Detection of MEA's flaws in PEMFC : "in-situ" Relaxometry combined with "ex-situ" Infrared Imagery

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Axane Fuel Cell systems

❑ A commercial scale activity

- **Commercial scaled global offer:** **(FC systems, H_2 logistic, services and measurement)**
- **From 0.1 to 2.5 kW**
- **Off-Grid, Bad-Grid (telecom antenna), events (sports, meetings)**
- **> 50 systems deployed since 2011 mainly in France**

  ➔ Europe and India in progress
- **System's availability (2012) > 99.4%**
- **11000h reached (and still working) with the first systems deployed**

Axane ⇔ Laboratories

To study MEAs degradation mechanisms and to develop mitigation strategies adapted to Axane system

> Analyse of system working data

> Development *in-situ*/*ex-situ* diagnostic and characterization tools

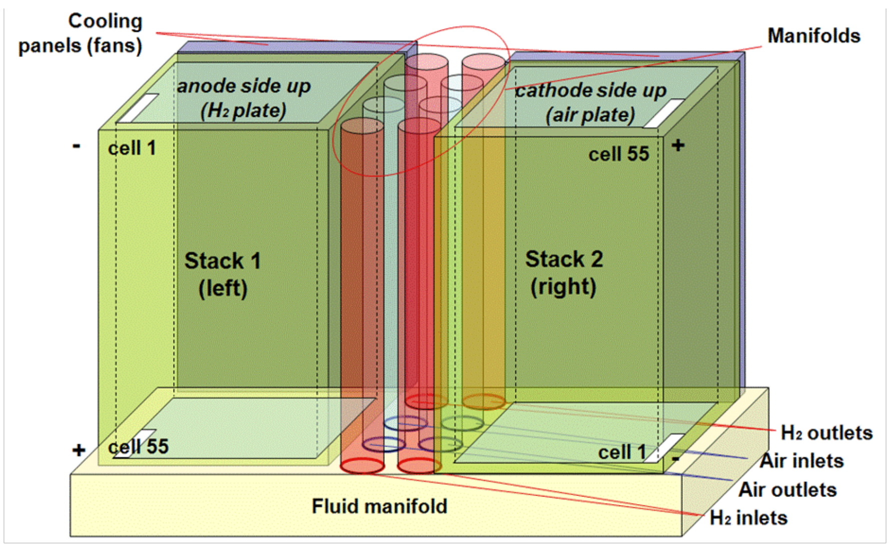
> Optimisation of MEA components and working conditions

in situ Stack diagnosis after/during operation

❑ Main obectives:

- Identify the cells with defects such as pinhole or short-cuts
- Localize precisely the flaw intra-MEA
- *Physico-Chemical characterization around the defect area*

✓ 3 Macroscopic Techniques



Sensitive to pinhole / H_2 leak

- Leak test by pressure drop (*in situ*)
- Infrared Imagery (*ex situ*)

Sensitive to pinhole, membrane thinning, etc... / electrical short-cuts

- Relaxometry (*in situ*)

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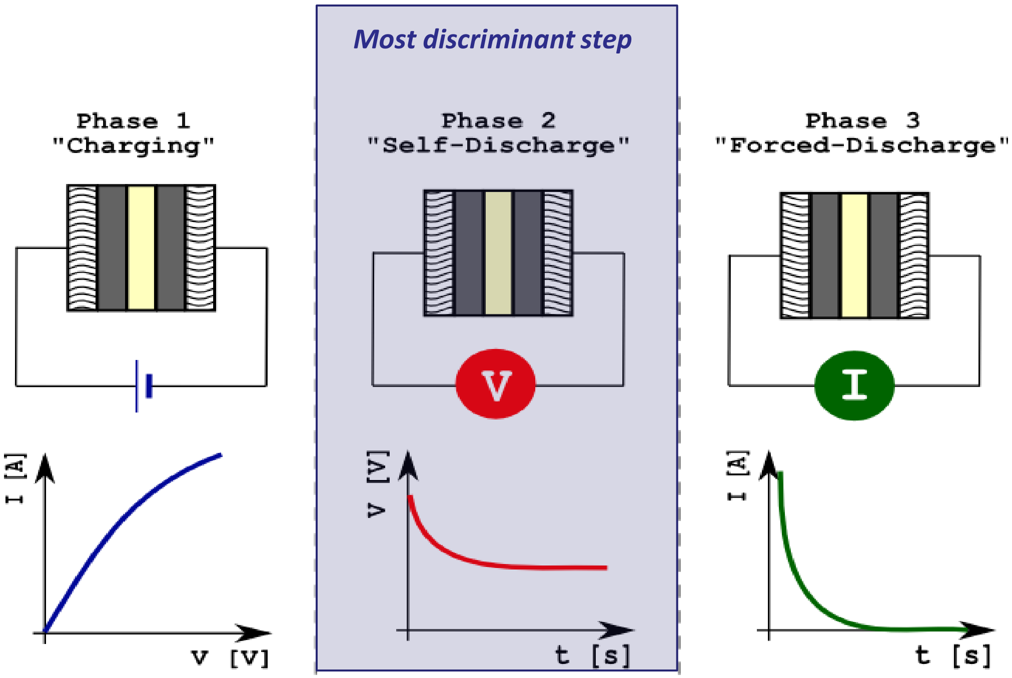
in situ Stack diagnosis during/after operation

❑ Electrical relaxometry[1] (method)

Passive state : No electrochemical reaction



- ✓ *Integrated in Fuel Cell (current source and voltage measurement)*
- ✓ *Fast and synchronous measurement of all the cells*
- ✓ *Electrical short-cut growth detection*

- ***Phase 1:*** **a forced charging – a current (few mA) is applied during few seconds**
- ***Phase 2:*** **a self discharge - the MEA is held at open circuit and freely discharges**
- ***Phase 3:*** **a forced discharge to return MEA at an equilibrium state**

[1] L. Flandin, A. S. Danérol, C. Bas, E. Claude, G. De Moor, N. Albérola, J. Electrochem. Soc. 2009, 156, B1117.

Horizon Hydrogène Energie

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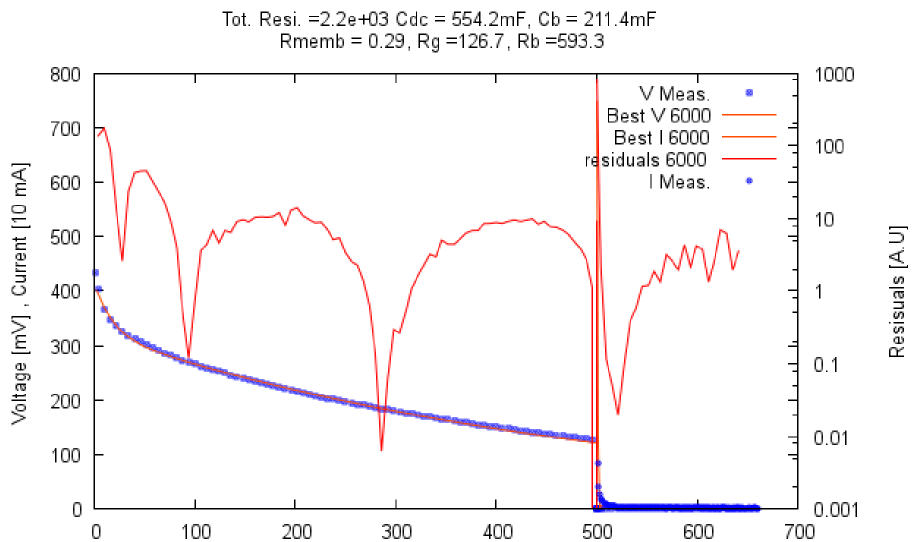
in situ Stack diagnosis during/after operation

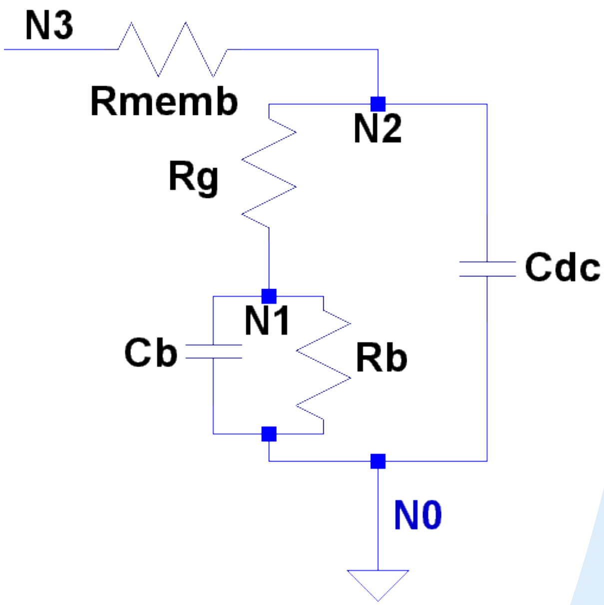
❑ Electrical relaxometry (Phase 2)

Kohlrausch (KWW) function simulated by a Monte Carlo numerical simulation ⇔ ***Equivalent circuit to fit the Phase 2***

$$V(t) = V_{source}\left[1 - exp^{\left(\left(-\frac{t}{\tau_c}\right)^{\beta}\right)}\right]$$

Rg, Rb related to electrical short-circuit





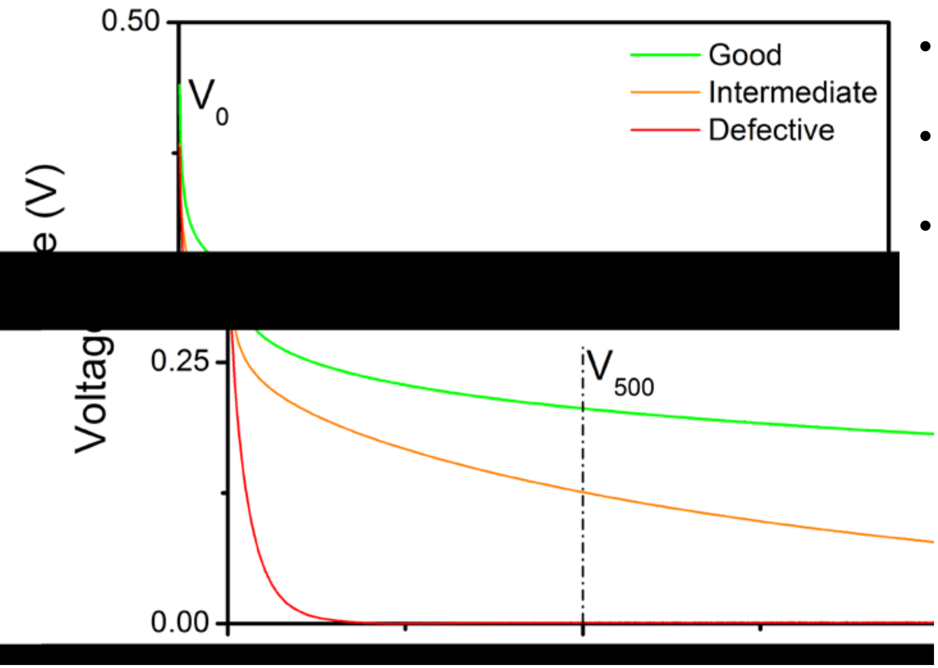
Estimation of $R_{short\text{-}circuit}$ with data from phase 2

in situ Stack diagnosis during/after operation

Horizon Hydrogène Energie

❑ Electrical relaxometry (sensitive to shortcuts)

Phase 2: the most discriminant step



- **The self discharge of the D_{LC} is governed by the electrical short-circuit resistance**
- **Equilibrium recovery for an unaged MEA is approximatively 10 hours**
- **A rapid drop of the voltage indicates a localized contact between the active layers**

Classification

Good : No electrical short-circuit
Intermediate : beginnings for short-circuit
Defective : Evident short circuit within the cell

Drawbacks: **Fuel Cell turned off, false negative**
Advantages: **Fast, easily integrated in FC system, sensitive**

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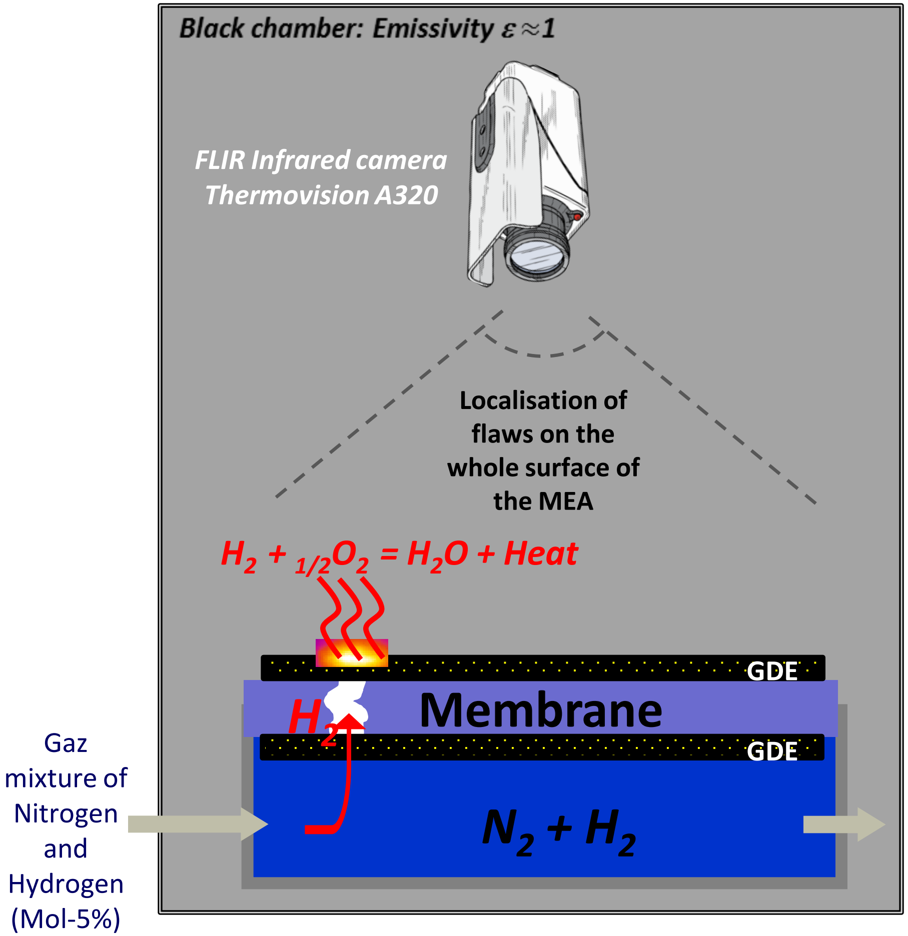
ex situ Stack diagnosis before/after operation

❑ Infrared Imagery[2]

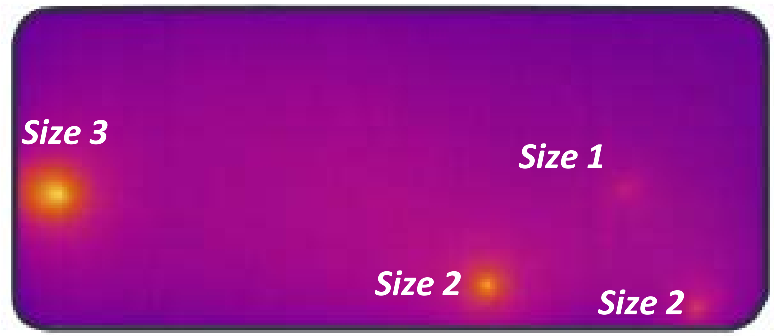
All the MEA are analysed after ageing



Classification

Flaws classified as a function of the generated heat

$$\Delta T\ (°C) = T_{max} - T_{min}$$



ΔT (°C)	0-0.9	1-1.9	2-4.9	5-14.9	>15
Flaw size	1	2	3	4	5

- Flaw sizes 1–2: *Not critical at short time*
- Flaw sizes 3–4: *May be critical at short time*
- Flaw size 5: *Highly critical (shut down of the fuel cell)*

[2]U.S. Patent No. 5,763,765 (issued Jun.9 , 1998).

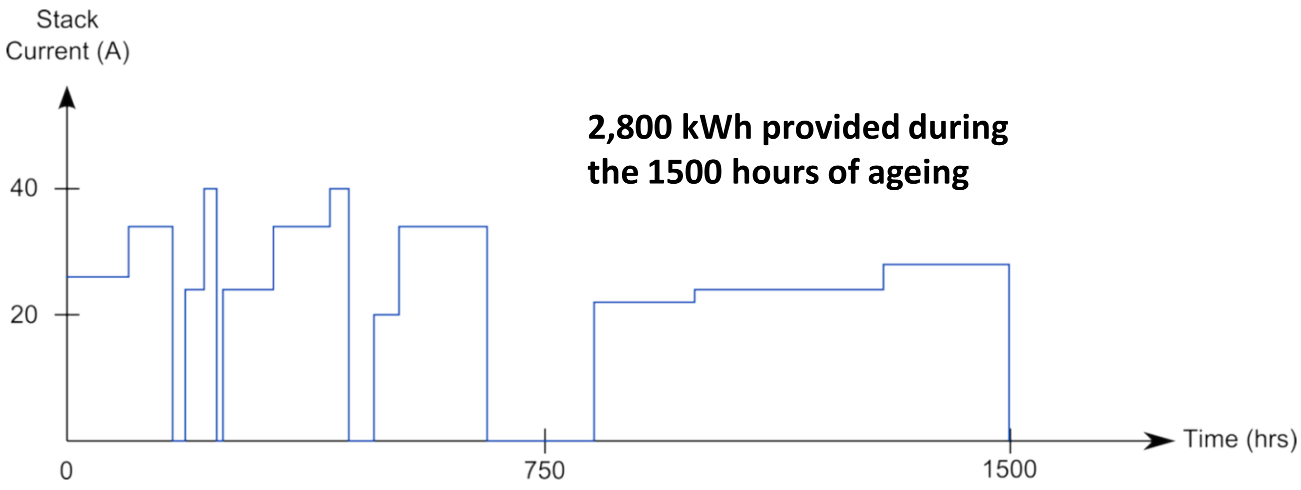
Stack characterization (old generation)

❑ Study of a particular case (back from customer)

- ***Materials***

  - Commercial CCB MEA with surface area close to 90 cm^2
  - Membrane type: Nafion NR211 (25 µm) with IEC of 0.91 $meq.g^{-1}$
  - Catalyst layers: Pt/C type at both anode and cathode side

- ***Load profile of the system studied and its specificity***



- ***End of life***

Shut down of the Fuel Cell due to unsafety level of H_2 leak

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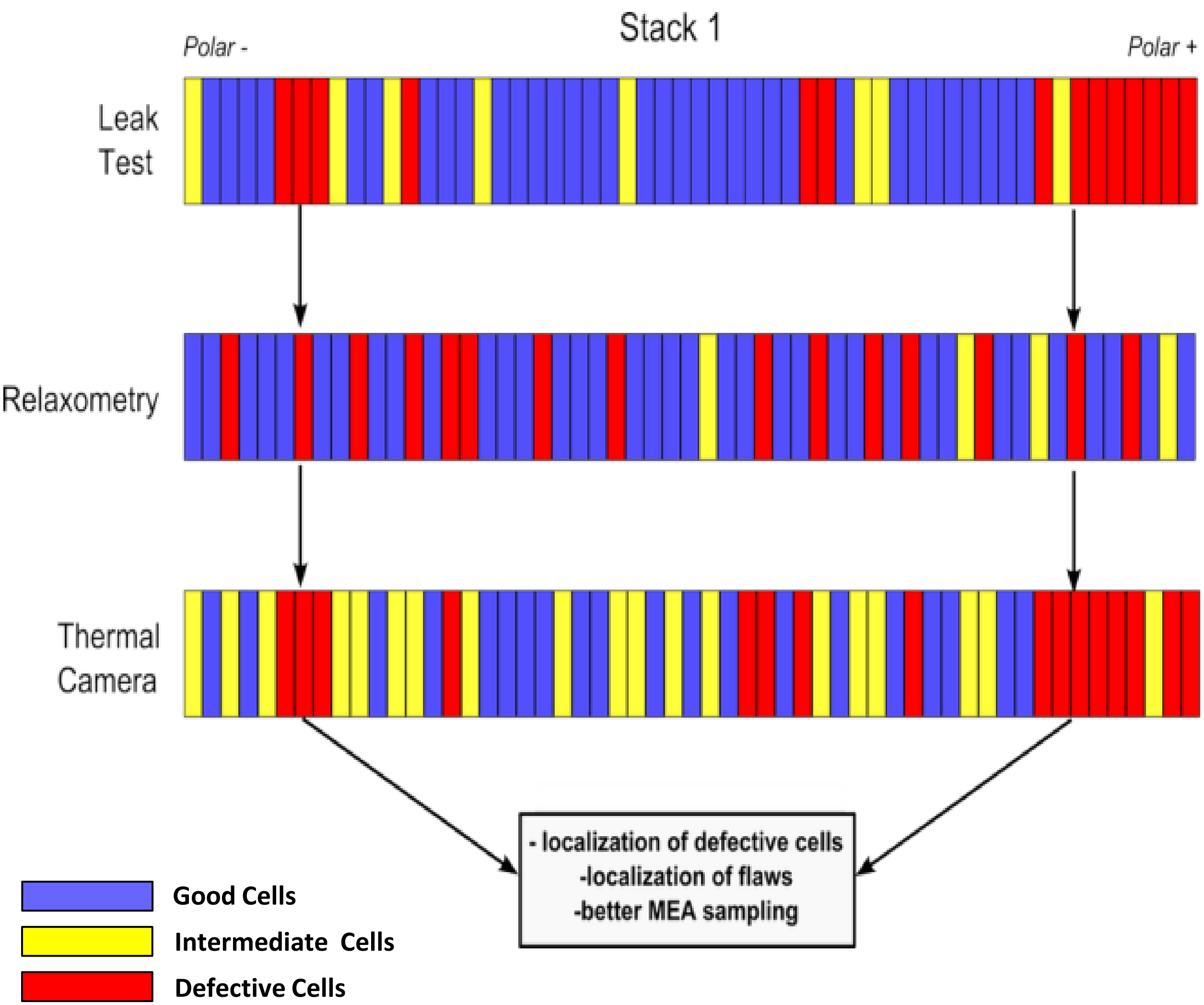
Macroscopic Characterizations

❑ Defective cells position



Leak test:

- Degradation at the bottom part of the stack
- Degraded cells at the same position than those observed in infrared imagery

Relaxometry:

- Shortcuts : randomly spread along the stack

Infrared Imagery:

- Cells identified with flaws are the sum of those identifed by relaxometry and leak test
- Intermediate cells → relaxometry
- Defective cells → leak test

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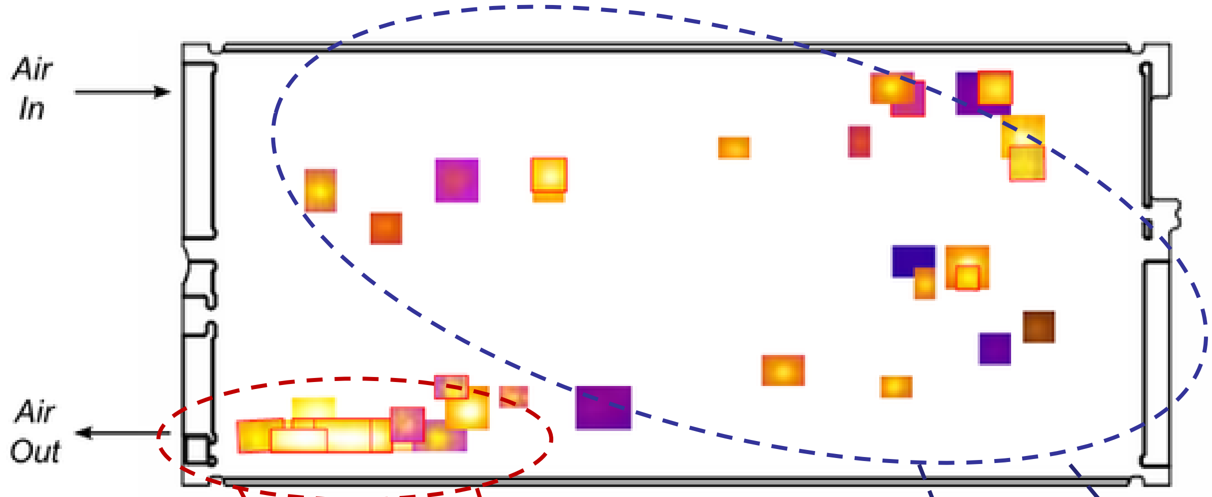
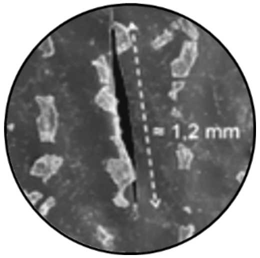
Flaw localisation

❑ Overlay of the flaws position within MEA

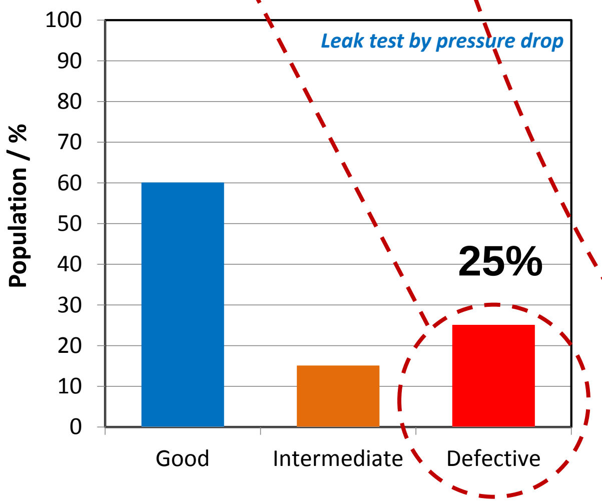


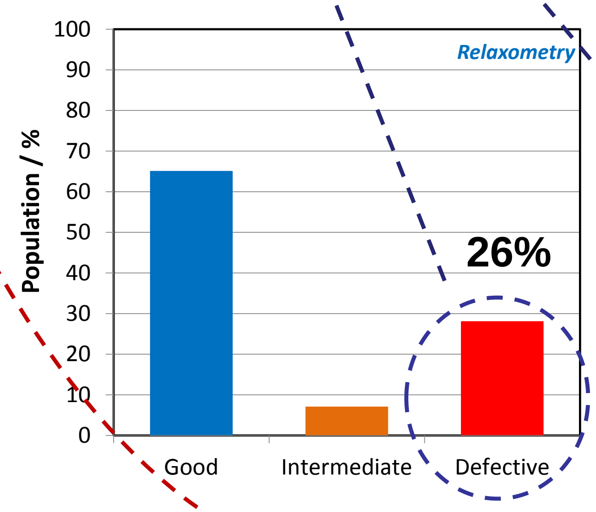
Responsible for stack shut-down

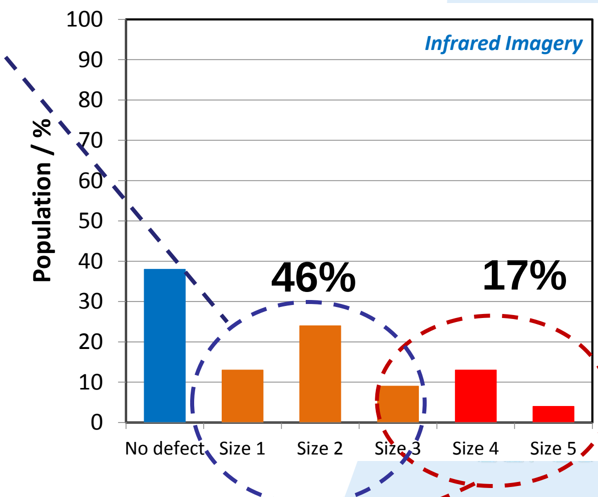


Cracks with lengths ranging from 0.5 to 1.2 mm promoting unsafety level of H_2 leak

- **Localized H_2 leak in the air outlet region**
- **Random distribution of the short-cuts**







Conclusions

✓ **Macroscopic tools used for FMEA (Failure Mode and Effect Analysis)**

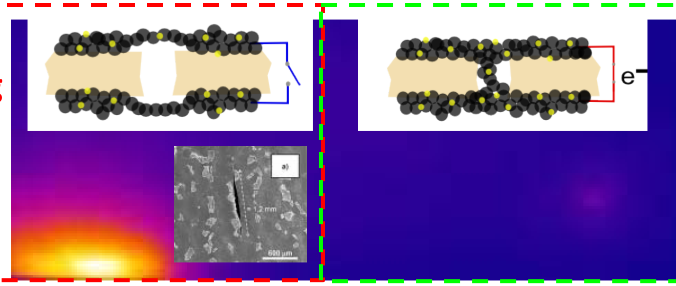
- **Identification of defective Cells and MEA defective areas**
- **Statistical analysis of the degradation occurrence as a function of MEA type, membrane type, current load profile, system configuration**

✓ **In the present study**

- **Heterogeneous ageing**
- **Large pinholing of the membrane in air outlet region due to the failure of one humidifier that induced operation under large air sub-stoichiometry and with large flooding**
- **Two different types of defect**

Case 1: large pinholing and tearing that appear during ageing due to operating conditions

→ End of Life of FC



Case 2: small pinhole/microstructure imperfections that appear during ageing or initially present before ageing

→ Not dramatic at short-term but at long time?

✓ **Current focusings**

- **Deeper physico-chemical characterization around the defects**
- **Accelerated Degradation Technique (ADT) to evaluate the impact of local short-circuit defects on membrane durability**

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Thank You For Your Attention.

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