: nicolas.guillet@cea.fr

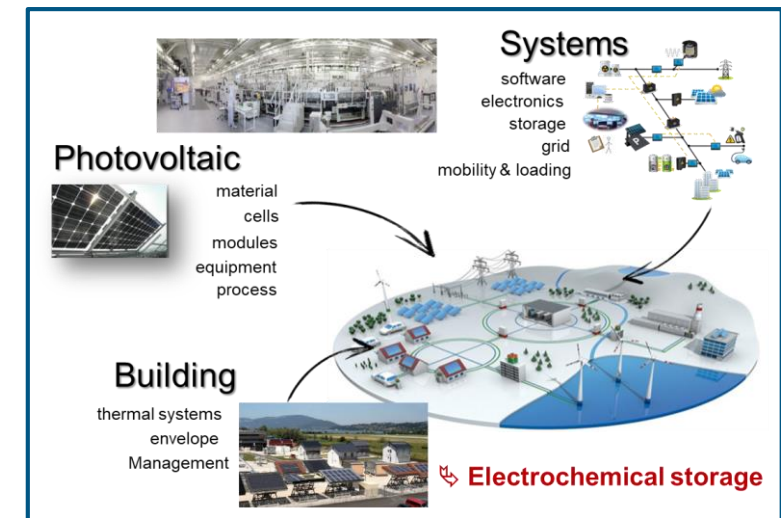
CEA - LITEN ?

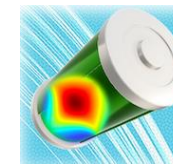
- CEA : French Alternative Energies and Atomic Energy Commission (since 1945)
- Liten : Research institute dedicated to the energy transition



Liten headquarters at **Grenoble** ~ 1100 researchers,

~300 at INES campus **Le Bourget-du-Lac**





Stand-alone systems



Grid-connected systems



Integration in buildings



Experts
Electrochemistry,
Modelling, iElectrical
engineering...



Test facilities
350 battery testing
channels, abusive
conditions and safety
tests, high voltage
platform



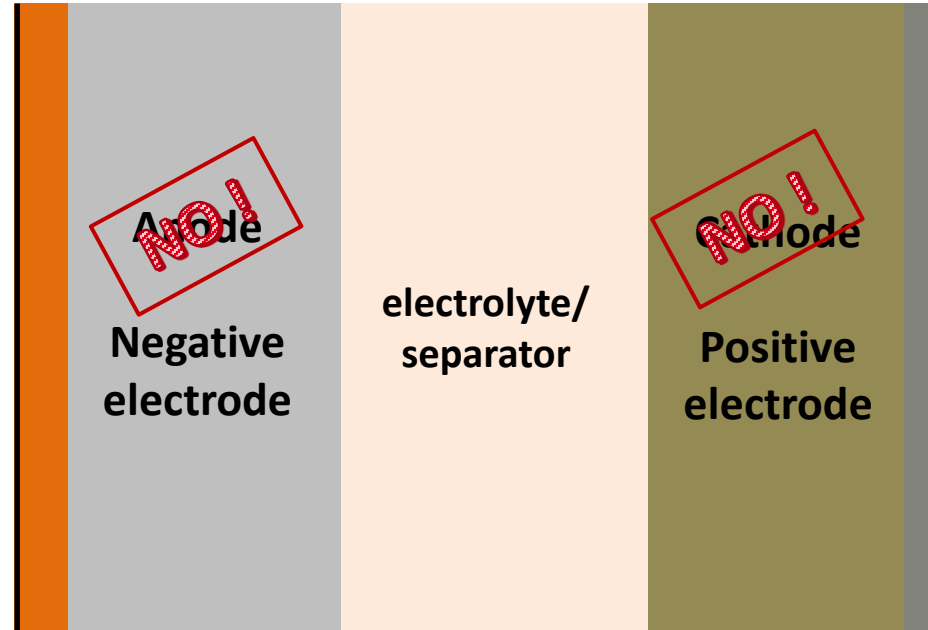
1) Select the most appropriate storage systems for the intended application

2) Development of battery of advanced management strategies

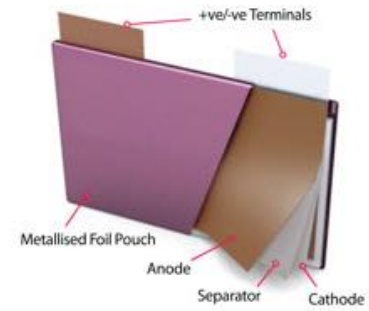
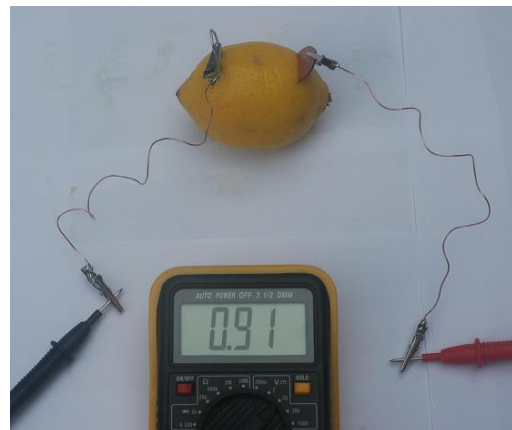
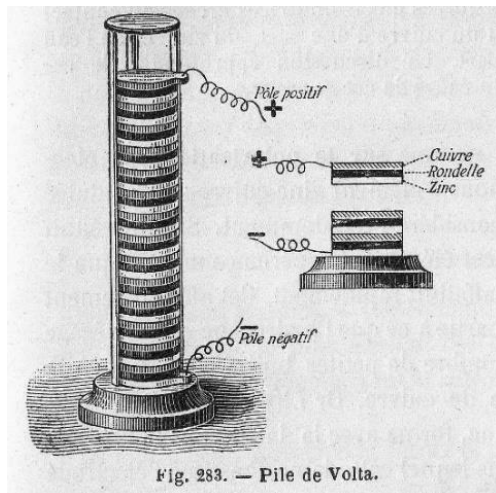
A BATTERY : A SIMPLE SYSTEM...

- In summary, essential constituents of an elementary battery cell :

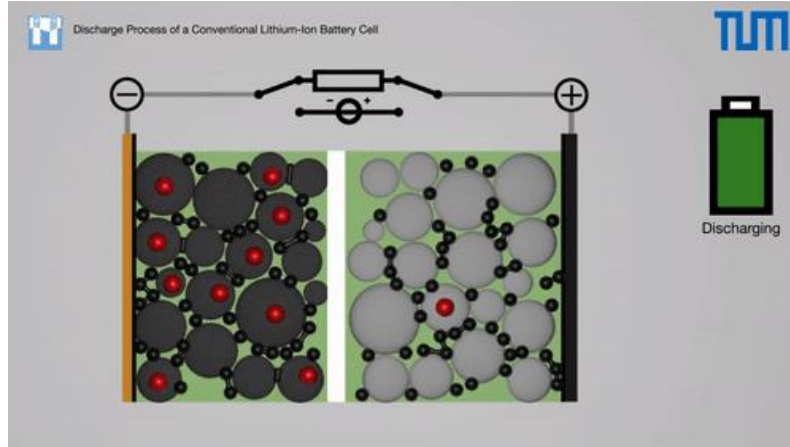
Current collector
negative electrode



Current collector
positive electrode



A BATTERY : A SIMPLE SYSTEM ... BUT COMPLEX MECHANISMS



During cycling

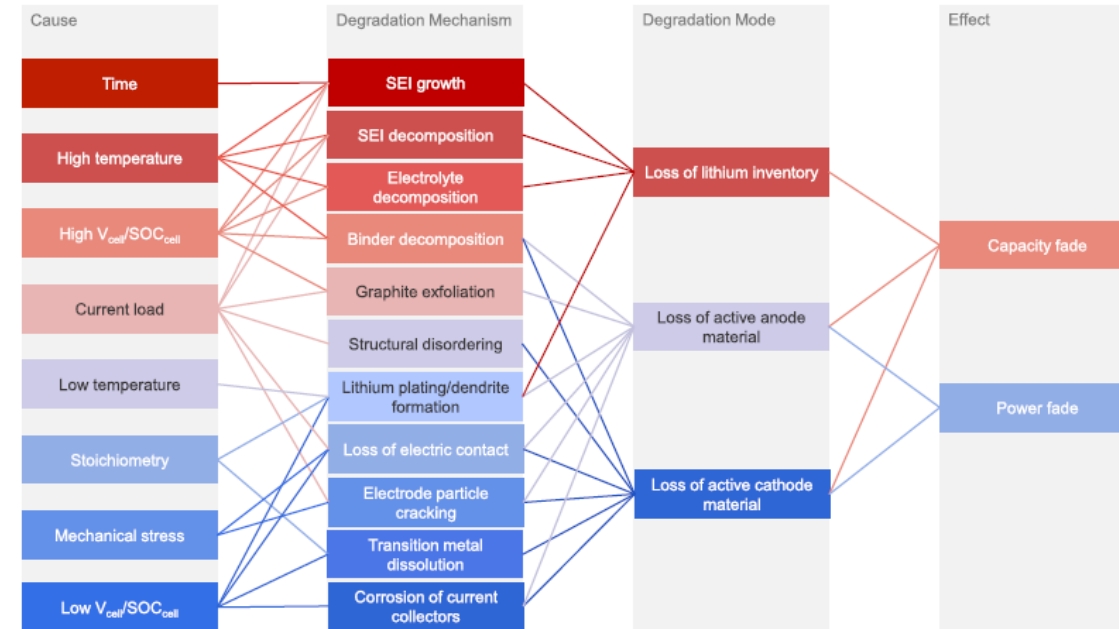
Li⁺ ion displacement from one electrode to the other:

- For positive NMC electrodes, the volume change is almost zero in the range $x = 0$ to 0.67. Then, 5 % of the volume change is noted in the last third of Li⁺ insertion [1,2].
- The volume change related to graphite lithiation is about 10 % [3,4], and the main volume change occurs during the first 20% of lithium insertion.

↪ Change in electrode volume (breathing) during operation

↪ The volume change can lead to microcracks in the electrodes and passivation layers

During calendar / cycling aging



R. Birkl, M.R. Roberts, E. McTurk, P.G. Bruce, D.A. Howey «Degradation diagnostics for lithium ion cells», *J. Power Sources*, vol.341, p.373-386 (2017)

- Multiple causes for similar consequences
- Strongly coupled mechanisms
- Phenomena that add up (battery history)

[1] N. Yabuuchi *et al.*, "Novel lithium insertion material of LiCo1/3Ni1/3Mn1/3O2 for advanced lithium ion batteries" *Journal of Power Sources* Volumes 119–121, 1 June 2003, Pages 171–174

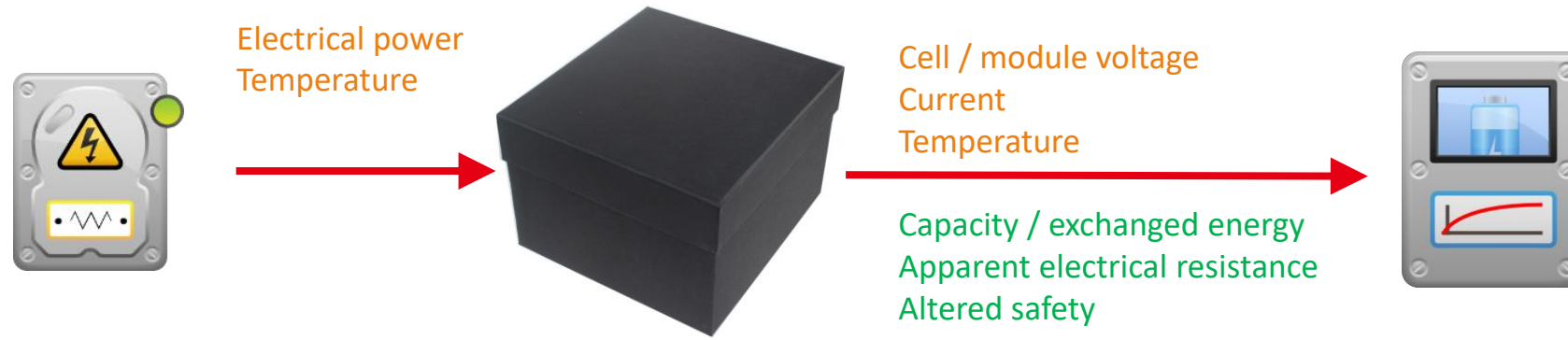
[2] A. K. Padhi *et al.* "Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries" *J. Electrochem. Soc.* 1997 volume 144, issue 4, 1188-1194

[3] M. Broussely *et al.*, "Main aging mechanisms in li-ion batteries" *J Power Sources*, vol. 146, no. 1-2, pp. 90–96, 2005.

[4] Naoki Nitta *et al.*, "Li-ion battery materials: present and future" *Materials Today* Volume 18, Number 5 June 2015 pp. 252 - 264

A BATTERY : A SIMPLE SYSTEM ... BUT COMPLEX MECHANISMS

- Only few information available during operation : the battery, a black box?

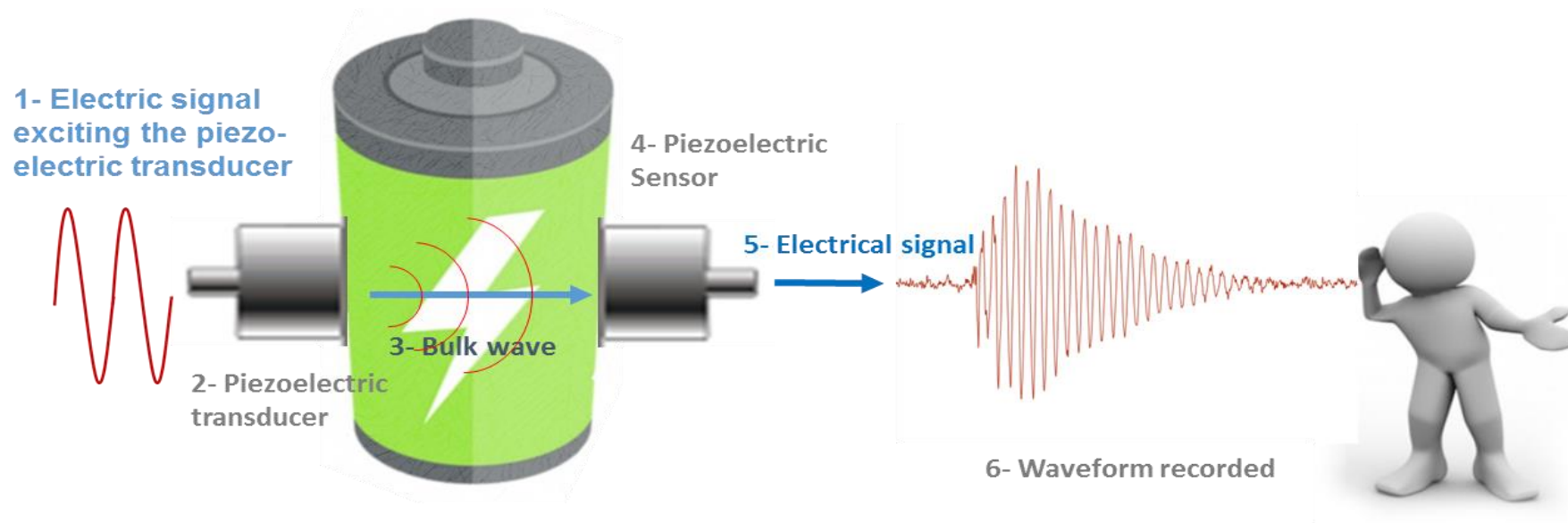


↳ Only 3 independent parameters used for battery monitoring & SoC, SoH estimation :

Cell voltage, current & temperature (and their evolution with time)

➔ Additional independent parameters are required for a more accurate monitoring

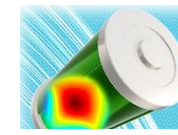
- Physical change of materials (???)



- **Non-destructive test (NDT) method;**
 - Study the propagation of acoustic waves throughout the battery's materials;
 - Acoustic waves interact with materials and interfaces

➤ **Detect materials density variations, discontinuities, defects, bubbles generation...**

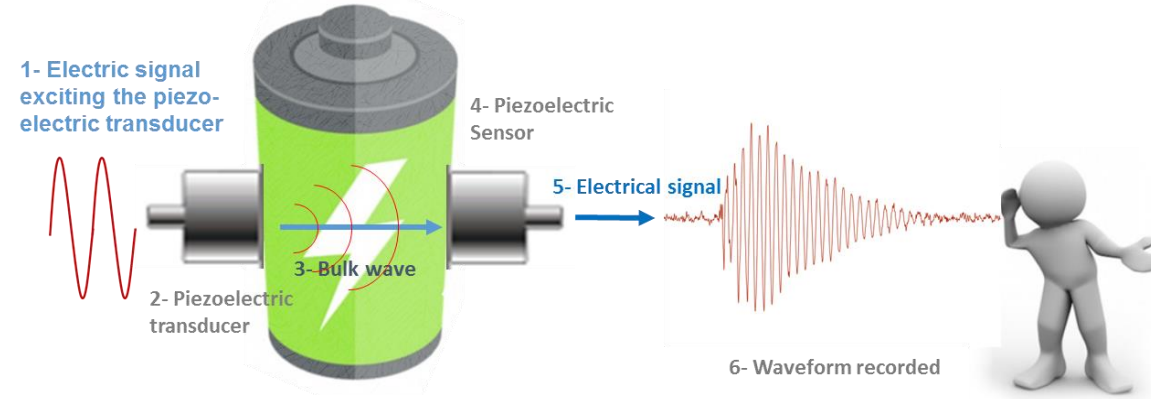
ULTRASOUND INTERROGATION FOR BATTERY MONITORING ?



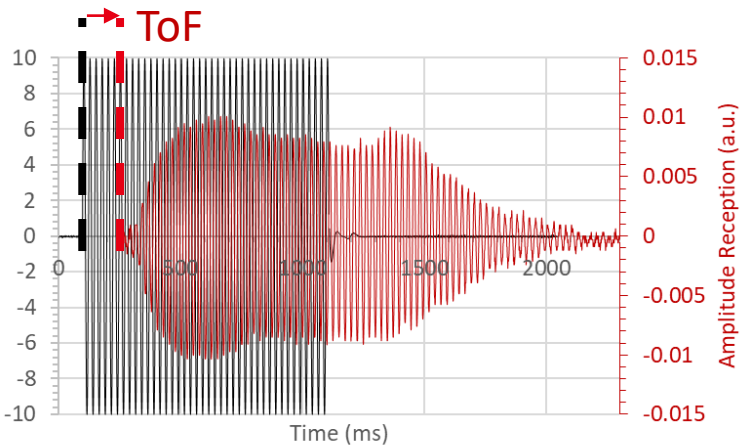
International Operando Battery Days

Grenoble, France, 16-18 May 2022

- Parameters of interest

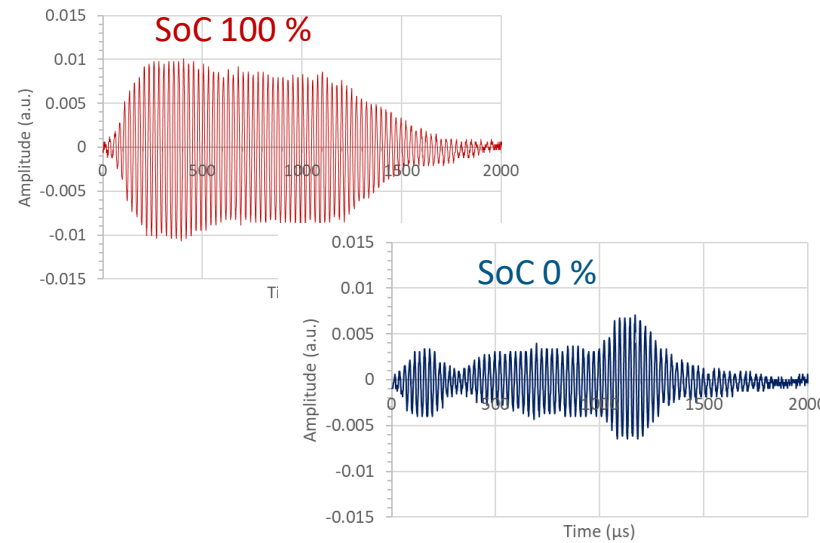


Time of Flight (delay between emission and reception)



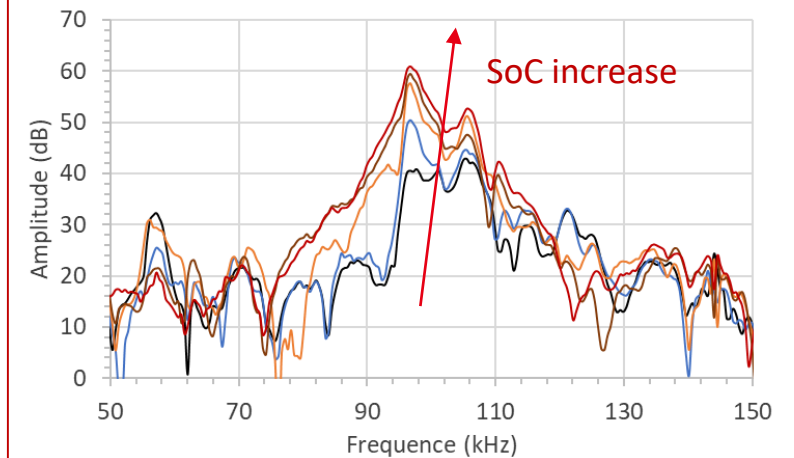
Depending on the distance between the transducers and the sound speed in the materials (related to density / young modulus)

Shape of the waveform



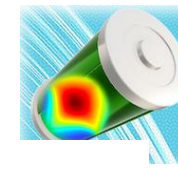
Depending on the interactions of the acoustic wave with the materials / interfaces inside the battery (porosity / interfaces)

Power spectrum density



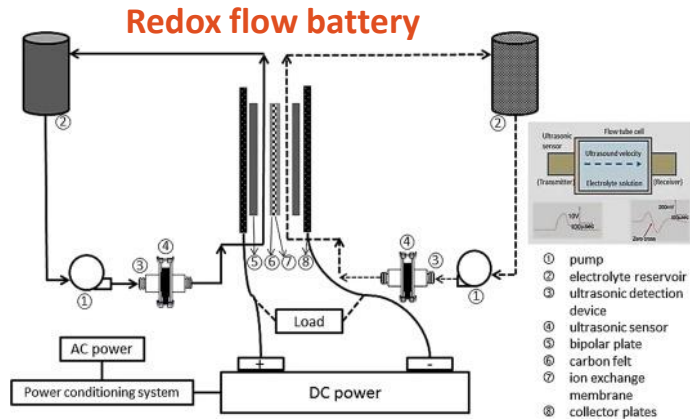
Energy and strength of the signal transmitted depending on the properties of the materials (density, Young modulus, porosity etc...)

3- ULTRASOUND INTERROGATION FOR BATTERY MONITORING ?



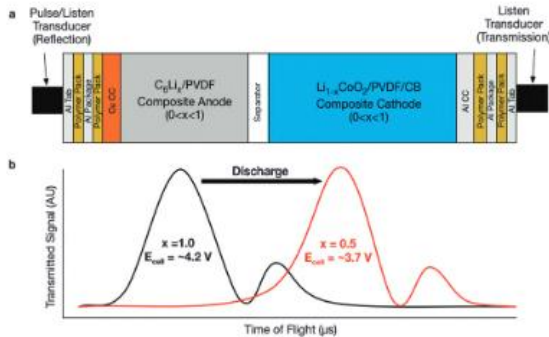
- Previous works

- Density of electrolyte measurement

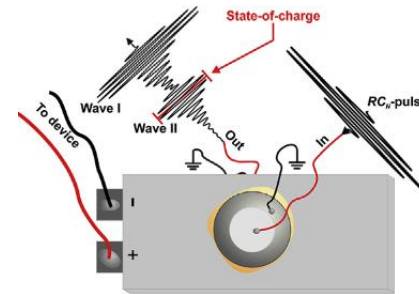


Y-S. Chou, N.-Y. Hsu, K.-T. Jeng, K.-H. Chen, and S.-C. Yen, "A novel ultrasonic velocity sensing approach to monitoring state of charge of vanadium redox flow battery," *Appl. Energy*, vol. 182, pp. 253–259, 2016.

- Material change during cycling & ageing (Li-ion batteries)



A. G. Hsieh et al., "Electrochemical-Acoustic Time of Flight: In Operando Correlation of Physical Dynamics with Battery Charge and Health," *Energy Environ. Sci.*, vol. 8, no. 5, pp. 1569–1577, 2015



L. Gold et al., "Probing lithium-ion batteries' state-of-charge using ultrasonic transmission – Concept and laboratory testing," *J. Power Sources*, vol. 343, pp. 536–544, 2017.

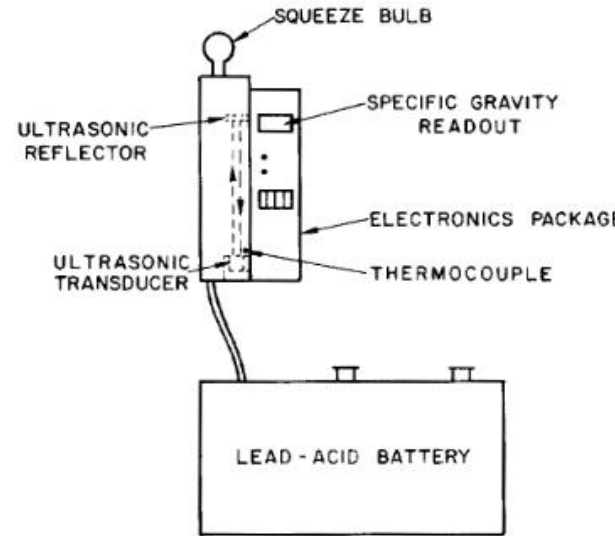
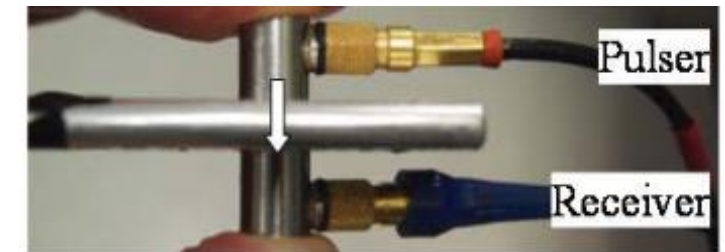


Fig. 10. Conceptual design of improved hydrometer.

Lead – acid battery

C. A. Swoboda et al., "Development of an Ultrasonic Technique to Measure Specific Gravity in Lead-Acid Battery Electrolyte," *IEEE Trans. Sonics Ultrason.*, vol. 30, no. 2, pp. 69–77, 1983

J. X. Liu, G. F. Li, W. Q. Xiong, H. J. Xiao, and L. Wang, "An ultrasonic approach to measure the density of battery electrolyte," *Proc. - Int. Conf. Electr. Control Eng. ICECE 2010*, no. 1, pp. 414–418, 2010.



B. Sood et al., "Health Monitoring of Lithium-ion Batteries," in *Proc. 2013 IEEE Symposium on Product Compliance Engineering (ISPC)*, 2013, pp. 3–8.

ULTRASOUND INTERROGATION FOR BATTERY MONITORING ?



- Experimental setup:
 - Piezo-electric transducers

PZT ceramic ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$)



EVERLASTING
<https://everlasting-project.eu/>

TEESMAT
 Open Innovation Test Bed for Electrochemical Energy Storage Materials
<https://www.teesmat.eu/>

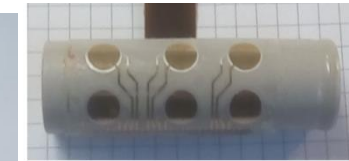
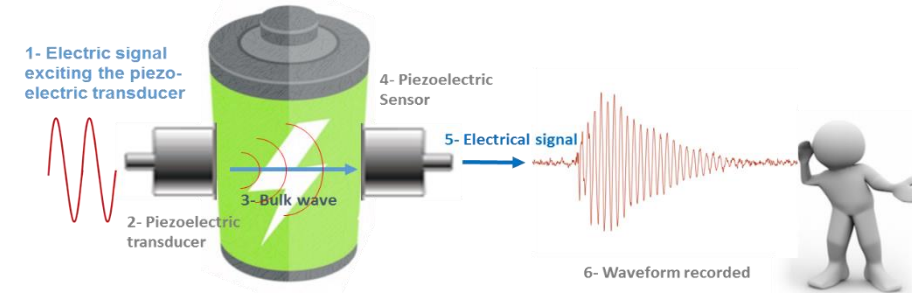
Ø20mm,
 thickness 600 µm
 ~ 0.3 €

PZT ceramic piezoelectric transducer (22.4 mm x Ø19 mm)
<https://www.physicalacoustics.com/by-product/sensors/F15a-100-450-kHz-High-Sensitivity-Flat-Frequency-Response-AE-Sensor>

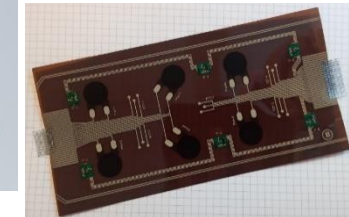
Polymer P(VDF-TrFE)



cea



Hi-C
<http://www.hi-c.eu/>

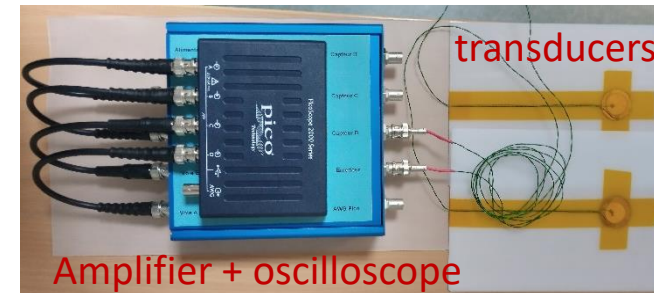


SPARTACUS
<https://www.spartacus-battery.eu/>

- Data acquisition / Signal analysis :
 - Amplifier
 - Digital oscilloscope (~600 €)
 - Mini PC (~150 €)



Oscilloscope (Emission + 4 channels reception)



Amplifier + oscilloscope



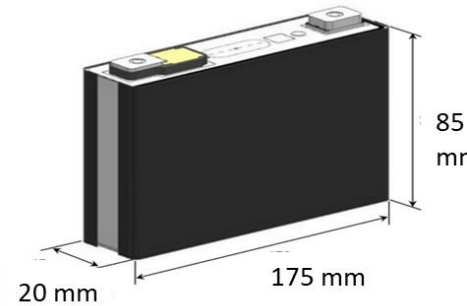
Mini PC

ULTRASOUND INTERROGATION FOR BATTERY MONITORING ?

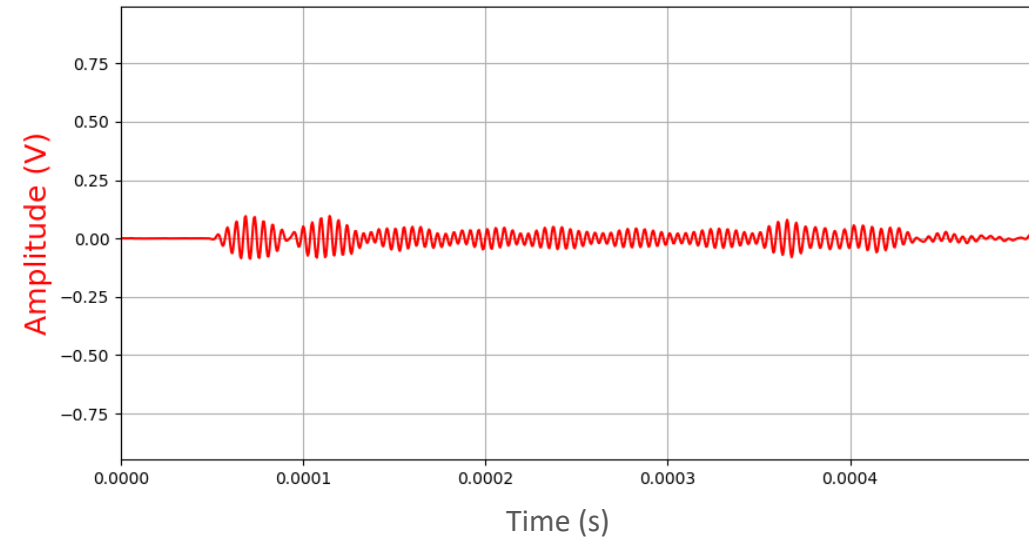
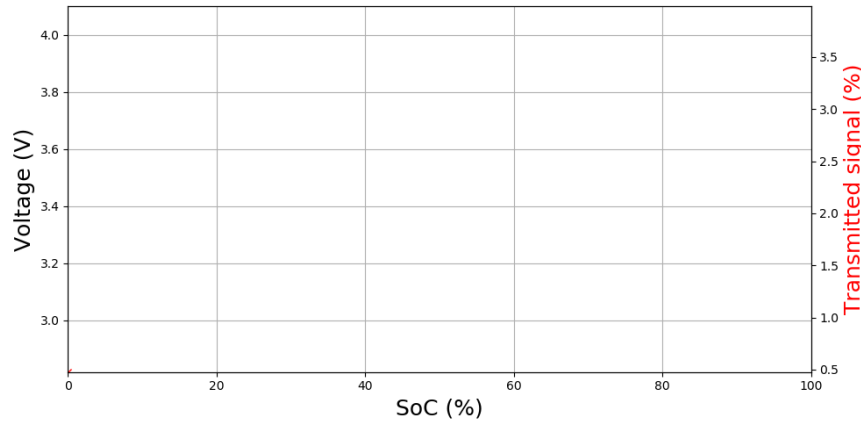
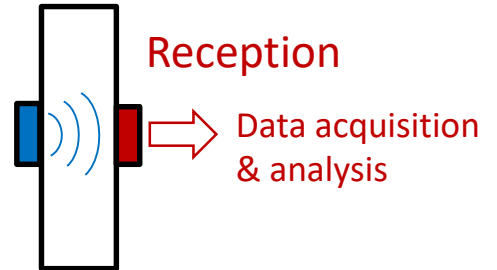


- Exemple of results:

- Prismatic NMC+LMO blend / Graphite 23 Ah



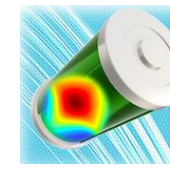
Emission
220 kHz, 2 V
0.5 ms



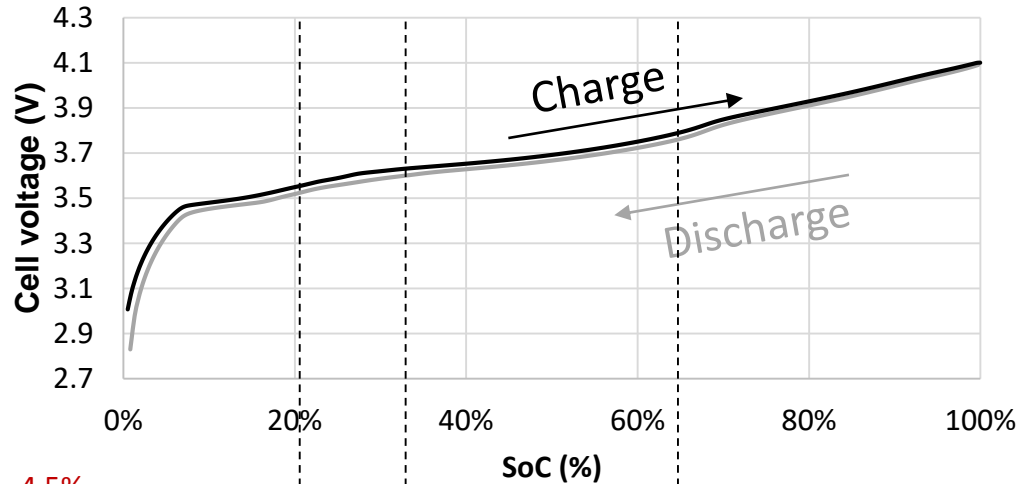
↪ Significant evolution of the transmitted acoustic signals during cycling

↪ Very good repeatability over successive charge – discharge cycles

ULTRASOUND INTERROGATION FOR BATTERY MONITORING ?



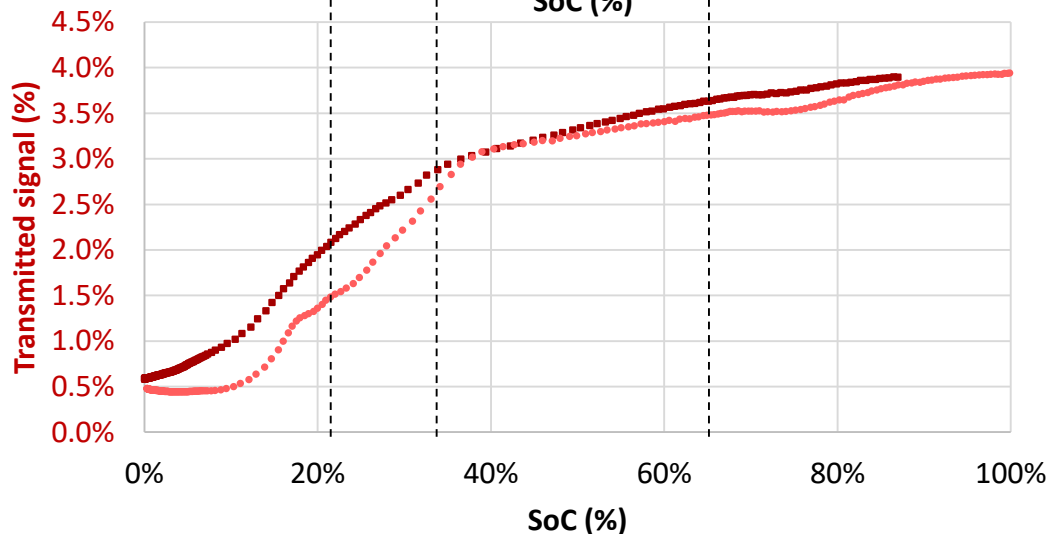
- Acoustic signal evolution during charge – discharge cycling
 - Prismatic NMC+LMO blend / Graphite 23 Ah



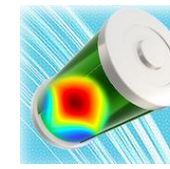
↳ The **transmitted signal** goes back to its initial value at the end of the charge/discharge cycle

↳ The slope change are characteristic of the redox couples of materials inside the battery

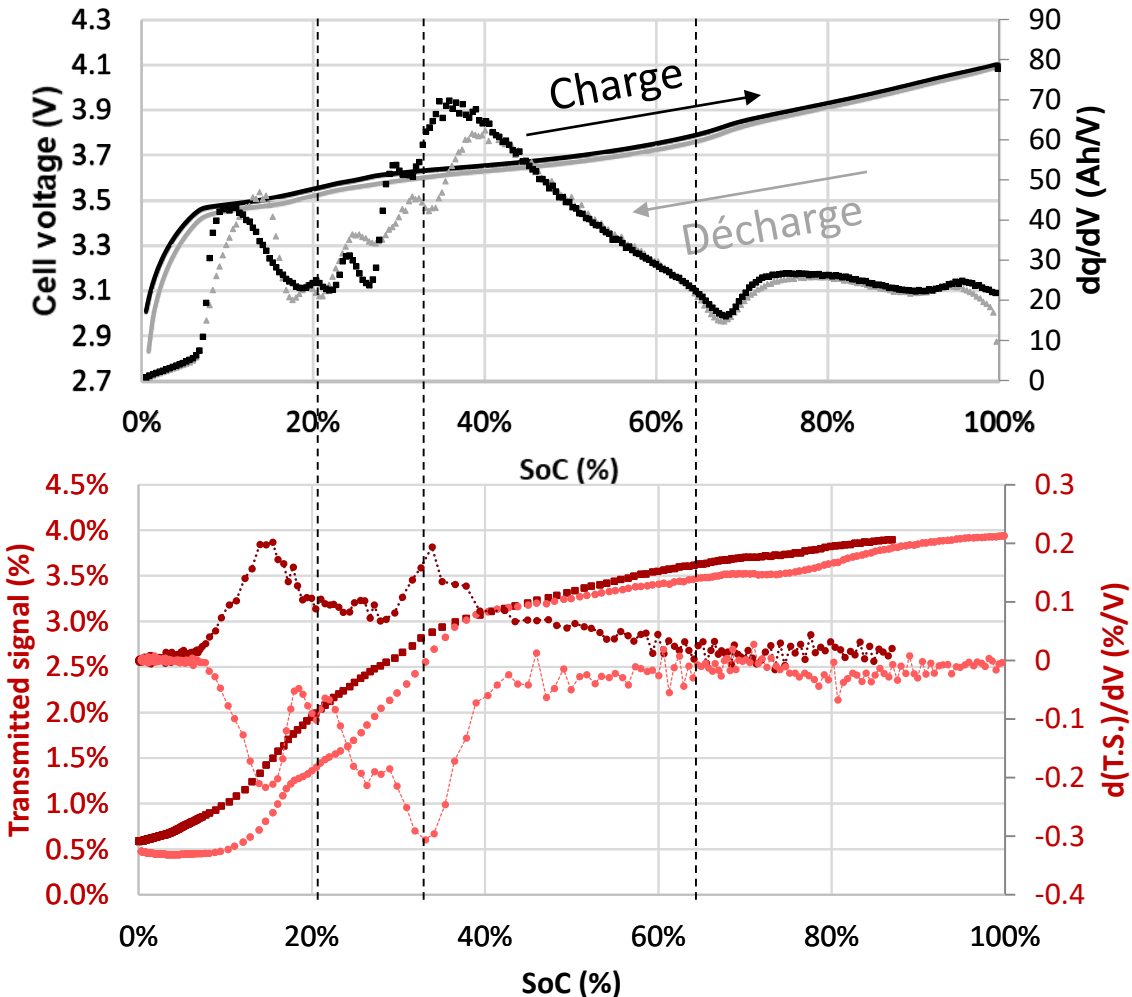
↳ Slope change observable on the **transmitted signal** curves occur at the same SoC as those in voltage



ULTRASOUND INTERROGATION FOR BATTERY MONITORING ?



- Acoustic signal evolution during charge – discharge cycling
 - Prismatic NMC+LMO blend / Graphite 23 Ah



↪ The **transmitted signal** goes back to its initial value at the end of the charge/discharge cycle

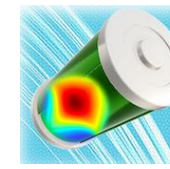
↪ The slope change are characteristic of the redox couples of materials inside the battery

↪ Slope change observable on the **transmitted signal** curves occur at the same SoC as those in voltage

➔ One way to study slope breaks is to represent dq/dV

➔ Representation of $d(T.S.)/dV$ plot allow to better visualize the slope change of the **transmitted signal**

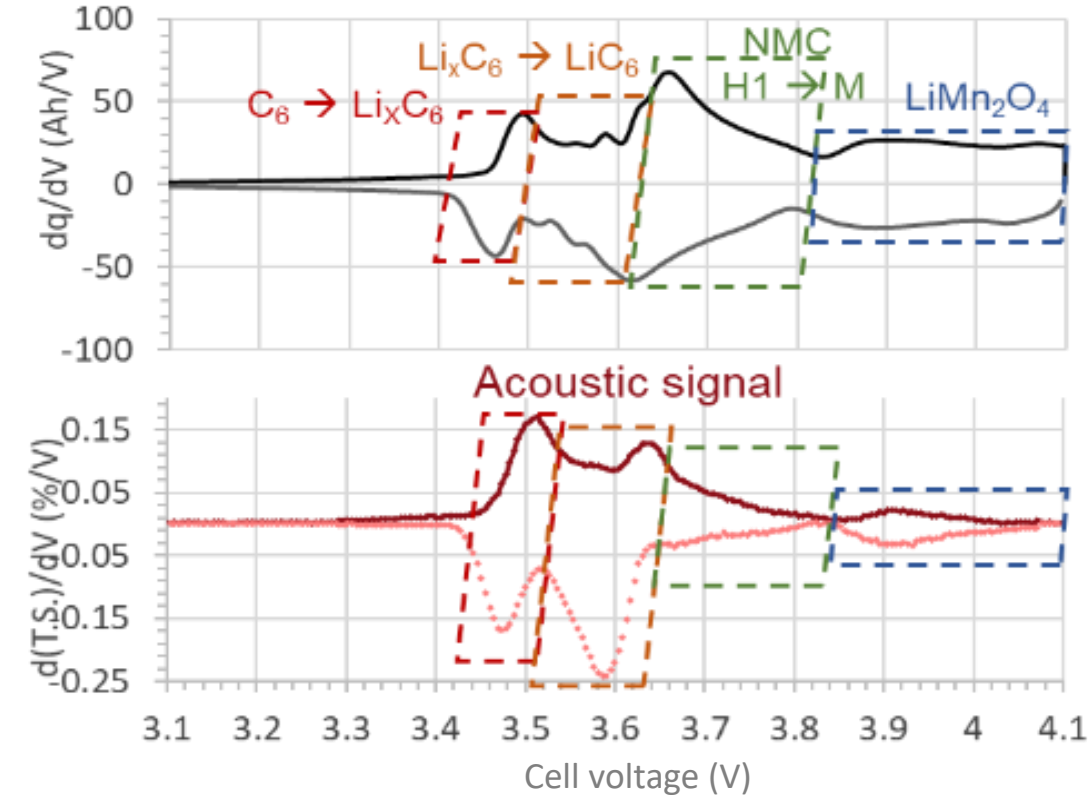
ULTRASOUND INTERROGATION FOR BATTERY MONITORING ?



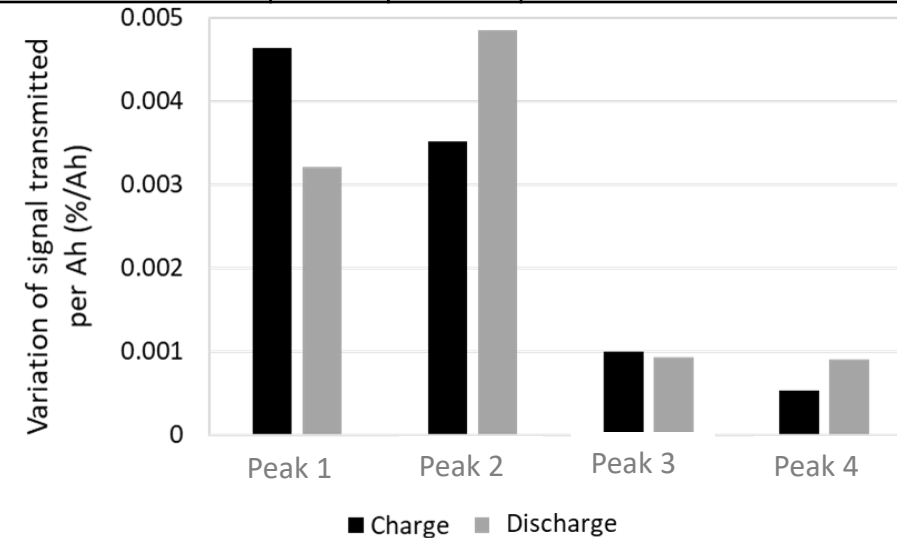
Acoustic signal evolution during charge – discharge cycling

- Prismatic NMC+LMO blend / Graphite 23 Ah

Cyclic voltammetry 5, 10 & 15 $\mu\text{V}\cdot\text{s}^{-1}$ at 25 °C



| | Redox peak | | Identification | Acoustic | |
|------------------------|---------------|-----------------|--|---------------|-----------------|
| | $E_{1/2}$ (V) | ΔE (mV) | | $E_{1/2}$ (V) | ΔE (mV) |
| Peak 1 (3,40 – 3,55 V) | 3,48 | 37 | Attributed to the graphite lithiation / delithiation | 3,49 | 41 |
| Peak 2 (3,55 – 3,60 V) | / | / | Secondary peaks of graphite lithiation / delithiation | / | / |
| Peak 3 (3,60 – 3,85 V) | 3,64 | 41 | Attributed to the H1 → M à la transition of NMC | 3,62 | 45 |
| Peak 4 (3,85 – 4,10 V) | 3,90 | / | Double peak attributed to the lithiation of the LMO spinel structure | 3,91 | / |



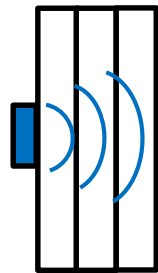
➡ Largest variation of acoustic signal (in % per Ah) is observed during graphite lithiation

SOC ESTIMATION OF BATTERY CELLS AND MODULES

- Acoustic signal evolution during charge – discharge cycling
 - LiPo battery pack 3S, 2200 mAh



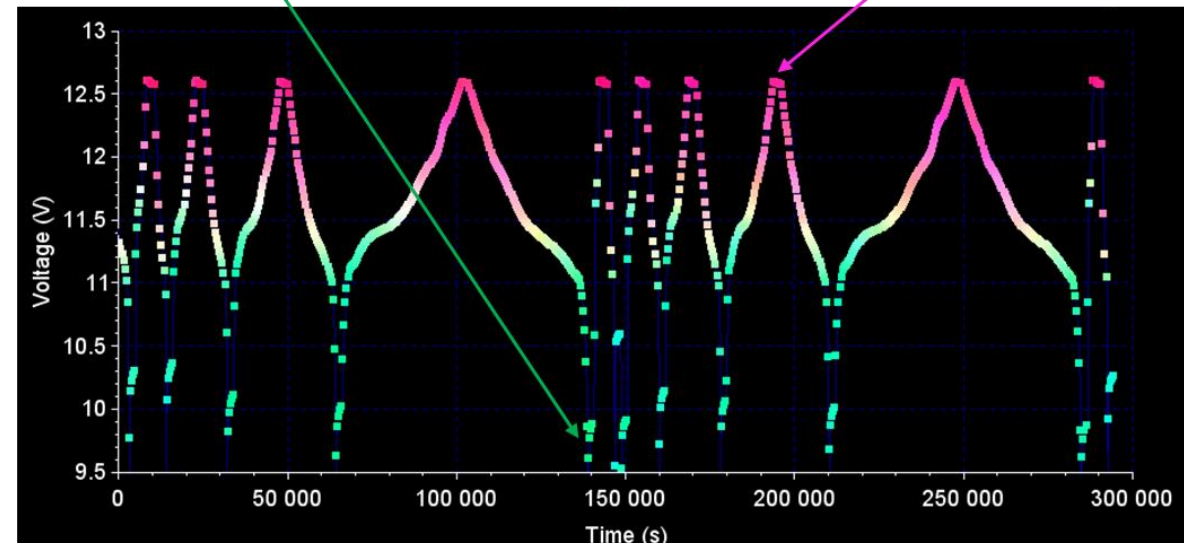
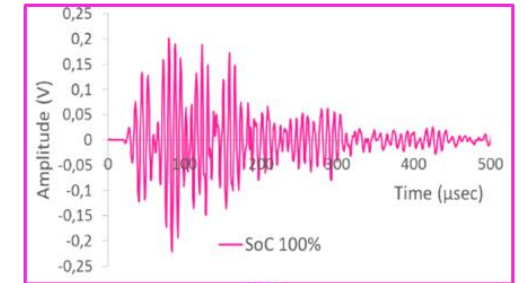
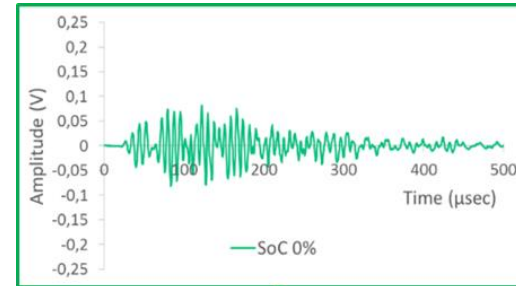
Emission
220 kHz, 2 V
0.5 ms



Reception

⇒ Data acquisition & analysis

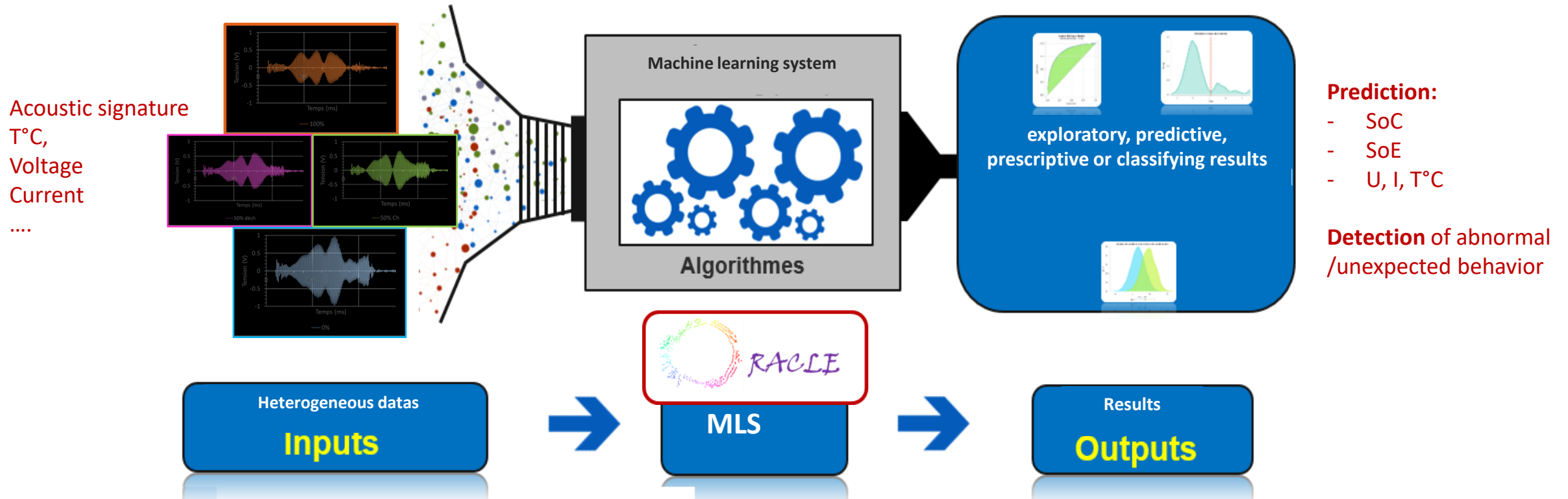
Cycling at 25 °C and different C-rates: 2C, 1C, C/2, C/4, C/10



↪ Very good repeatability over successive charge – discharge cycles at different C-rates

➔ Possible to estimate the state of charge from variations of the physical properties of the materials, independently of the electrochemical parameters (U, I, Q)

- Simple machine-learning tools ?



SOC ESTIMATION OF BATTERY CELLS AND MODULES

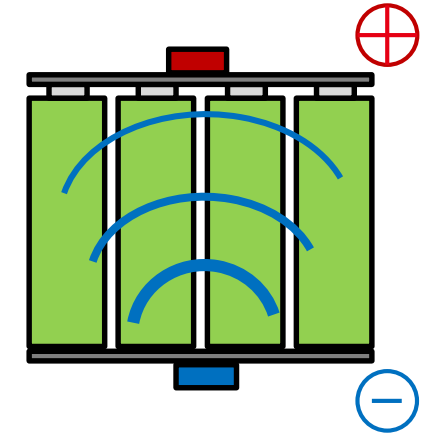
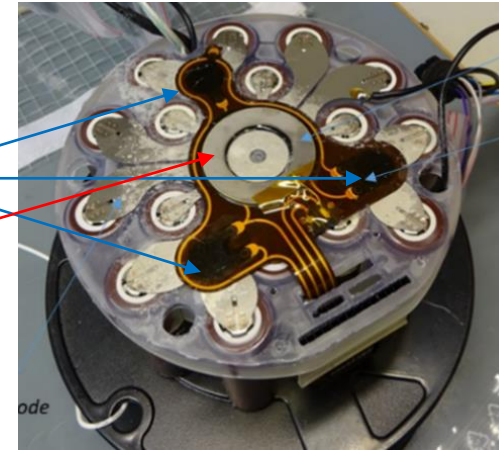
- Exemple of results:
 - Module OASIS : 18S (NMC/Graphite, 18650 cells) - 45 Ah



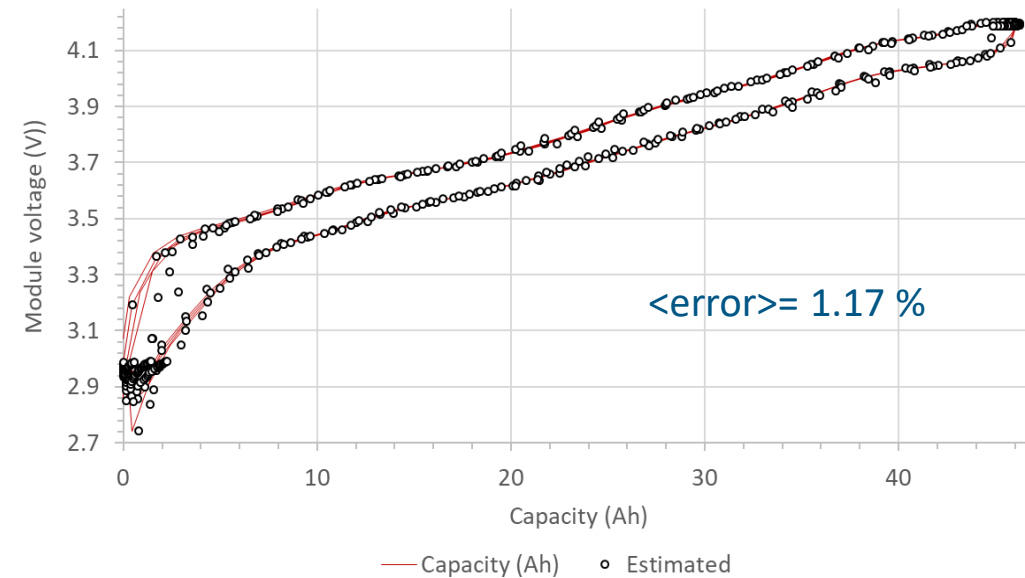
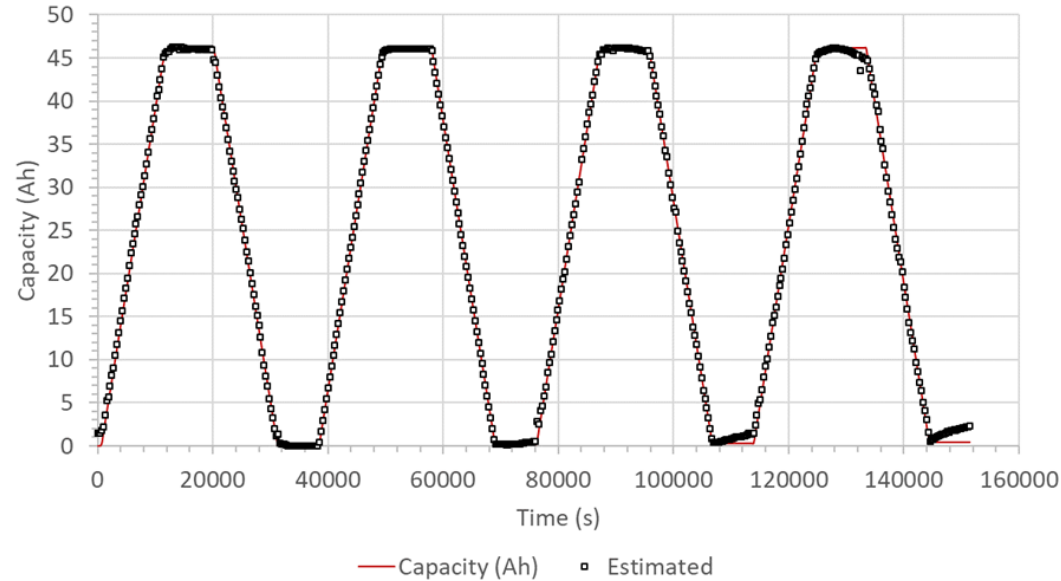
<https://project-oasis.eu/>

P(VDF-TrFE) transducers (Liten -DTNM)

PZT transducer (commercial)



↪ Estimation of stored capacity from acoustic data (red line = measurement; black dots = estimates)

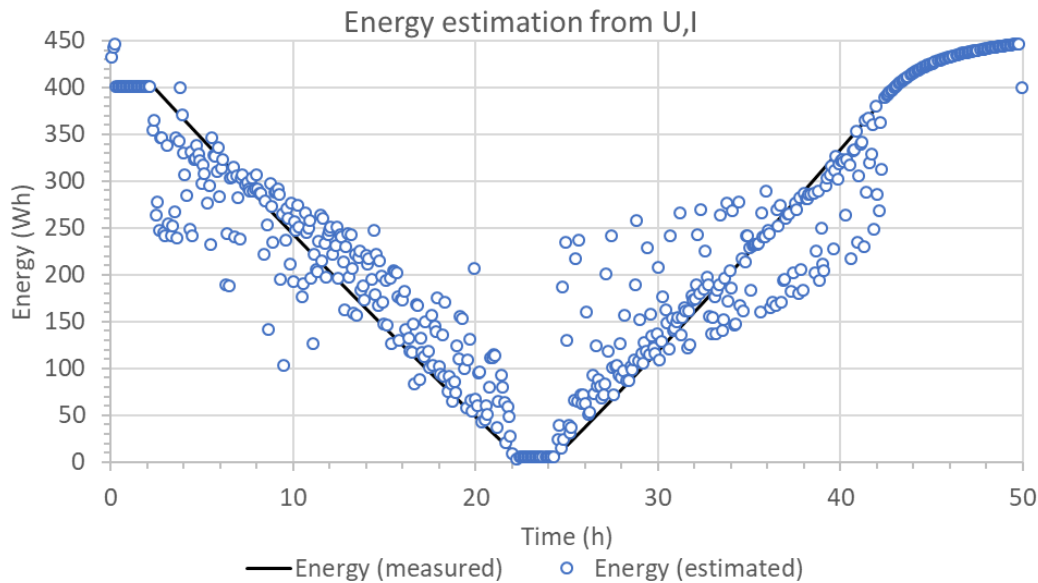


SOC ESTIMATION OF BATTERY CELLS AND MODULES

- **Pb-acid battery** : GNB Sprinter XP6V2800 (6 V / 195 Ah)
(l x H x P) 309 x 241 x 172 mm; 32.6 kg



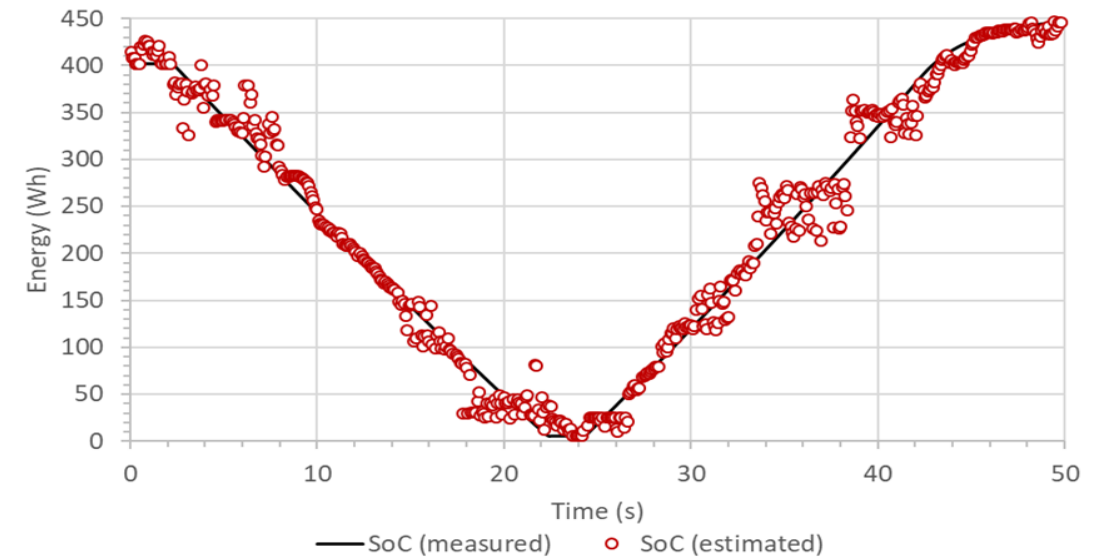
→ « Oracle » algorithm (machine learning)



→ Mean error on full cycle = 6.8 %

→ SoCMax error on full cycle = 48.7 %

Energy estimation using acoustic data



→ Mean error on full cycle = 3.1%

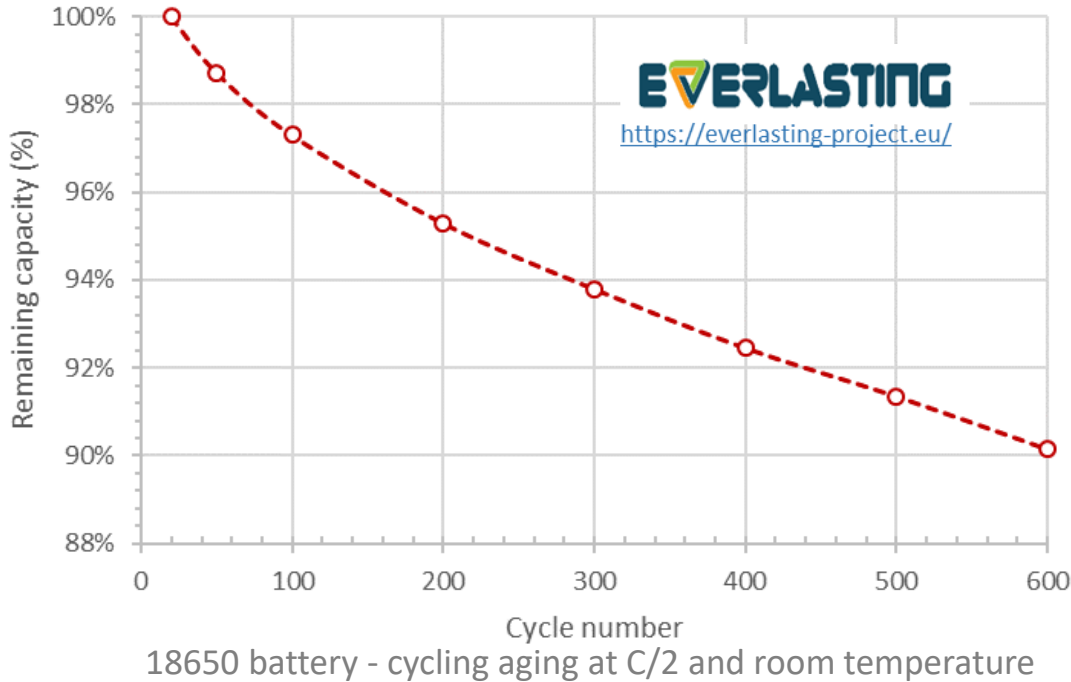
→ Max error on full cycle = 17.6%

→ Possible to estimate accurately the remaining energy available in the battery independently of the electrochemical data

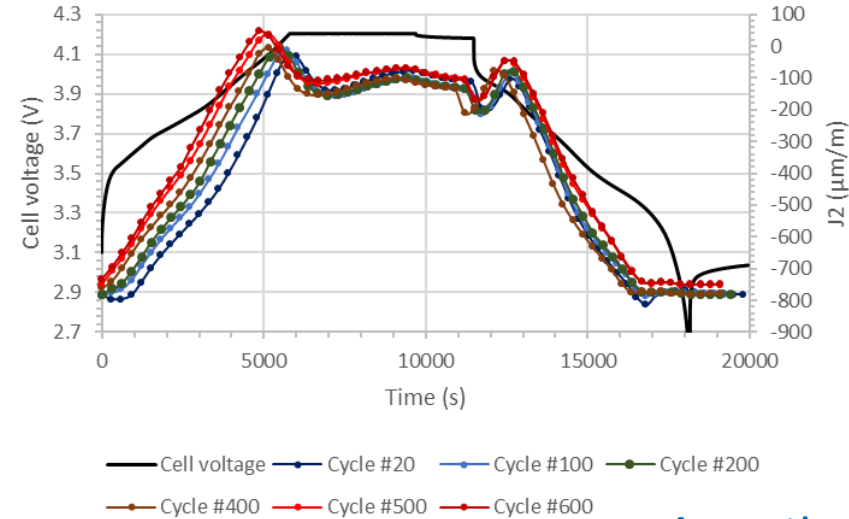
N. Guillet *et al.* 11th International Conference on Lead-Acid Batteries - LABAT'2021, June 2021

EVOLUTION DURING AGEING OF THE BATTERY CELLS

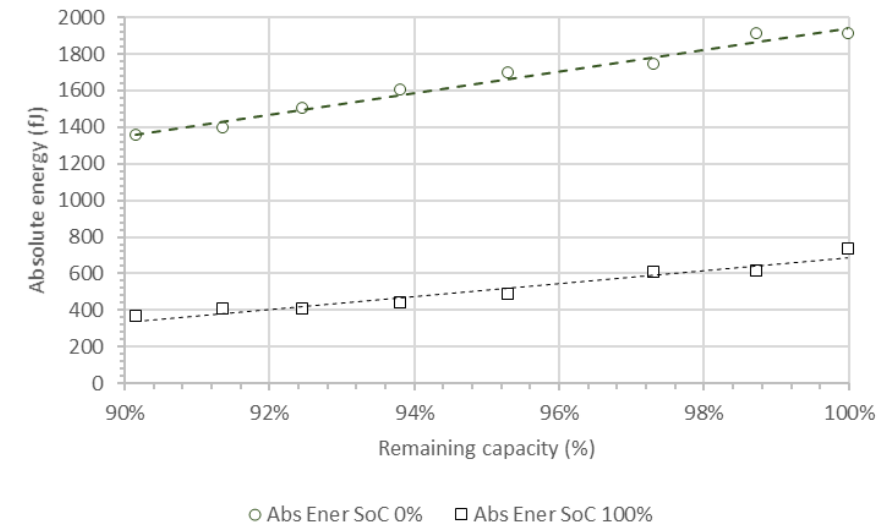
- LG MJ1 INR 18650 3500mAh Battery



Deformation evolution (strain gauges)



Acoustic signal (absolute energy)

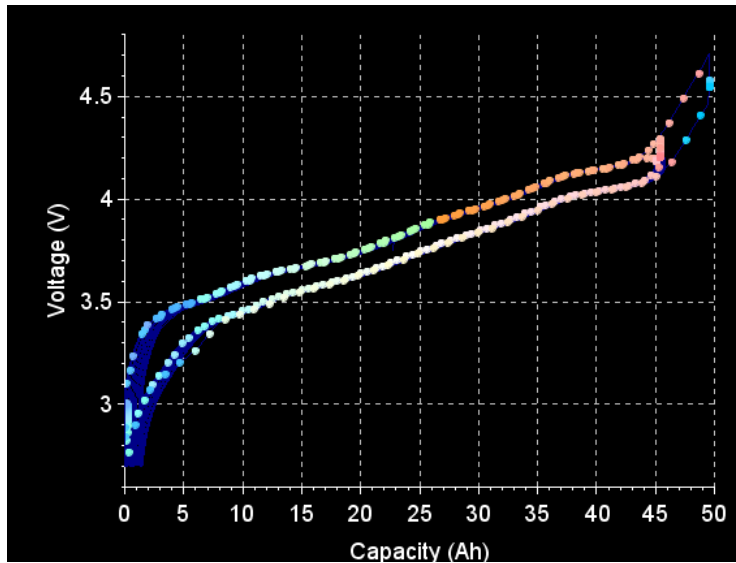
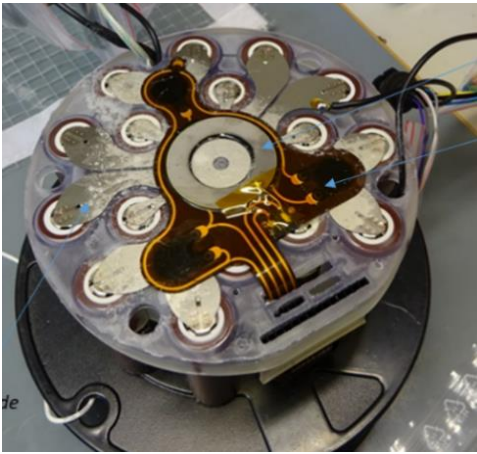


↳ slow and irreversible evolution of the cell deformation (strain gauges) and of the acoustic signal with the state of charge during ageing

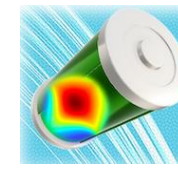
➔ Possible to estimate the remaining useful life of the battery

DETECTION OF DEFECTS DURING OPERATION

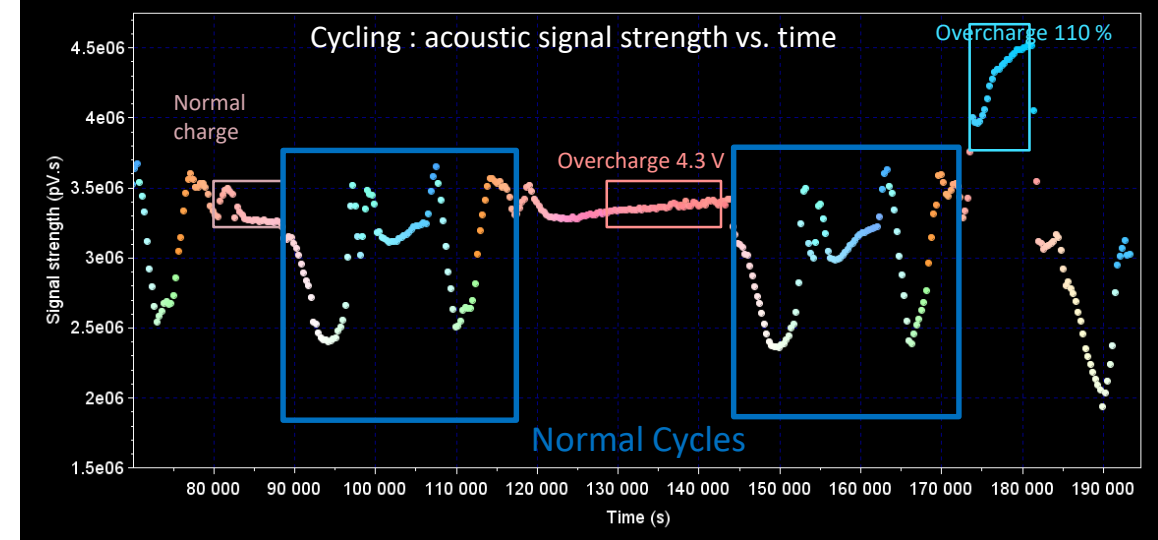
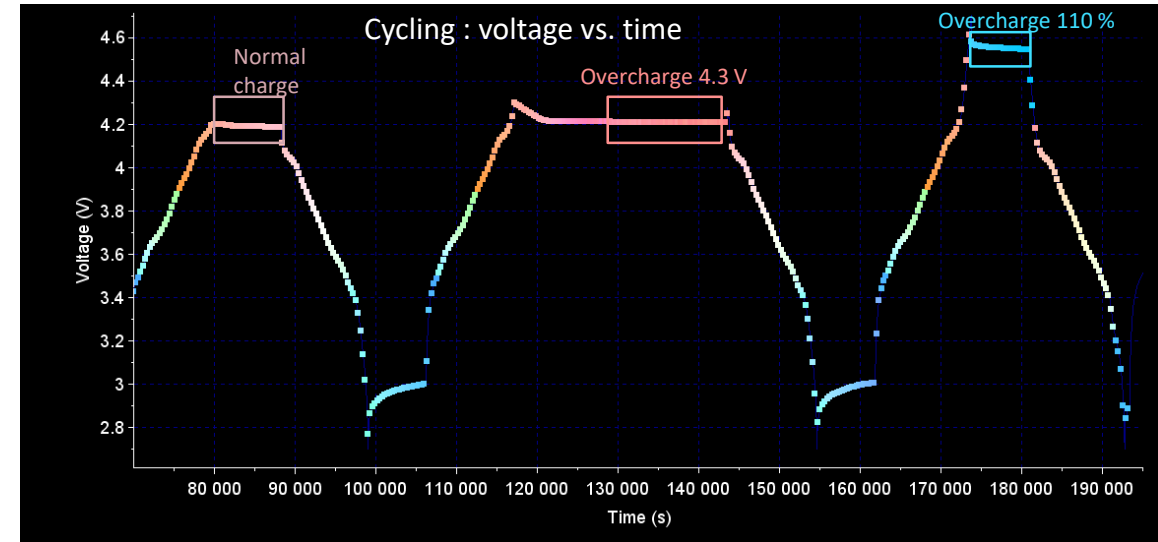
- Example of the overcharge of a 45 Ah module
 - Normal cycling (2.5 V – 4.2 V)
 - Overcharge 4.3 V , followed by normal cycle
 - Overcharge 110 % SoC , followed by 10 normal cycles



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➔ Immediate detection of overcharge

↪ No significant influence of the 4.3 V overcharge on the transmitted acoustic signal

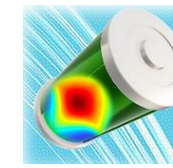
↪ Significant change after 110% SoC overcharge

DETECTION OF DEFECTS DURING OPERATION

- Example of the overcharge of a 45 Ah module
 - Normal cycling (2.5 V – 4.2 V)
 - Overcharge 4.3 V , followed by normal cycle
 - Overcharge 110 % SoC , followed by 10 normal cycles

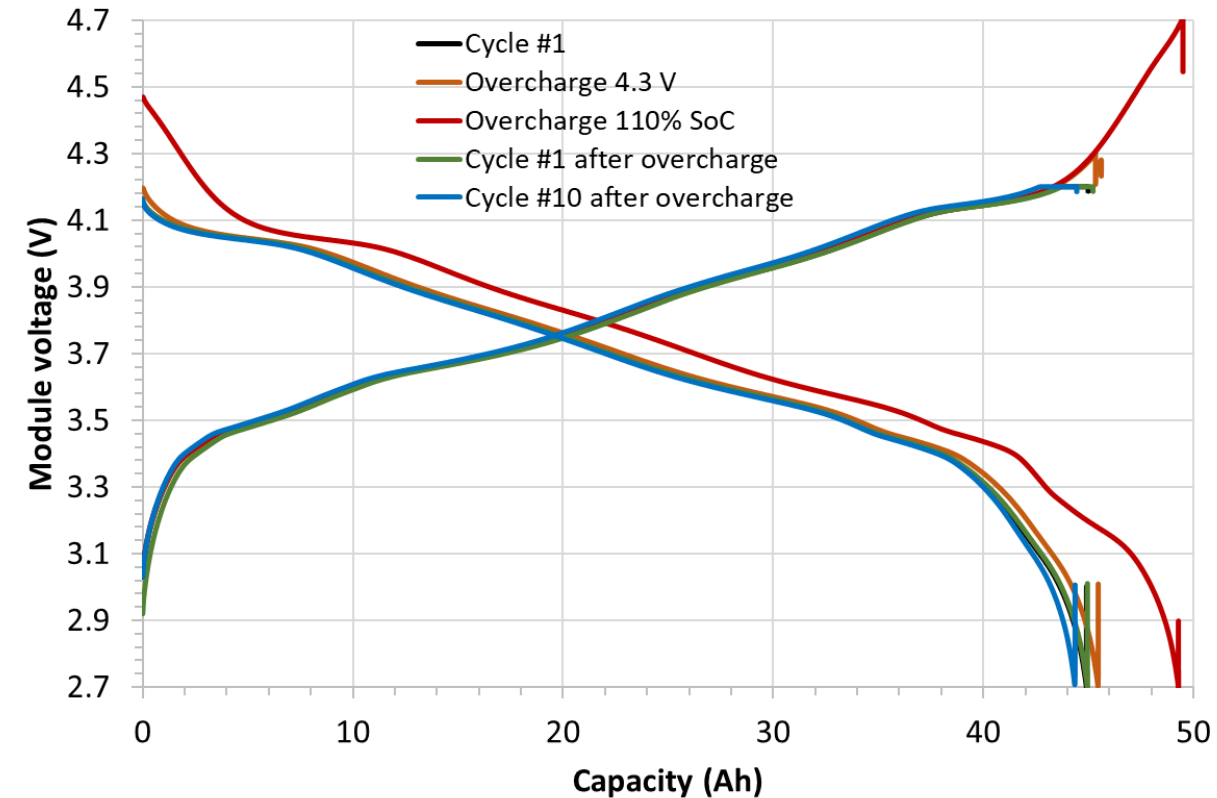
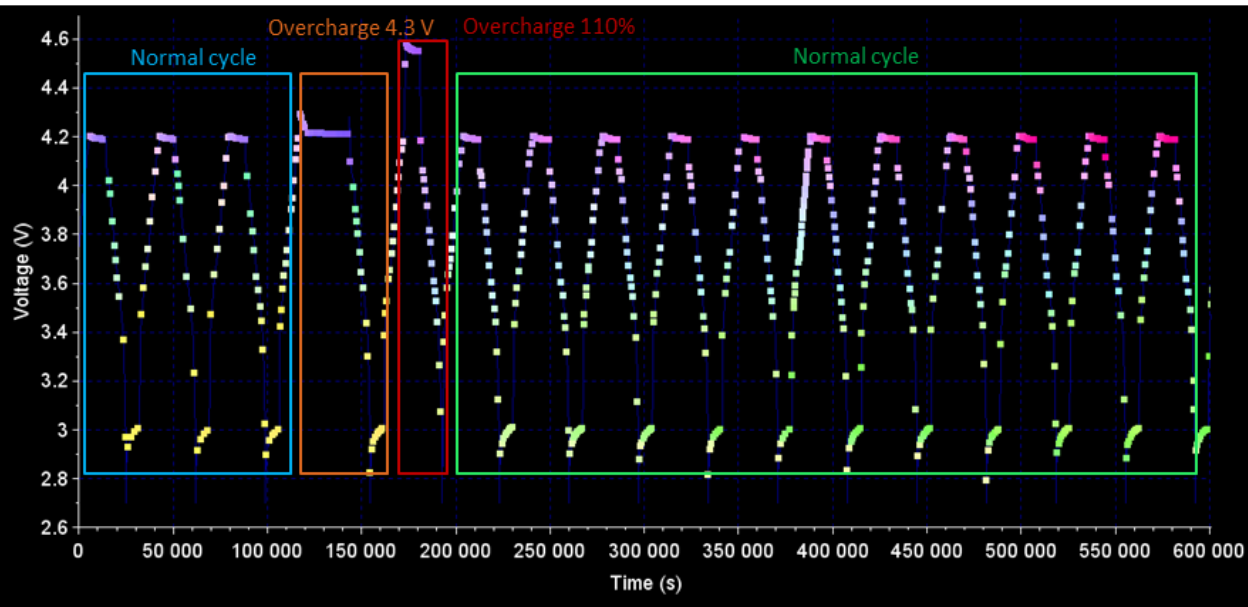


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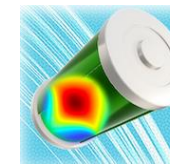
➔ **No visible impact on the charge and discharge curves of the battery**

↪ Only a slight decrease in capacity, 10th cycle after the overcharge (44.95 → 44.35 Ah – 98.6% SoH)

DETECTION OF DEFECTS DURING OPERATION



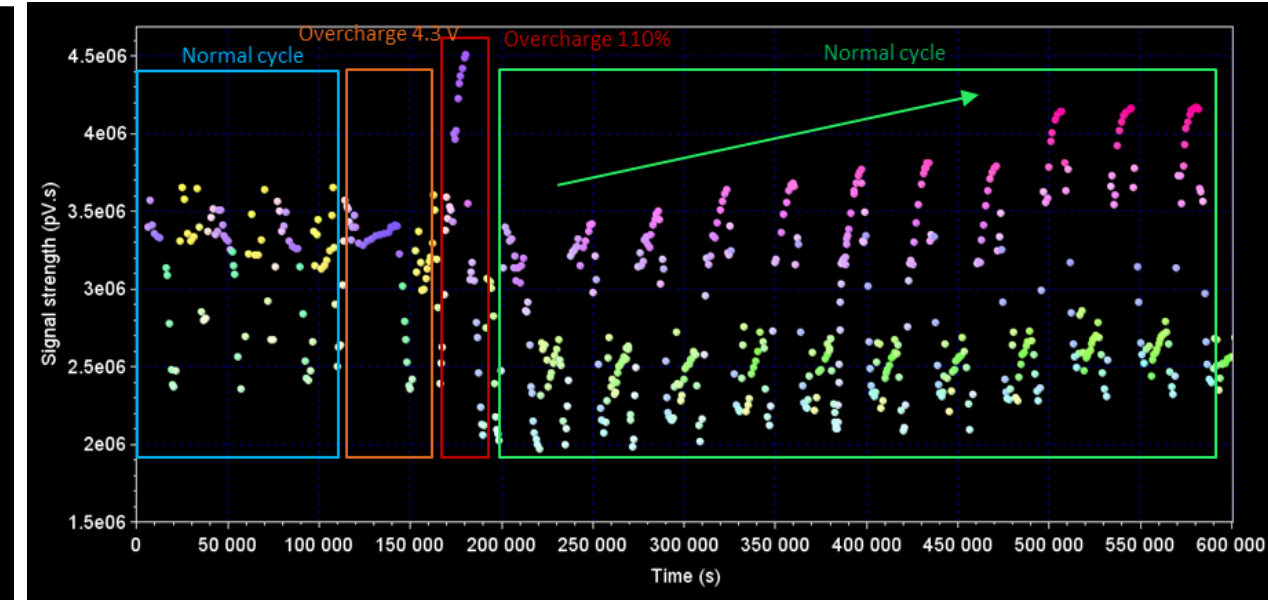
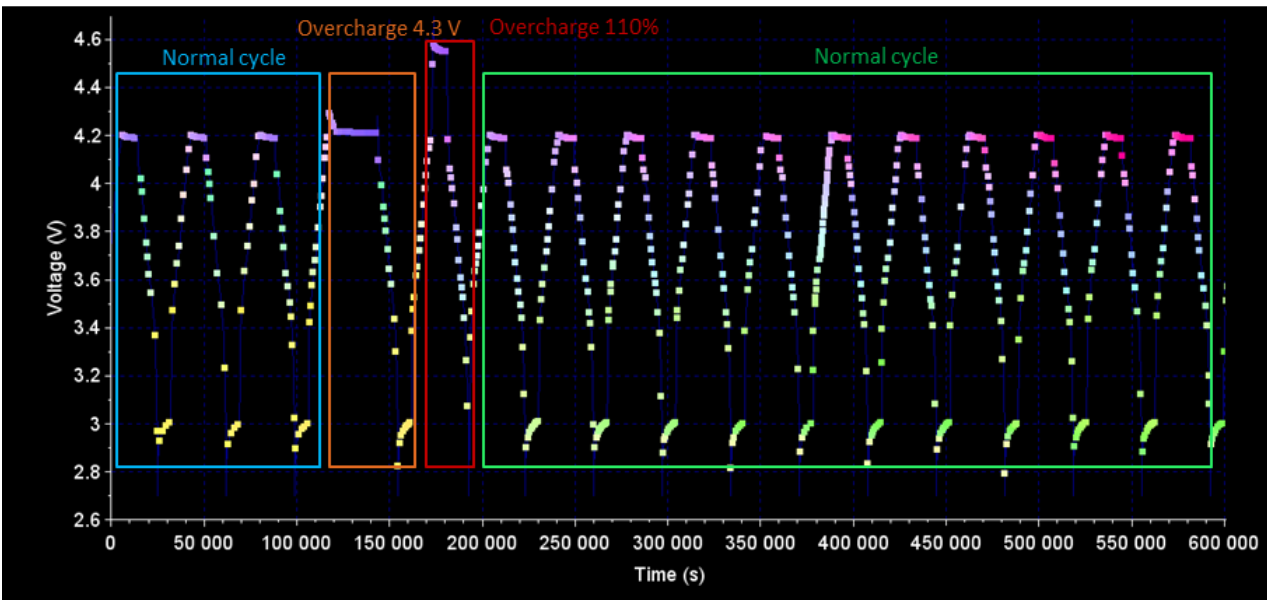
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- Example of the overcharge of a 45 Ah module
 - Normal cycling (2.5 V – 4.2 V)
 - Overcharge 4.3 V , followed by normal cycle
 - Overcharge 110 % SoC , followed by 10 normal cycles



➔ **Acoustic signal strongly modified after 110% overcharge**

↪ Different acoustic signature → physical properties of the materials significantly impacted

↪ Very clear evolution of the acoustic signal from cycle to cycle → the battery becomes unstable

- **Advanced instrumentation for operando monitoring & management of the batteries:**
 - Non-destructing testing methods- non intrusives
 - Simple to put in place and non expensive
- **Can be useful for monitoring and management batteries**
 - Identification of the main changes in physical properties of the materials inside the battery during operation
 - Improve the estimation of SoC and SoE
 - Detect abnormal behavior and prevent safety issues
 - Quality check for manufacturers...
- **Next works !**
 - Improvement of the testing setup
 - Integration to the BMS for better performance and longer uselife of the batteries
 - Ageing test / SoH estimation (sensors / transducers + battery 😊)

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- Cédric Ducros (UGA, CEA –Liten)
- David Brun-Buisson (UGA, CEA-Liten)
- Lionel Serra (UGA, CEA –Liten)
- Olivier Masson (UGA, CEA –Liten)
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- Sylvain Lespinats (UGA, CEA –Liten)
- Vincent Gau (UGA, CEA –Liten)

Thank you for your attention

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SPARTACUS

<https://www.spartacus-battery.eu/>

EVERLASTING
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OASIS

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Any questions?

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