ALPE PROJECT – LECTURE
PEMFC COMPONENTS: DESIGN, MANUFACTURING AND TESTING

MICOUD Fabrice – R&D Engineer at CEA LITEN
Email : fabrice.micoud@cea.fr

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PRESENTATION OUTLINE

- **Description & Manufacturing of PEMFC components**
  - Single cell architecture / PEMFC Principle
  - Membrane Electrode Assembly (MEA)
  - Bipolar Plate (BP)
  - Cell/Stack Assembly

- **PEMFC testing**
  - Different possible testing configurations
  - Initial Conditioning – Break-in phase
  - Performances assessment
  - Complementary Electrochemical characterizations
  - Durability Testing

PEMFC SINGLE CELL ARCHITECTURE

- **Proton Exchange Membrane Fuel Cell Principle**

$T_{operation}$: Ambient-95°C (Low T° PEMFC)

Anode (-): Hydrogen Oxidation Reaction (HOR)

$H_2 \rightarrow 2\ H^+ + 2\ e^-$

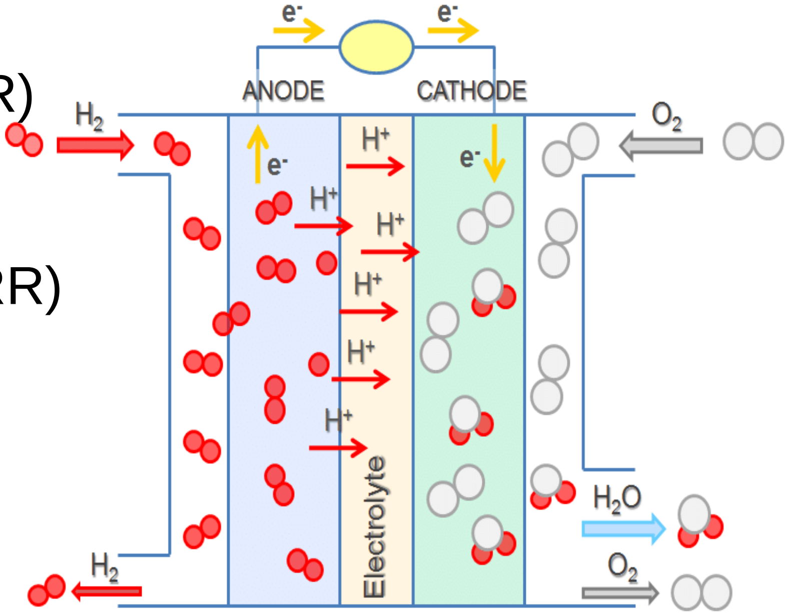
Cathode (+): Oxygen Reduction Reaction (ORR)

$½\ O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O$

Overall reaction

$H_2 + ½\ O_2 \rightarrow H_2O$ *(+ electricity + heat)*

$\Delta E° = 1{,}23\ V$



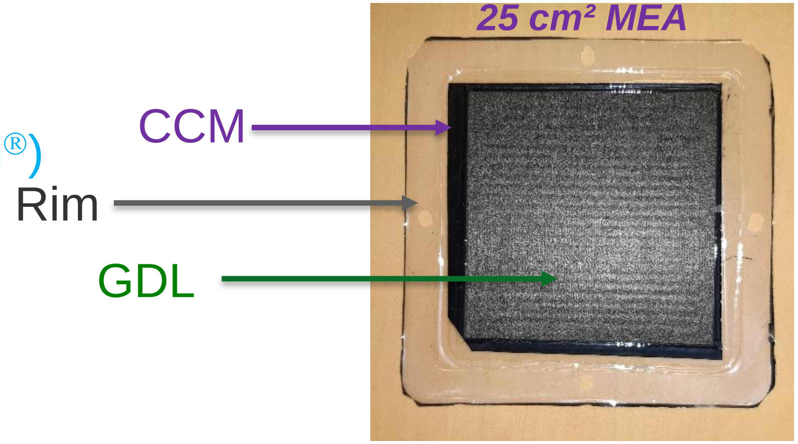
(PEM)FC : "Open" electrochemical generator vs. batteries "closed systems"

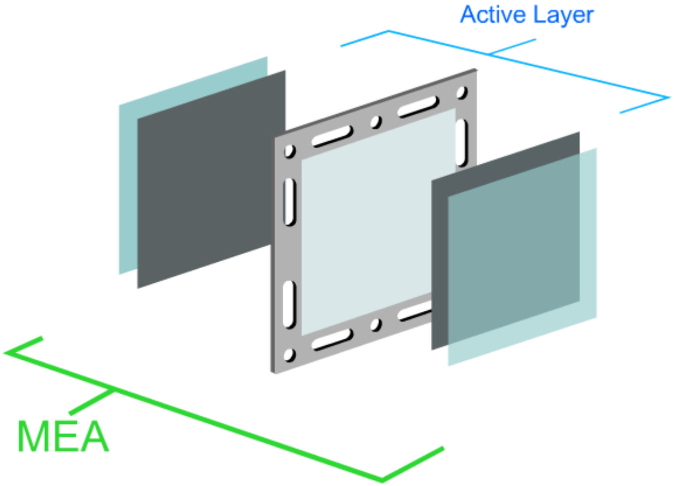
Energy (H_2 storage capacity) and Power (FC size) are clearly dissociated

PEMFC COMPOSITION & ARCHITECTURE

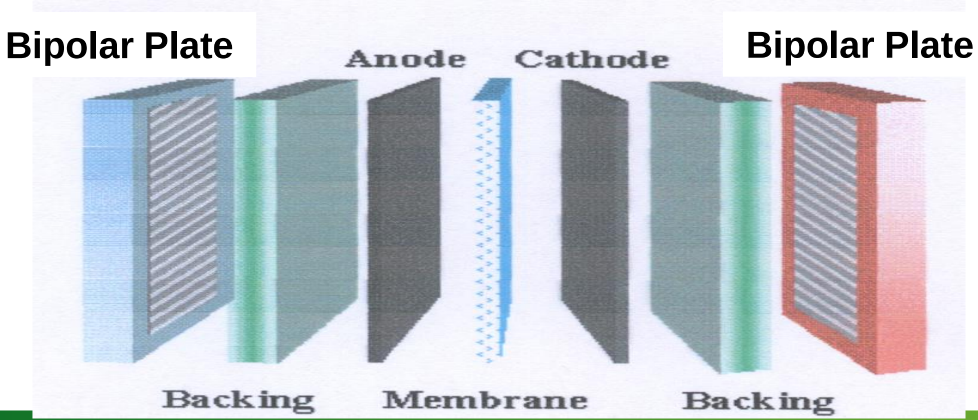
Constitution of an elementary cell:

- **Electrolyte:** polymer membrane (Nafion®)
- **Electrodes : Active layer**
  - **Pt/C (catalyst)**
  - **Ionomer**
- **Gas diffusing Layer (Backing)**
  - Carbon paper/fabric
  - Hydrophobic compounds
- **Bipolar plates**
  - **Reactant supply / Products exhaust**
  - **e- collection**
  - **Heat management**





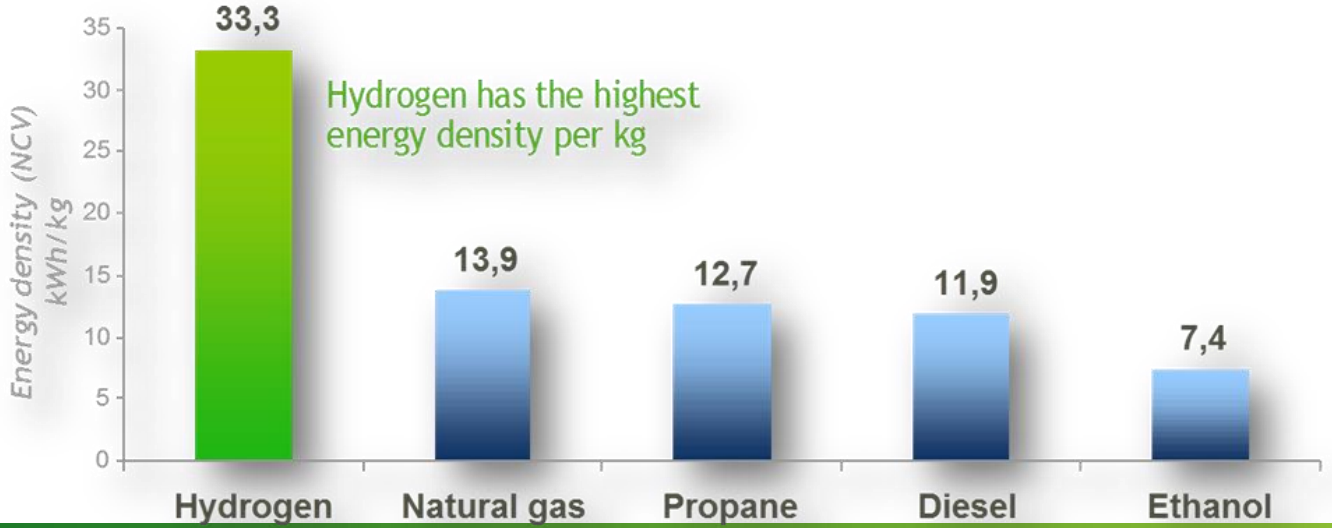
Membrane Electrode Assembly



GENERAL INFORMATION ABOUT HYDROGEN

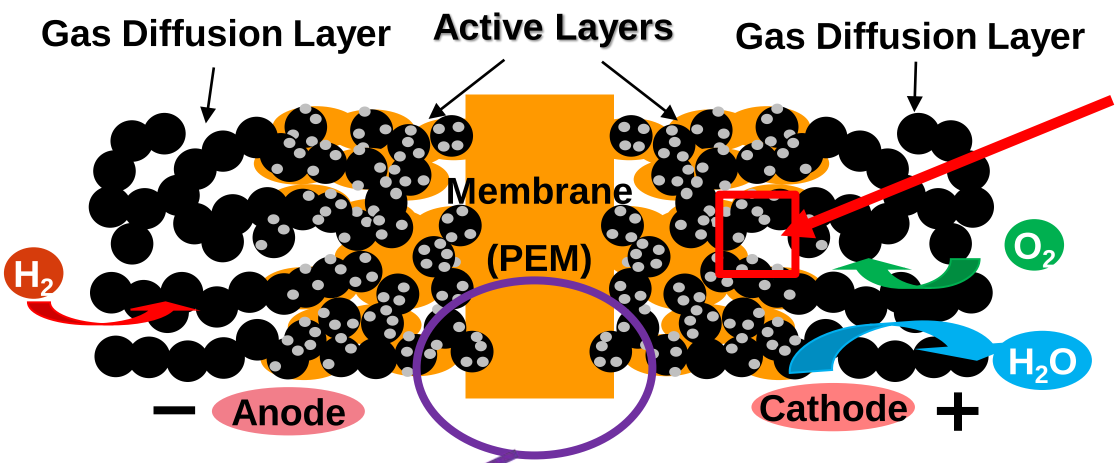
1 kg of hydrogen corresponds to :

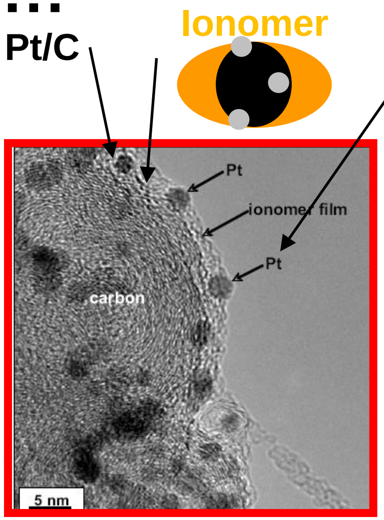
- 33,33 kWh (Lower Heating Value, 120 MJ)
- ~ 16 kWh (FC electric output power) → electrical efficiency ~ 50%
- 1-2 days of autonomy for domestic supply (except heating)
- ~ 100 km for a typical car
- 3,7 L (2.75 kg) of gasoline
- ~ 25 L @ 700 bars (storage weight ca. 20 kg/kg H_2)
- 2 to 10 € depending on the production processes



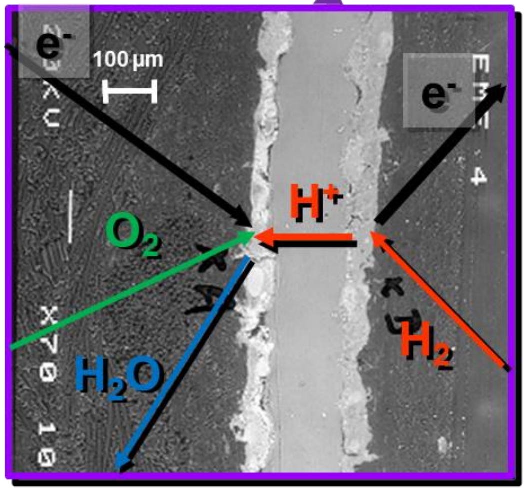
MEA NANO & MICRO-STRUCTURES

- **Further insights into MEA operation…**

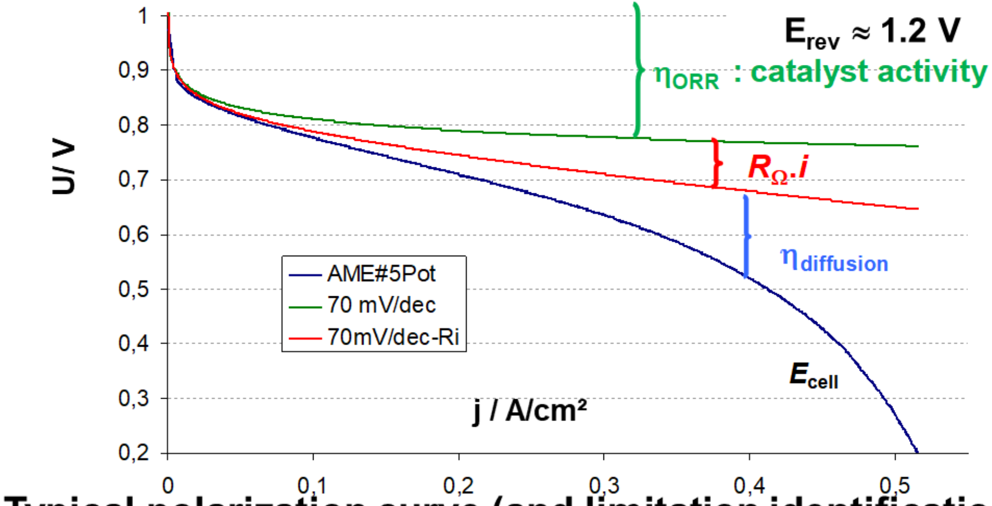




Triple contact
- Reactant
- Ionomer
- Catalyst (e-conduction)



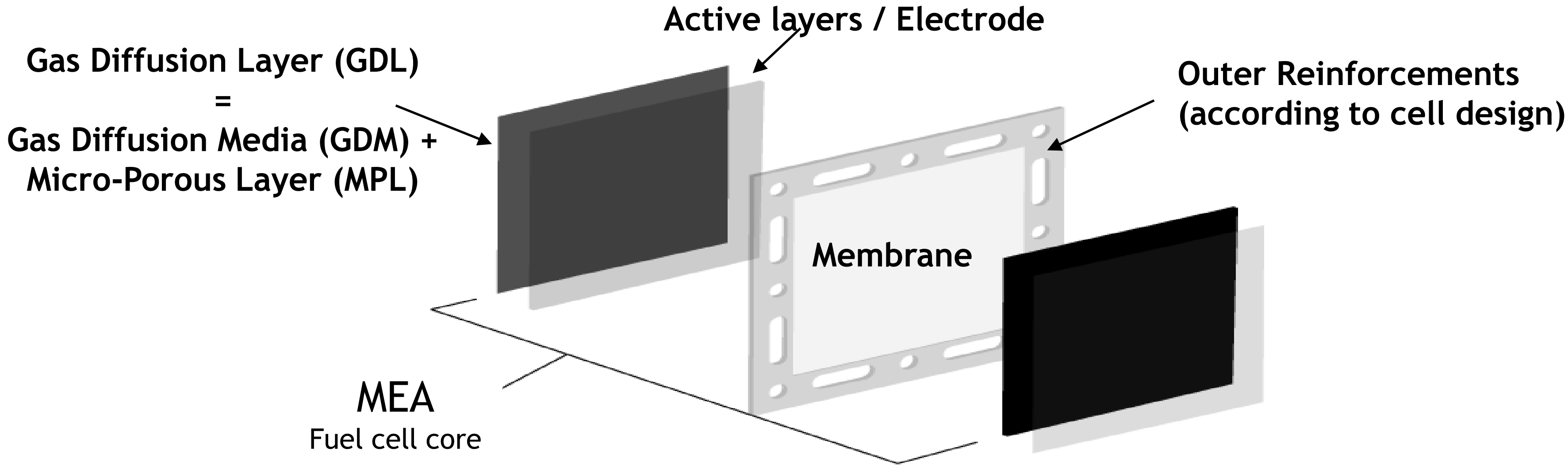
$$E_{cell} = E_{rev}(p_{H2},p_{O2},T) - \eta_{ORR} - i\,R_{\Omega} - \eta_{diffusion}$$



Typical polarization curve (and limitation identification)

MEA MANUFACTURING

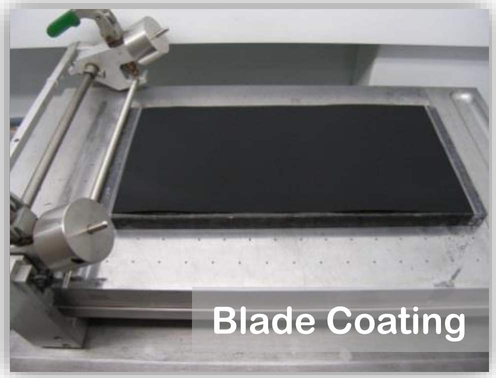
- **MEA : Assembly of up to 7 layers**



- **Core-component “3-layer” : Membrane + both active layers**
  - **CCM-type : Catalyst-Coated Membrane**
    - Active layer deposited onto a flat inert support (PTFE film)
    - Decal-transfer onto the membrane
    - Soft assembly of the two GDL and outer reinforcements
  - **CCB-type : Catalyst-Coated Backings**
    - Active layer deposited on the GDL
    - Hot pressing then needed onto the membrane to assembly the MEA with outer reinforcements

MEA MANUFACTURING

- **Ink Preparation**
  - Catalyst: Pt nanoparticles onto carbon support
  - Ionomer: Nafion® solution
  - Solvent: shall disperse well all components (mixture of water/organic solutions)
  - Details of preparation: key-parameters (confidential)
    - Rheological properties: to be adjusted according to the fabrication process
    - Order of addition of components
    - Dispersion method : mechanical stirring, ultrasonic probe, ball milling
    - Dispersion duration / Rest time before use
- **Different processes possible to deposit the active layers**
  - CCM (onto inert support) or CCB types (directly onto GDL)
  - Drying process to be controlled to ensure coating homogeneity



Blade Coating

Spray

Screen printing

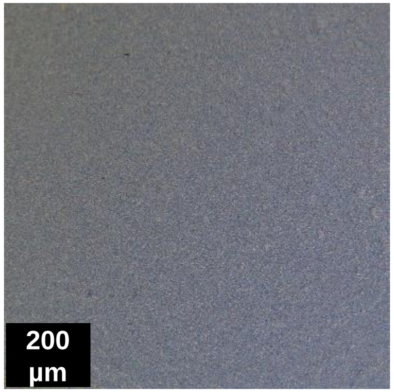
MEA MANUFACTURING

Quality control of electrodes

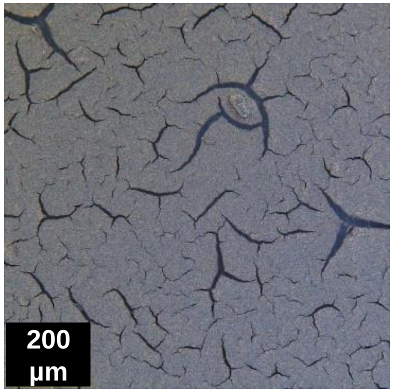
- Visual control / Optical Microscopy / Scanning Electron Microscopy

Cathode active layer top view

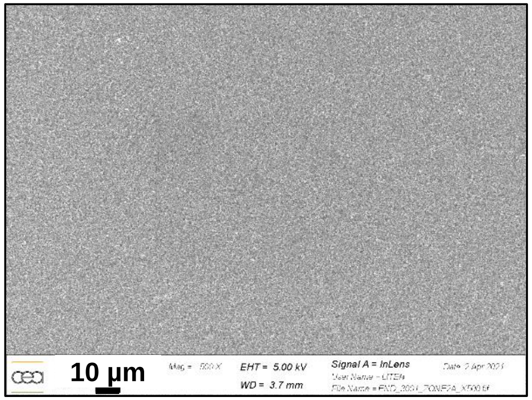
Homogeneous layer



Heterogeneities and cracks



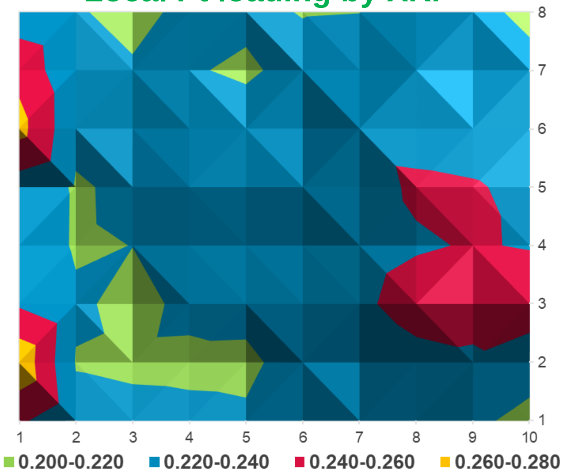
Homogeneity checked at the µ-scale



- Catalyst loading assessment / Transfer and interfaces quality

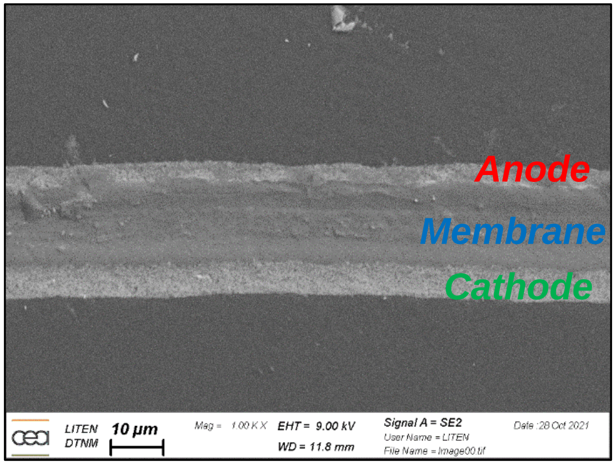
Electrode homogeneity (SEM and Pt loading by XRF)

Local Pt loading by XRF

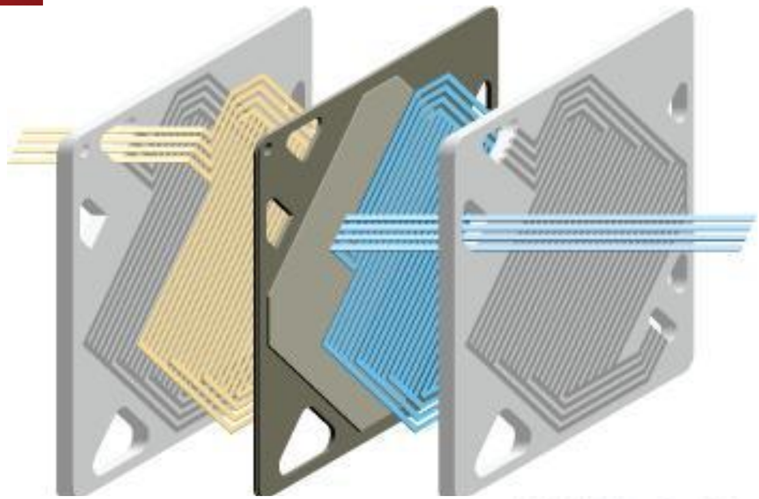


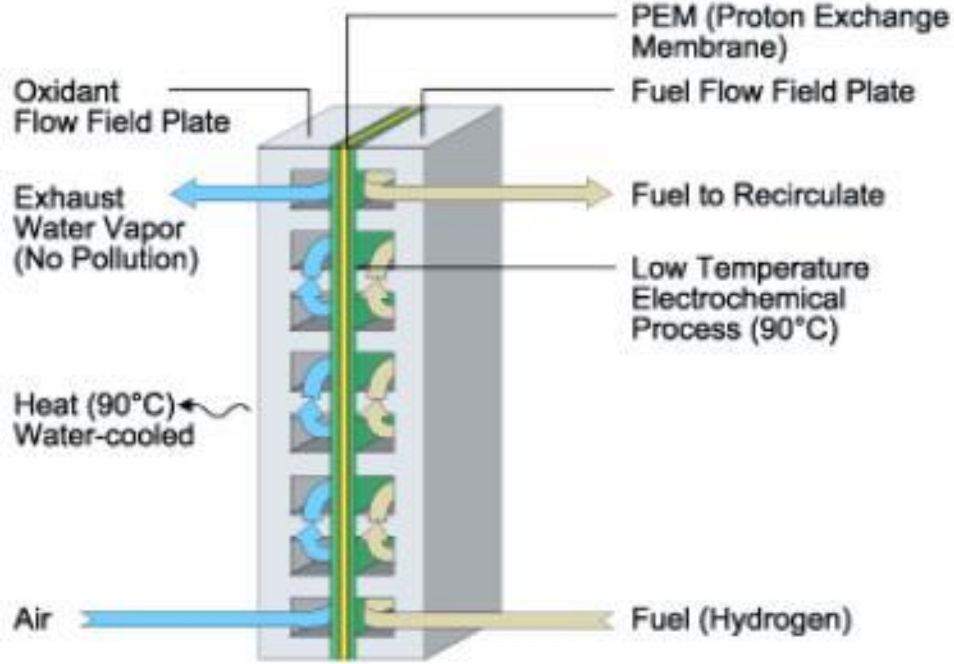
Global Pt loading also checked by weight before assembly / decal transfer (hot pressing) onto the membrane

MEA cross-section by SEM



BIPOLAR PLATE : TECHNICAL FUNCTIONS





BP manage the inlets/outlets of the cell

- **Uniform gas distribution**

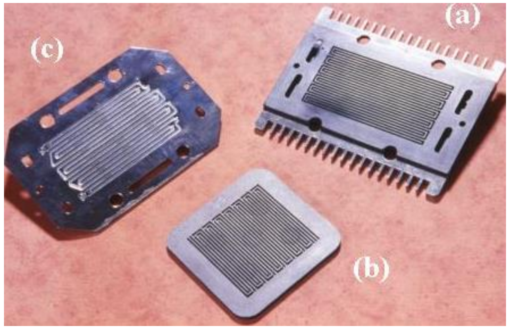
(intracell and inter-cells for stacks)

- **Heat management**
- **Water management**
- **Fluid circulation**
- **Gas tightness (separation)**
- **Current collection**

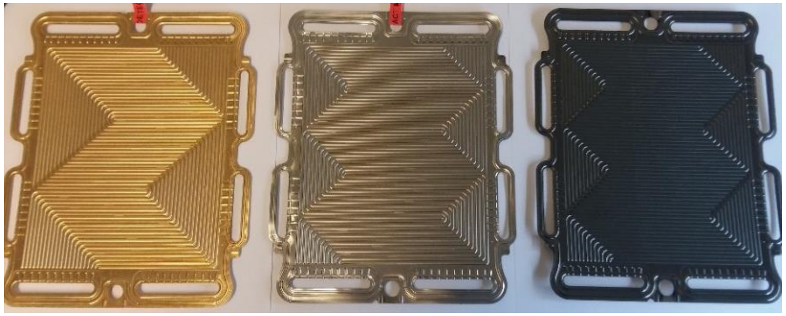
BIPOLAR PLATE MATERIALS

FUEL CELLS AND HYDROGEN
JOINT UNDERTAKING

Examples of
single cell plate



Coated metallic BP (serpentine design)



SoA metallic BP
(linear design)

Issues

Volume

Weight

Material cost

Machining cost (duration)

(a) Graphite → Machining

Performances OK but high cost, fragile

(b) Carbon / polymer composite → Moulding, injection

Pb : conductivity, mechanical strength

(c) Metal plate (stainless steel) → Stamping

Pb : corrosion, interfacial contact resistance C/metal

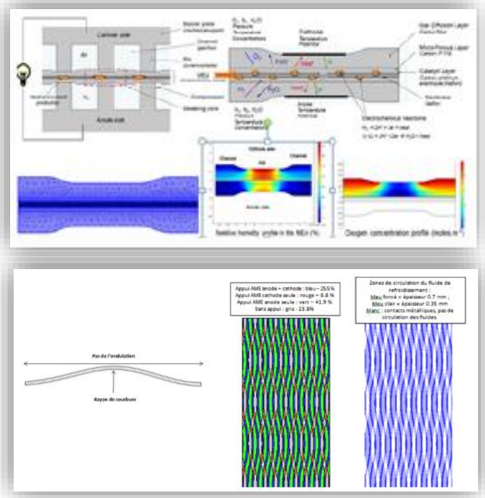
Cost

Importance of the BP design|GDL interface

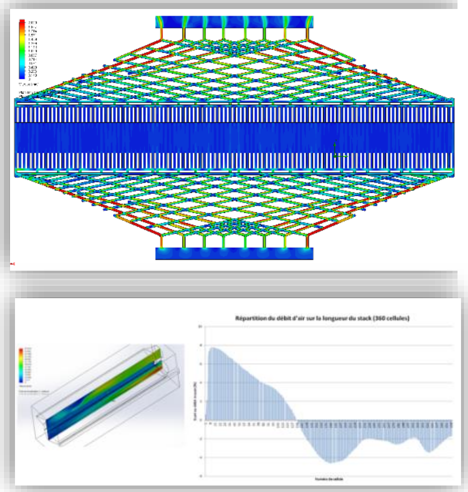
BIPOLAR PLATE AND STACK DESIGN : DIMENSIONING

- **Bipolar plate design**

Channel design



Flow homogeneity



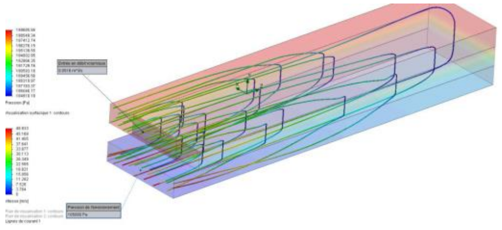
CAD

Numerous parameters to be considered

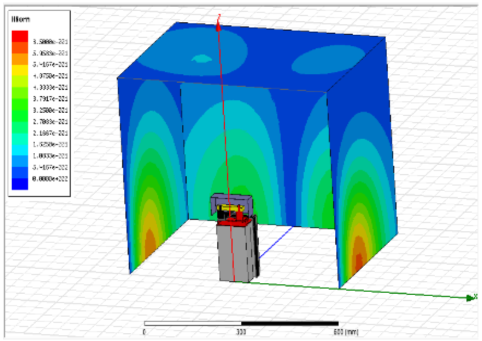
→ BEST COMPROMISE to be found

- **Stack design**

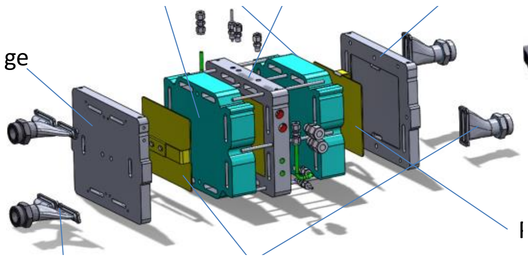
Fluidic modeling



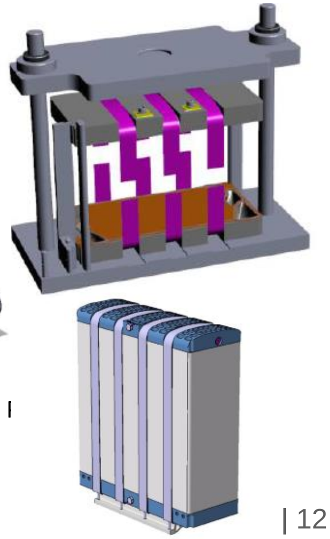
CEM simulation



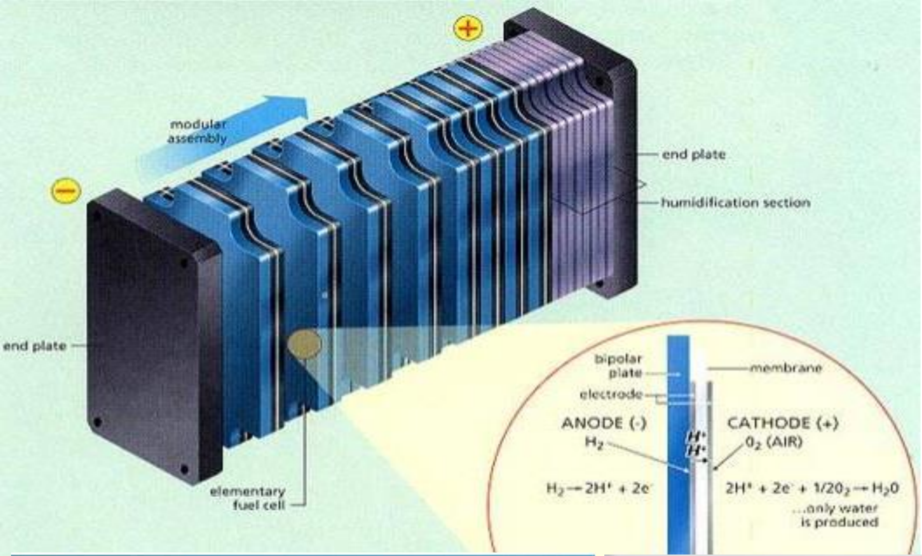
Assembly

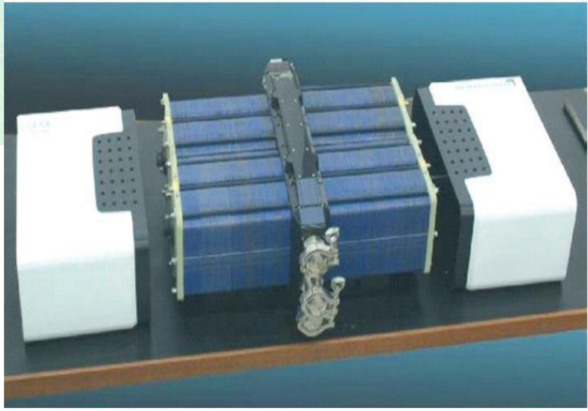


Mechanical simulation

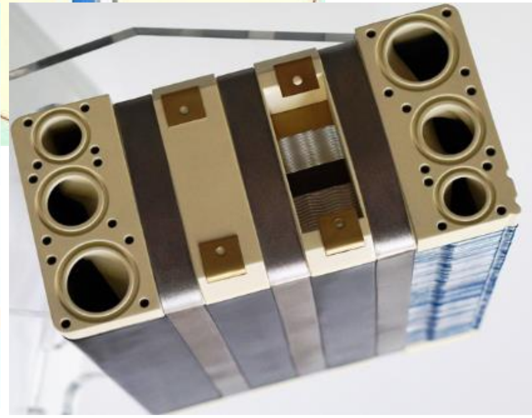


CELL STACKING





4 x 20 kW PEMFC Stack CEA-PSA for automotive applications (2005)



Single 80 kW PEMFC Stack CEA for automotive applications (2020)

Cells : associated in series (→ output voltage)
Cell size : related to the output current
Gas supply : in parallel
Cooling supply: in parallel

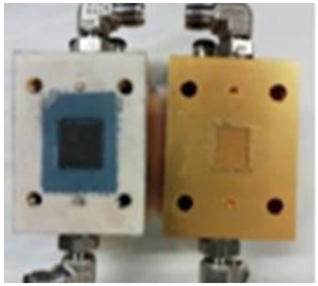
- → **Mechanical aspects**
- → **Thermal aspects**
- → **Fluidic aspects**
- → **Electrochemical aspects**

TO BE CORRELATED WITH THE OPERATING CONDITIONS AND APPLICATIONS SPECIFICATIONS !

WHAT ABOUT PEMFC TESTING ?

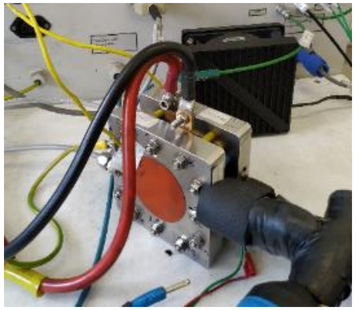
- **Different configurations and scales available**

Differential Cell
ca. 1-2 cm²



- Homogeneous operating conditions (high stoichiometries)
- Reproduction of local operating conditions
- Suitable for fast testing: components & MEA intrinsic properties and durability

Small Single Cell
ca. 25-50 cm²

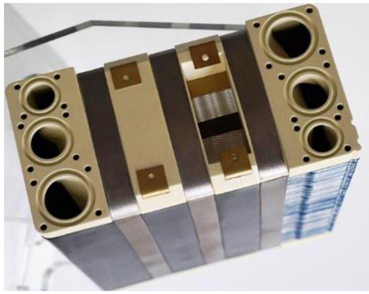


- Evaluation of MEA performances and durability under realistic/technical operating conditions
- Low amount of materials needed for performances and durability assessement

Large Single Cell
ca. 100-350 cm²

- Usually same plate design as stack
- « True » evaluation of MEA performances and durability under technical operating conditions
- Characterizations of MEA and cell design properties

Short / Full Stack

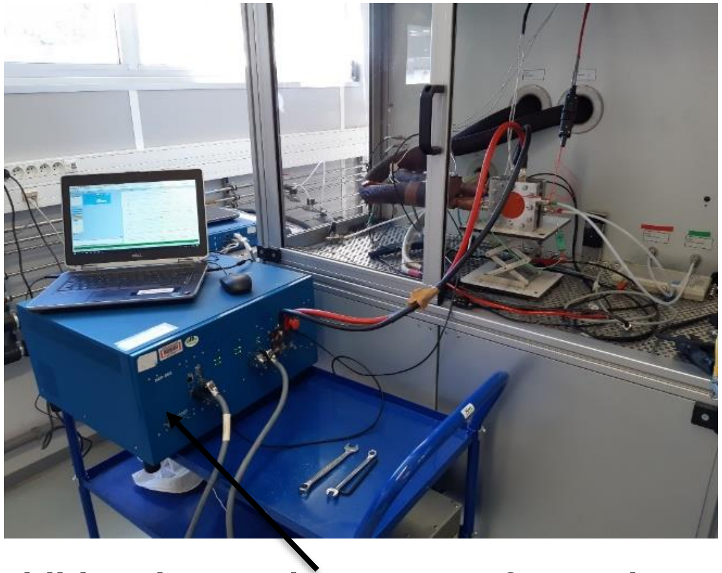


- Useful to assess « real » performances/durability in stack configuration
- Thermal heterogeneities & inertia taken into account
- Global fluidic behavior : inter-cell homo/hetero-geneity

PEMFC TESTING EQUIPMENT / FACILITIES

- **Examples of fuel cell test benches in the laboratory**

Single cell test bench



Additional potentiostat to perform advanced electrochemical measurements (Cyclic voltammetry, EIS, …)

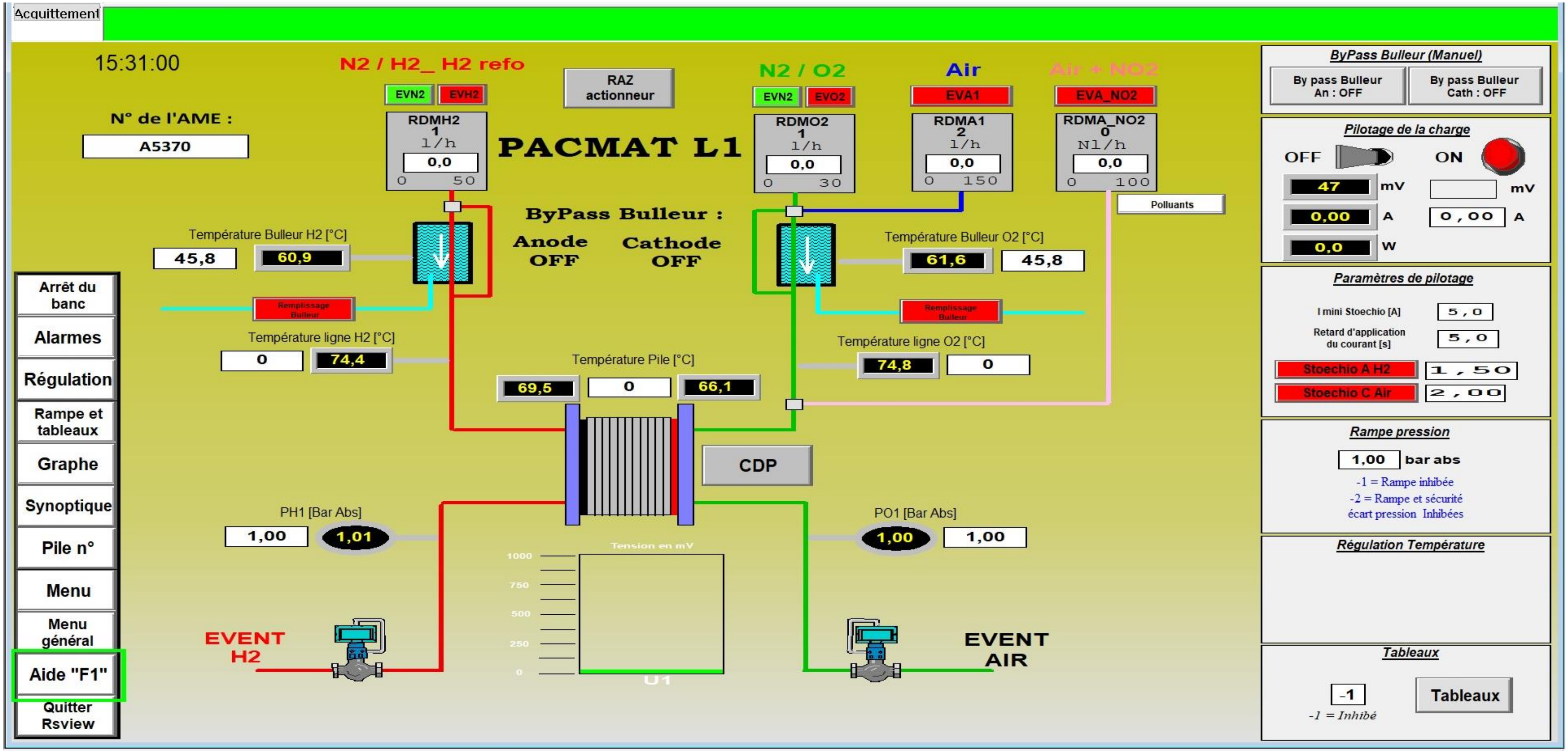
100 kW stack test bench

Facilities needed:

- H_2 / air / N_2/ O_2 gas supplies
- DI water supply
- Gas sensor (H_2) for safety
- Vents for gas exhaust / purge
- External Cooling circuit
- Room with controlled ventilation system

PEMFC TEST BENCH DESCRIPTION

- **How does a test bench work ?**
  - General control panel
  - Hydrogen line (anode) / Air line (cathde) + N2 for inerting
  - Control for RH, Pressure, Temperature, Current or Voltage, Safety thresholds

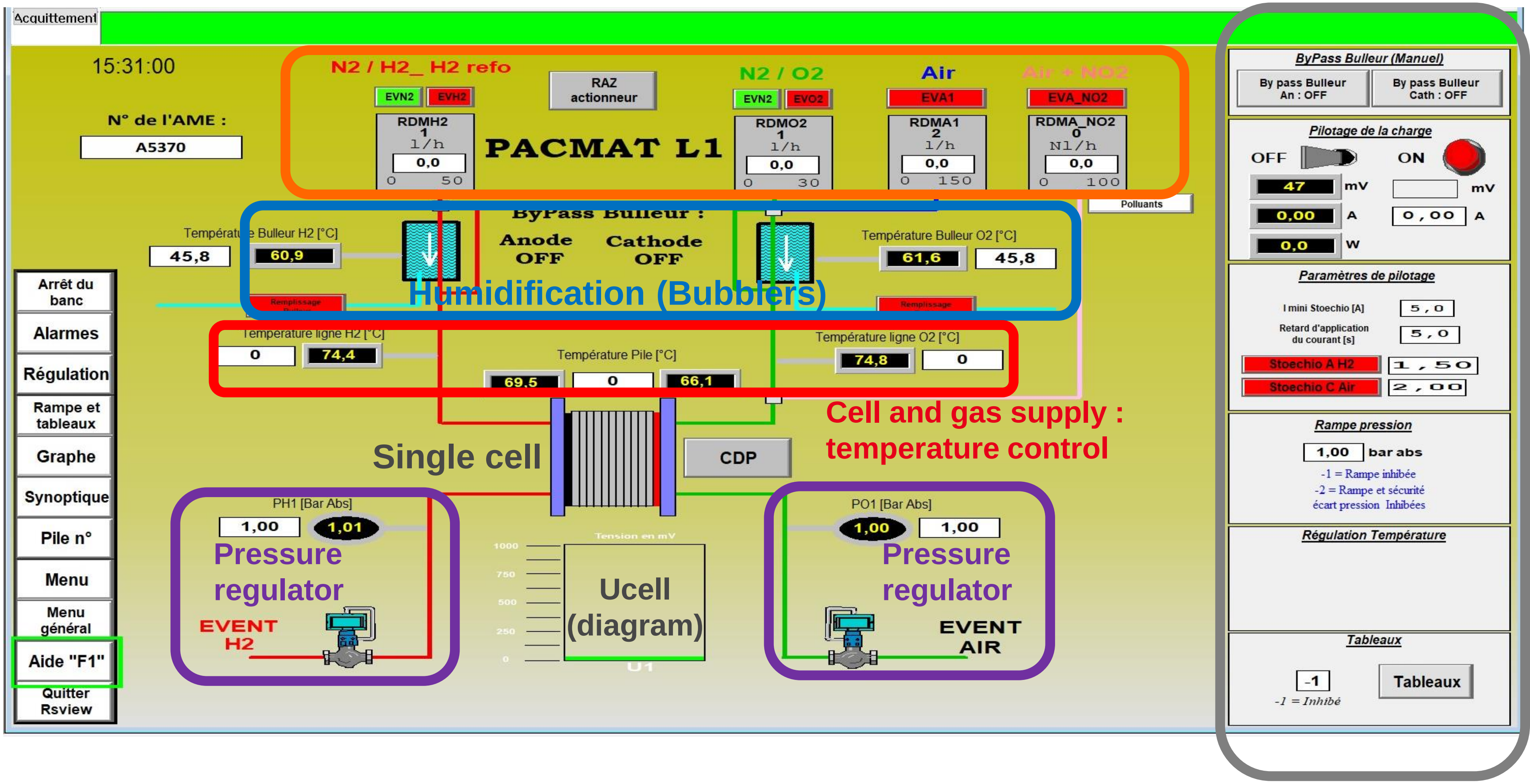


PEMFC TEST BENCH DESCRIPTION

- **How does a test bench work ?**

Operating parameters
I / Ucell / P
Stoichiometries
Minimum Flow rates
Test program / cycles

Gas selection / Flow-rate set points



Humidification (Bubblers)

Cell and gas supply : temperature control

Single cell

Pressure regulator

Ucell (diagram)

Pressure regulator

15:31:00

N° de l'AME : A5370

RDMH2 1: 0,0 l/h (0 – 50)

RDMO2 1: 0,0 l/h (0 – 30)

RDMA1 2: 0,0 l/h (0 – 150)

RDMA_NO2 0: 0,0 Nl/h (0 – 100)

Température Bulleur H2 [°C]: 45,8 / 60,9

Température Bulleur O2 [°C]: 61,6 / 45,8

Température ligne H2 [°C]: 0 / 74,4

Température Pile [°C]: 69,5 / 0 / 66,1

Température ligne O2 [°C]: 74,8 / 0

PH1 [Bar Abs]: 1,00 / 1,01

PO1 [Bar Abs]: 1,00 / 1,00

ByPass Bulleur (Manuel)

By pass Bulleur An : OFF

By pass Bulleur Cath : OFF

Pilotage de la charge

OFF ON

47 mV

0,00 A — 0,00 A

0,0 W

Paramètres de pilotage

I mini Stoechio [A]: 5,0

Retard d'application du courant [s]: 5,0

Stoechio A H2: 1,50

Stoechio C Air: 2,00

Rampe pression

1,00 bar abs

-1 = Rampe inhibée

-2 = Rampe et sécurité écart pression Inhibées

Régulation Température

Tableaux

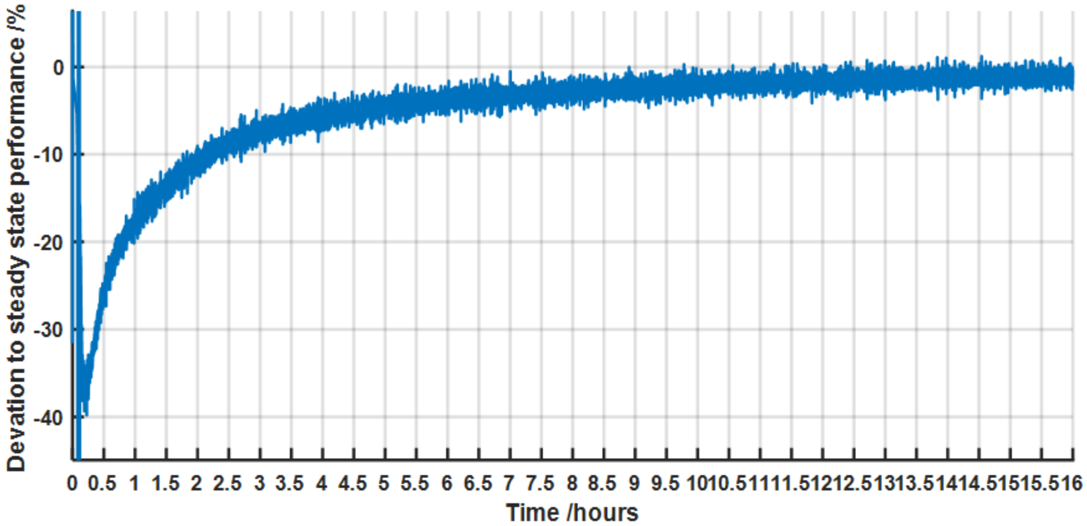
-1 Tableaux

-1 = Inhibé

INITIAL CONDITIONING – BREAK-IN PHASE

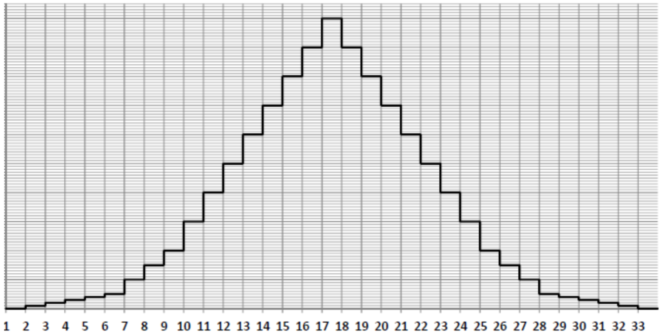
- **Break-in : very first operation of the PEMFC**
  - Similar to the « first formation » cycle for Li-ion batteries
  - Necessary step: operation under favorable and well-controlled conditions
  - Allow to increase and reach nominal performances before system integration
  - Can last several hours to reach steady-state/final performances

- **Different (electro)chemical processes**
  - Membrane hydration
  - Ionomer hydration in the active layers
  - Activation/Depollution of the catalyst particles



PEMFC TESTING: PERFORMANCES ASSESSEMENT

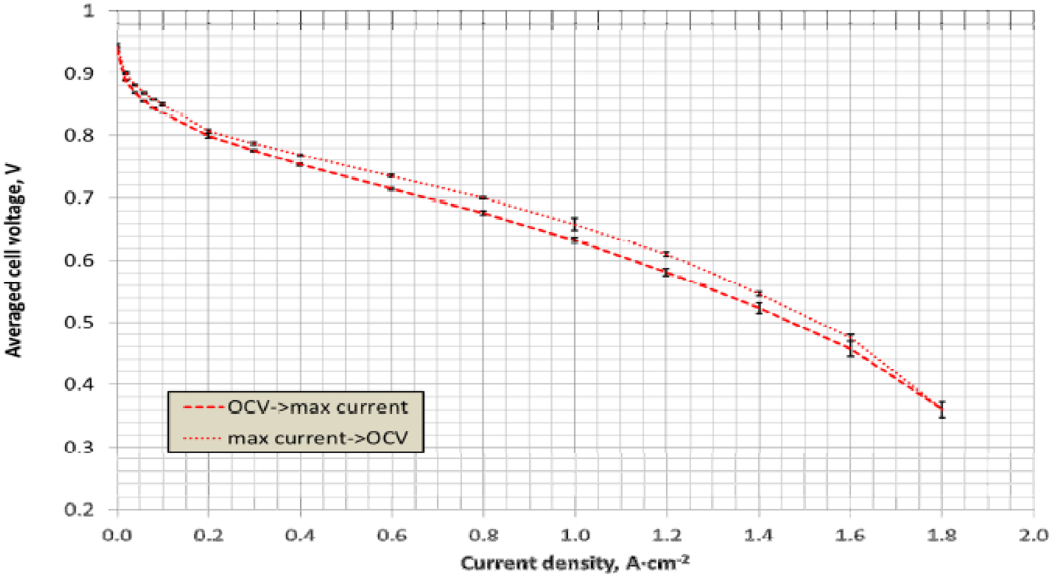
- **Polarization curve measurements**
  - i-E response of the FC



Measurement usually carried out by current steps

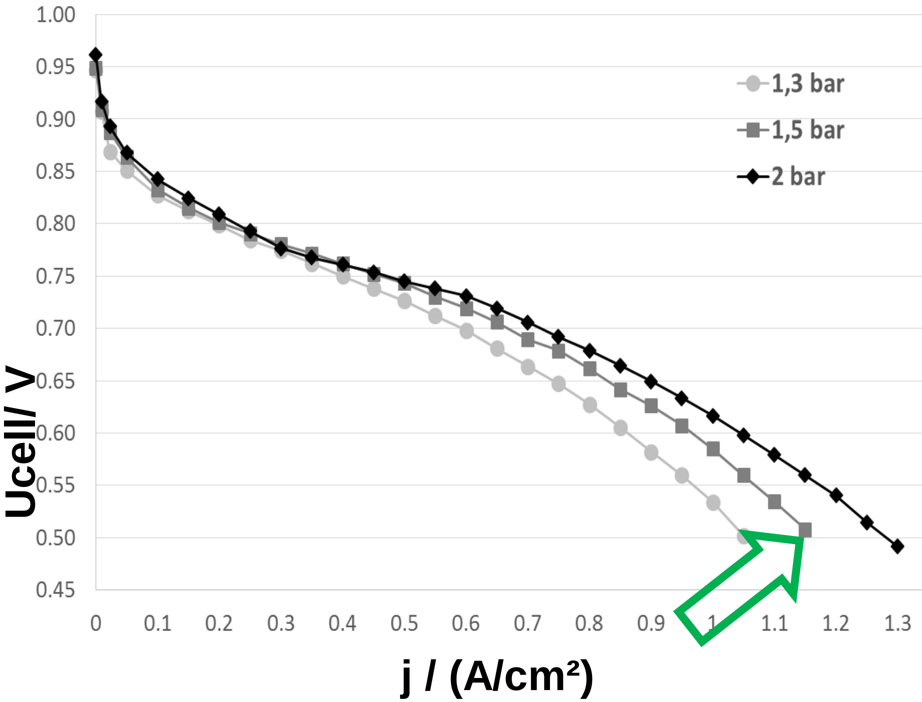
Experimental protocol has an influence on the results

- Conditioning phase before measurement
- Increasing/Decreasing current steps (hysteresis due to RH effect within the cell / Pt oxide formation)
- Stability criteria
- Step duration
- Minimum gas flow / Maximum current reached



PEMFC TESTING: EFFECT OF OPERATING CONDITIONS

- **Gas Pressure**
  - Favors mass transport (especially at the cathode air side) vs. compressor power consumption
- **Relative Humidity**
  - Improves ionomer conductivity vs. drying (low RH) / flooding (> 100%)
- **Temperature**
  - Enhances FC reaction kinetics / Avoid liquid water condensation
  - Thermal exchanger size
  - Drying effect
  - Also enhances degradation reaction kinetics
- **Stoichiometry**
  - Fluid velocity within the cell : homogeneous supply and liquid water removal
  - H2 efficiency & storage capacity (recirculation loop / dead-end mode)
  - Pressure drops / Air compressor capability / energy consumption

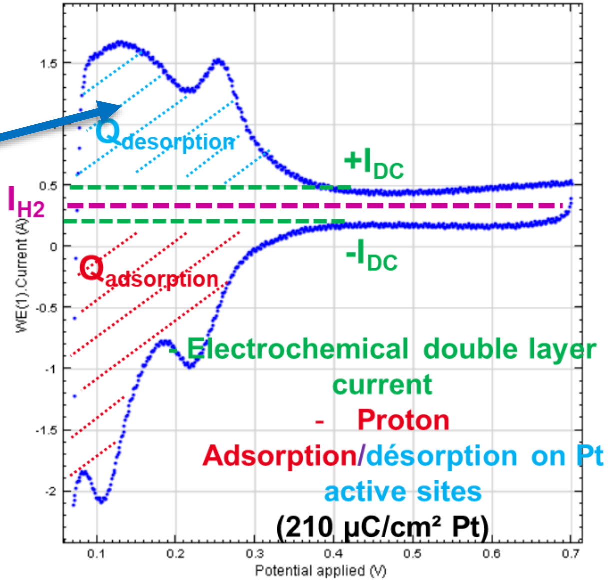


Impact of gas absolute pressure on the performances of a PEMFC short stack. H_2/air, 80°C, RH 50/50, Sto 1.5/2, Minimum flowrates equivalent to 0.1 A/cm².

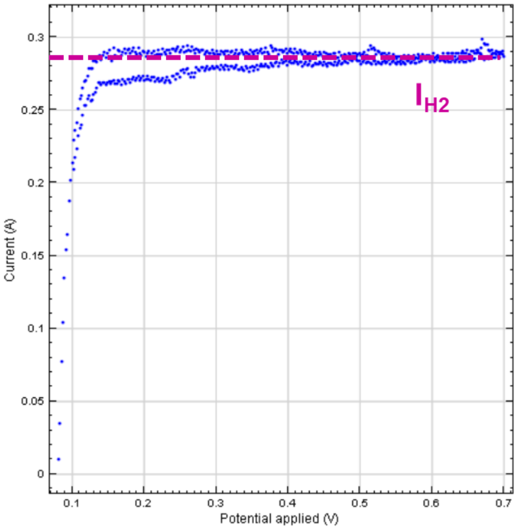
Best trade-off / compromise to be found between performances, durability and system balance of plant

PEMFC TESTING: EXAMPLE OF ADDITIONAL CHARACTERIZATIONS

- **Pt ECSA Measurement by cyclic voltammetry (high scan rate)**

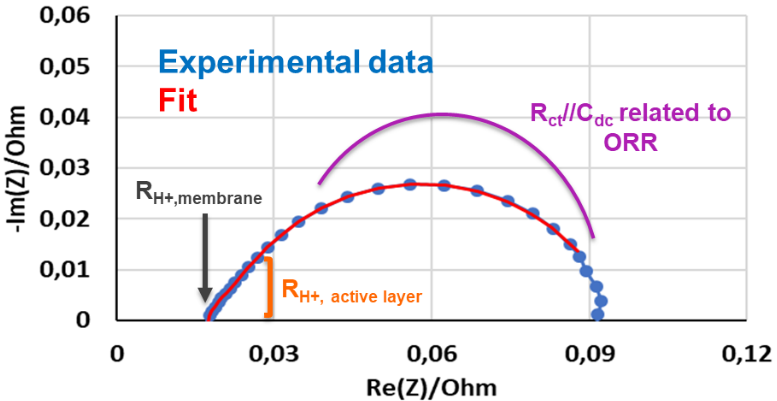


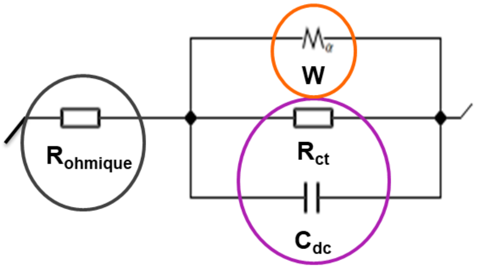
- **H2 permeation measurement by cyclic voltammetry (low scan rate)**



EIS example on differential cell (no mass transport limitations) Equivalent electrical circuit

- **EIS measurement**





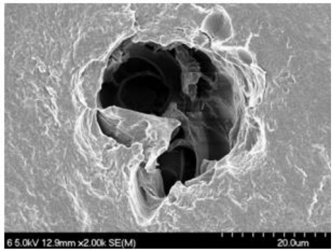
PEMFC TESTING: DURABILITY ASPECTS

- **Overview of the main degradation mechanisms**
- **Membrane Degradation**

  - Stress due to RH cyles (swelling/shrinking)
  - Mechanical stress (assemblage cell/stack asembly)
  - Chemical Stress

  → **Loss of ionic conductivity**

  → **H_2 crossover**

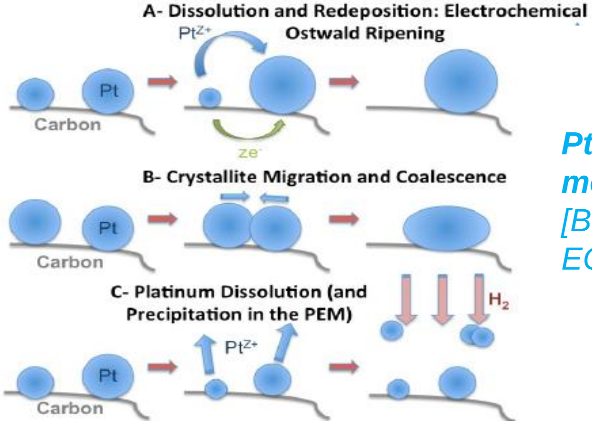


SEM image: membrane pinhole

- **Pt Nano-Particles Degradation**

  - Ostwald ripening
  - Pt NP coalescence/agglomeration
  - Pt NP dissolution and reduction/redeposition

  → **Loss of electroactive area**



Pt NP degradation mechanisms

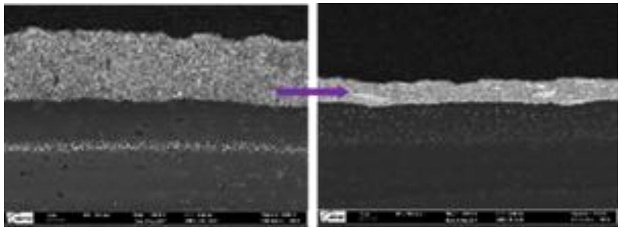
[B. Vion-Dury 2011 ECS Trans. 41 697]

- **Carbon Support Degradation**

  - Carbone corrosion

  → **Loss of porosity (mass transport)**

  → **Loss of electronic conductivity**



SEM image: Cathode thinning due to carbon corrosion

PEMFC TESTING: DURABILITY ASPECTS

- **Durability study usually performed at small single cell / short stack level**
  - Component characterizations by Accelerated Stress Tests (Single cell)
  - Realistic ageing tests can last hundreds/thousands of hours : evaluation of degradation rate
  - Estimation/ Prediction of PEMFC lifetime under given operating conditions ?

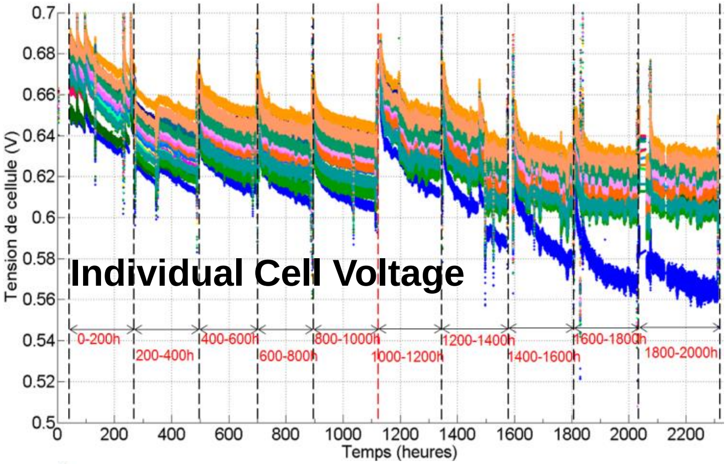
- **Ageing protocols usually depend on the application and operating conditions**
  - **Constant load durability**
    - Very simple protocol but not realistic
    - Operating conditions relevant according to system conditions
  - **FC-DLC : Fuel Cell Dynamic Load Cycle**
    - Former New European Driving Cycle
    - « Representative » of automotive application
  - **Accelerated Stress Tests**
    - Dedicated to MEA and component ranking/selection for fast benchmarking
    - Not realistic / Require external equipment (potentiostat) for potential cycling
    - Specific protocols exist for:
      - Membrane
      - Catalyst
      - Catalyst support
    - AST representative of real-world ageing for automotive applications under development:

EU Project ID-FAST(http://id-fast.eu)

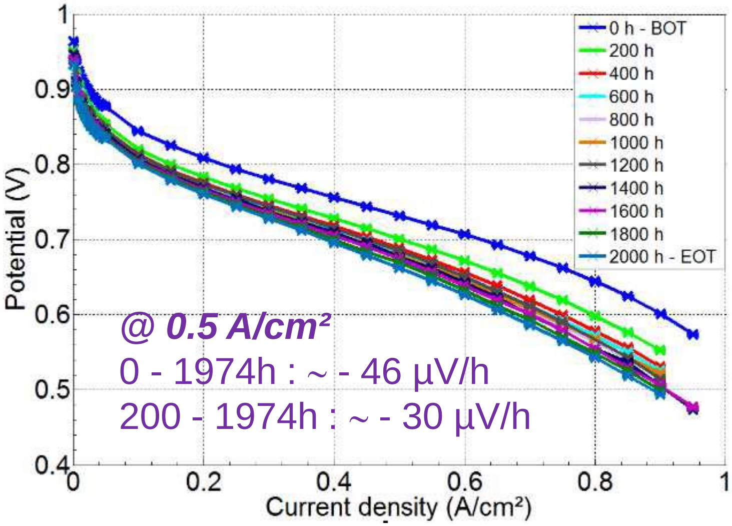
PEMFC TESTING: CONSTANT LOAD AGEING

- **Durability study usually performed at small single cell / short stack level**

Fixed current @ 0.4 A/cm² on a short stack



Individual Cell Voltage



@ 0.5 A/cm²

0 - 1974h : ~ - 46 µV/h

200 - 1974h : ~ - 30 µV/h

<u>Degradation rate is not constant during PEMFC operation !!!</u>

Important performance losses during the first 200-300 h of operation

- Fast evolution of active layer (Ostwald ripening, small NP dissolution & NP growth)
- « More constant rate » after this first stage

Performance losses can be partly recoverable/reversible after shutdown/characterizations:

- RH heterogeneities, water management
- Catalysts pollution/depollution
- Reduction of Pt oxides

Irreversible losses are caused by physical degradation of components (BP, GDL, Pt NP, carbon support, membrane) and cannot be recovered

Degradation rate is not a single value !!!

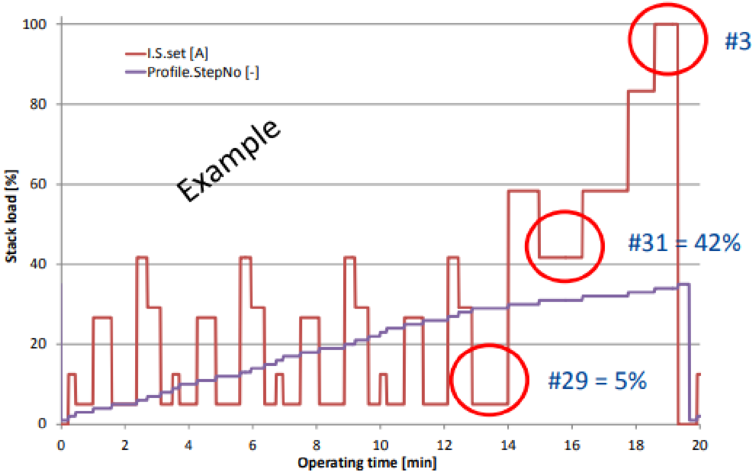
Both reversible and irreversible performance losses

F. Nandjou, PhD thesis CEA-INPG 2015
C. Robin et al., J. Pow Sources, 326 (2016) 417
M. Gérard, présentation ECS Prime 2016

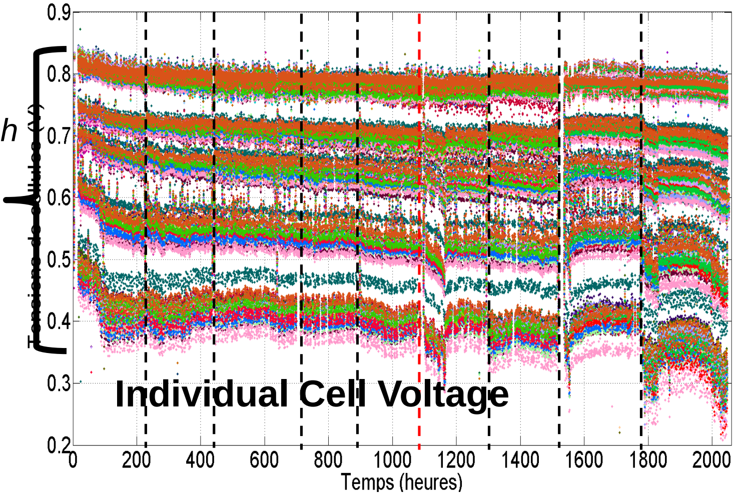
PEMFC TESTING: FC-DLC AGEING

- **Reference cycle used for automotive applications**

FC-DLC ageing on a short stack

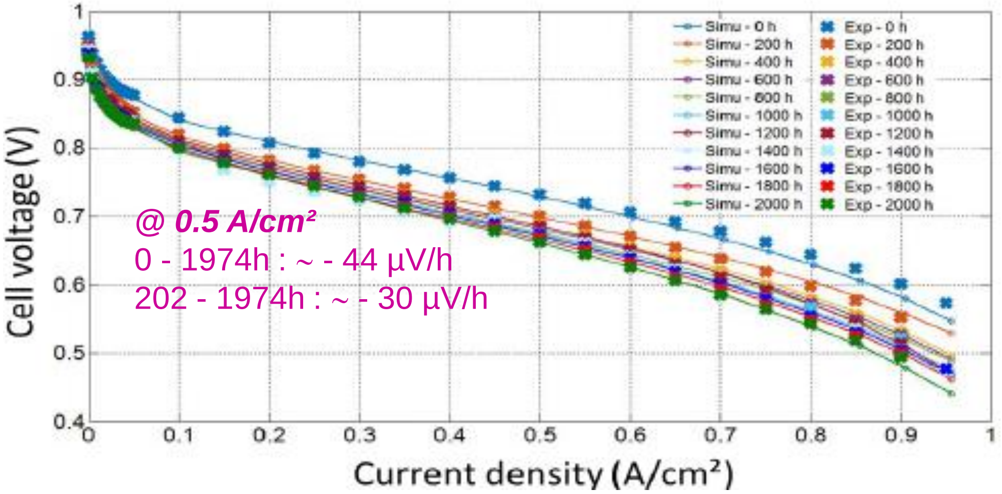


Different cell voltages for each current



Current load profile during FC-DLC (ex-NEDC)

Current values to be adapted to cell/MEA/stack performances (% values)



@ 0.5 A/cm²
0 - 1974h : ~ - 44 µV/h
202 - 1974h : ~ - 30 µV/h

F. Nandjou, PhD thesis CEA-INPG 2015
C. Robin et al., J. Pow Sources, 326 (2016) 417
M. Gérard, présentation ECS Prime 2016

Degradations are mostly irreversible

CONCLUSIONS ABOUT PEMFC TESTING

- **Recommendations exist about PEMFC testing at single cell and stack levels from previous EU projects**

European Commission

JRC SCIENCE FOR POLICY REPORT

EU HARMONISED TEST PROTOCOLS
FOR PEMFC MEA TESTING IN
SINGLE CELL CONFIGURATION FOR
AUTOMOTIVE APPLICATIONS

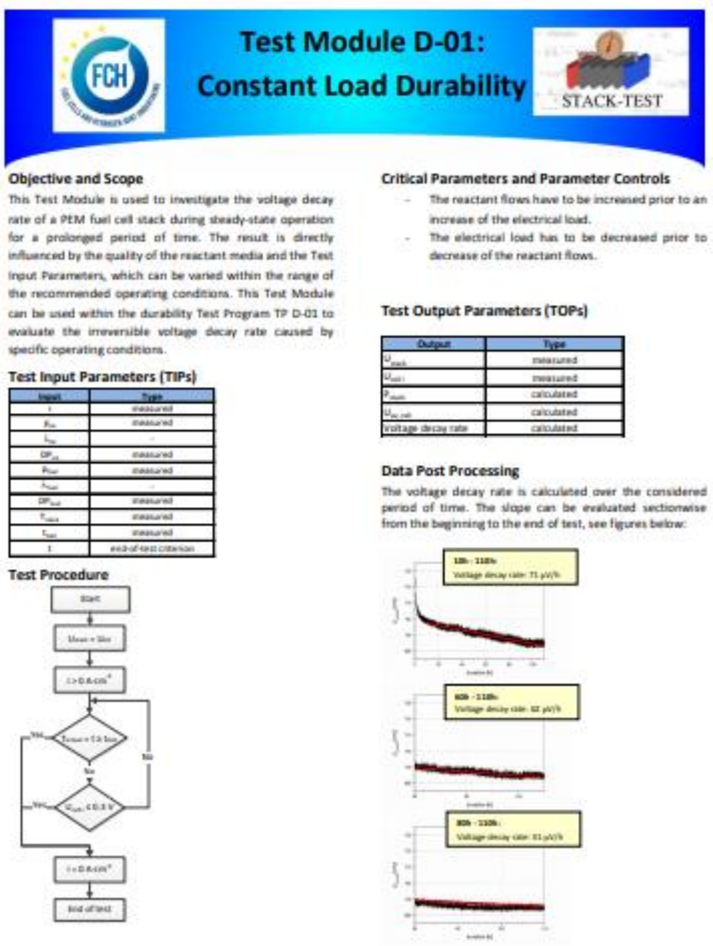
Georgios Tsotridis, Alberto Pilenga, Giancarlo De Marco, Thomas Malkow

2015

Joint Research Centre

EUR 27632 EN

https://op.europa.eu/en/publication-detail/-/publication/82c28cc6-cef7-11e5-a4b5-01aa75ed71a1/language-en



Test Module D-01:
Constant Load Durability

STACK-TEST

Objective and Scope

This Test Module is used to investigate the voltage decay rate of a PEM fuel cell stack during steady-state operation for a prolonged period of time. The result is directly influenced by the quality of the reactant media and the Test Input Parameters, which can be varied within the range of the recommended operating conditions. This Test Module can be used within the durability Test Program TP D-01 to evaluate the irreversible voltage decay rate caused by specific operating conditions.

Test Input Parameters (TIPs)

Input	Type
I	measured
[illegible]	measured
[illegible]	-
[illegible]	measured
[illegible]	measured
[illegible]	-
[illegible]	measured
[illegible]	measured
[illegible]	measured
t	end-of-test criterion

Test Procedure

Critical Parameters and Parameter Controls

- The reactant flows have to be increased prior to an increase of the electrical load.
- The electrical load has to be decreased prior to decrease of the reactant flows.

Test Output Parameters (TOPs)

Output	Type
U_{stack}	measured
$U_{cell\ i}$	measured
P_{stack}	calculated
[illegible]	calculated
Voltage decay rate	calculated

Data Post Processing

The voltage decay rate is calculated over the considered period of time. The slope can be evaluated sectionwise from the beginning to the end of test, see figures below:

http://stacktest.zsw-bw.de

Thank you for your attention !

Any questions ?

Commissariat à l’énergie atomique et aux énergies alternatives
17 rue des Martyrs | 38054 Grenoble Cedex
www-liten.cea.fr

Établissement public à caractère industriel et commercial | RCS Paris B 775 685 019