LoCEL-H2

Low-cost, Circular, plug & play, Off-grid Energy for remote Locations including Hydrogen

Durability and degradation of lead electrodes under battery/electrolyzer hybrid operational conditions

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LoCEL-H2 project objectives and impact

Project goal: development and demonstration of affordable and clean off-grid energy solutions

- 24/7 access to electricity for basic needs (light, communication, refrigeration, local business uptake)
- Green hydrogen for safe cooking (the use of open wood and coal fires for cooking is causing the loss of over 3 million lives per year, women and children being most of the victims of such practices)
- Market uptake supported by a sustainable business model based on results from SSH studies

Sustainable business model

48V Smart grid for renewable energy sharing (PV, wind, etc.)	Advanced & Affordable Energy Storage (HPPL battery)	Combined Green Hydrogen production and energy storage (Battolyzer)

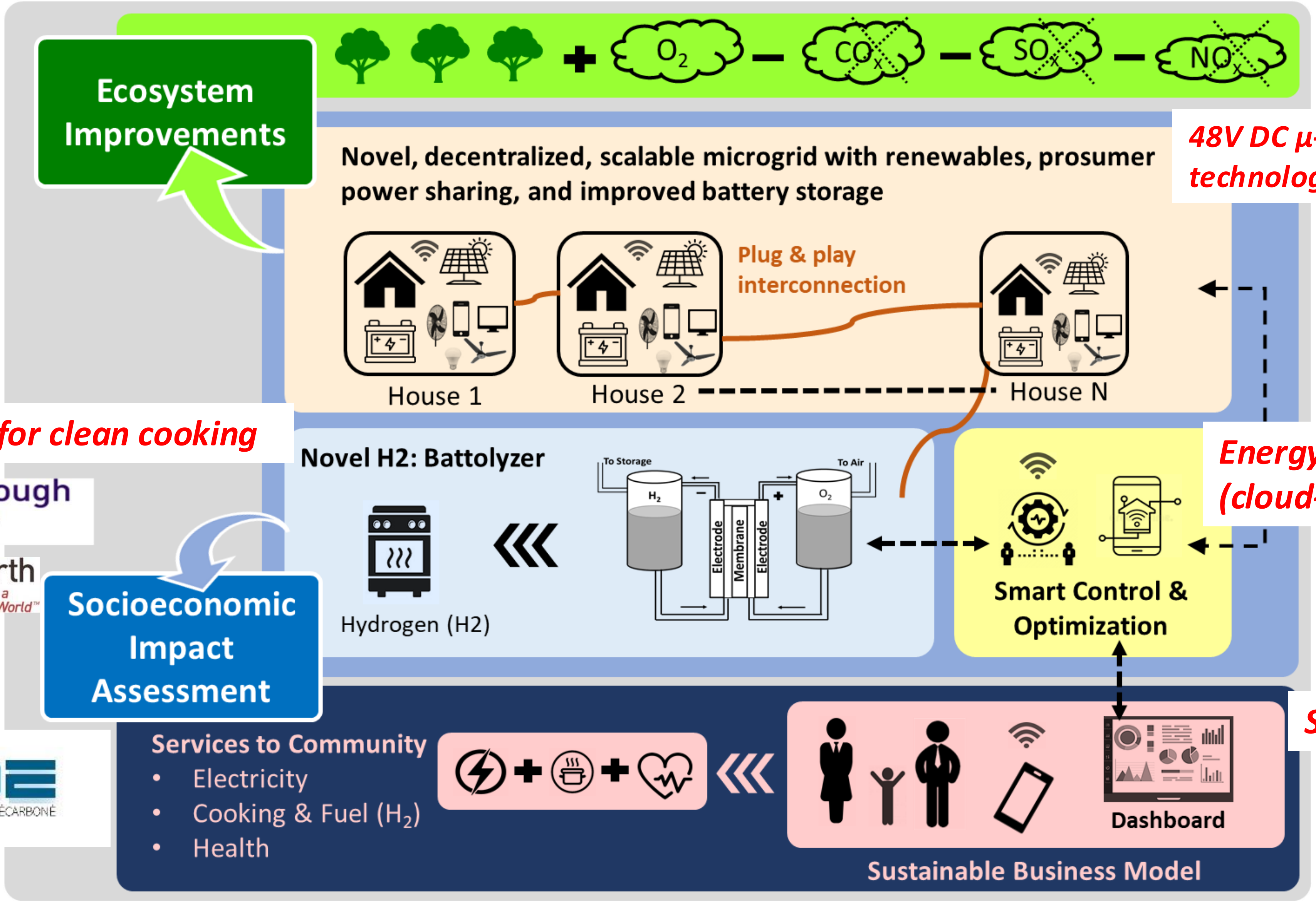
LoCEL-H2 approach at glance

48V DC µ-grid using HPPL battery technology for PV energy storage

Hydrogen for clean cooking

Energy Management System (cloud-based)

Supported by SSH studies



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LoCEL-H2 challenges and beyond

Safety

- Extra-low voltage (<50V) and very safe energy storage at household level
- Existing practices and knowledge about the spent batteries and electronics waste value and disposal
- Lacking on non-existing legislation and standards related to the hydrogen production, storage and use

Availability and affordability

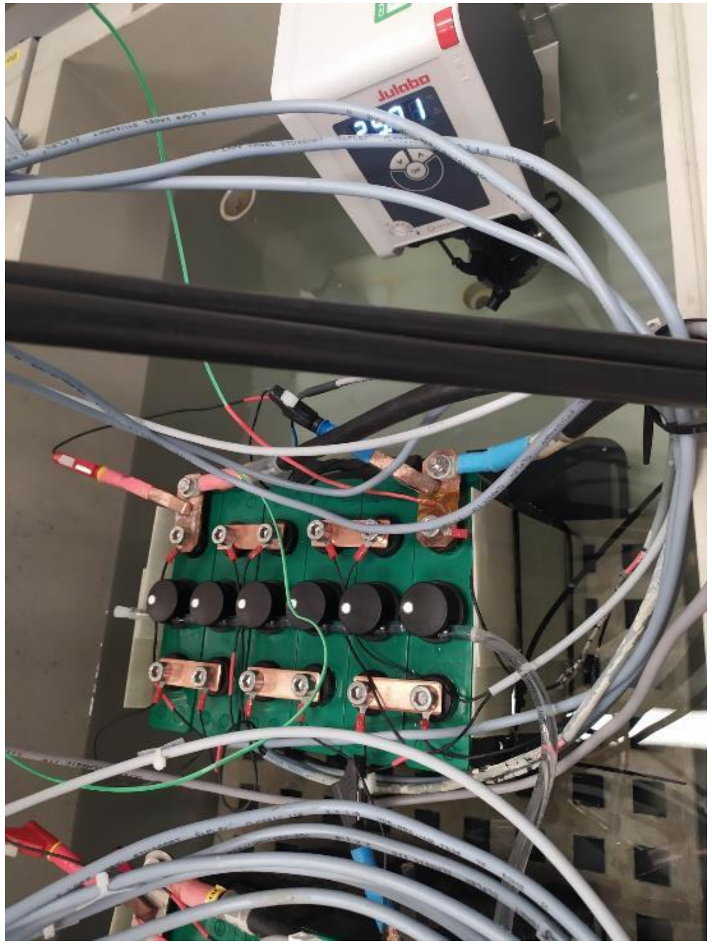
- Record low PV modules pricing observed recently
- Electrochemical technologies employing lead electrodes (cost-efficient manufacturing and recycling)
- Growing access to satellite internet services (a must for cloud based EMS)

Durability

- Most user locations are in regions with hot climate (Africa and South Asia)

⇒ Electrodes/Battery lifetime limitations (corrosion, AGM dry-out, high DOD PSOC operation)

Test set-up and ageing experimental protocol



Cycling profile #1 "Deep cycling":
Depth of Discharge (DOD) = 70%
Charge Factor (FC) = 143%
<u>Charge input per cycle: 120Ah</u>
H_2 production: 36 Ah/cycle
- One string at T = 25°C
- One string at T = 45°C

Cycling profile #2 "Moderate DOD cycling":
Depth of Discharge (DOD) = 50%
Charge Factor (FC) = 200%
<u>Charge input per cycle: 120Ah</u>
H_2 production: 60 Ah/cycle
- One string at T = 25°C
- One string at T = 45°C

Cycling profile #3 "Shallow cycling":
Depth of Discharge (DOD) = 20 %
Charge Factor (FC) = 500 %
<u>Charge input per cycle: 120Ah</u>
H_2 production: 96 Ah/cycle
- One string at T = 25°C
- One string at T = 45°C

Cycling profile #4 "Continuous overcharge":
Depth of Discharge (DOD) = 1 %
Charge Factor (FC) = 10 000 %
<u>Charge input per cycle: 120Ah</u>
H_2 production: 118,8 Ah/cycle
- One string at T = 25°C
- One string at T = 45°C

- Electrochemical cells: 2 HPZS 120 (Hoppecke Batteries, flooded tubular type 2 V / 120 Ah) connected in 12V strings
- Electrodes technology identic to those used in the Loughborough University's Battolyzer cells
- Positive grid alloy: Sb 4,2% / Sn 0,09% / Se 0,012%
- Periodic cells removal from the strings for tear down analysis (2, 4, 5, 6 months on test etc…)

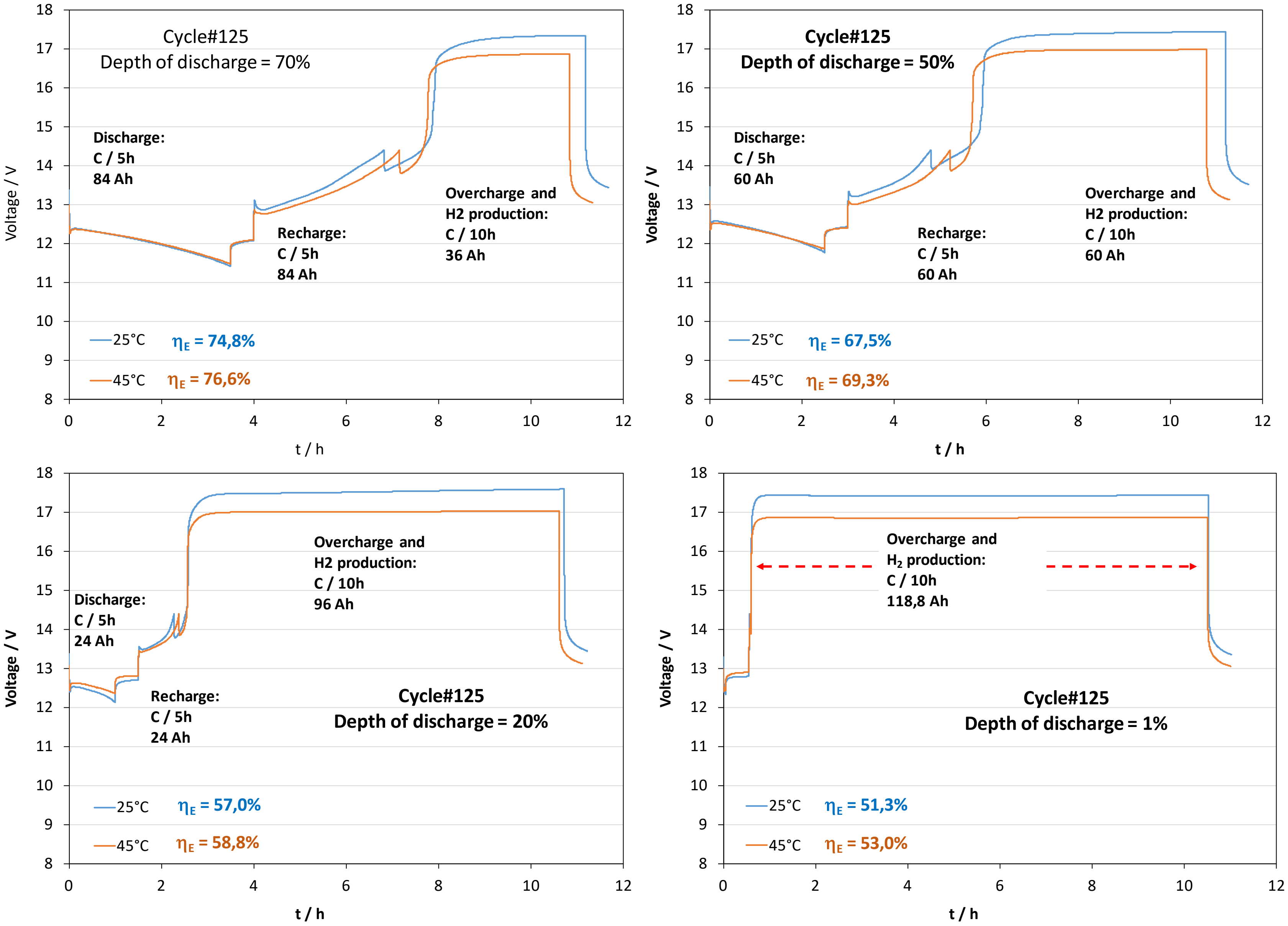
Combined energy efficiency in hybrid operation mode

$$\eta_E = 100\,\frac{Wh_{\,dsch} + Wh_{\Delta H2}}{Wh_{\,charge}}$$

$Wh_{\Delta H2}$ is the burning heat of the produced hydrogen according to the Faraday’s law, considering H_2 oxidation enthalpy of 285,8 kJ/mol

Efficiency gain: ~ 0,1 %/°C

Cell voltage factor: ~ 3-4 mV/°C



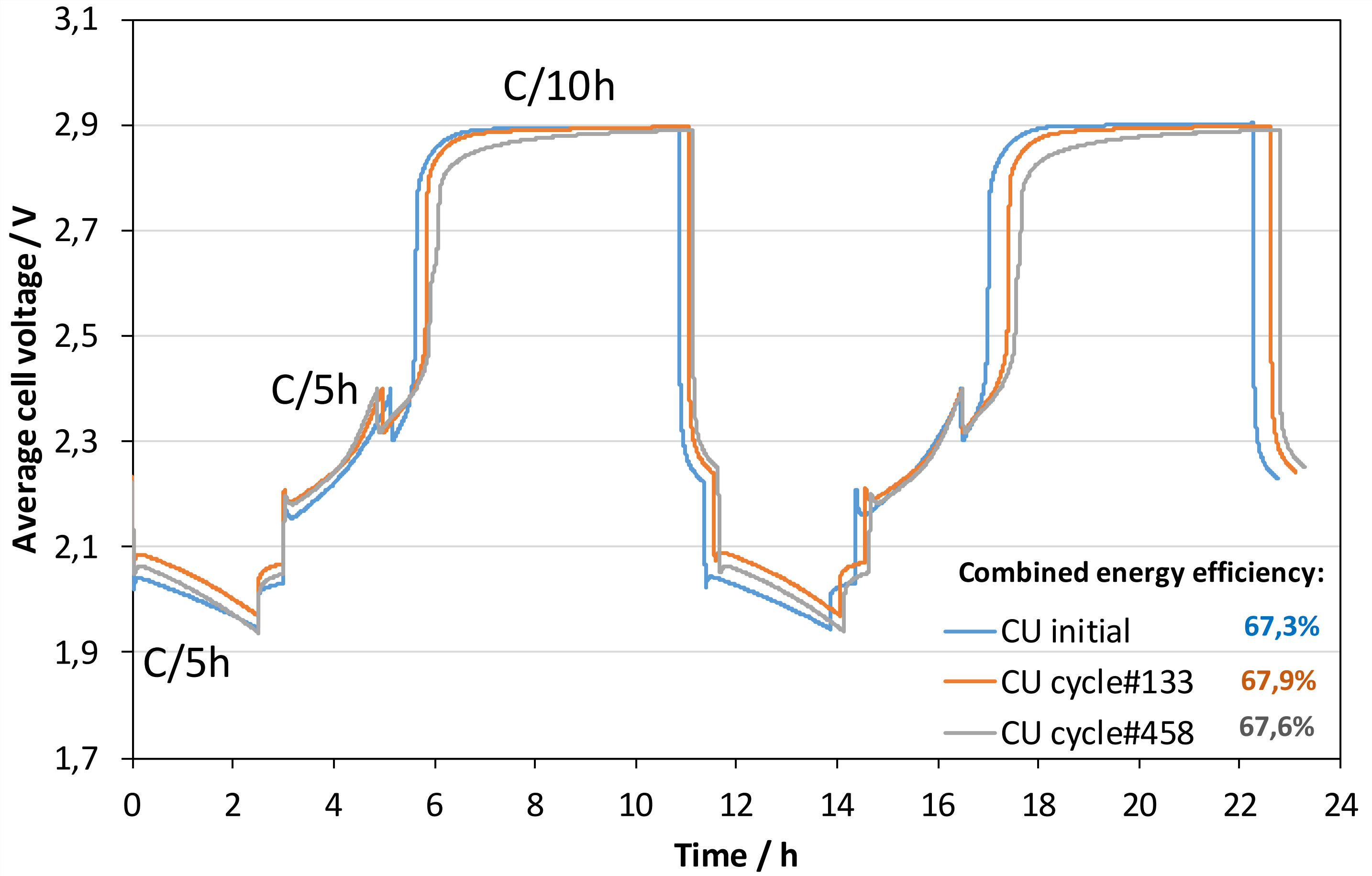
Ageing effects: efficiency

Example: cycling profile #2

- **DOD = 50%**
- **FC = 200%**
- **T = 25°C**

Main observations

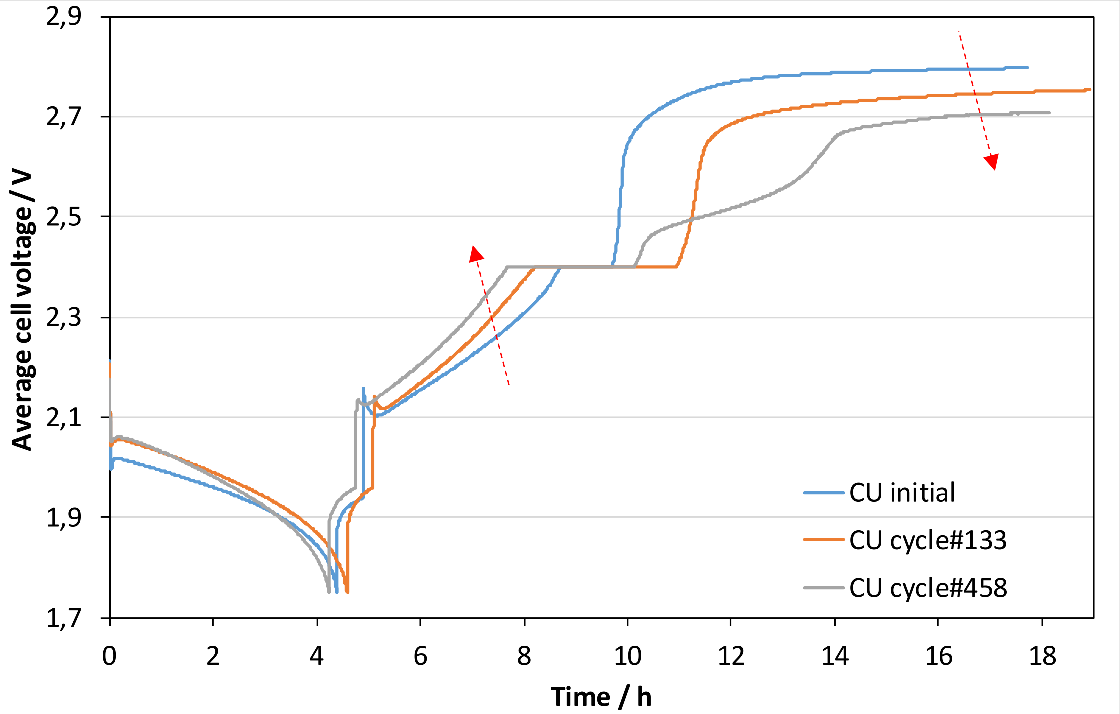
- **Very small change of the voltage profile**
- **Nearly constant efficiency**
- **Absence of Sb poisoning indications**

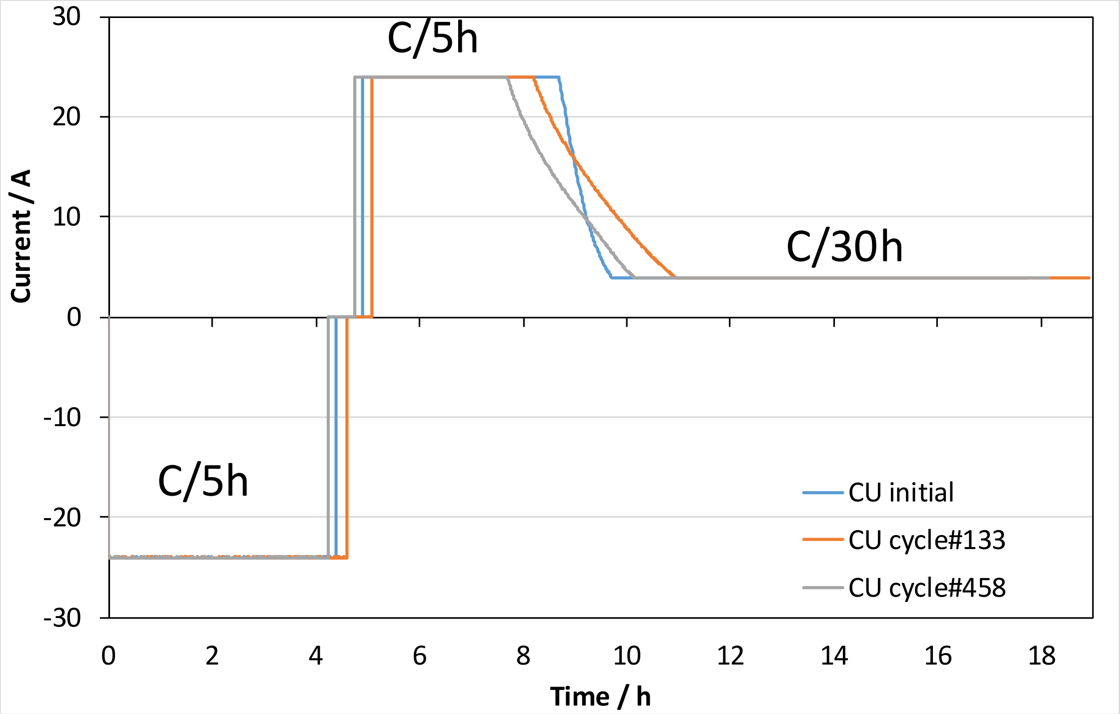


Ageing effects: capacity

Ageing effects: capacity

- Example: cycling profile #2 (DOD = 50% / FC = 200% / 25°C)
- Capacity estimation: 5h rated discharge followed by 5h rated IUi recharge at 25°C (3 cycles)
- Relatively small capacity loss after 458 cycles
- Minor resistive ageing and Sb poisoning indications during the charge process





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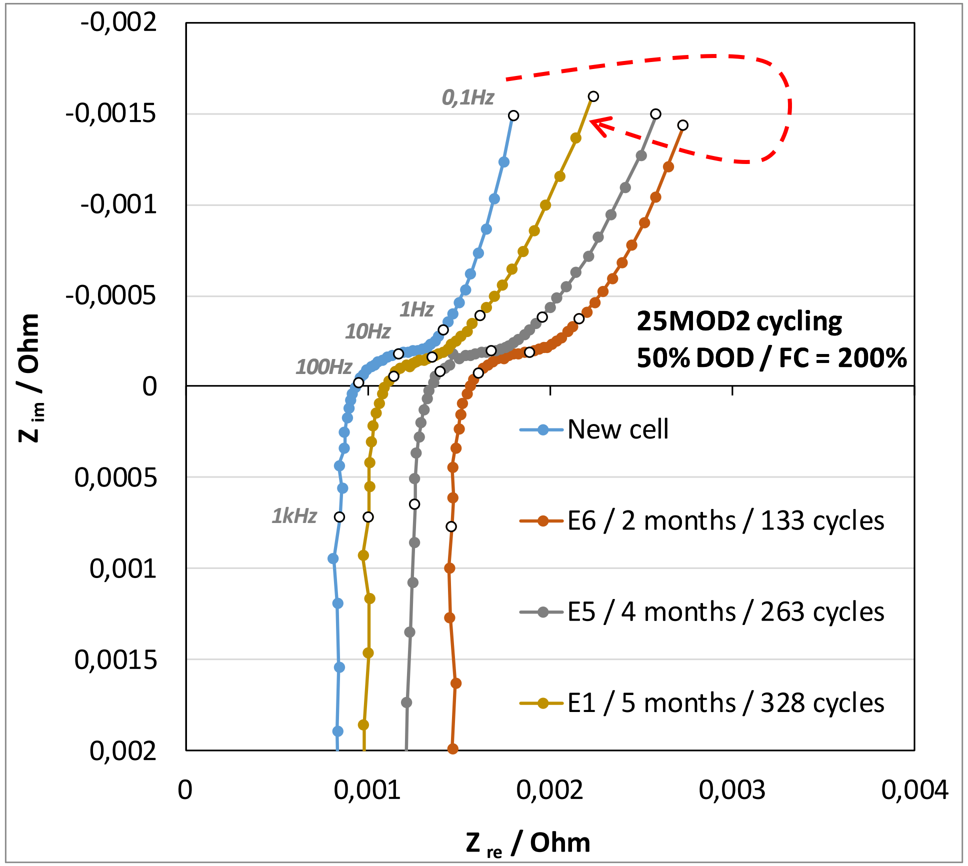
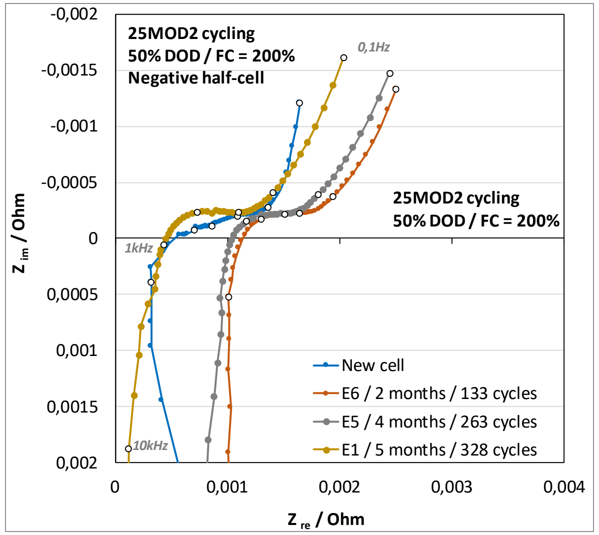
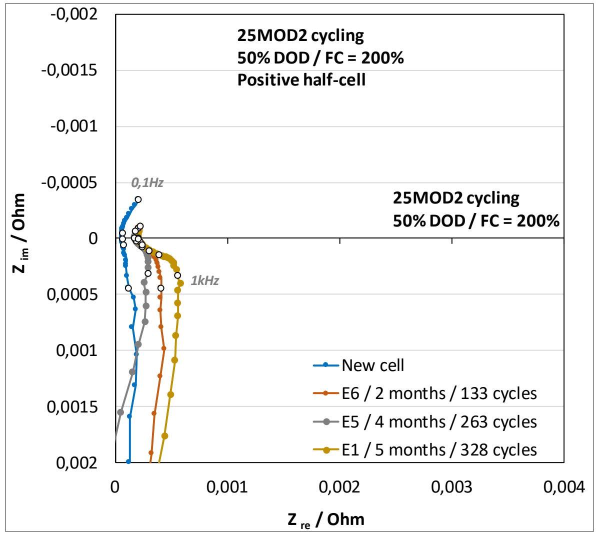
Ageing effects: impedance

- **Example: cycling profile #2 (DOD = 50% / FC = 200% / 25°C)**
- **The ageing impact is focused almost entirely on the ohmic resistance of the cells**
- **Irregular (loop-like) evolution of the ohmic resistance**





The negative half-cell impedance repeats closely the total cell impedance spectra

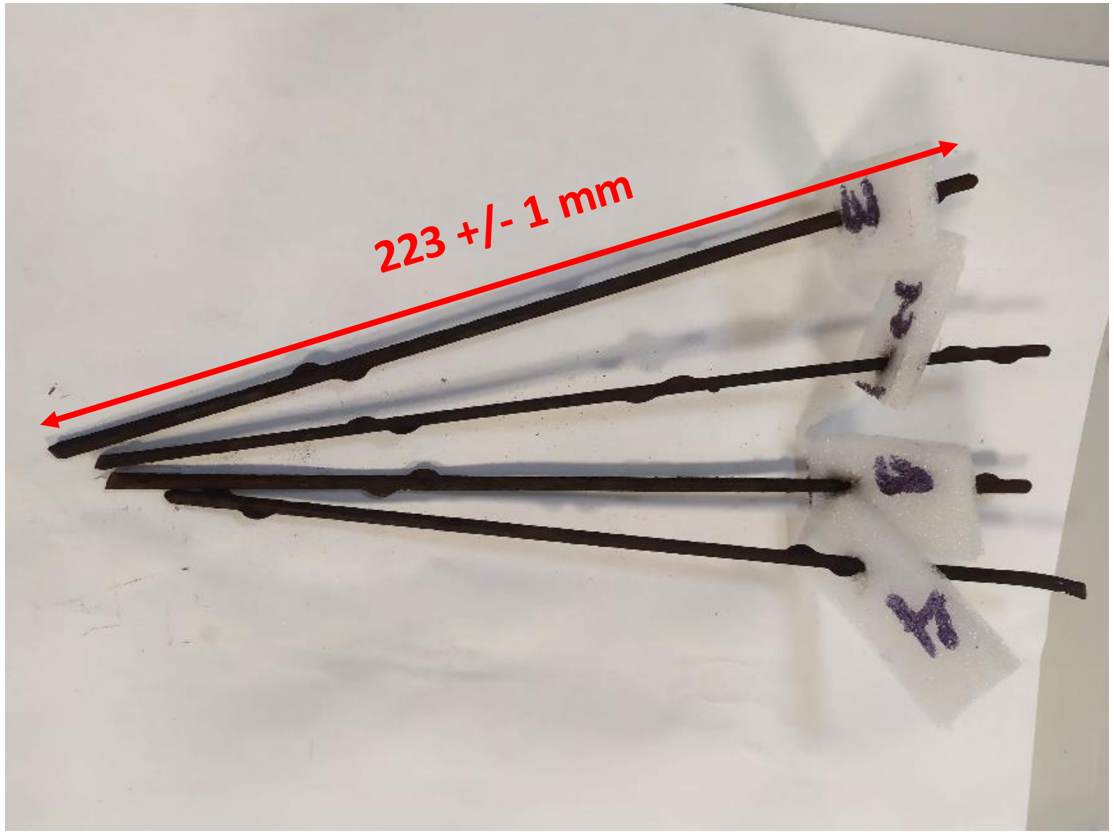


The medium and low-frequency positive half-cell impedance becomes constant shortly after the beginning of the ageing tests

The electrochemical tests results show that the effects from ageing of the cells remain hidden over long periods of time, making the diagnostic process very challenging despite the aggressive test conditions

Ageing effects: positive grids corrosion rate measurement

Weight loss method: G. Papazov, T. Rogatchev, D. Pavlov, J. Garche, K. Wiesener, *J Power Sources 6 (1981) 15*



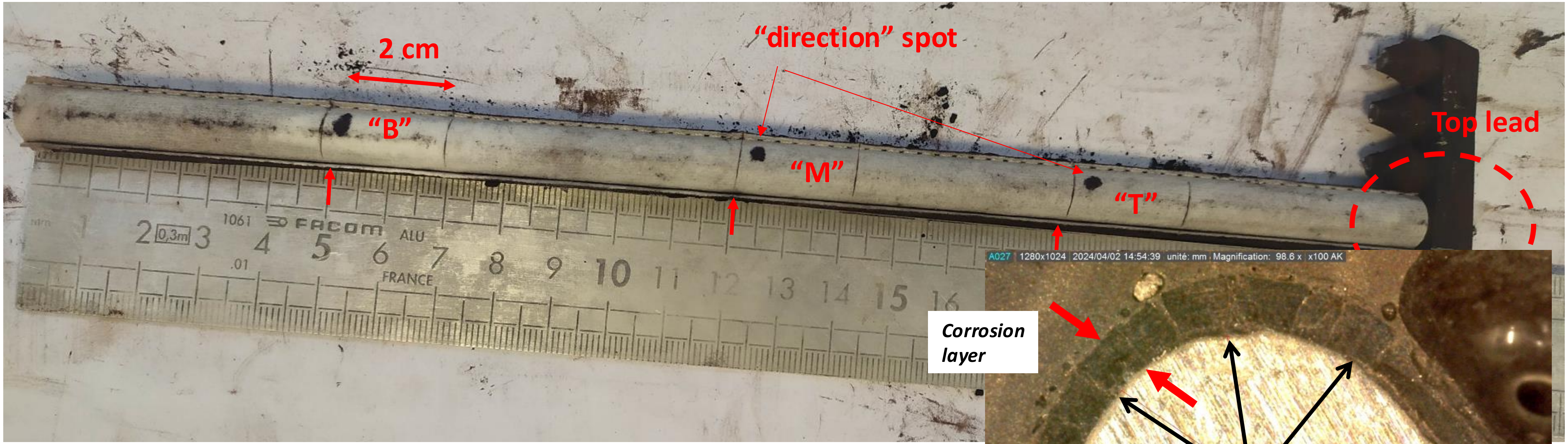
- Four positive grid spines are extracted and PAM is removed
- Controlled cutting at length of 223 mm from the bottom end of the spine

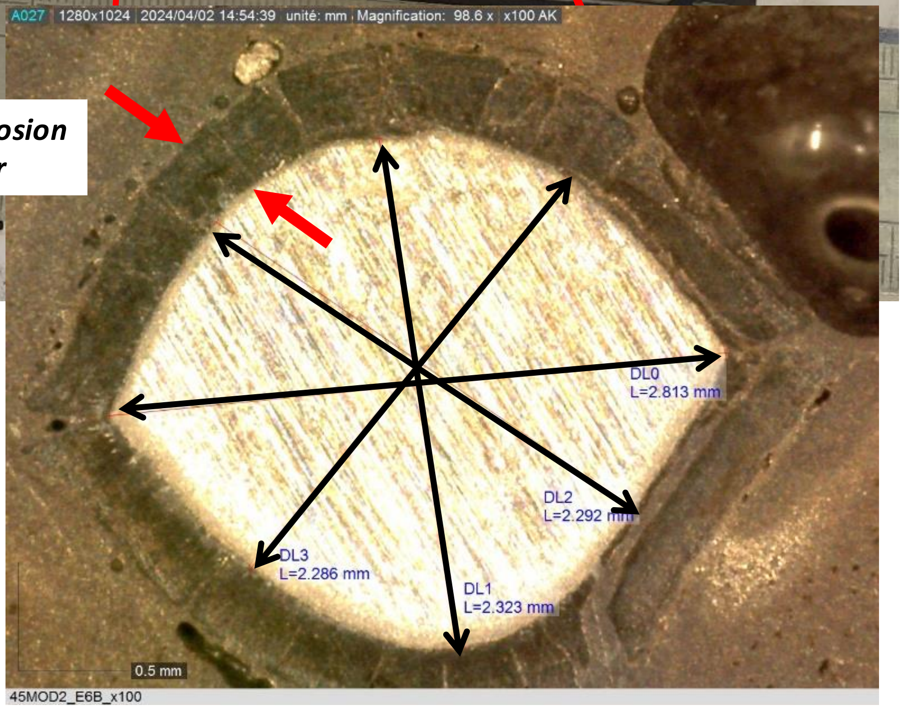
- Corrosion layer stripping in boiling in solution of 100g/L NaOH + 20g/L mannitol + 4g/L hydrazine (3h)
- Weight loss calculated vs. the weight of striped spines from a new cell subjected to 3 capacity measurement cycles and short Tafel test

Ageing effects: positive grids corrosion rate measurement

Optical method

Samples from entire PAM-filled gauntlet are cut at controlled length and fixed in epoxy resin moulds for metallographic characterisation





Top / Middle / Bottom samples + 1 top lead sample

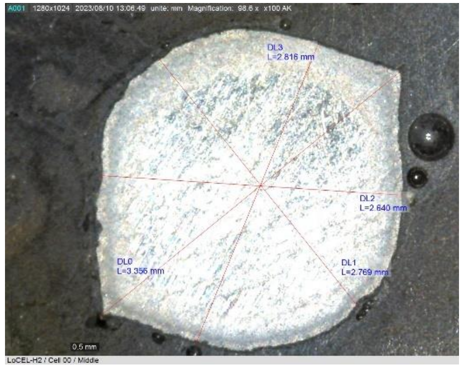
- **Four characteristic spine diameters are measured optically**
- **The average diameter is used to calculate the area of a round shape (πr^2)**
- **The corrosion rate is calculated as a loss of volume of Pb per cm of spine surface**

Ageing effects: positive grids corrosion mechanism

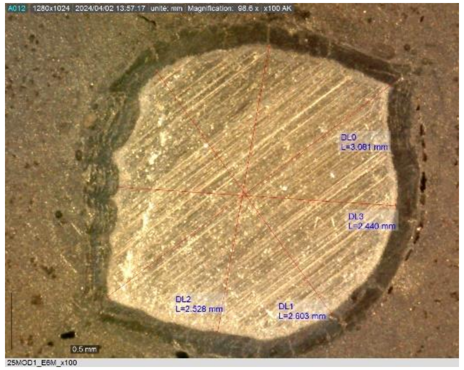
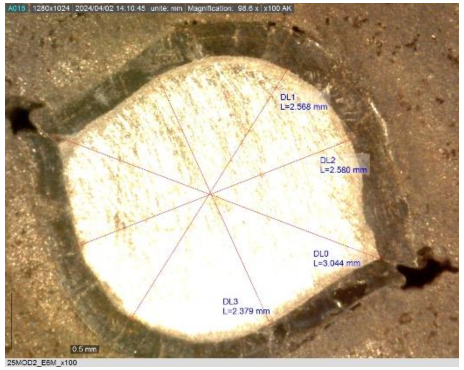
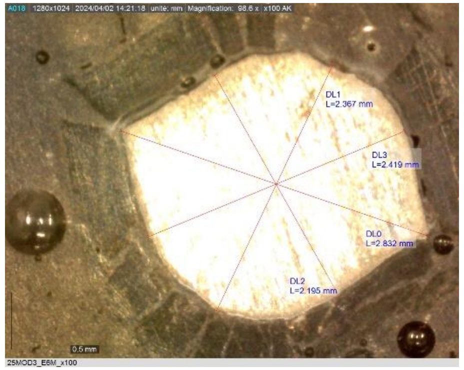
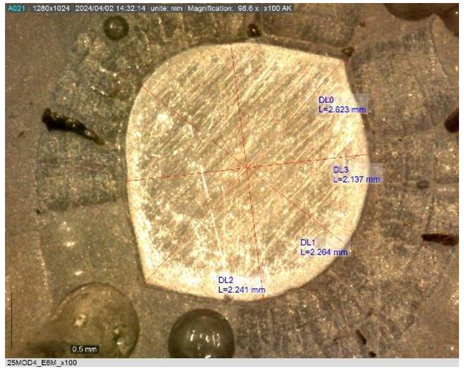
	DOD = 70%	DOD = 50%	DOD = 20%	DOD = 1%

25°C

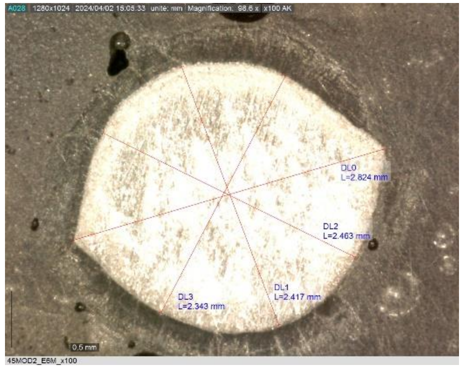
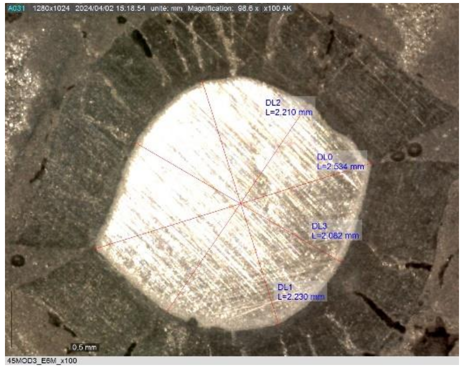
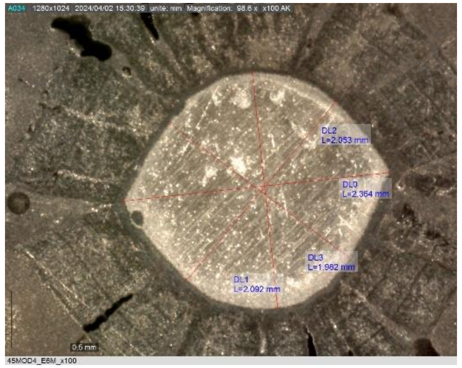
At the reception test



Middle section

45°C

Cumulative overcharge	≈ 4600 Ah ≈ 38 equiv. cycles	≈ 7800Ah ≈ 65 equiv. cycles	≈ 12500Ah ≈ 104 equiv. cycles	≈ 15500Ah ≈ 129 equiv. cycles

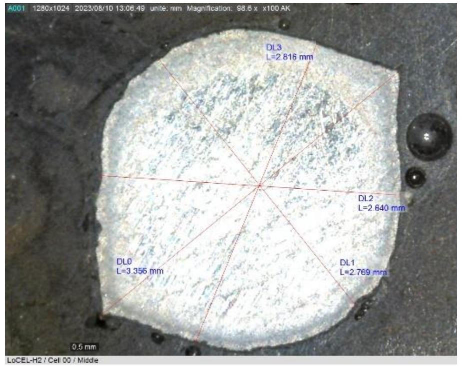
The Depth of Discharge does not change significantly the mechanism

The effect of the temperature seems to be much lower than the expected

Ageing effects: positive grids corrosion mechanism

At the reception test

25°C

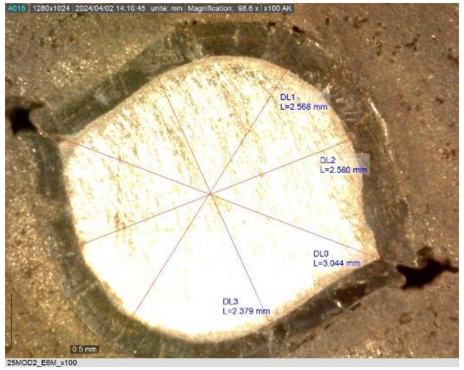


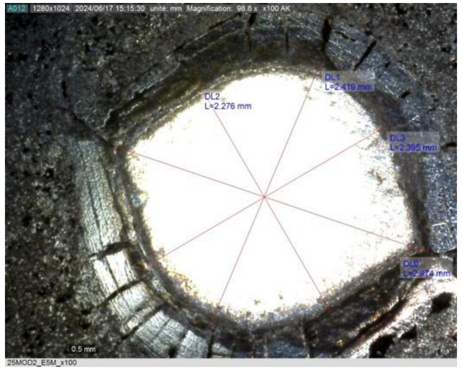
Middle section

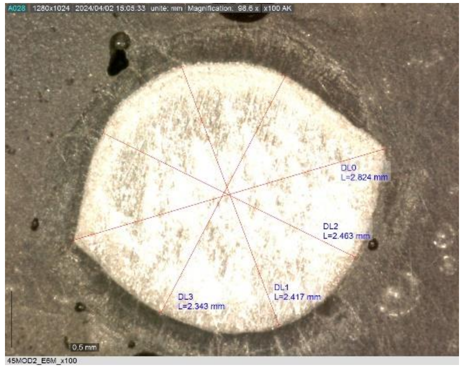
45°C

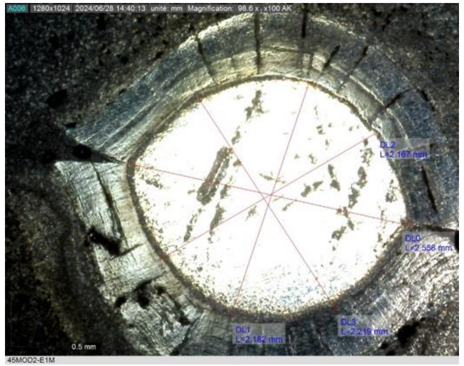
Cumulative overcharge

DOD = 50% / FC = 200%





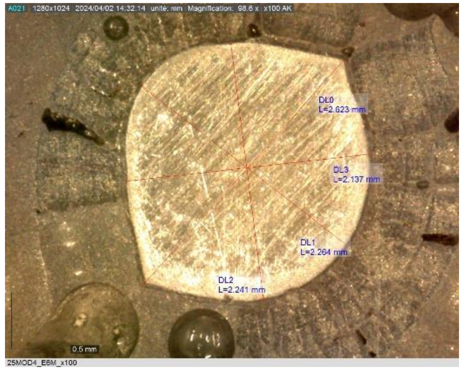


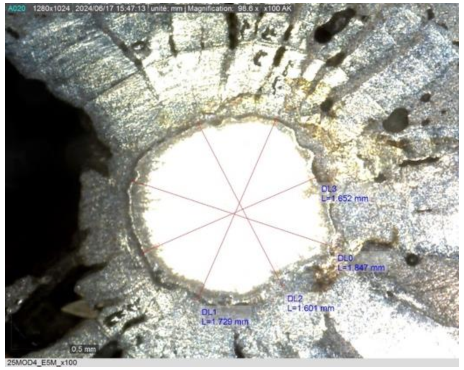


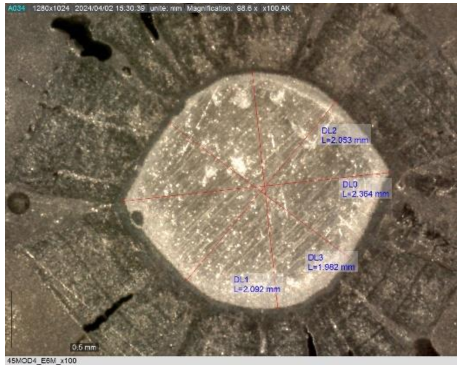
≈ 7800Ah
≈ 65 equiv. cycles
(2 months test)

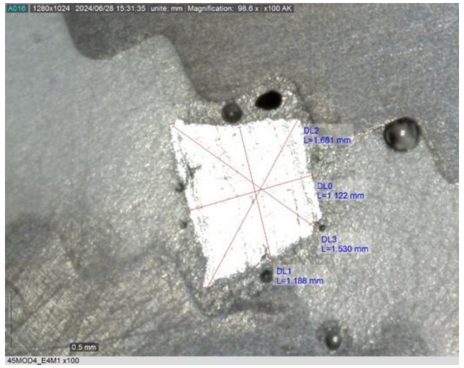
≈ 15600Ah
≈ 130 equiv. cycles
(4 months)

DOD = 1% / FC = 10 000 %







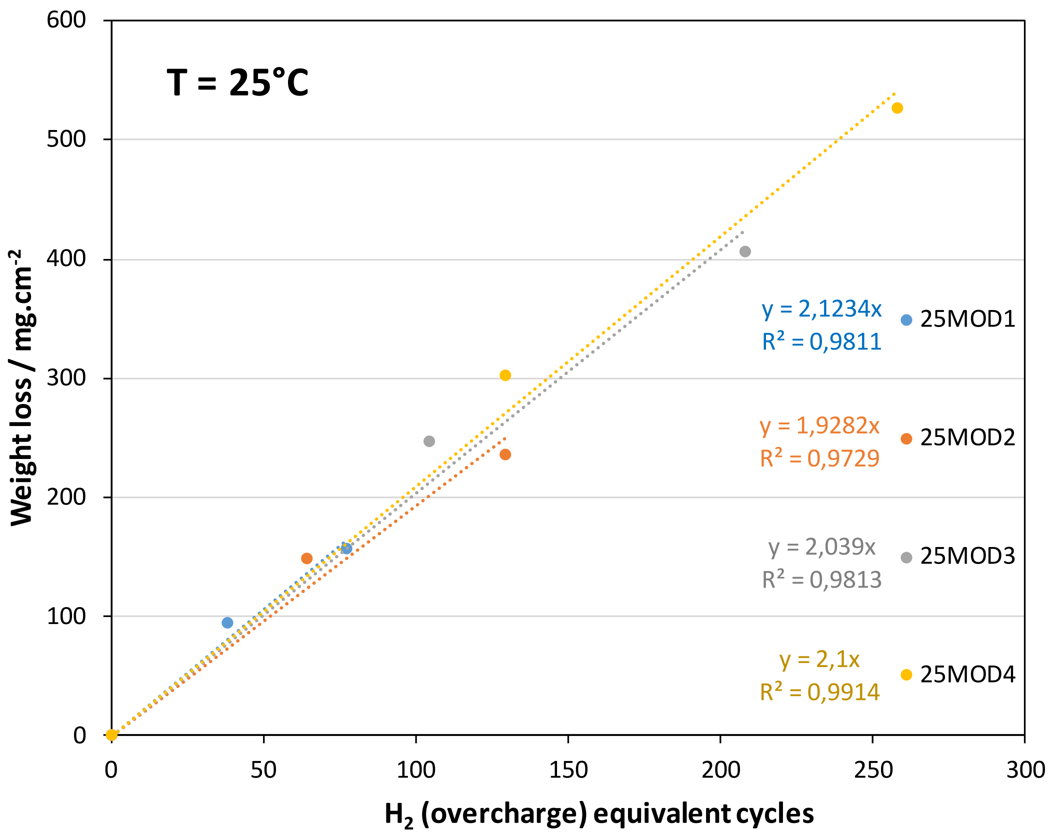


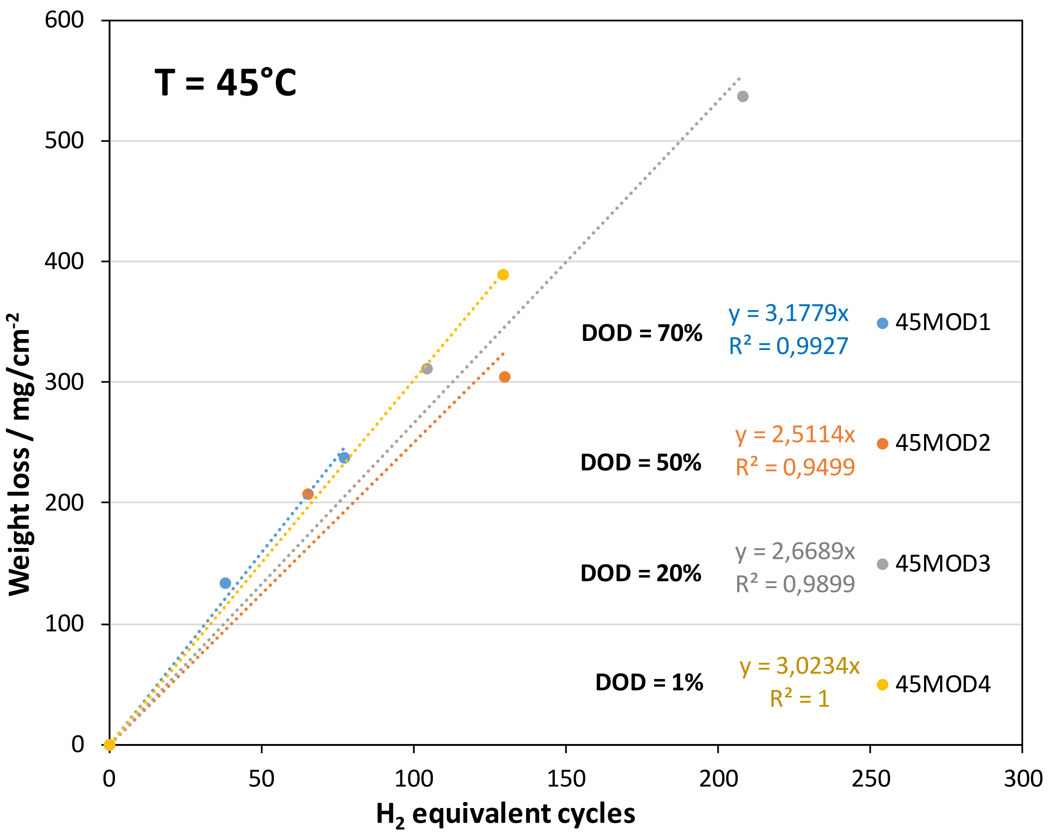
≈ 15500Ah
≈ 129 equiv. cycles
(2 months)

≈ 30600Ah
≈ 258 equiv. cycles
(4 months)

- Very strong correlation between the cumulative overcharge (e.g. H_2 production) and the corrosion process
- Significant increase of the gauntlets diameter (e.g. positive plate thickness growth) causing gauntlets rupture in the final test stage

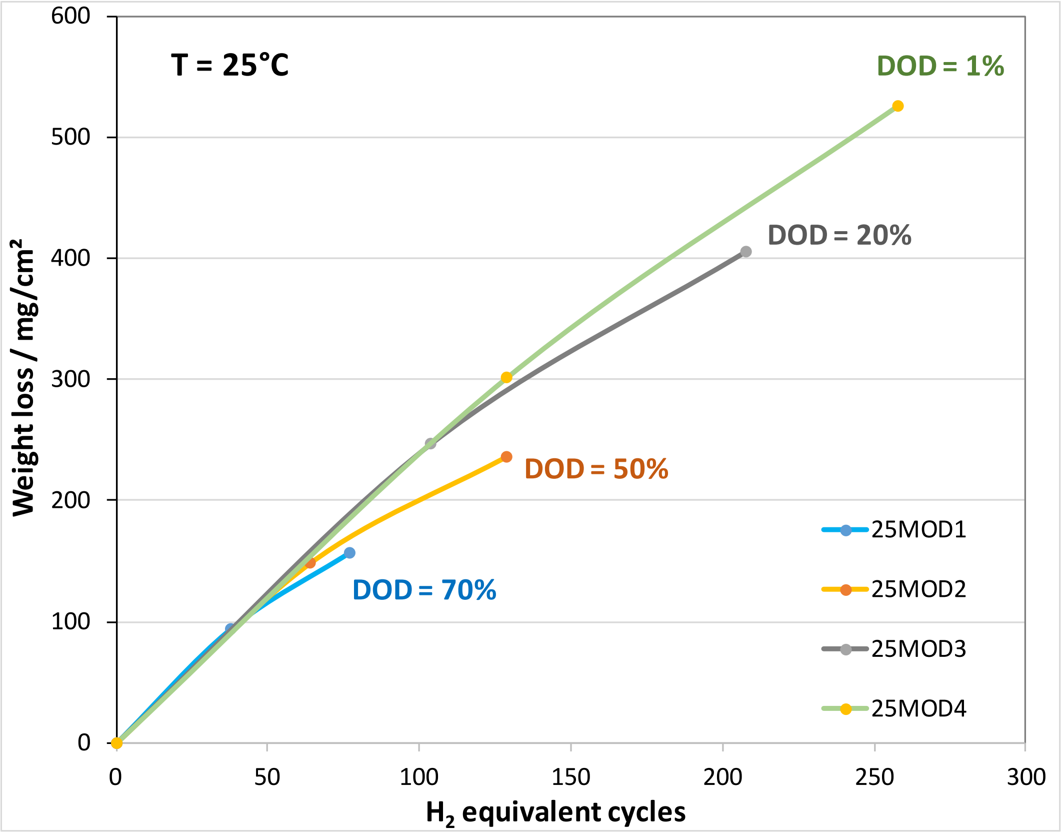
Corrosion rate estimation: weight loss data

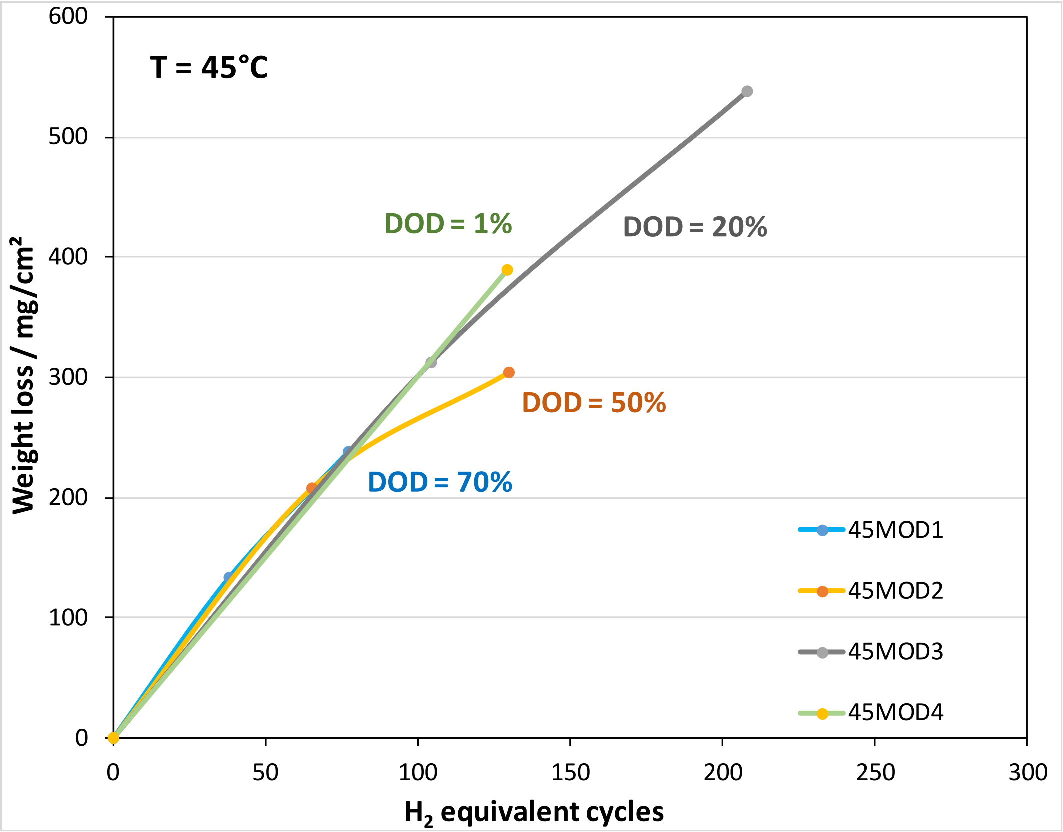




- **Close to linear relationship between the weight loss and the overcharged electricity (H_2 production)**
- **Minor impact of the Depth of Discharge on the corrosion process**
- **The impact of the temperature is far below the expected values according to the Arrhenius equation**

Corrosion rate estimation: weight loss data



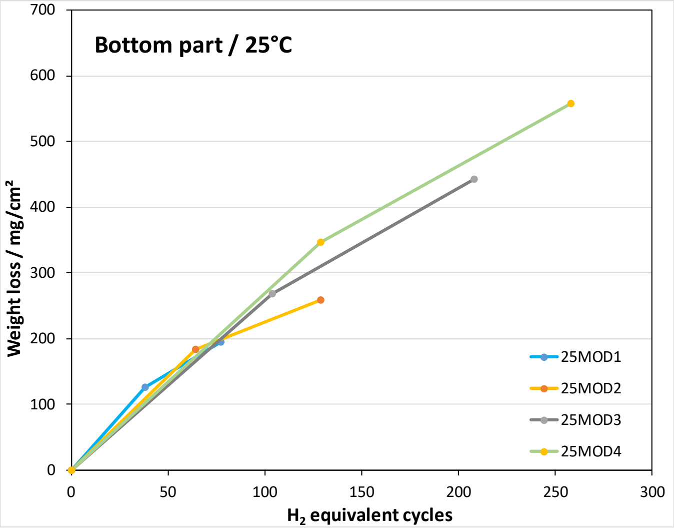


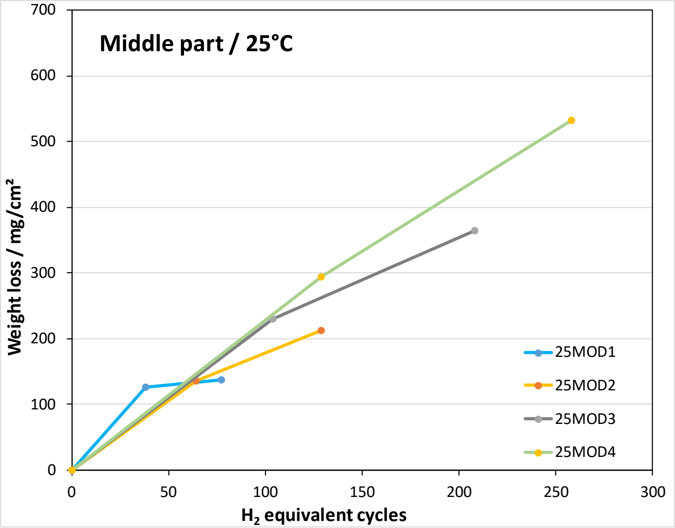
- More careful inspection of the data indicates that the higher DOD tends to slow-down the corrosion rate with the time
- The above effect coincides with the observations of more adherent and difficult to strip corrosion layer at DOD = 70% and 50%

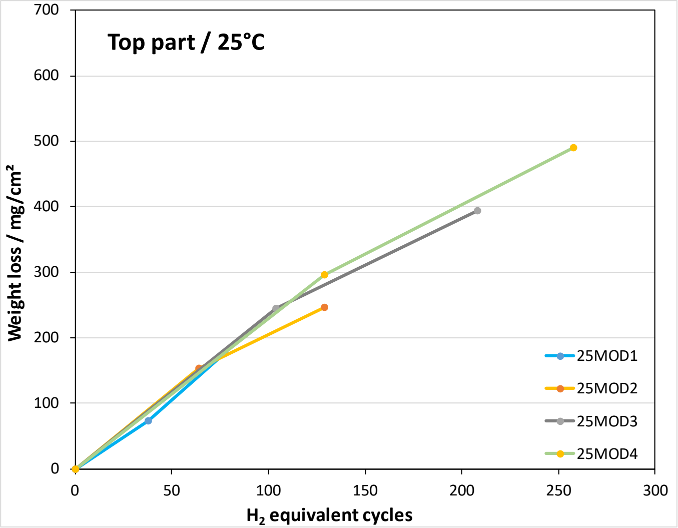
Hypothesis: the cycling creates "fresh" catalytic sites for O_2 evolution inside the PAM volume

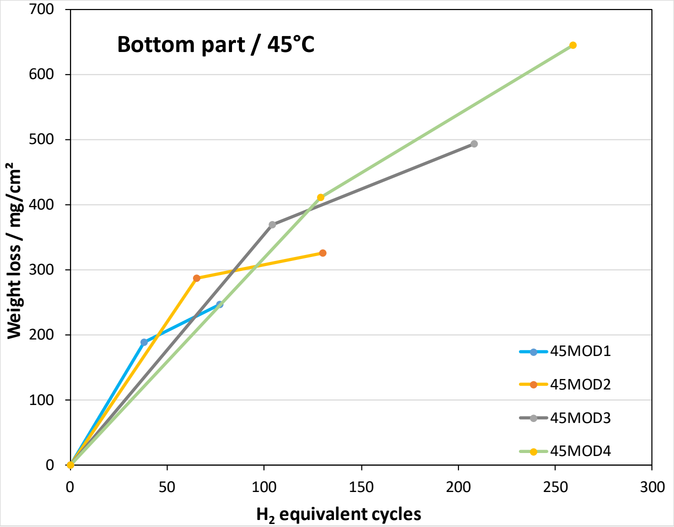
- The H_2 production should be considered as a "secondary" function of the Battolyzer, prioritising the battery function

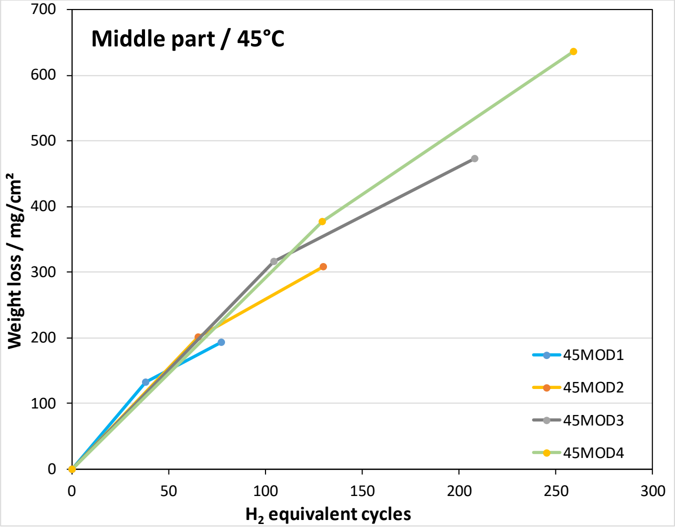
Corrosion rate estimation: optical measurements

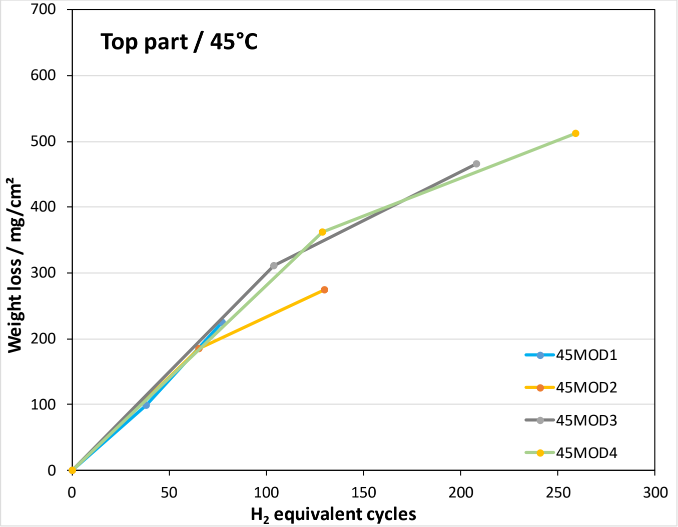








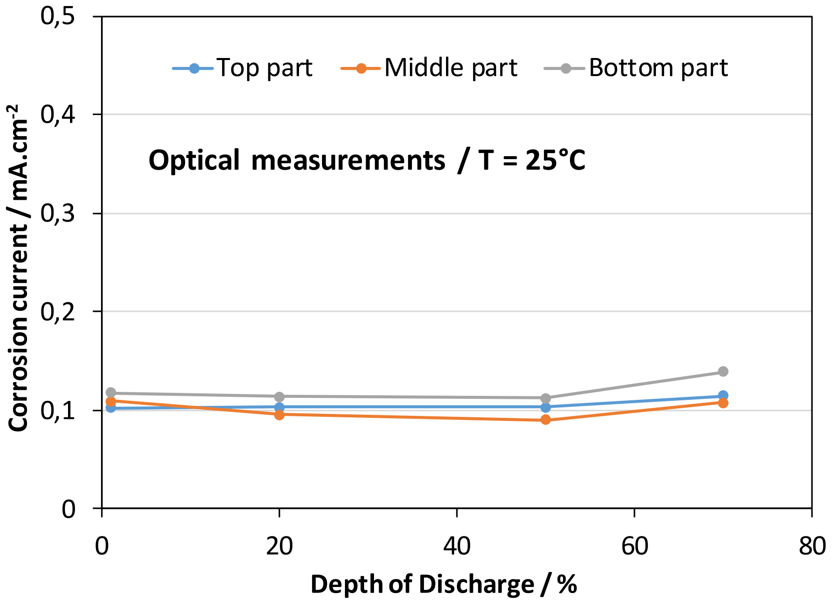


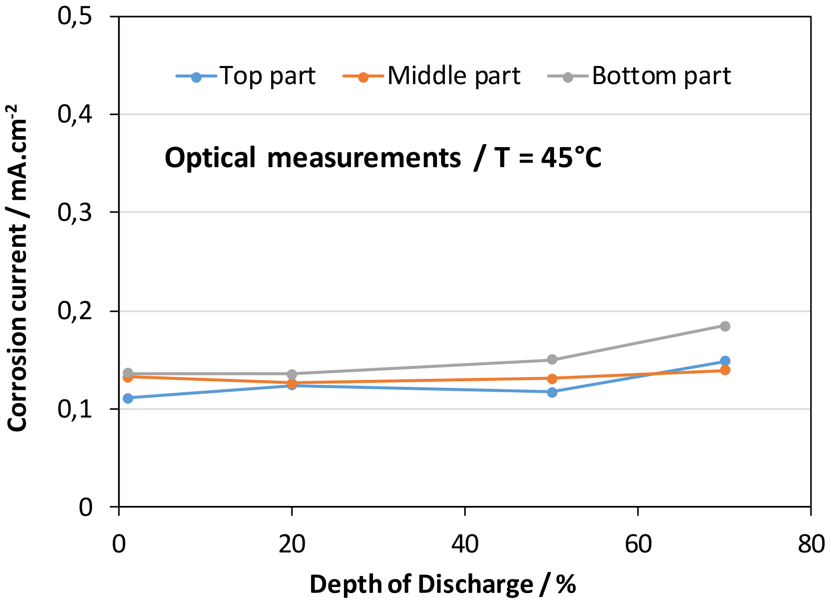


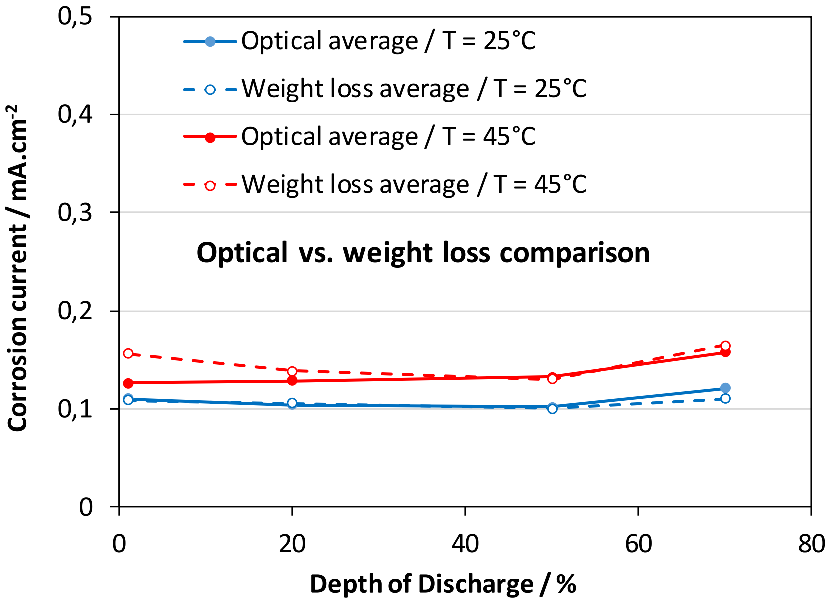
- **Slightly higher corrosion rate observed in the bottom section of the plates**
- **Slightly lower corrosion rate observed in the middle section of the plates**

Competing effects of the electrolyte stratification and special distribution of the O_2 evolution

Corrosion current: optical vs. weight loss measurements







Corrosion reaction: $Pb_{spine} + H_2O \rightarrow PbO_2 + 4H^+ + 4e^-$

$$\text{Corrosion current} = \frac{4\,\Delta m_{spine}\,F}{\Delta t_{H2\ electrolysis}\,A_{Pb}}$$

$$\Delta t_{H2\ electrolysis} = Q_{overcharge} \times 3600s\ /\ 12Amps$$

- The corrosion current remains rather constant (at T = const)
- The thermal dependence of the corrosion process under C/10h regime is much lower that expected according to the Arrhenius equation)
- The impact of the overcharge current is under investigation (overcharge tests @ DOD = 20% and C/20h and C/40h) in order to track down the dependence of the corrosion current on the water electrolysis current (or the Tafel plot of the corrosion process)*

* *D. Pavlov and T. Rogatchev, Electrochimica Acta 23 (1978) 1237*
T. Rogatchev, St. Ruevski, D. Pavlov, J Appl Electrochem 6 (1976) 33

Conclusions and perspectives

- **The tubular positive electrodes are suitable for rechargeable "anodes" for lead-based hybrid battery/electrolyzer cells**
- **The efficiency of the hybrid operation increases with the increased share of the "battery function", exceeding 75% under profiles combining deep cycling and intense overcharge**
- **The ageing of the hybrid battery/electrolyzer cells proceeds without any significant degradation of the electric performance over significant periods of time**
- **The tear down analysis of the cells subjected to hybrid cycling profiles showed that the positive grid corrosion is the main degradation mechanism**
- **The corrosion process follows closely the applied total overcharge (i.e. the quantity of the produced H_2)**
- **The increase of the depth of discharge (i.e. the "battery function") results in minor decrease of the corrosion rate in medium term, indicating that the hybrid Battolyzer use with H_2 production as "by-product" can be profitable**
- **The impact of the temperature on the corrosion rate under all tested cycling profiles is much smaller than the expected according to the Arrhenius equation. This result may change the overall perception of the lead-acid battery performance at elevated temperatures if precise and adequate overcharge monitoring and control are set in place**

Acknowledgements

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- AK would like to thank Professor Dani Strickland, Dr Eduardo Cattaneo and Dr Goetz Langer for the helpful discussions of the tests design and the obtained results

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