



Некоторые физические проблемы, связанные с функционированием и диагностикой топливных элементов

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Research Institute in Materials, Mechanics and Energetics

Application to Transport, Energy and Environmental Engineering

Director : Yves GERVAIS

Vice Director : Jean-Claude GRANDIDIER

- Institute of the CNRS : INSIS et INP
- Section CNRS (Chercheur) : 5, 9 et 10
- Section CNU (Enseignant Chercheur) : 26, 28, 30, 60, 62, 63 et 74
- Component of affectation : UFR SFA, ENSIP, IUT 86, IRIAF, IUT 16 et l'ENSMA



Where is Poitiers ?



An Old Medieval City (Roman Art) ...



... of cheese and wine !

Research and Education Context



Research and Education



School of Engineers in
Aeronautics

Within the ISAE Toulouse group



Faculty of Sciences
(Physics and Mech Engg)

School of Engineers ENSIP
(environment)

Faculty of Sports Sciences

The Pprime Institute

- **People : ~ 600 personnes**

Academic staff	Technical staf	PhD students	Contractual (post-doc, engineers, ...)
199 (58 % d'HDR)	101	156	> 150

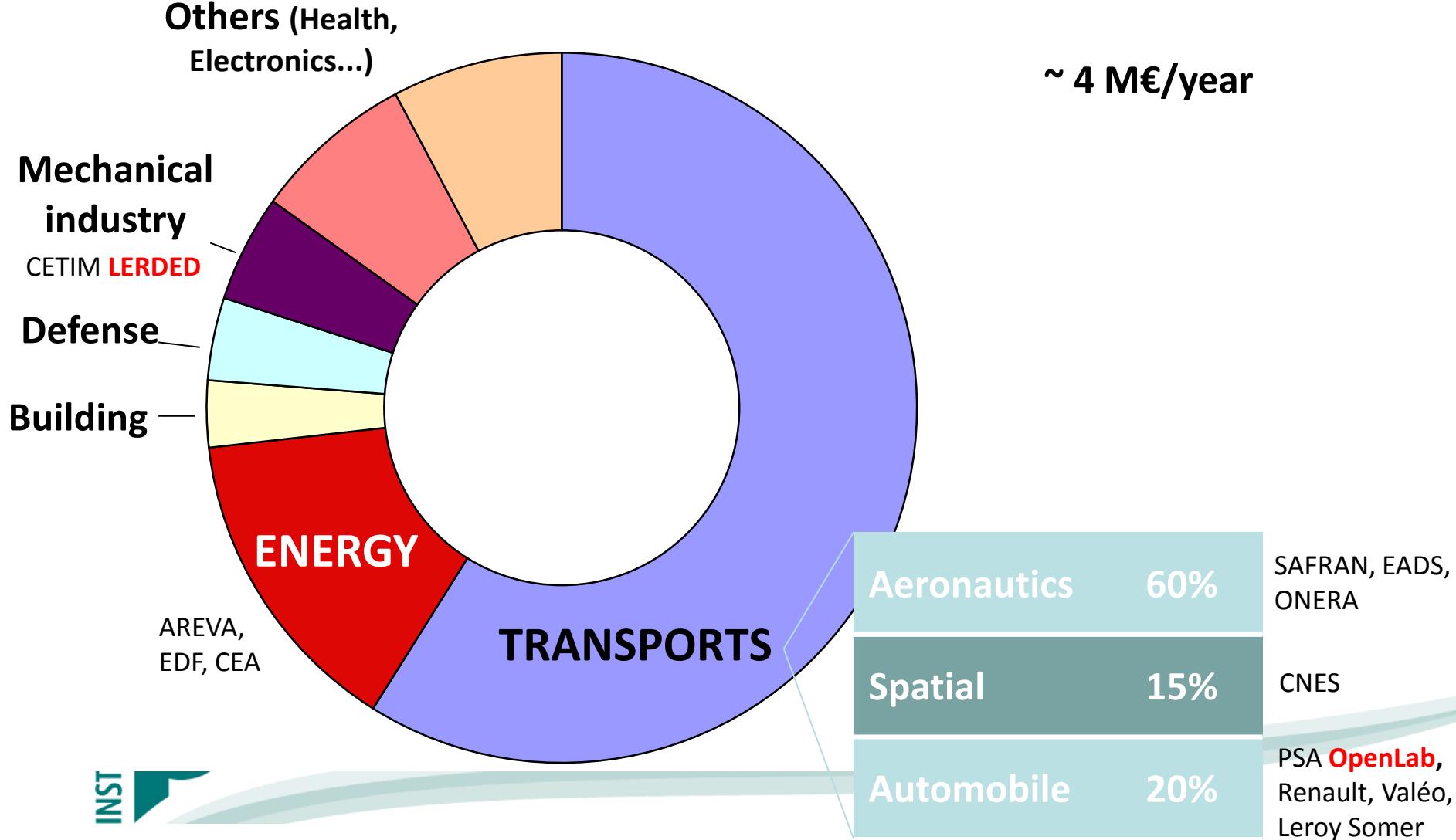
- **Annuel Budget : ~ 25 M€**

Salaries	Government annual fundings	Local (regional) funds CPER, FEDER	Grants, Industrial sponsors and contracts
14,5 M€	1,5 M€	2 M€	7 M€

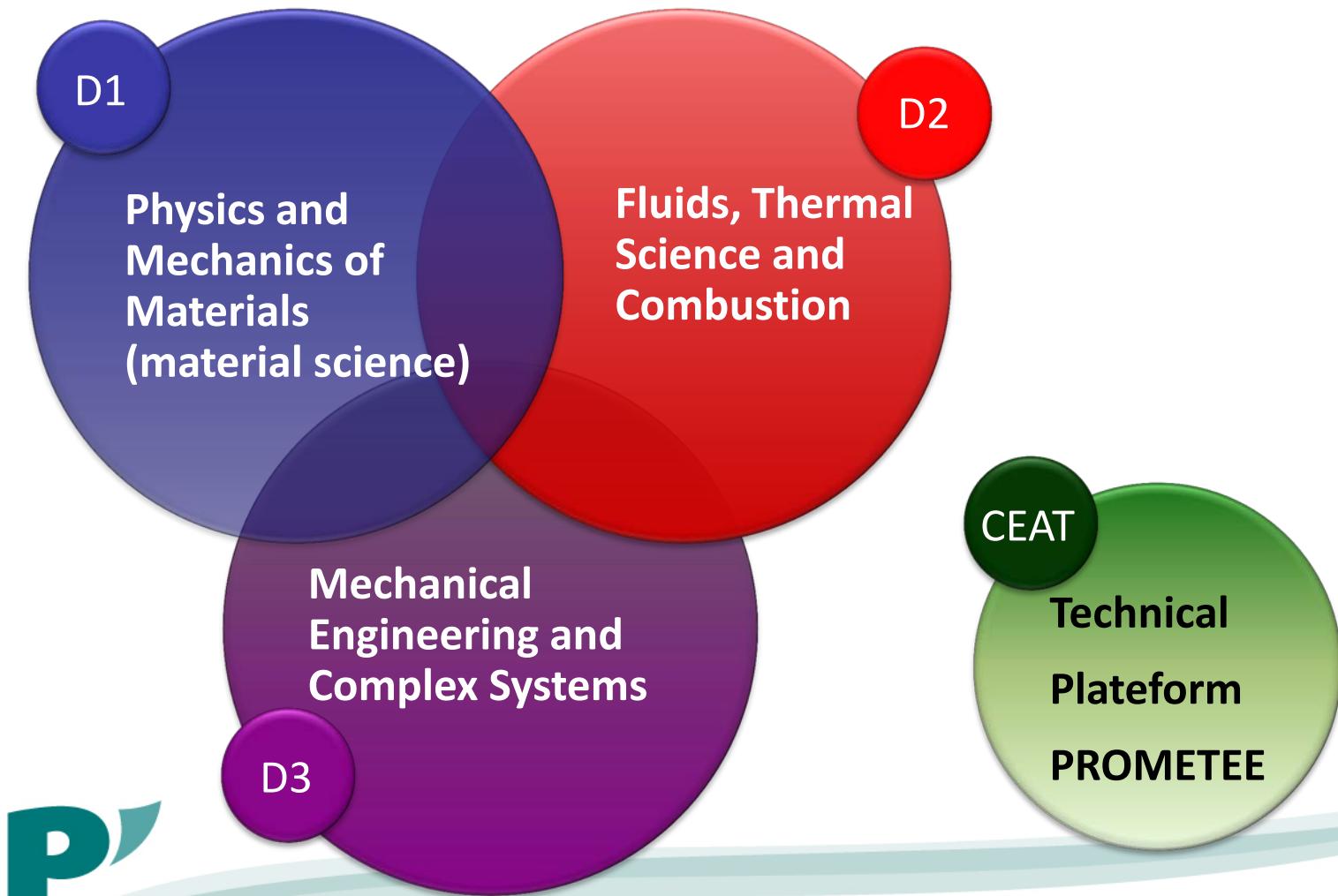
- **Scientific and Technical Production : 250 international publications/year (+ about 500 communications) ; 45 ANR; 1 FUI ; 9 FP7 in progress, ~ 15 active patents**



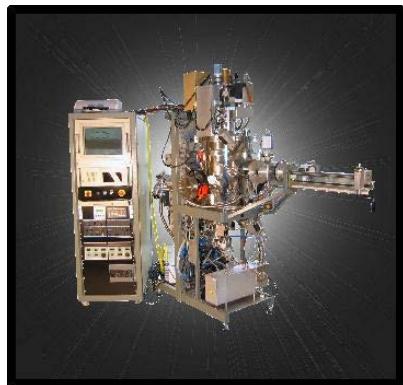
Connected Industrial Sectors



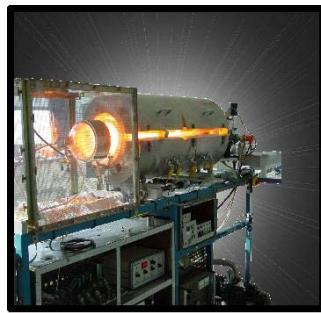
3 Scientific Departments



Dept. Physics and Mechanics of Materials



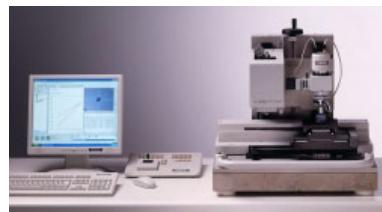
Elaboration



Surface plasma treatments



Ion implantation



Nano,
microindentation

Equipment
*Elaboration-treatment-Characterization
calculations*



INSTITUT

DMA DSC



X-ray analysis



Dept. Physics and Mechanics of Materials



Fatigue apparatus
under controled environment
(gas)



Fatigue (thermal)



Creep under
environment



Vibrophore

≠ thermomechanic loading & ≠ Environnements



Deformation under gas
or hydrostatic
pressure



Fatigue apparatus
(temperature and bi-
dimensional)

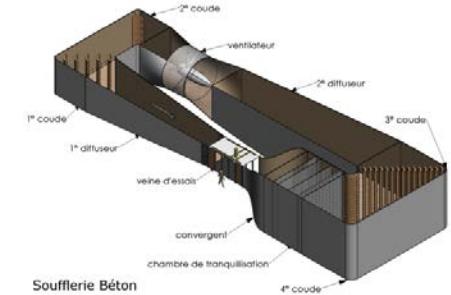
Dept. Fluids, Thermal Science, Combustion



**Test bench : Martel High speed, high temp.
aeroacoustic
2400K, M 2-3**



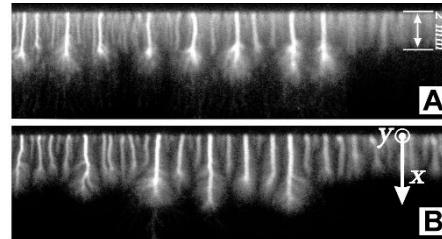
**Wind tunnels Supersonic,
Anechoic**



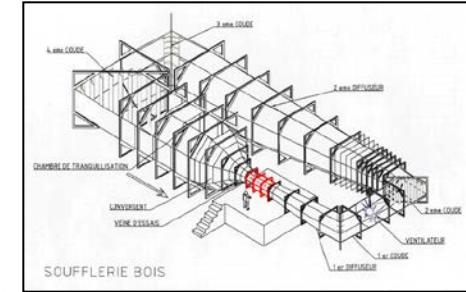
Subsonic Wind Tunnels
Béton: $2.4 \times 2.6 m^2$, 50m/s



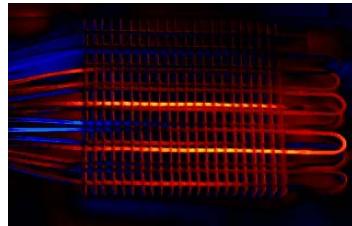
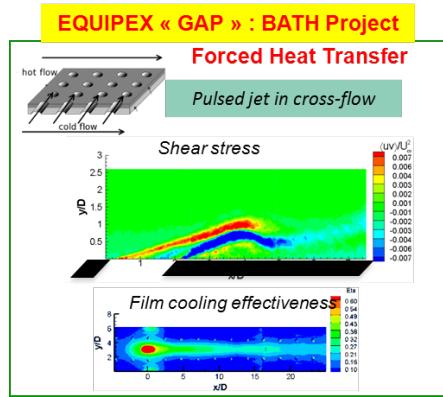
Towing Tank
Length: 20m ; Width: 1.5m



**Test benches :
Plasma actuators in flight conditions**



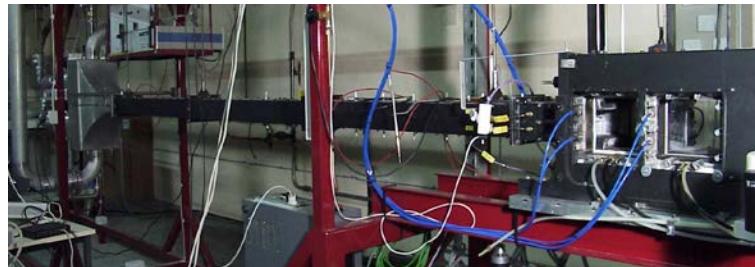
Dept. Fluids, Thermal Science, Combustion



Heat Drains From Lab to
industrial scale



FTC :
Some Large experimental facilities



Oracle Test Bench
Partially premixed combustion



Pulsed detonation
engine



Rotating detonation
engine

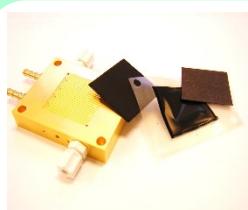
Cavity Ra=10¹¹

EQUIPEX « GAP » : RDE Project

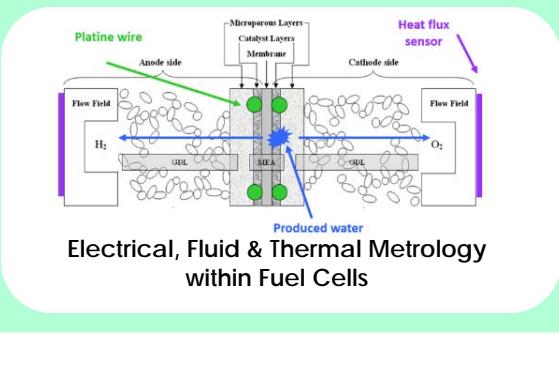
EDE Team Research Activities

Fuel Cells / Electrolyzers

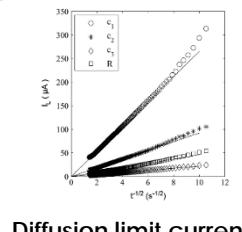
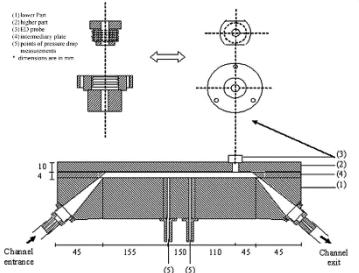
MEA optimization
Cell Test & Systems
Mechanical Effects /
Durability



Membrane
Electrode
Assembly



Mass Transfer in Turbulent Flow

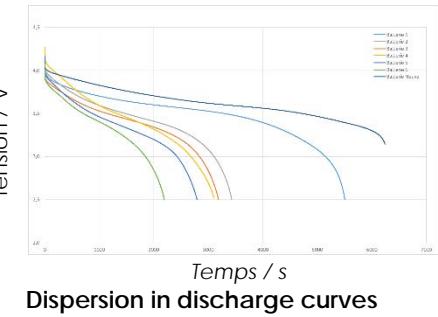


Modelling -Electrodiffusion Effects

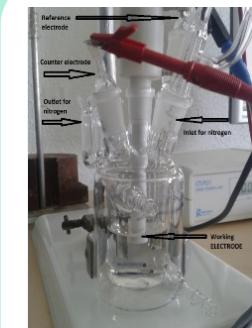
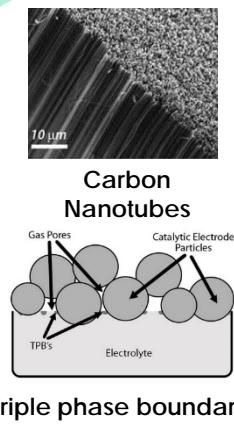
Batteries / Supercapacitors



Electrochemical Noise
Aging Tests
Diagnosis / Prognosis

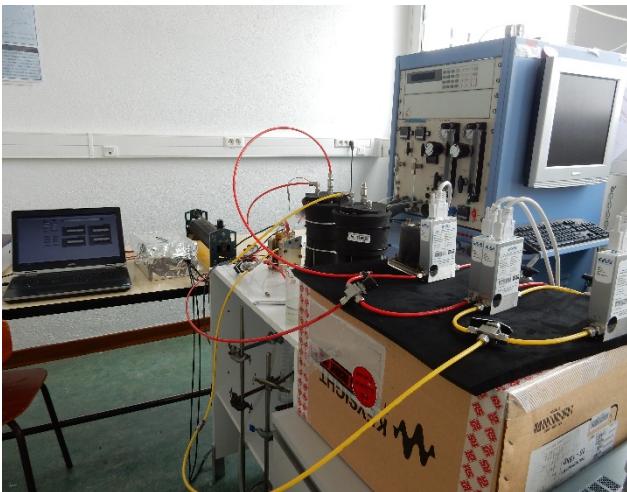


Interface Structuring / EDL



Nanostructure / Electrical Double Layer
Cyclic Voltammetry - Impedance

Experimental Resources



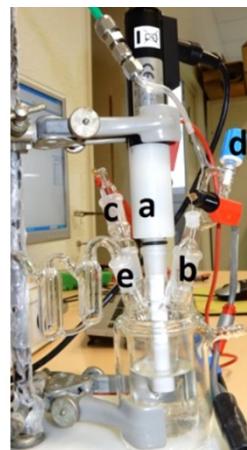
2 Fuel Cell bench



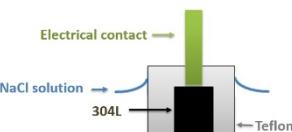
2 Lithium-ion bench



1 electrodiffusion loop

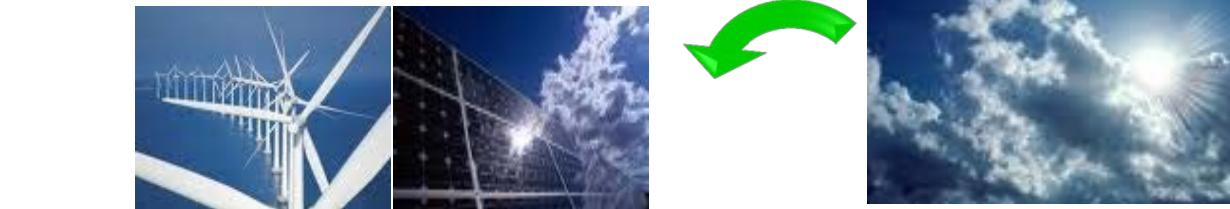


- (a) Working electrode :
 - polished 304L
 - fixed in a Teflon holder
 - 0.196 cm^2 area exposed to NaCl solution (0.01 M)
- (b) Counter electrode : Pt solid : large surface area (2 cm^2)
- (c) Reference electrode : Ag wire/AgCl (saturated KCl)
- (d) / (e) Nitrogen flushing



One analysis bench and electrochemical cells

Intermitent Renewable Energy



Smart Grid

Li-ion battery

Electrolyzer

**H2 vector
Conversion
& Storage Energy**



- Electrochemical Storage of Intermittent Renewable Energy (Electrolyzer + Fuel Cell + Batteries)
- Power generation for isolated sites (Household Cogeneration Electricity / Heat)
- Power for transportation and mobile applications¹⁴



- Mirai commercialized since 2015
- Production capacity = 3,000 / yr
- 30,000 / yr from 2020



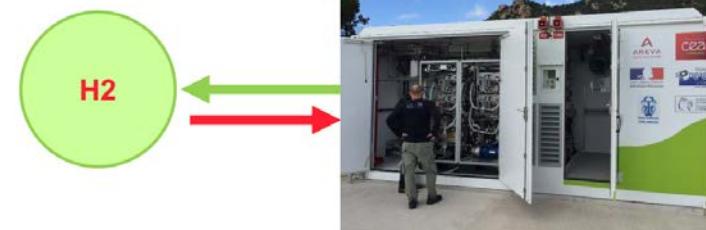
- Tucson commercialized since 2014
- Production capacity = 1 000 / yr
- 6,000 / yr from 2018

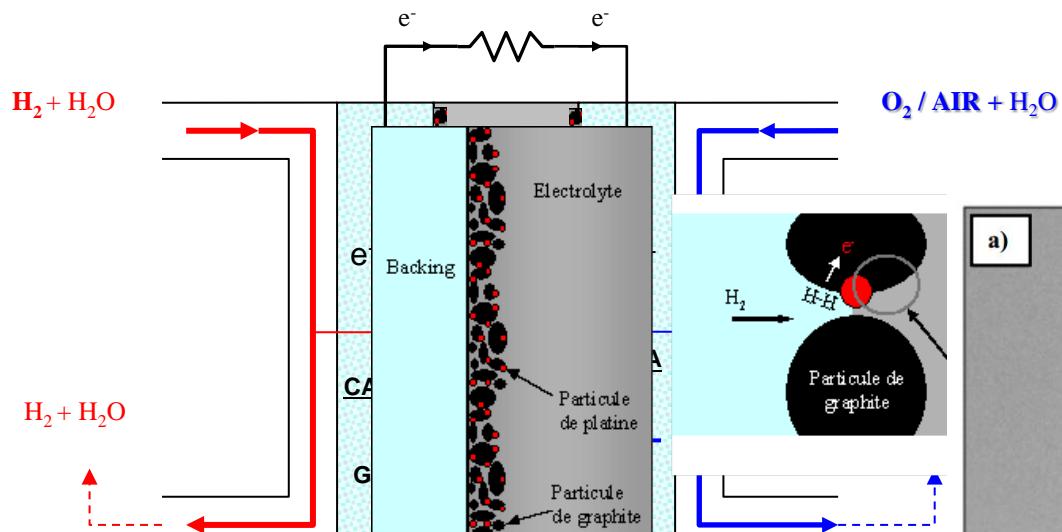


- Clarity commercialized since 2016
- Production capacity = 1,000 / yr

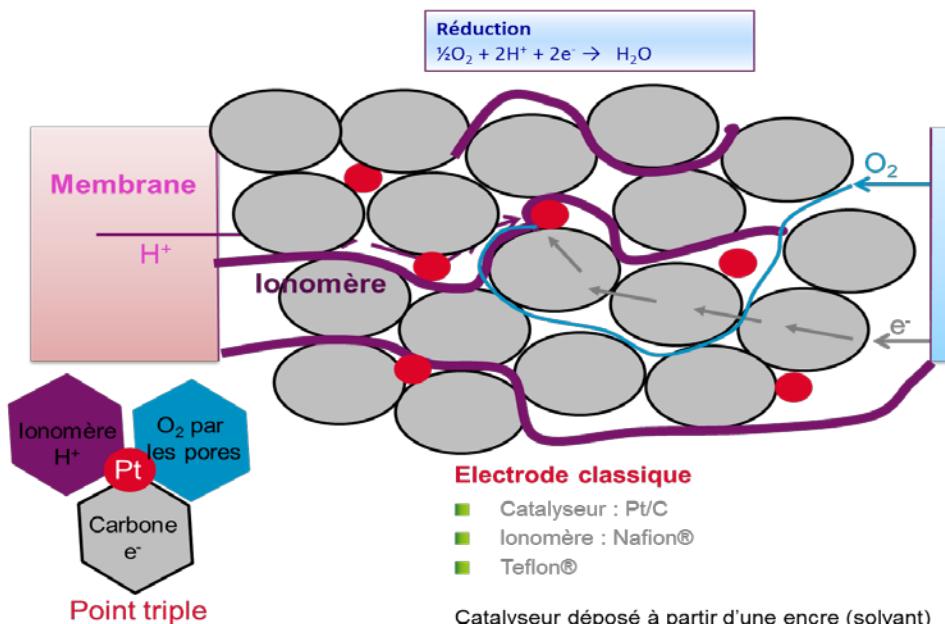


MYRTE - Ajaccio

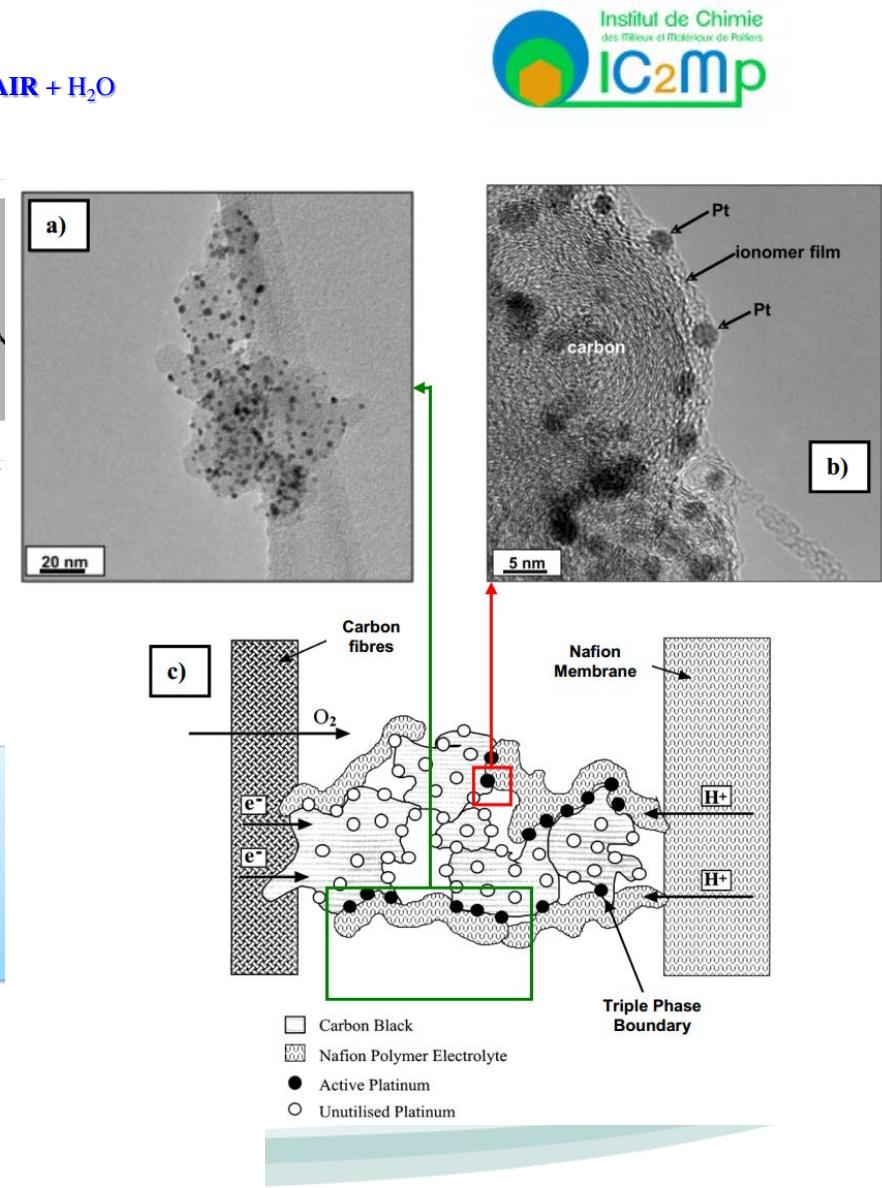




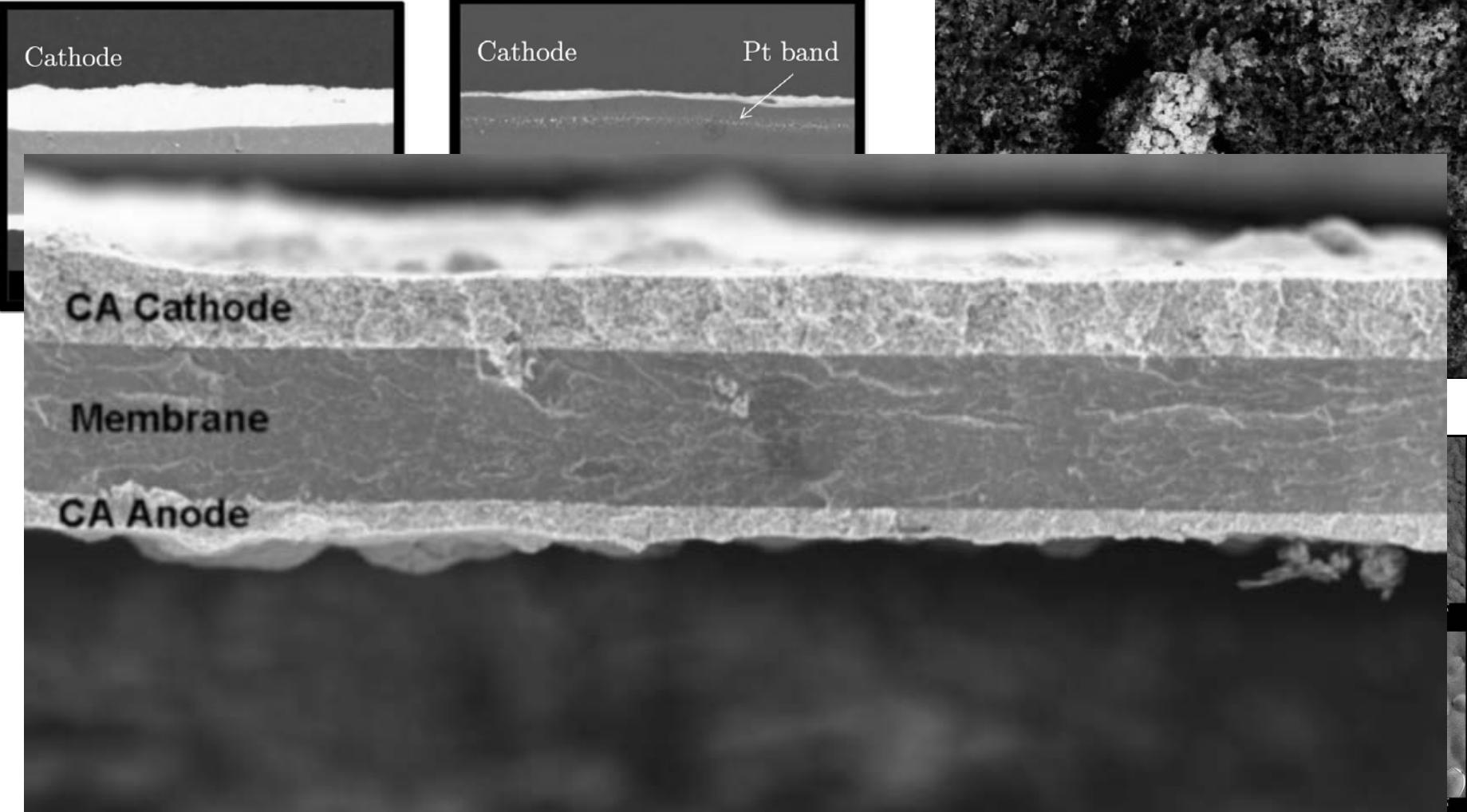
Problème de la Catalyse à la cathode



Catalyseur déposé à partir d'une encre (solvant)



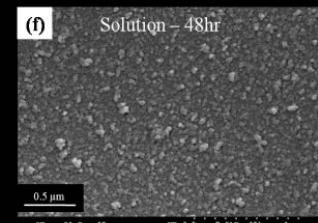
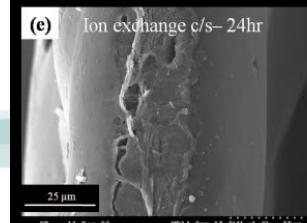
Only 20-30% activate Pt



Fresh MEA

Delamination – mechanical stress

→ Structured and Robust MEA



Membrane cracks (humidity changes)¹⁷

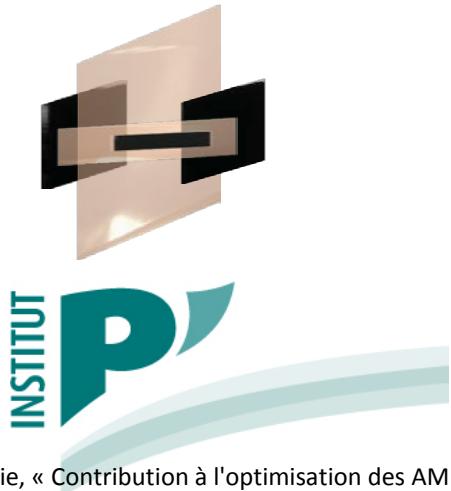
Hot pressing

- Simple method
- Control 3 parameters : Temperature, Pressure and Time
- Ensure a good interface between CL - membrane

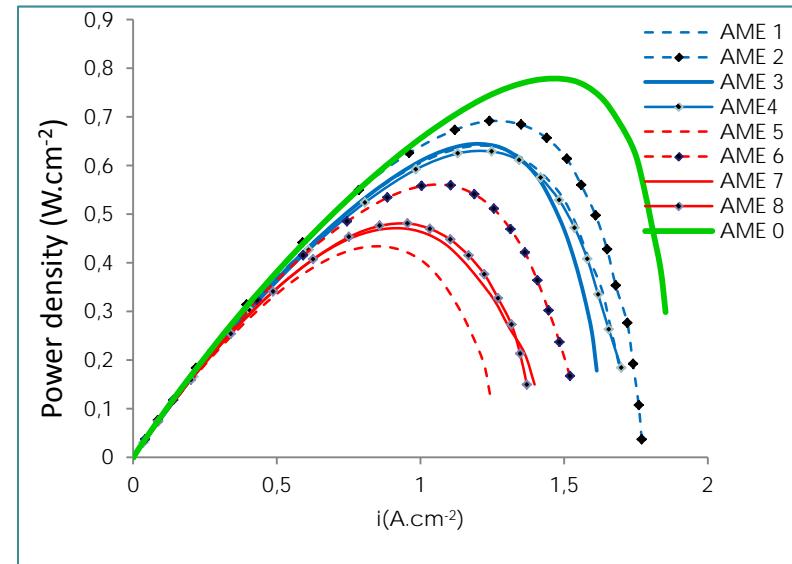


Prospects

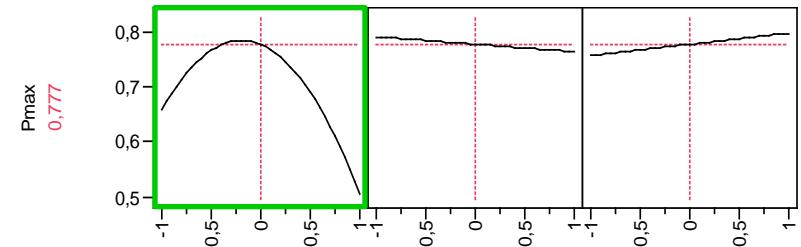
- Objective 1 : Robustness and Stability of MEA
- Objective 2 : Industrialization (automatisation) of the process
- Control mechanical and thermal behavior
- Optimize MEA manufacturing like in batteries area
- Use similar process than microelectronics area (PVD – CVD, Lithography,...)



MEA	T_{pressing} (° C)	P_{pressing} (kg / cm²)	t_{pressing} (s)	P (mW/cm²)
1	100	50	90	638
2	100	50	180	684
1	100	100	90	670
4	100	100	180	639
5	130	50	90	470
6	130	50	180	589
7	130	100	90	468
8	130	100	180	495
9	115	75	135	760
10	115	75	135	753
11	115	75	135	812

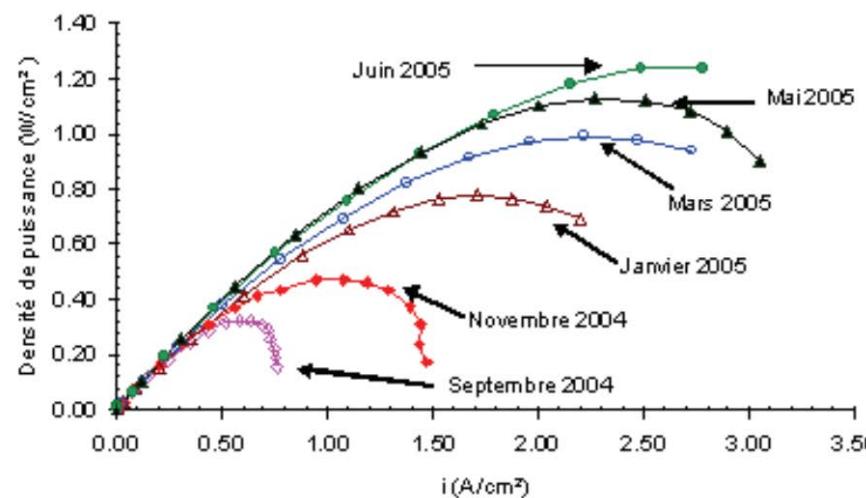
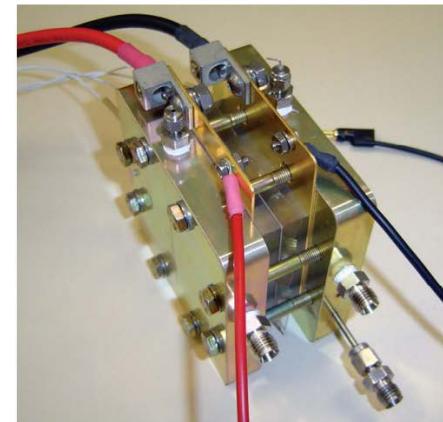
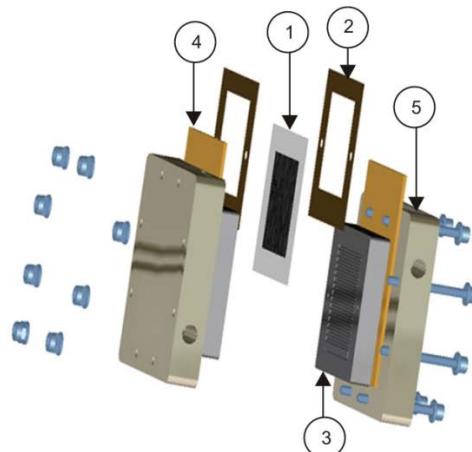


Domain of study			
Level	T (° C)	P (kg / cm²)	t (s)
-1	100	50	90
0	115	75	135
+1	130	100	180

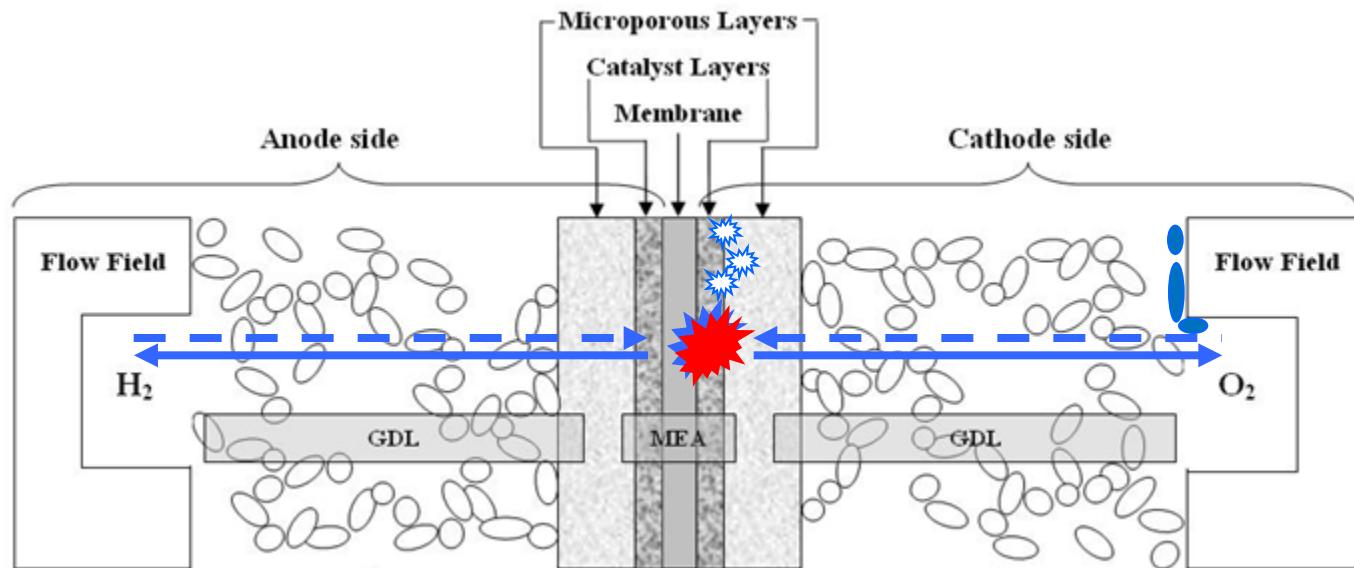


- Increase of 25% to 50% electrical performance with good control of temperature

$T_{\text{pressing}} \sim T_{\text{glass}}$ (little cooler $115^{\circ}\text{C} < 117^{\circ}\text{C}$)



	AME – L.A.C.C.O.			
	Membrane / épaisseur (μm)	GDL/épaisseur (μm)	Charge en Pt / poids mg/ cm^2 / %	Solution de Nafion %
Septembre 2004	Nafion 117 / 180	Papier de carbone/220	0,5 / 20	25
Novembre 2004	Nafion 117 / 180	Papier de carbone/220	0,4 / 20	25
Janvier 2005	Nafion 115 / 100	Tissu de carbone /270	0,35 / 30	25
Mars 2005	Nafion 112 / 50	Tissu de carbone /270	0,35 / 40	25
Mai 2005	Nafion 112 / 50	Tissu de carbone /270	0,35 / 40	25
Juin 2005	Nafion 112 / 50	Tissu de carbone /270	0,35 / 40	25

**Water management :**

- Good hydration of membrane => good proton conductivity
- Flooding issues on CL and GDL with the presence of liquid water

Thermal management :

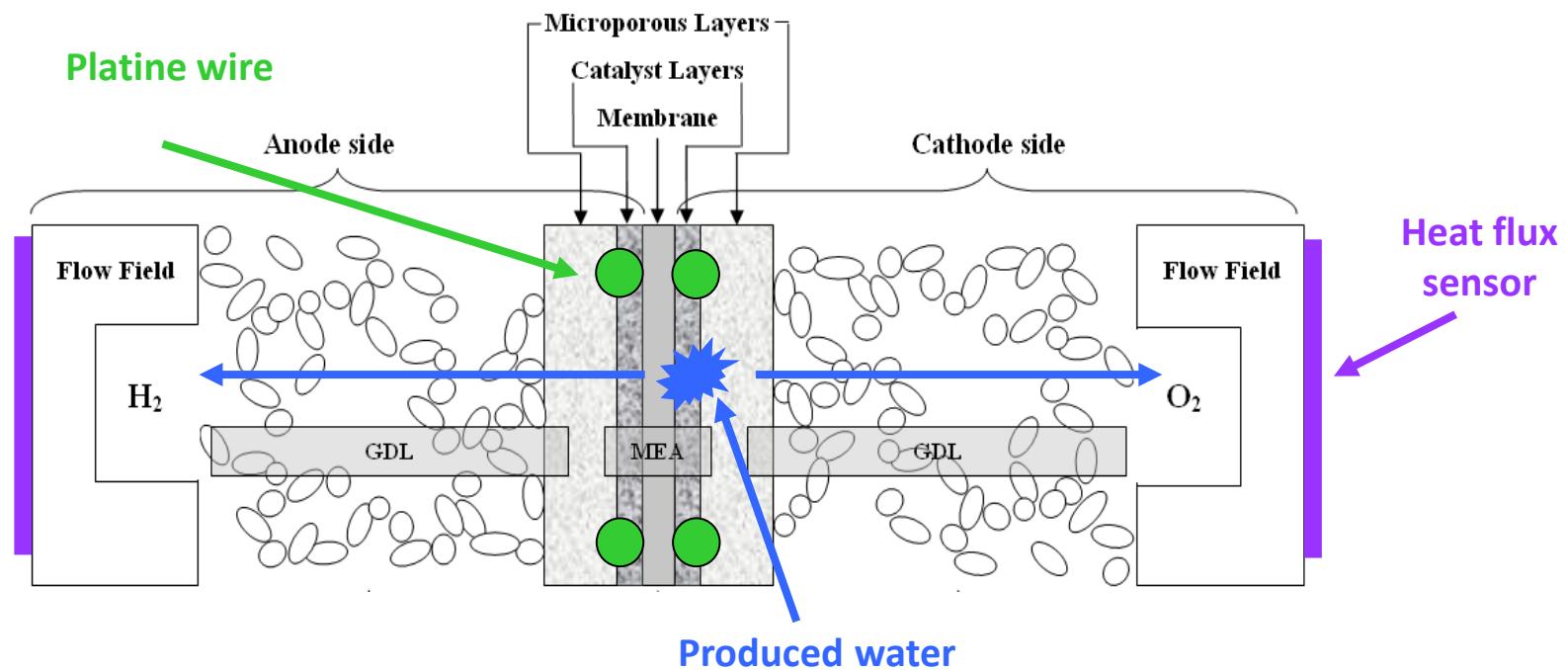
- High temperature → Hydration and deterioration problems
- Low temperature → increased risk of flooding

Objective : To understand mechanisms of heat and water transfer

Usually, fuel cell is supposed isothermal and thermal regulation is provided by thermocouples in flow field plates.

Three complementary water/heat measurements

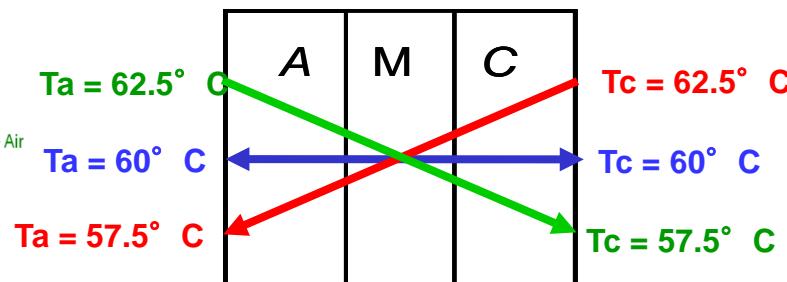
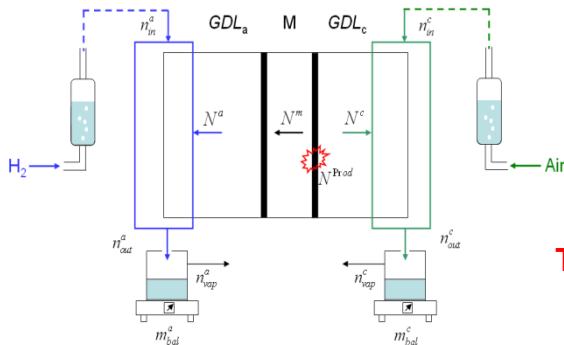
- Electrode temperature** → Temperature profile in the thickness direction
- Heat fluxes** → Heat fluxes through the GDLs
- Water fluxes** → Effect of temperature profile on water transport



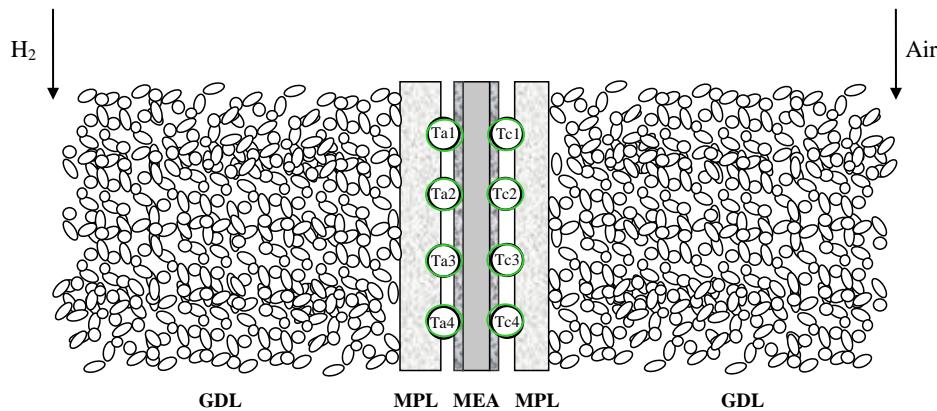
Three complementary water/heat measurements

→ Effect of temperature profile on water transport

Water fluxes

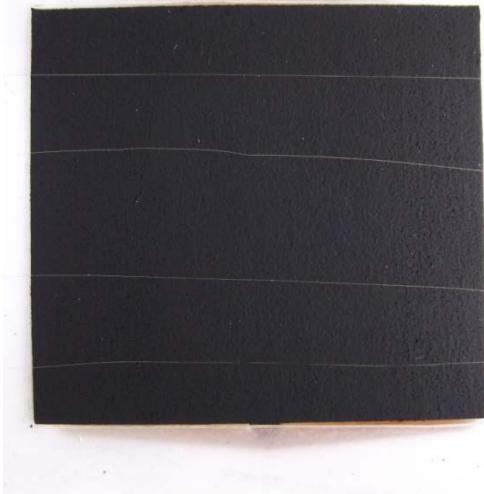
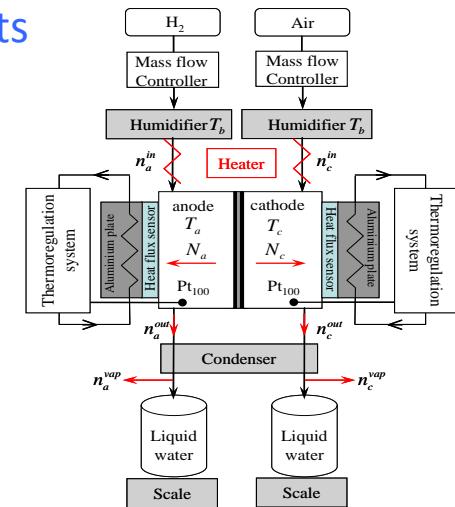
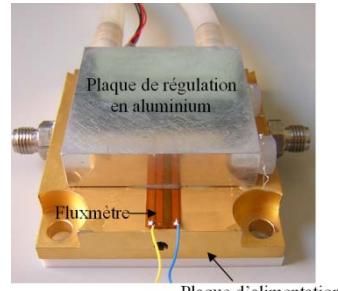
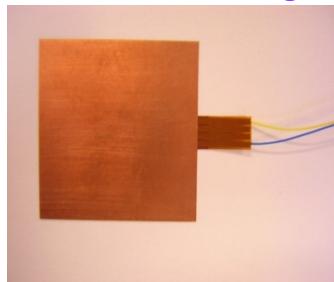


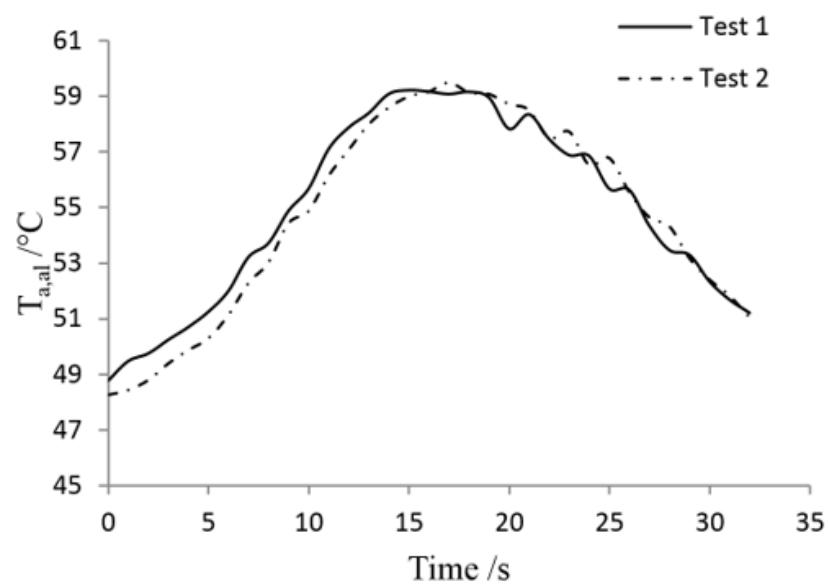
Electrode temperature → Temperature profile in the thickness direction



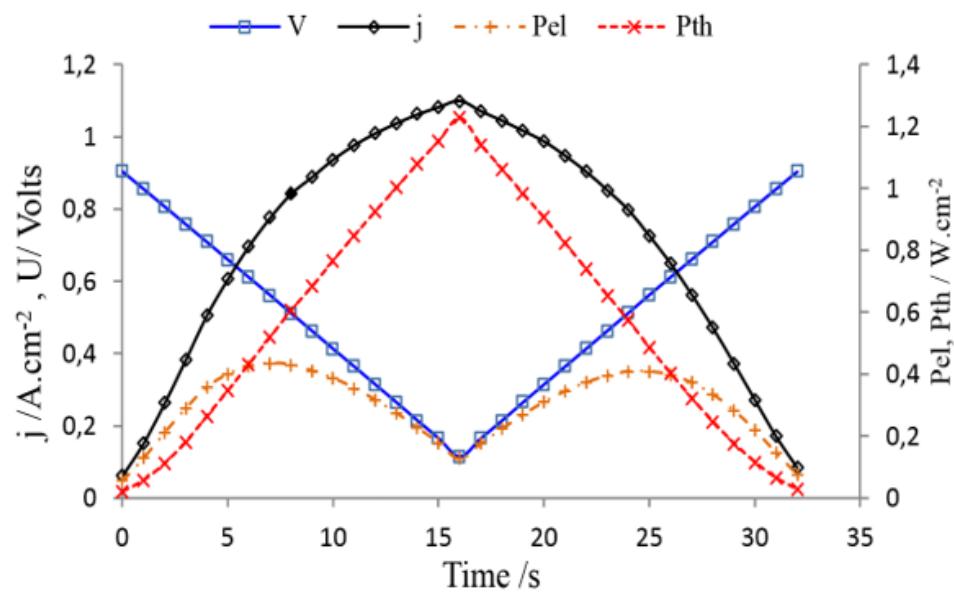
Heat fluxes

→ Heat fluxes through the GDLs

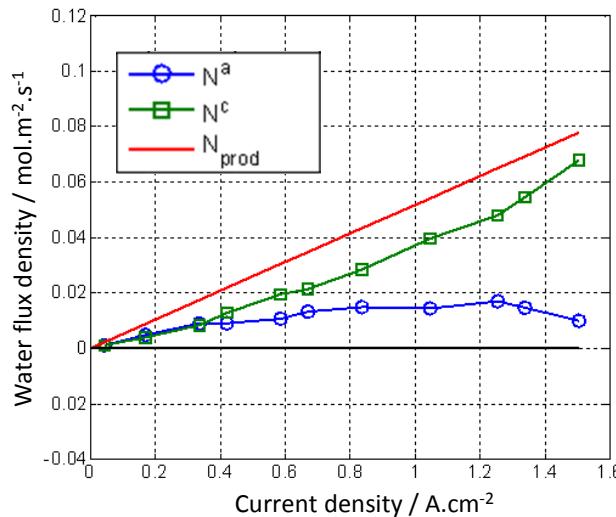
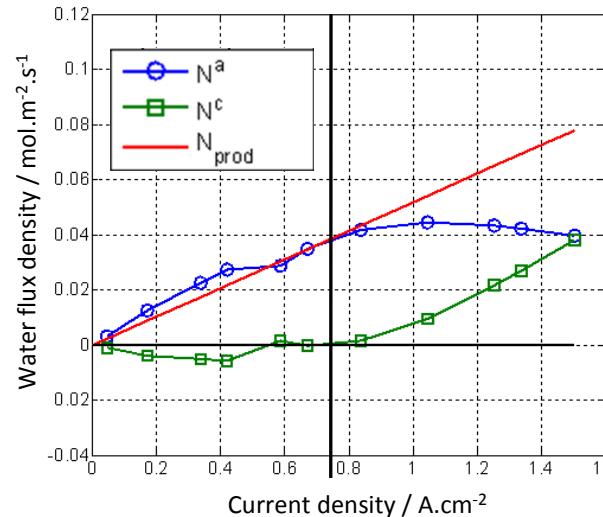
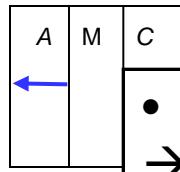
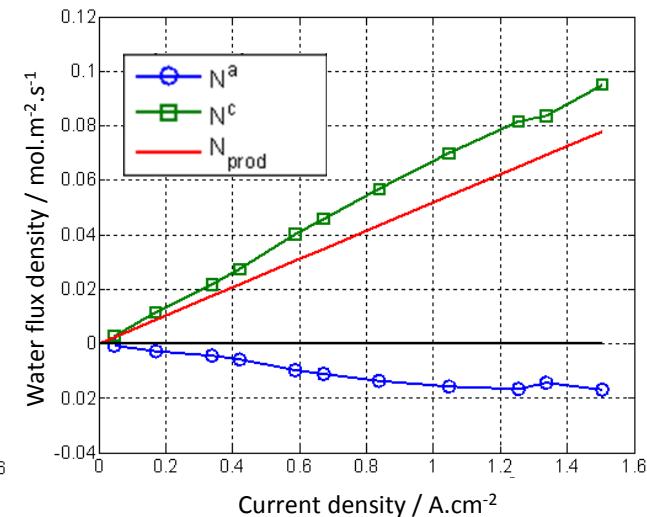




(a)

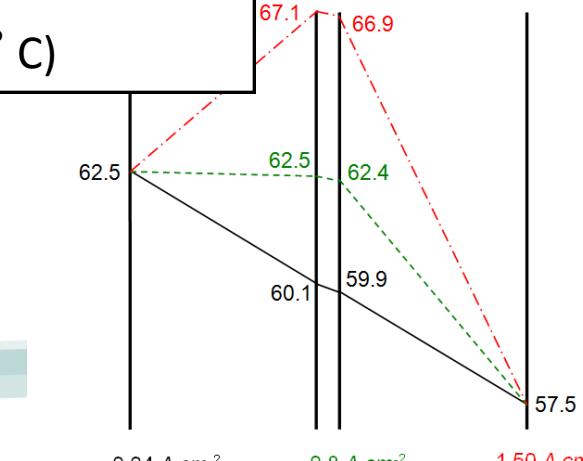
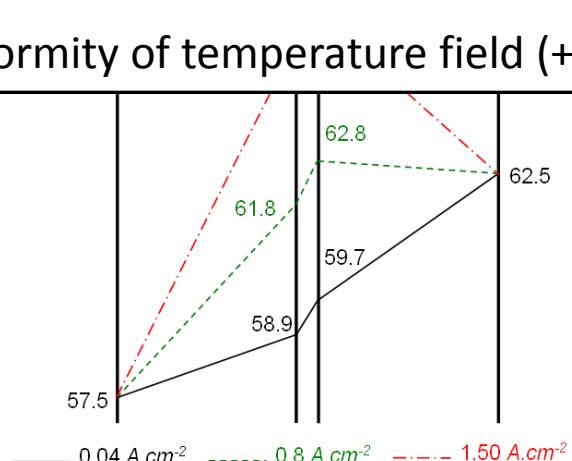
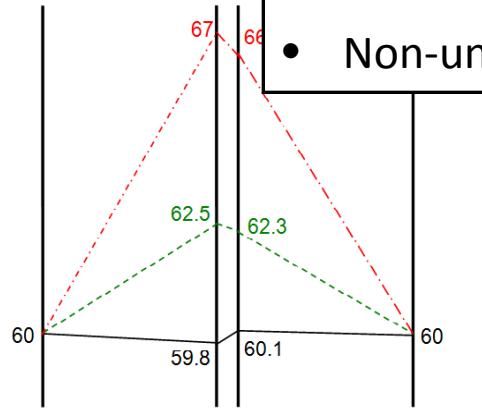


(b)

(i) $T_c = T_a = 60^\circ C$ (ii) $T_c = 62.5^\circ C > T_a = 57.5^\circ C$ (iii) $T_a = 62.5^\circ C > T_c = 57.5^\circ C$ 

- Strong impact of the temperature on water flux
→ Water (as heat) flows from hot to cold

- Non-uniformity of temperature field (+7° C)



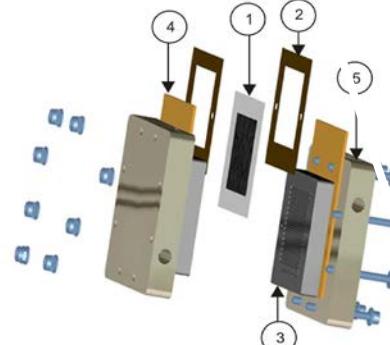
- **The main goals related with studying of mechanical effects**

1. Influence of compressive stress on the fuel cell performance
2. Mechanical damages of MEA

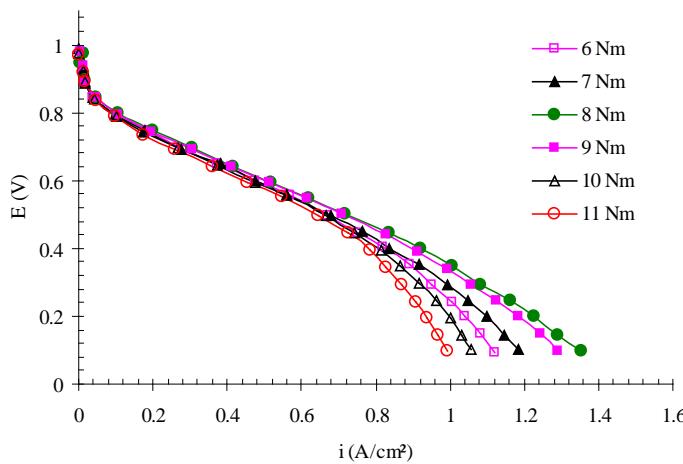
⇒ Bolts torque Effects ?



MEA with carbon cloth

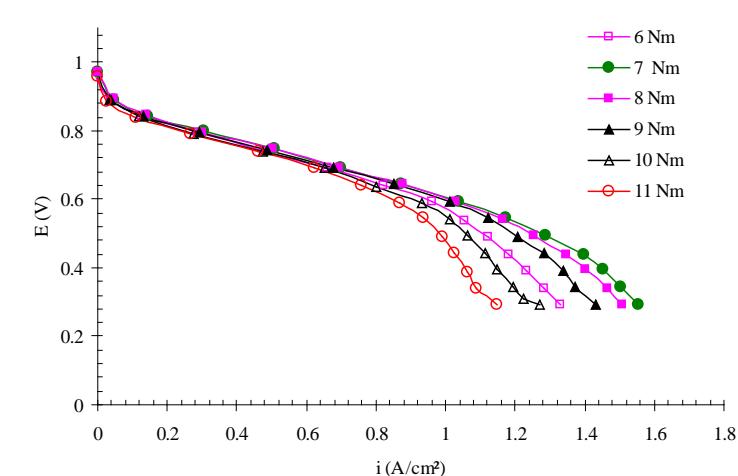


MEA with carbon paper



performances of the cell assembled with MEA-carbon cloth

$T_{\text{cell}}=70^\circ \text{ C}$, $T_{\text{hum}}=T_{\text{humc}}=80^\circ \text{ C}$, $d_a=500 \text{ ml/min}$, $d_c=1000 \text{ ml/min}$, $p_a=p_c=1 \text{ bar}$

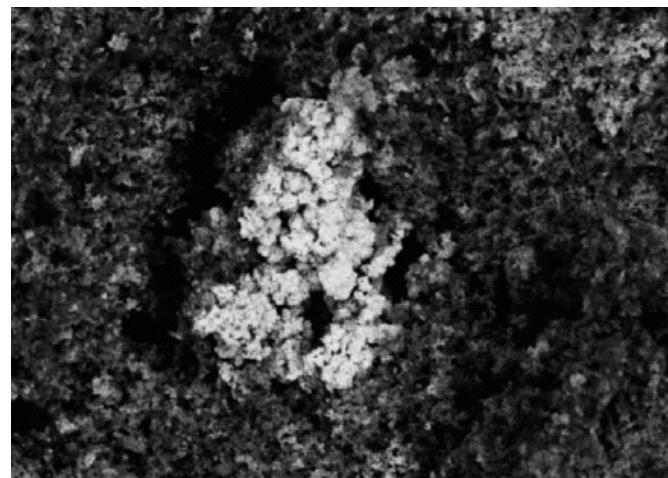
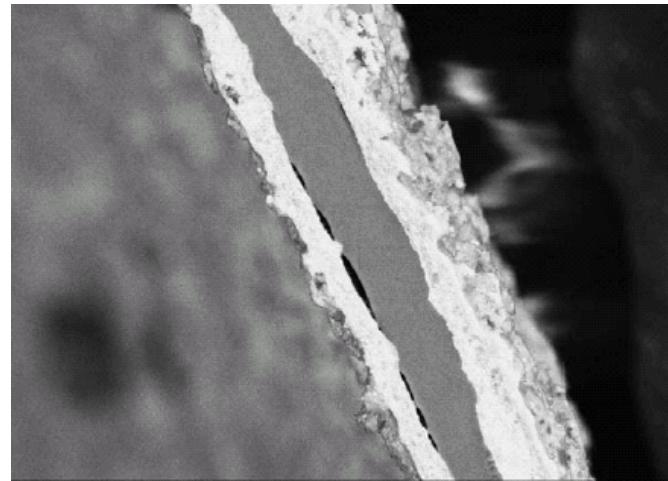


performances of the cell assembled with MEA-carbon paper

$T_{\text{cell}}=70^\circ \text{ C}$, $T_{\text{hum}}=T_{\text{humc}}=80^\circ \text{ C}$, $d_a=800 \text{ ml/min}$, $d_c=2000 \text{ ml/min}$, $p_a=p_c=3 \text{ bar}$

Durability

- Delamination between membrane and catalyst layer
- Holes in the membrane

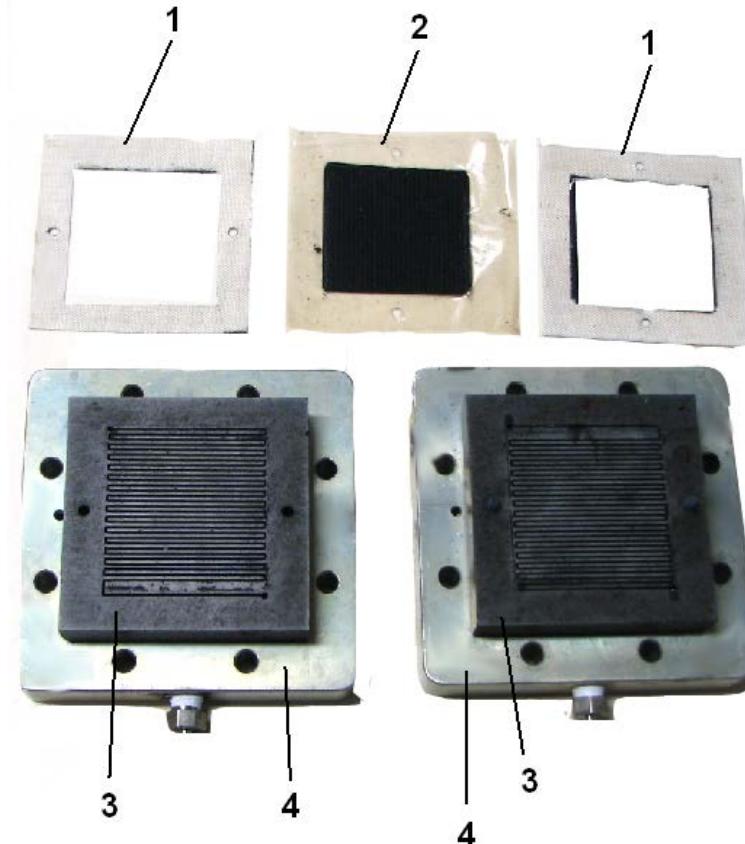


Modelling of mechanical effects

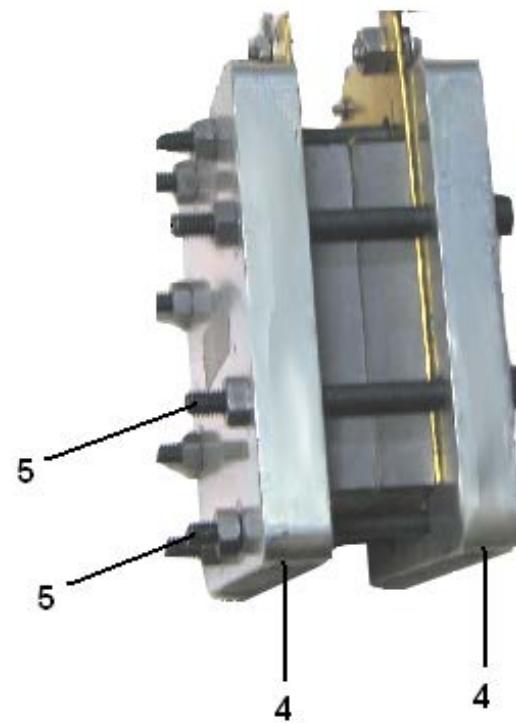
■ **Using tools**

- ✓ Numerical calculations of stress distributions in fuel cell by means of ABAQUS code
- ✓ Realistic modelling of the applied mechanical load
- ✓ Modelling of the single tooth / channel structure (local approach)
- ✓ Modelling of the entire fuel cell (global approach)

Fuel cell components



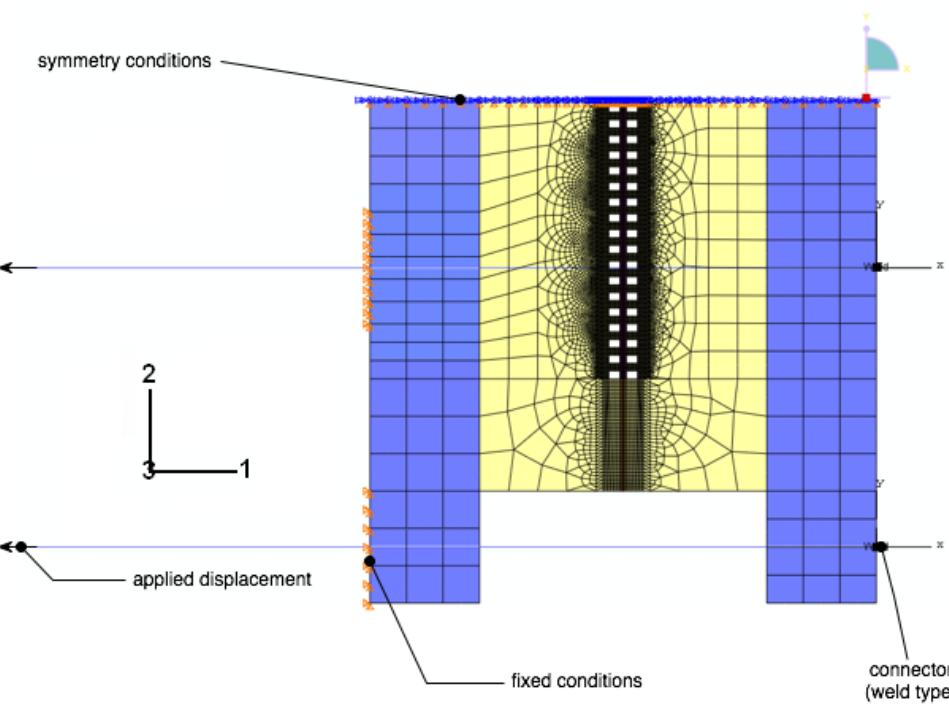
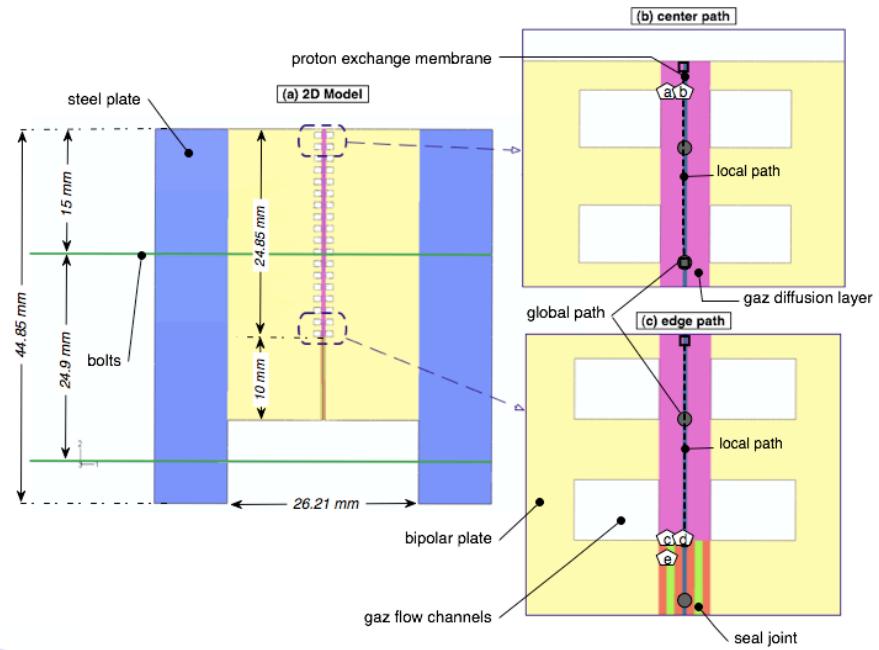
The Assembled fuel cell



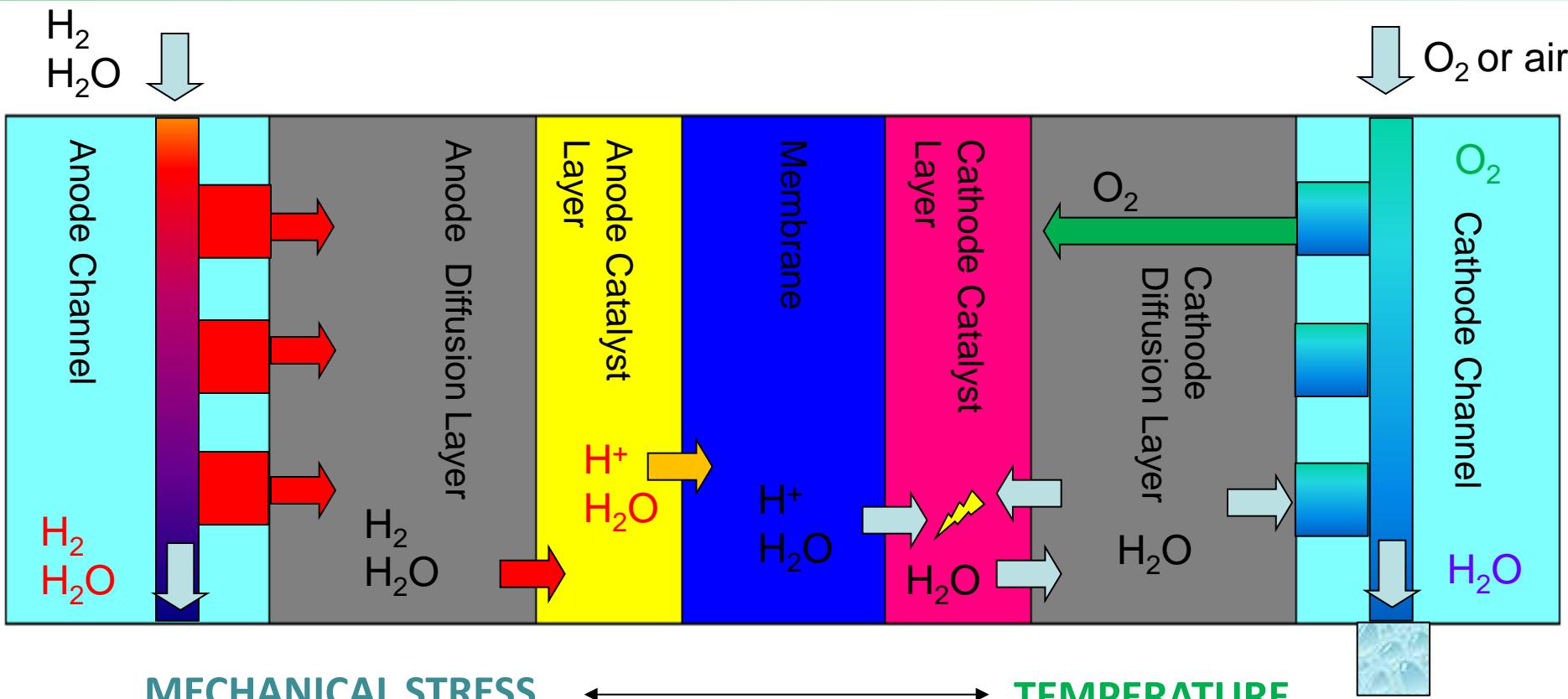
1 - Seal joints, 2 - MEA, 3 – Graphite plates,
4 - Steel plates, 5 - Bolts.

The model of fuel cell

The seal joints,
The membrane,
The graphite plates,
The steel plates,
The bolts.



The global and local scales



- Clamping effect on electrode, GDL and membrane (compression)
- Swelling effect (humidity)

- Exothermic reaction
- Joule effect



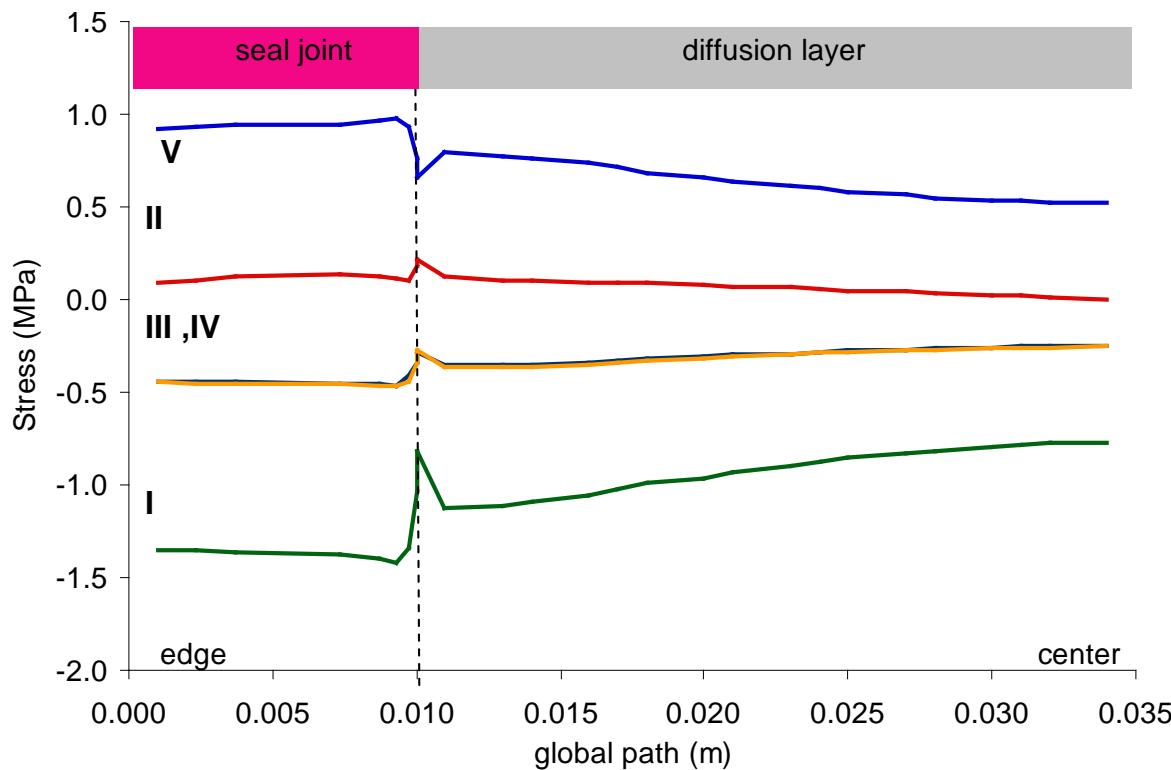
Modification on mechanical & thermal properties

[7] D. Bograchev, M. Gueguen , J.C. Grandidier, S. Martemianov, Journal of Power Sources, 2008 180, 393-401

[8] D. Bograchev, M. Gueguen , J.C. Grandidier, S. Martemianov, International Journal of Hydrogen Energy, 2008 33, 5703-5717

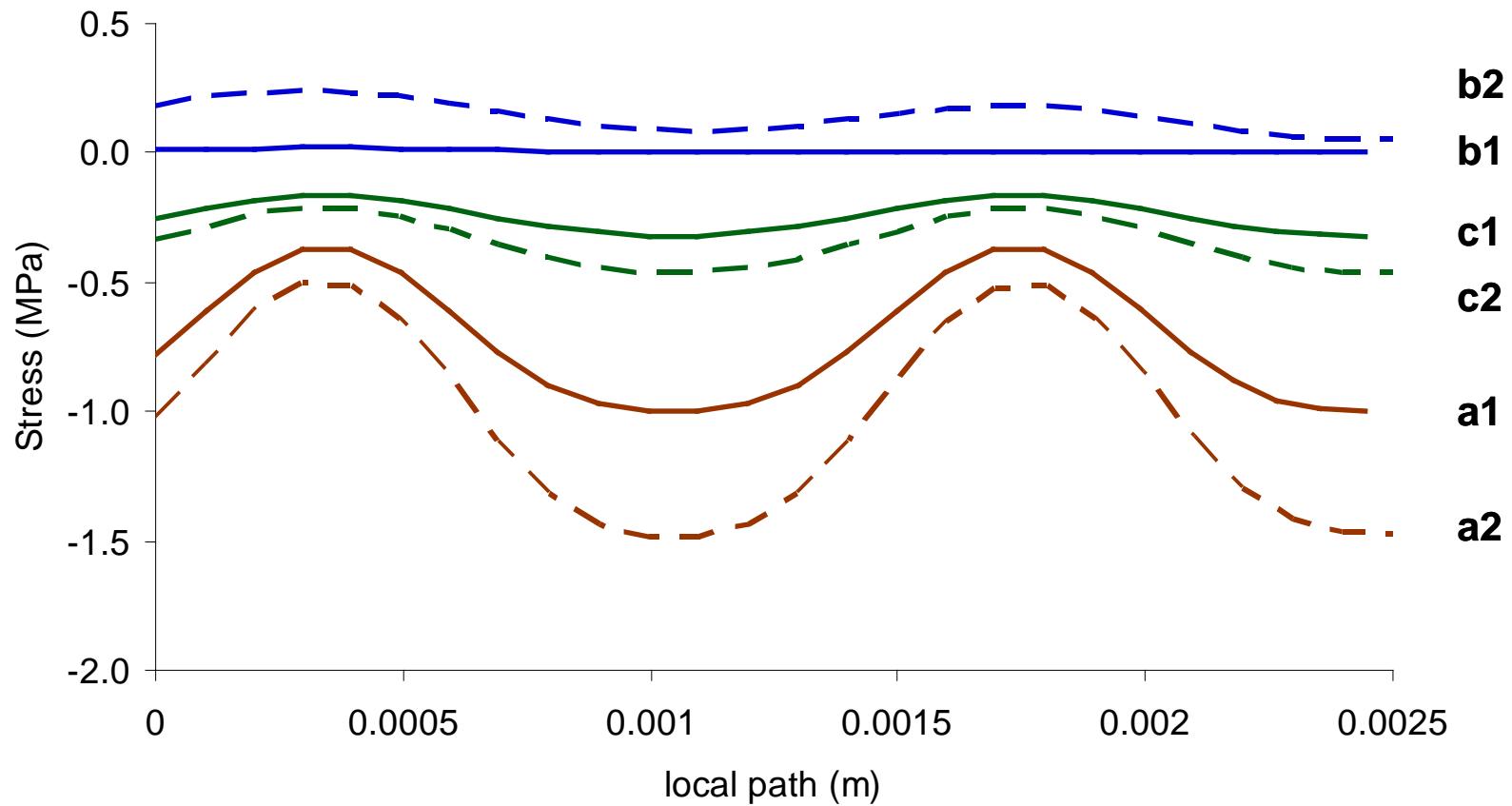
[9] J.C. Grandidier, S. Martemianov, M. Gueguen, D. Bograchev, M. Hamour, CFM, 2009

Cold assembly (global scale in the membrane)



I - Normal Stress , II – Shear stress, III – Tangential stress out of plane,
IV –Tangential Stress, V – Misses stress.

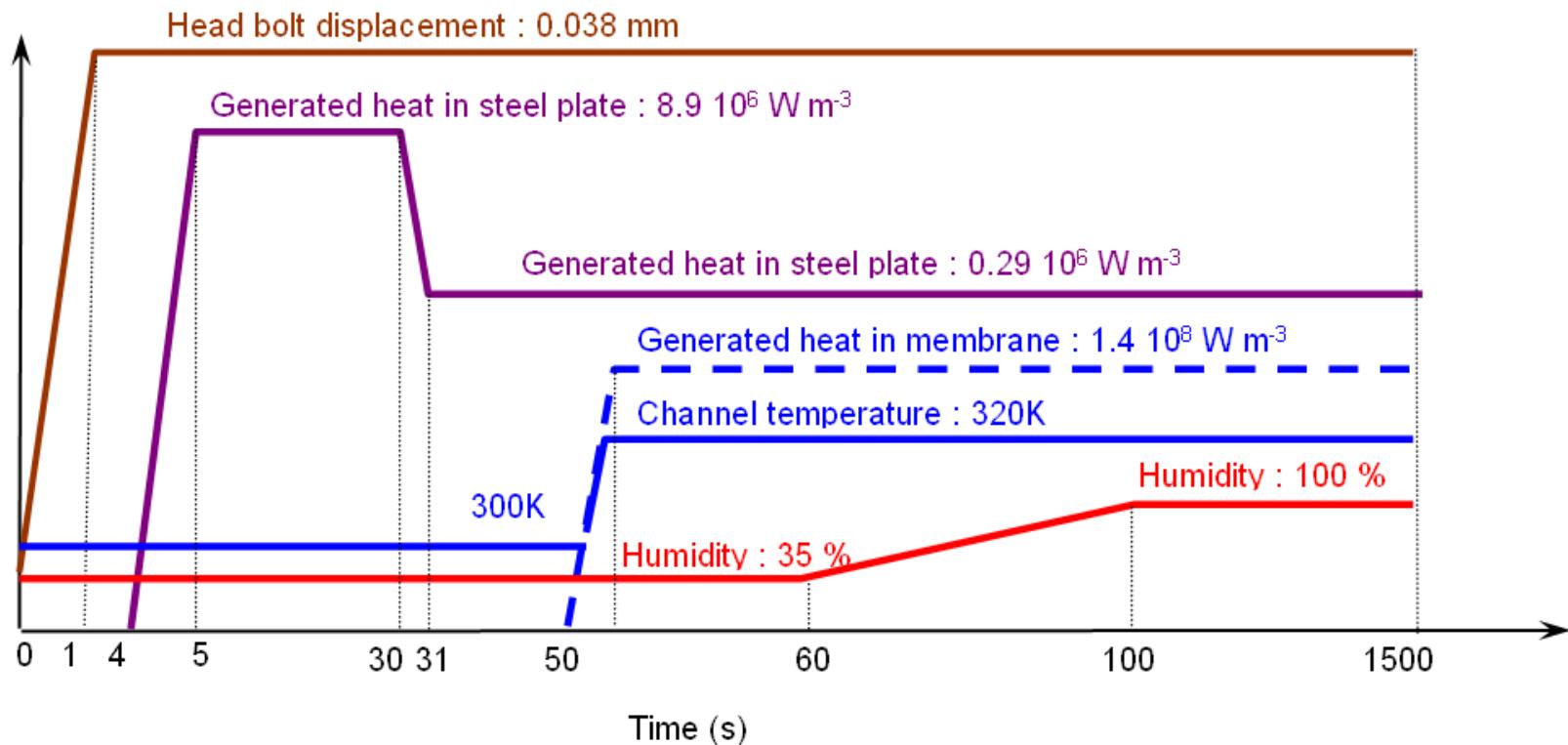
Cold assembly (local scale in the membrane)



Conclusions for «cold» model

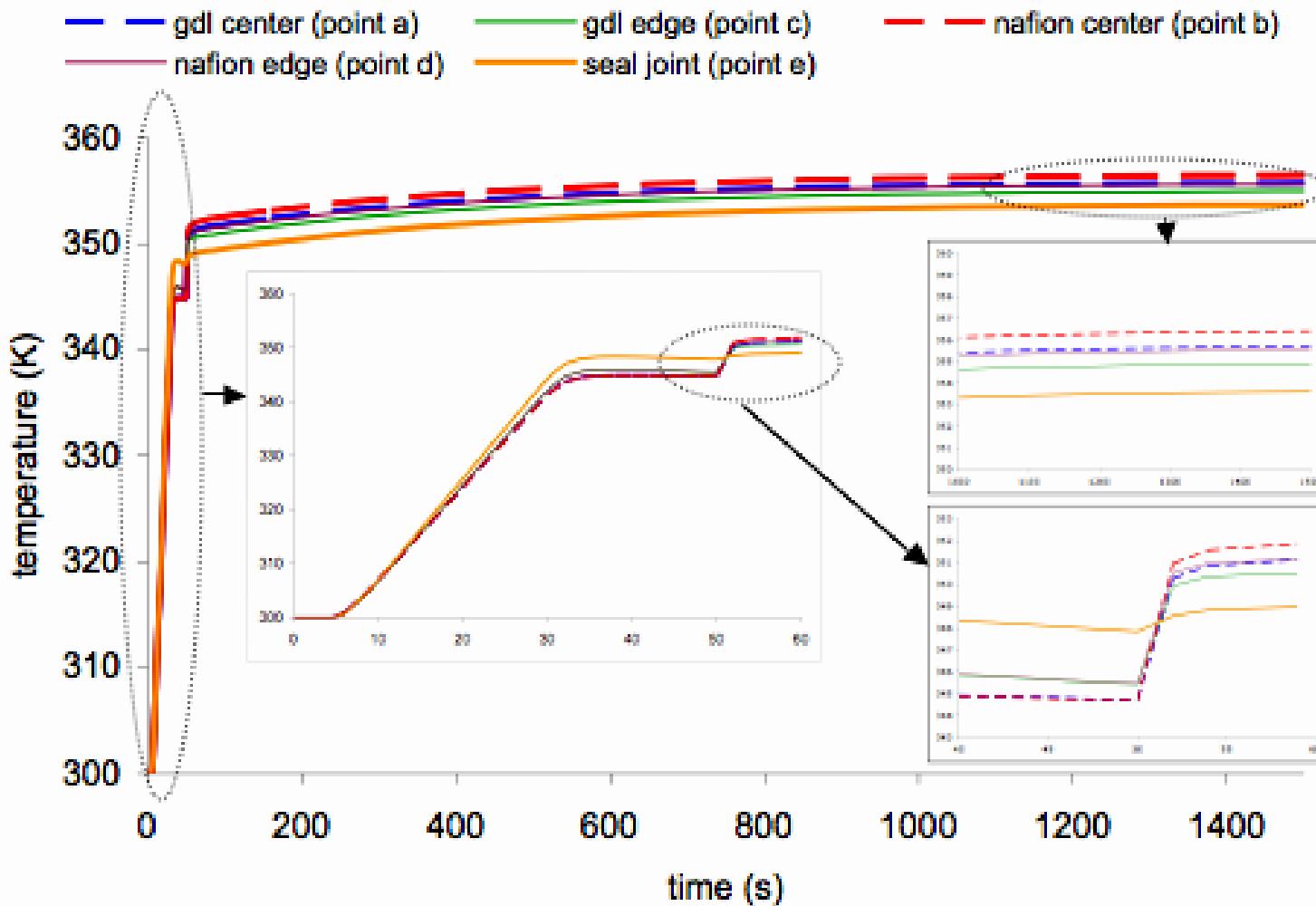
- stress distributions on the local and the global scales are determined
- there is a zone with strong heterogeneous stresses in the membrane under the junction seal joint/graphite plate
- difference between stiffness of seal joint and gas diffusion layer is very significant factor
- membrane does not reach the plasticity at the applied mechanical load corresponding to 1MPa

Hygro-thermal loading: running fuel cell



After fuel cell turn-on

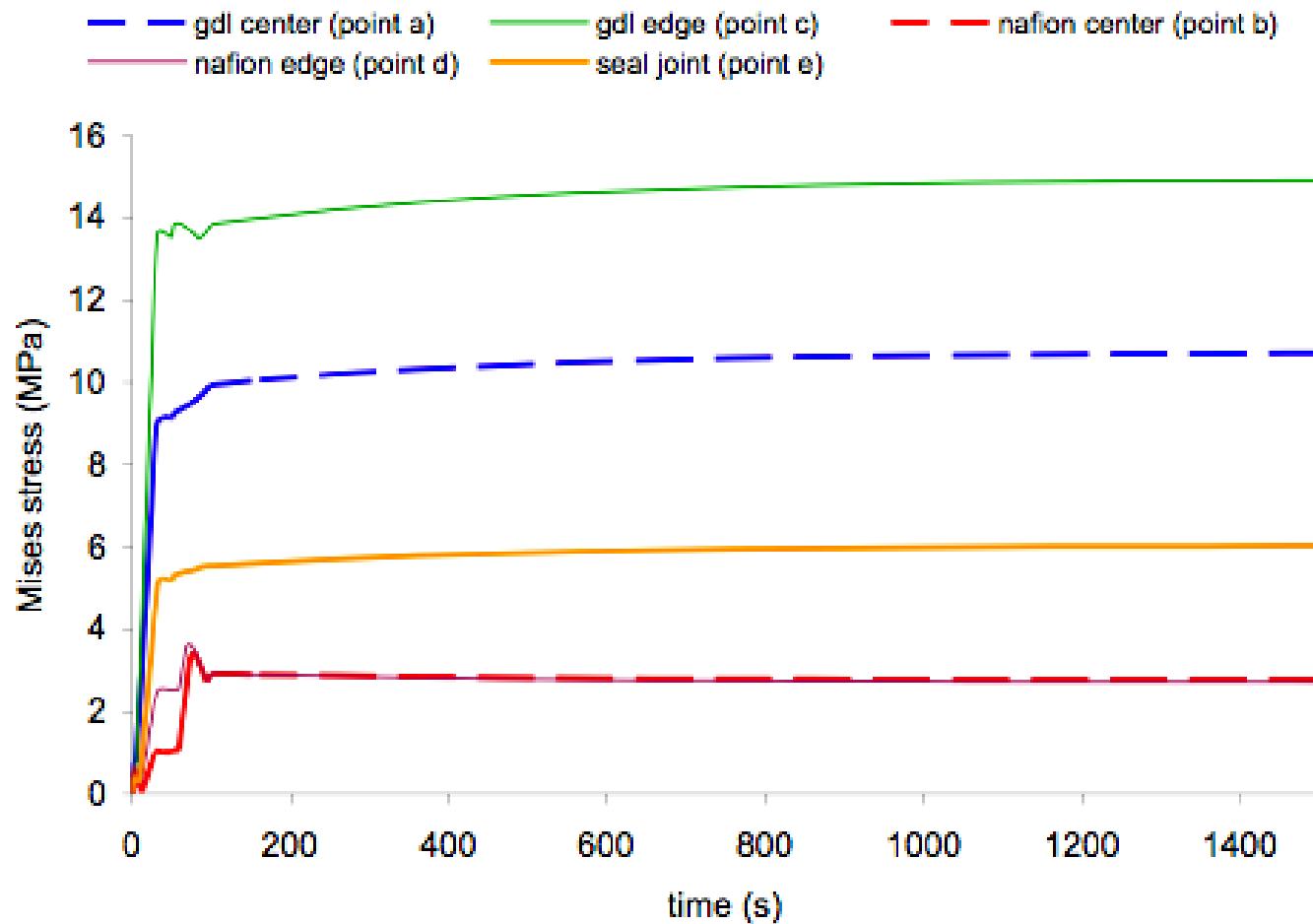
Time evolution of temperature



- The steady-state regime is achieved after about 1400s
- The highest temperature is in the membrane (center region), then GDL
- The seal joint temperature grows faster but reaches less level in comparison with membrane and GDL
- Characteristic temperature difference in MEA is about 5 ° C

After fuel cell turn-on

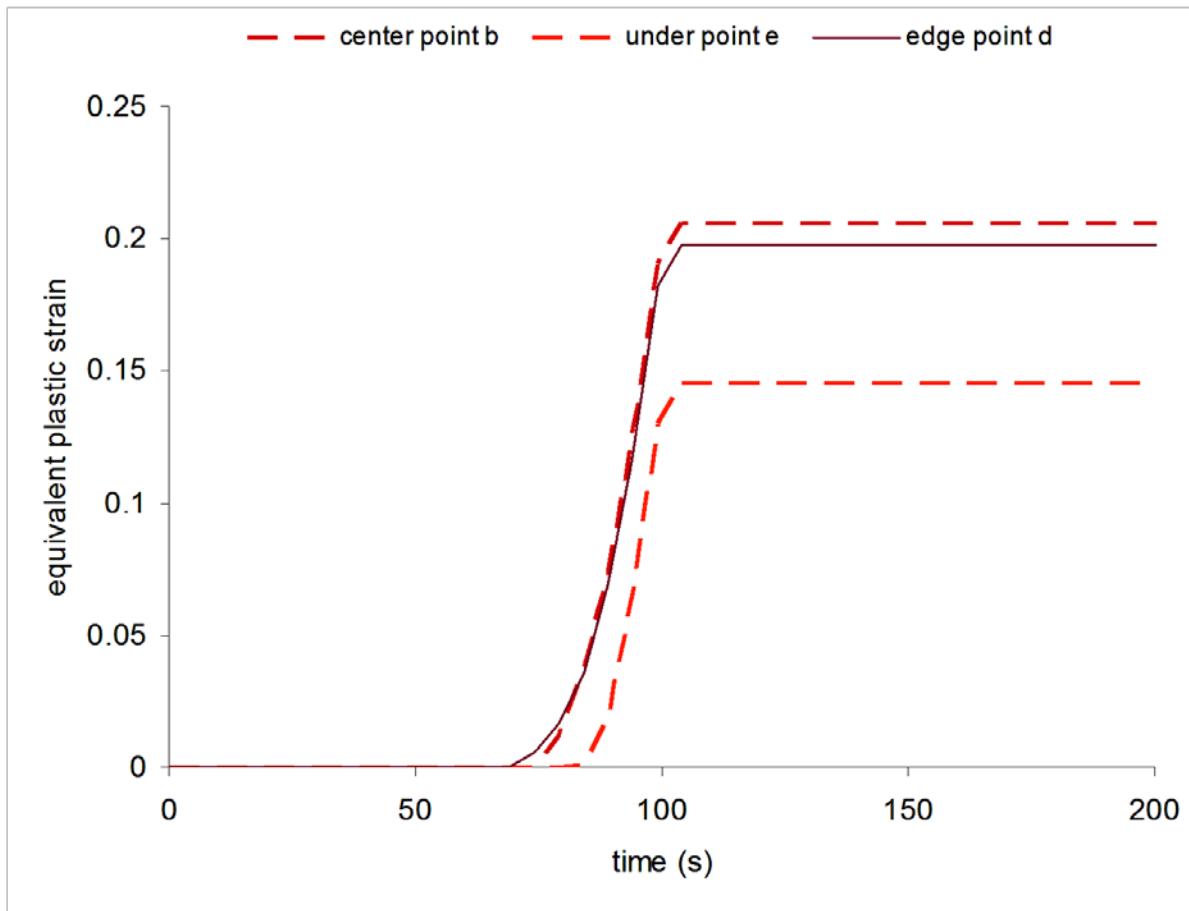
Time evolution of the Mises stresses



- The stresses change strongly during the first 100 seconds of the cell running, afterwards they stabilize with the achievement of the temperature steady-state regime
- The highest level of Mises stress is reached in the GDL, but plasticity effects don't occur in this zone
- From the other hand, the critical value of yield stress is achieved in the membrane and plasticity deformations arise

After fuel cell turn-on

The time evalution of the equivalent plastic strain



- The first plastic deformations in the membrane emerge only during the stage of the humidification
- The plastic deformation in the centre of the membrane arises later; however, it reaches a higher level
- The plasticity appears also in the membrane under the seal joint
- The plastic deformation remains constant at the end of the humidification stage
- It is important to note that its level is very high.

- The stress distribution along the membrane has a complex character during the transient phase
- This distribution stabilizes at the end of the humidification step and becomes quasi-homogeneous when the temperature field reaches steady-state
- It can be noted that the maximal stresses (higher than 3.5 MPa) occur during the humidification step
- These peak stresses are localized under the joint/GDL interface; especially in this part of MEA the failures are often observed.

Conclusions

Mechanical phenomena play very important role in fuel cell technologies influencing on cell performance and durability

In particular, one of the reasons of **membrane pinholes can be caused by accumulation of plasticity deformations** during work cycles

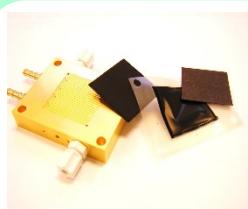
There is **strong coupling between mechanical, thermal and humidification effects**: numerical modelling shows that arising in MEA stresses depends on heat and humidity load regimes

Arising in MEA stresses reach important peak values (3 time **more than applied during assembly mechanical load**) in transient regime during humidification step

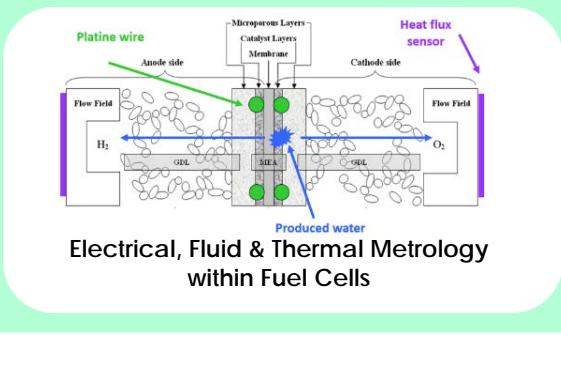
EDE Team Research Activities

Fuel Cells / Electrolyzers

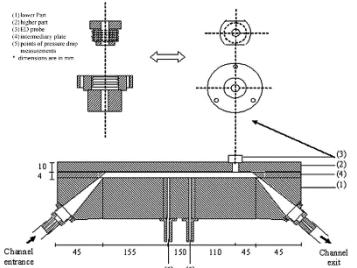
MEA optimization
Cell Test & Systems
Mechanical Effects /
Durability



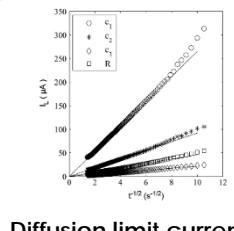
Membrane
Electrode
Assembly



Mass Transfer in Turbulent Flow



Flow loop with μ -electrodes

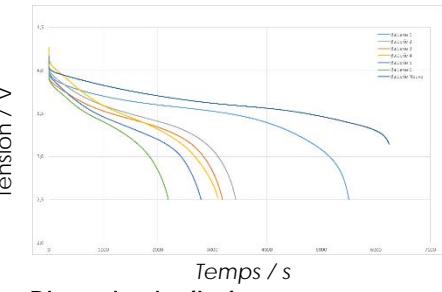


Modelling -Electrodiffusion Effects

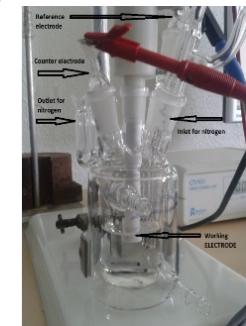
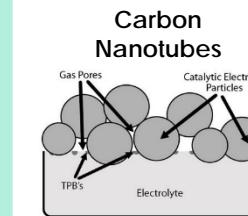
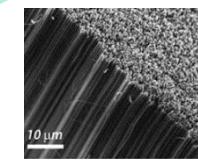
Batteries / Supercapacitors



Electrochemical Noise
Aging Tests
Diagnosis



Interface Structuring / EDL

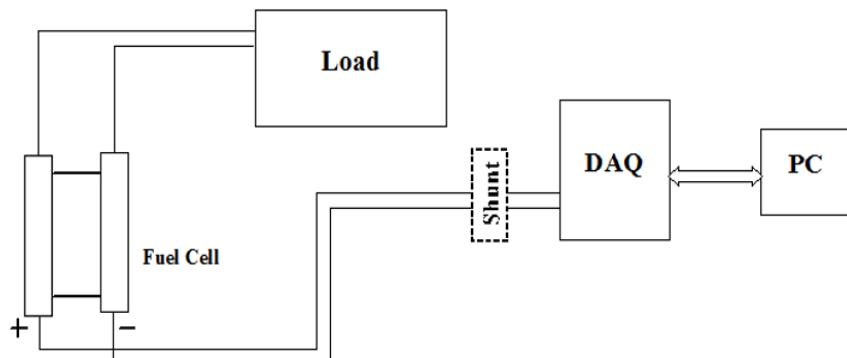


Nanostructure / Electrical Double Layer
Cyclic Voltammetry - Impedance

Electrochemical Noise = stochastic fluctuations of voltage (or current)
generated by mechanical and/or chemical degradations (cracks, dissolution, gas bubble formation,...)

Mostly use in Corrosion at metal-solution interface

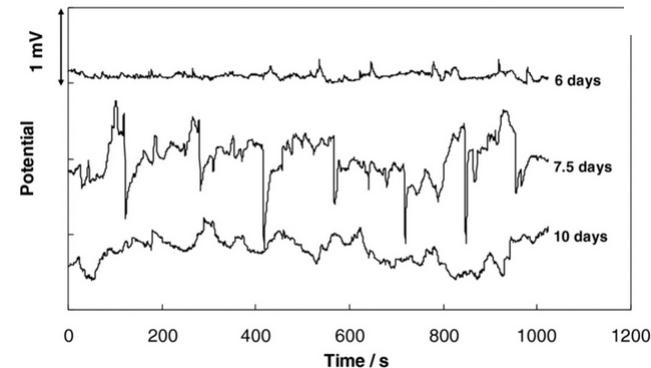
Experimental setup



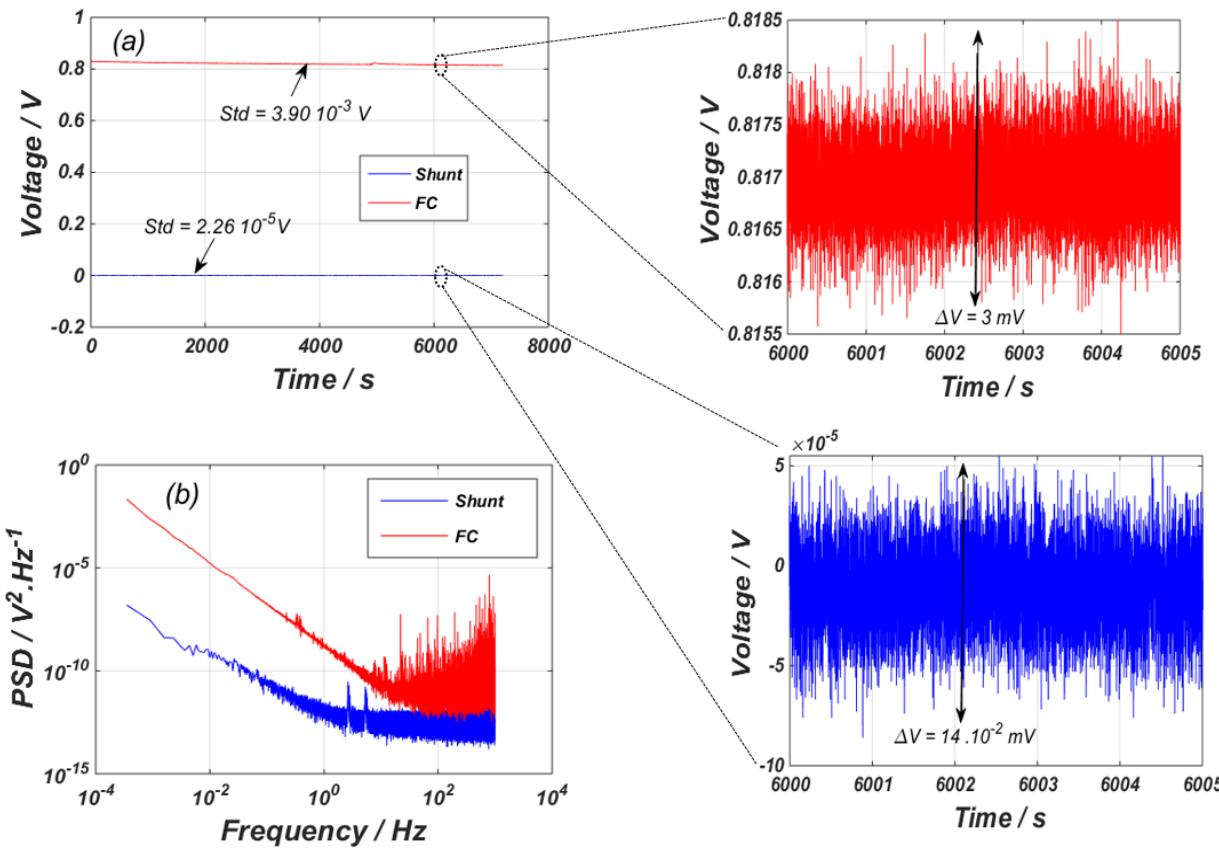
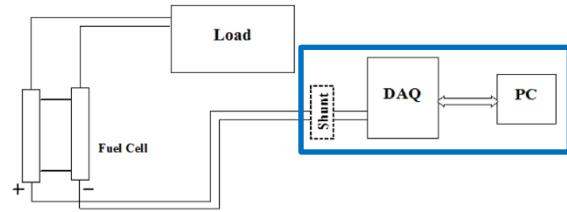
→ **Direct measurement**

No analog filter / No amplifier

Additional elements can impact final results



- **PEMFC single cell** Commercial MEA Nafion® 211 (25 cm²)
0,3 mg.cm⁻² Pt / Sigracet ® GDL 25BC
- **Fixed flow rate** H₂ : 122 ml.min⁻¹ and Air : 622 ml.min⁻¹
- **Tcell = 60 °C / Tbubbler (60 °C or more)**
 - 4 humidities : RH_{H₂} = 100% / RH_{Air} = 0%
 - RH_{H₂} = 100% / RH_{Air} = 100%
 - RH_{H₂} = 50% / RH_{Air} = 50%
 - RH_{H₂} = 20% / RH_{Air} = 20%
- **NI DAQ 9239** 24 bits (good accuracy) / anti-aliasing-filter sampling rate 2kHz
- **Load** = 0,1 Ω - 8 Ω Resistor
- **Shunt** : Intrinsic noise of experimental setup



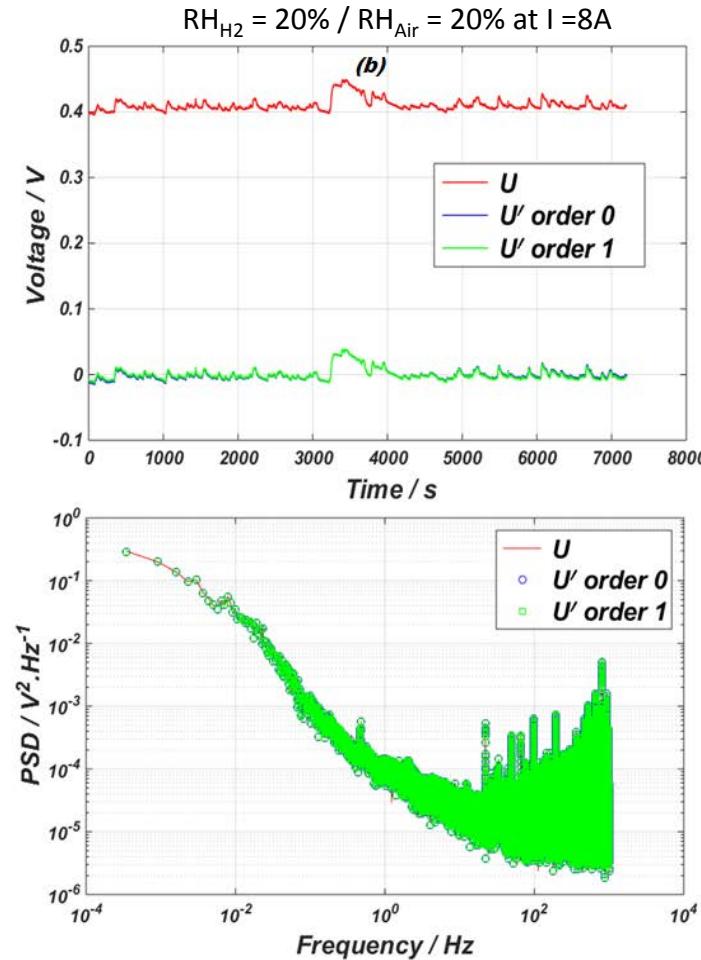
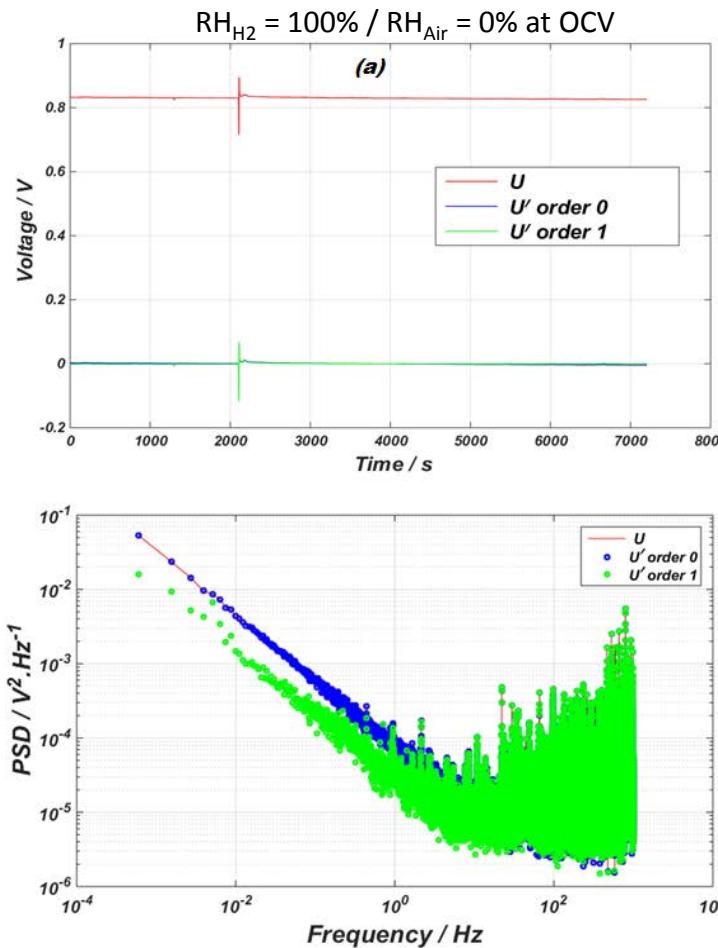
Voltage fluctuations measurements during 7200s at 2 kHz

- Fuel cell voltage fluctuations = $3 mV \gg_{x20}$ Shunt voltage fluctuations $0,14 mV$
- $STD_{FC} \gg_{x180} STD_{Shunt}$
- Spectrum amplitude $_{FC} >>$ Spectrum amplitude $_{Shunt}$ at low frequency range ($f < 100 Hz$)

Intrinsic noise of experimental setup two order smaller than electrochemical noise of the fuel cell

Apply FFT analysis to calculated Power Spectral Density (PSD) to:

- Raw signal U
- Signal fluctuations $U' = U - \bar{U}$ extracted with polynomial removal drift constant (order 0) or linear (order 1)

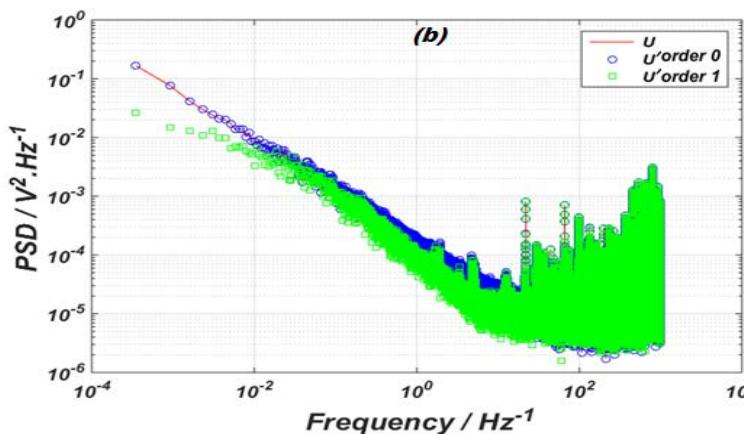
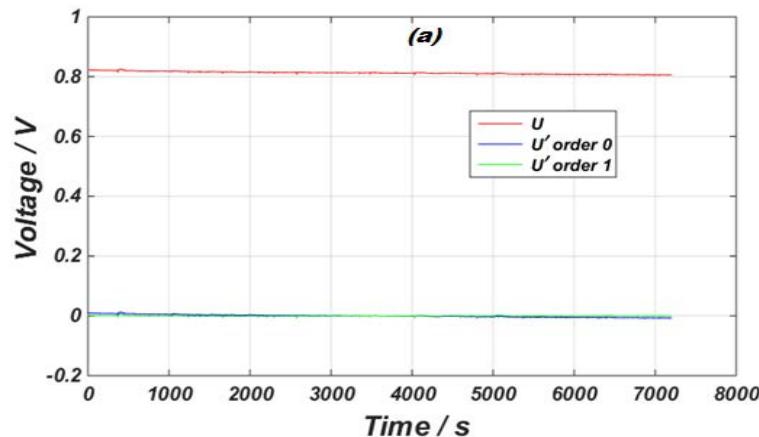


If PSD non-sensitive to drift removal \rightarrow Quasi-stationarity of signal

Apply FFT analysis to calculated Power Spectral Density (PSD) to:

- Raw signal U
- Signal fluctuations $U' = U - \bar{U}$ extracted with polynomial removal drift constant (order 0) or linear (order 1)

$$\text{RH}_{\text{H}_2} = 100\% / \text{RH}_{\text{Air}} = 100\% \text{ at OCV}$$



Higher drift (5mV.h^{-1}) \rightarrow preconditionning, flooding?

Changes appear in spectrum signatures :

\rightarrow Two linear slope U' order 1 (linear polynomial) at very low frequency ($f < 1\text{Hz}$)

Signal cannot be consider as stationary

Drift signal involves distortion of the results

Perform another drift removal procedure (piece-wise analysis – short term analysis)

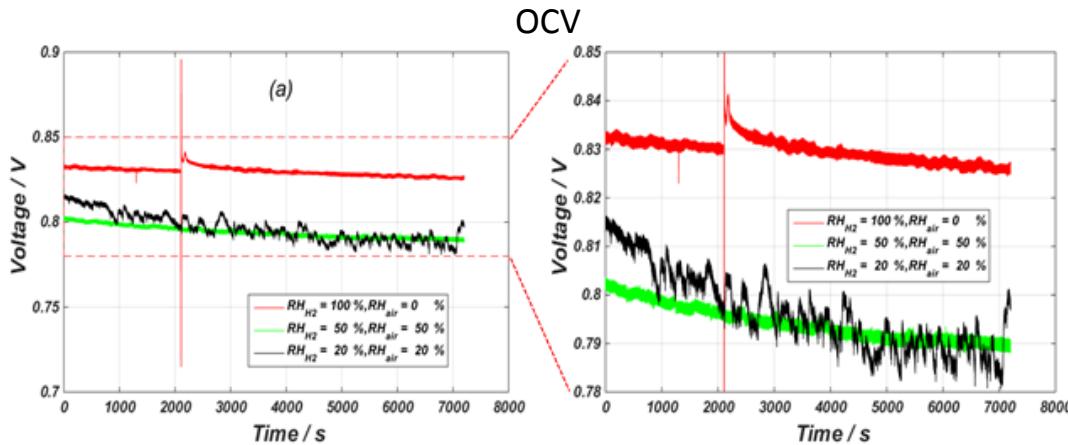
For all results we apply this methodology and present only quasi-stationary signals

Results

OCV

3 operating point : OCV, 2.5A and 8A

4 relative humidities $RH_{H_2} = 100\% / RH_{Air} = 0\%$ - $RH_{H_2} = 100\% / RH_{Air} = 100\%$ - $RH_{H_2} = 50\% / RH_{Air} = 50\%$ - $RH_{H_2} = 20\% / RH_{Air} = 20\%$



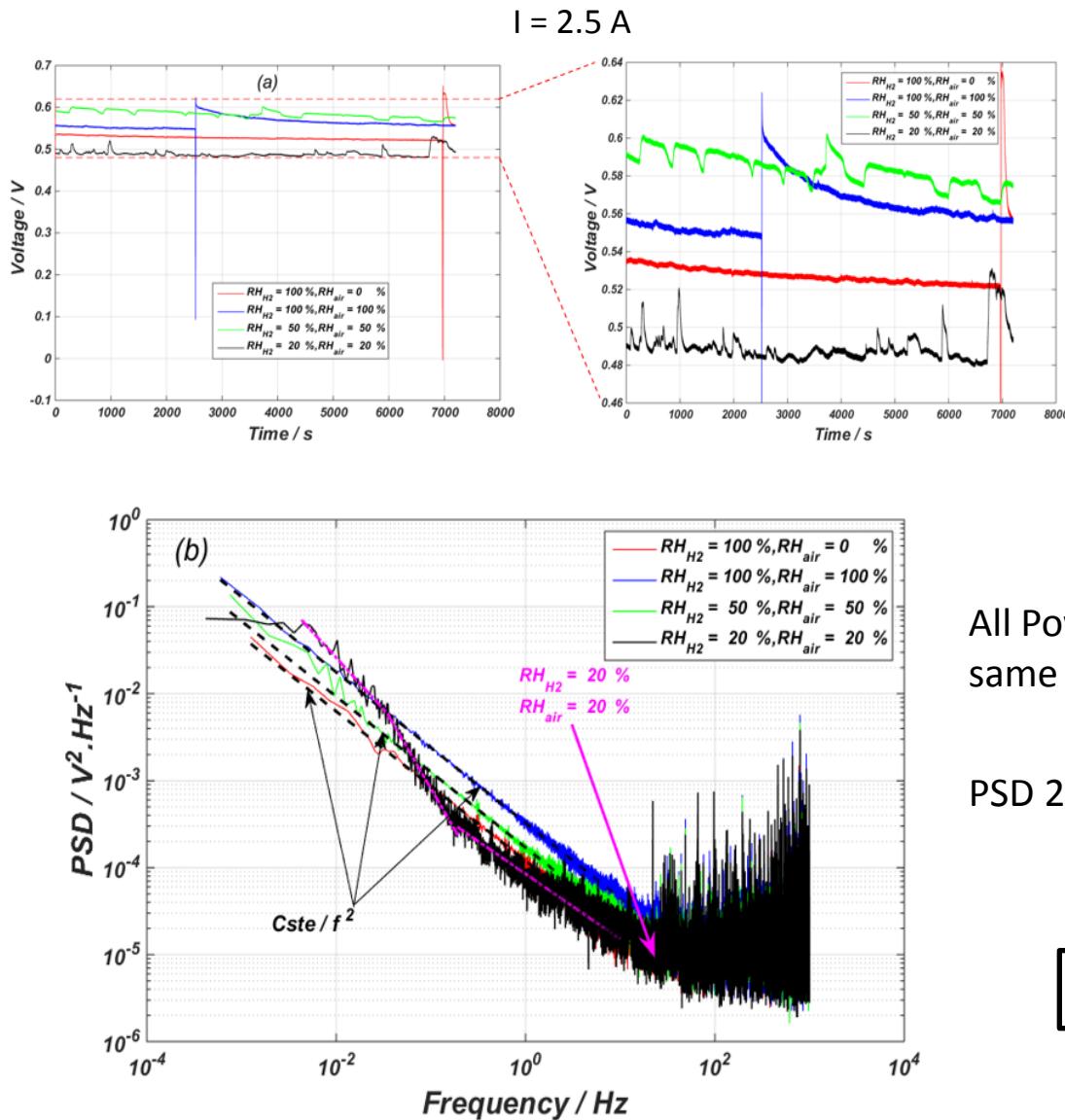
Voltage curves decrease smoothly

- $RH_{H_2} = 100\% / RH_{Air} = 0\%$ highest and stable voltage
 - $RH_{H_2} = 50\% / RH_{Air} = 50\%$ less stable
 - $RH_{H_2} = 20\% / RH_{Air} = 20\%$ the noisiest
- Fluctuations appears roughly 6 times larger*

All Power Spectral Density at OCV have the same shape :

- PSD highlight **linear slope $1/f^\alpha$** with $\alpha = 2$ (red noise) at low frequency ($f < 100$ Hz).

→ Fuel cell signature



As previously

- $\text{RH}_{\text{H}_2} = 100\% / \text{RH}_{\text{Air}} = 0\%$ highest and stable voltage
 - $\text{RH}_{\text{H}_2} = 20\% / \text{RH}_{\text{Air}} = 20\%$ **the noisiest**
- 100% / 0% and 100% / 100% potential peak drop (flooding phenomena)

All Power Spectral Density at 2,5 A have the same linear shape **except 20% / 20%:**

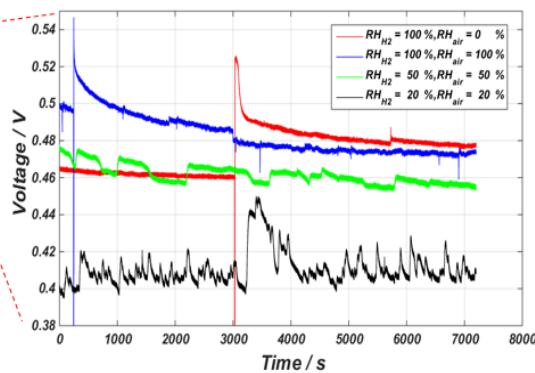
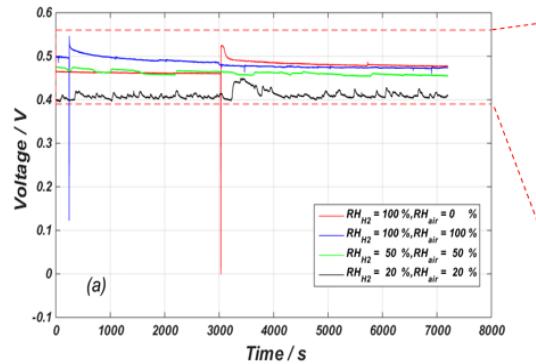
PSD 20% / 20% highlights **3 linear slopes**

→ Dry membrane signature
(spectral descriptor)

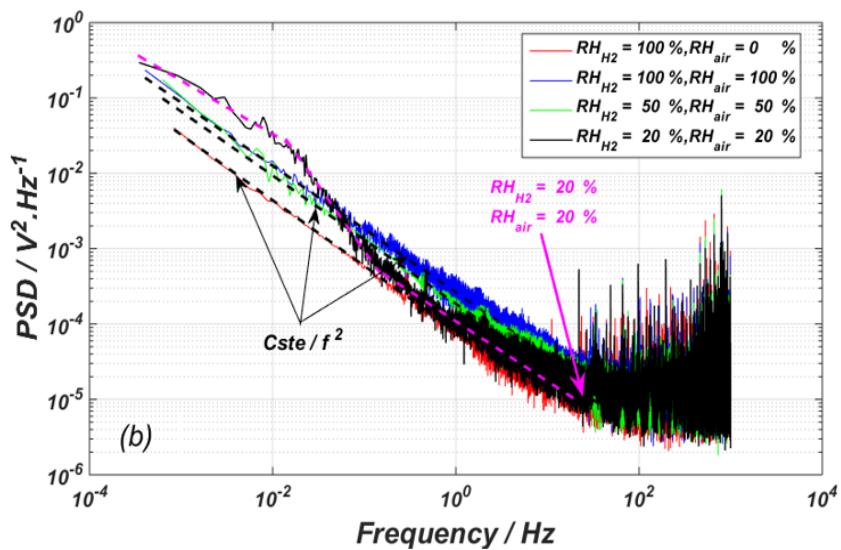
Results

$I = 8 \text{ A}$

$I = 8 \text{ A}$

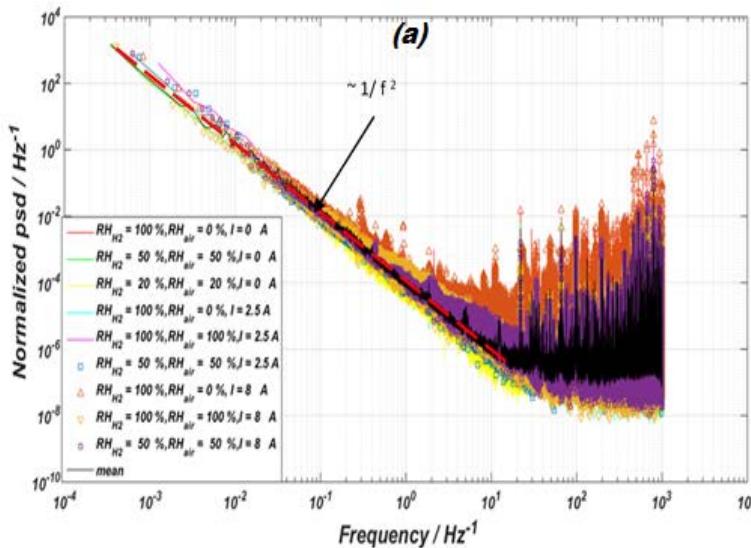


Increase of the voltage fluctuations



Increase of the **3 linear slopes** for PSD
at 20% / 20%

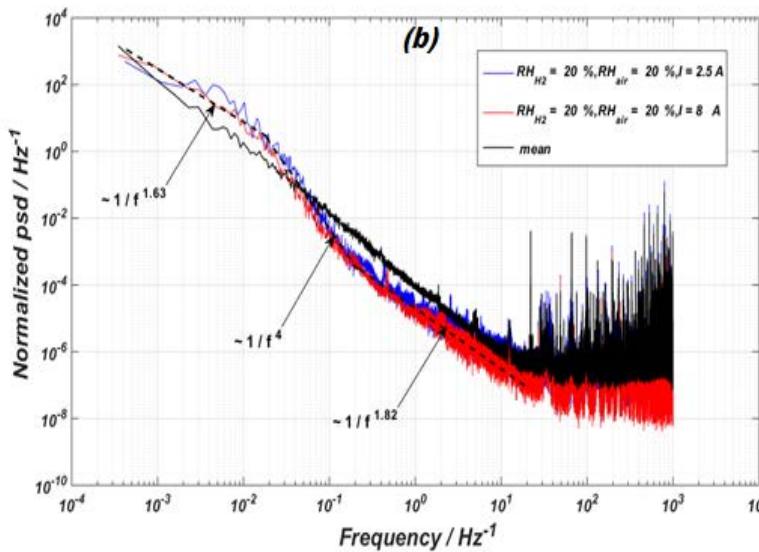
→ Dry membrane signature
(spectral descriptor)



All normalized PSD for \neq humidities except 20% / 20% for all operating point

Linear slope of $\alpha = 2$ (red noise)

→ Fuel cell signature



$\text{RH}_{\text{H}_2} = 20\% / \text{RH}_{\text{Air}} = 20\%$ for 2.5A and 8A

Three linear slope

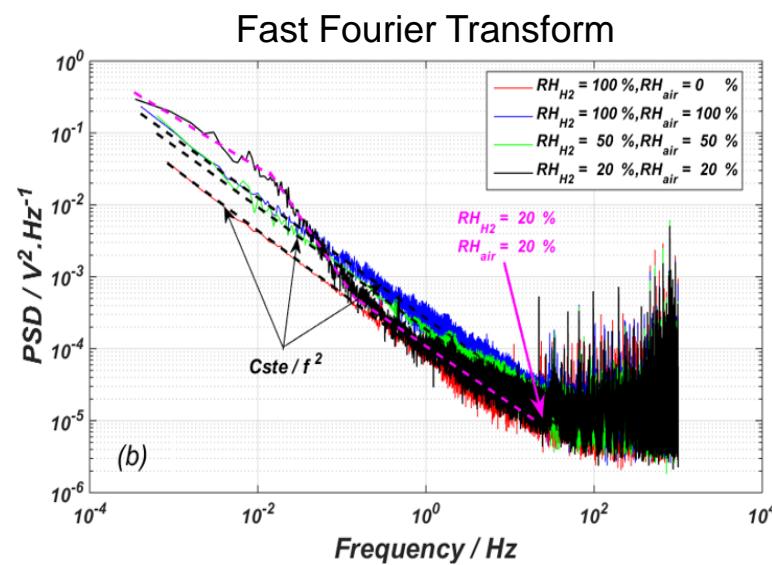
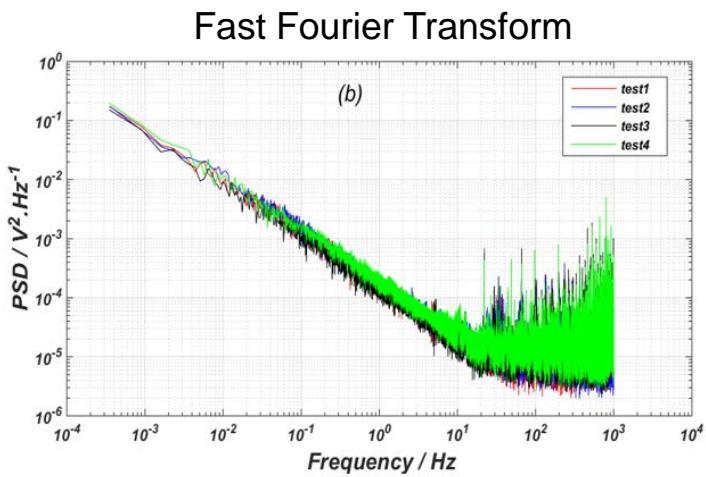
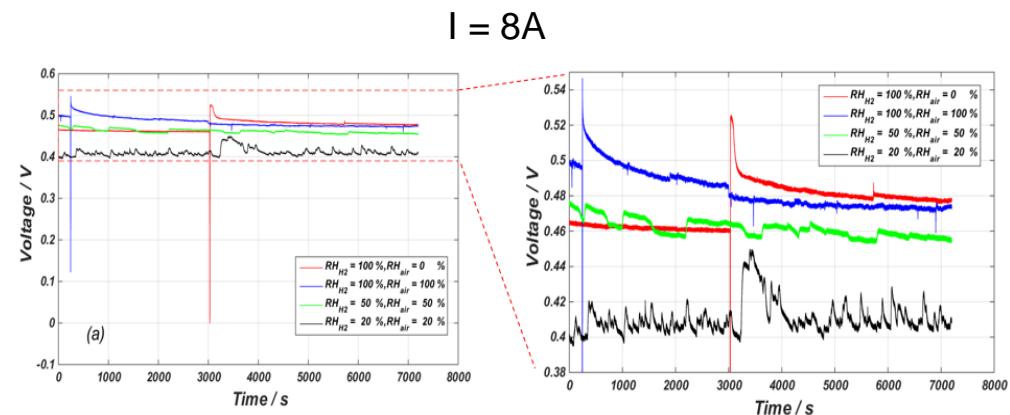
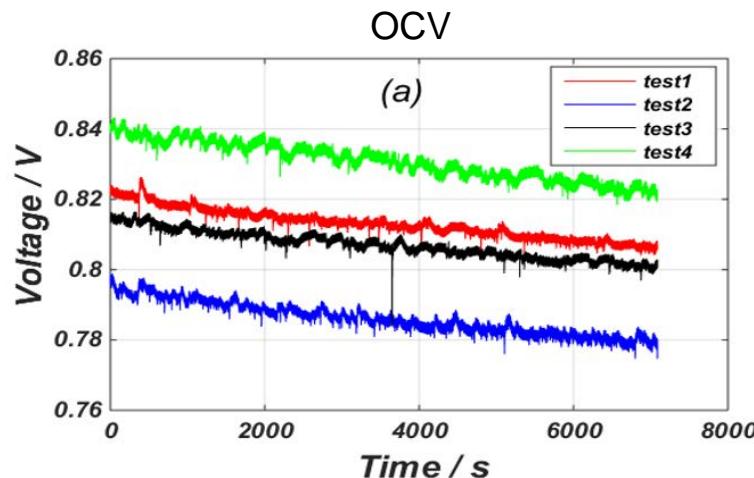
→ Dry membrane signature

PSD can be a spectral descriptor of drying membrane and diagnosis tool

Conclusions

- Electrochemical Noise Analysis (ENA) performed on PEMFC
 - *4 relatives humidities*
 - *3 operating point (OCV, 2.5A and 8A)*
- Spectral signature of fuel cell : linear slope $1/f^\alpha$ with $\alpha = 2$ at low frequency ($f < 100$ Hz)
- EN is sensitive to water management
 - *Three linear slope in dry conditions (higher mass & charge transfer resistance)*
- Methodology proposed to evaluate quasi-stationarity
 - *Non-sensitivity of spectrum for polynomial drift removal (order 0 & 1)*
- ENA is an interesting tool for the diagnosis of PEMFC
 - *Complete impedance spectroscopy and interrupt current methods*
- Remarkable advantage of ENA is its non-destructive nature
 - *Apply in on-line industrial application (prognostics)*

- Bejaia
 - Durability, Water & Thermal management of fuel cells systems

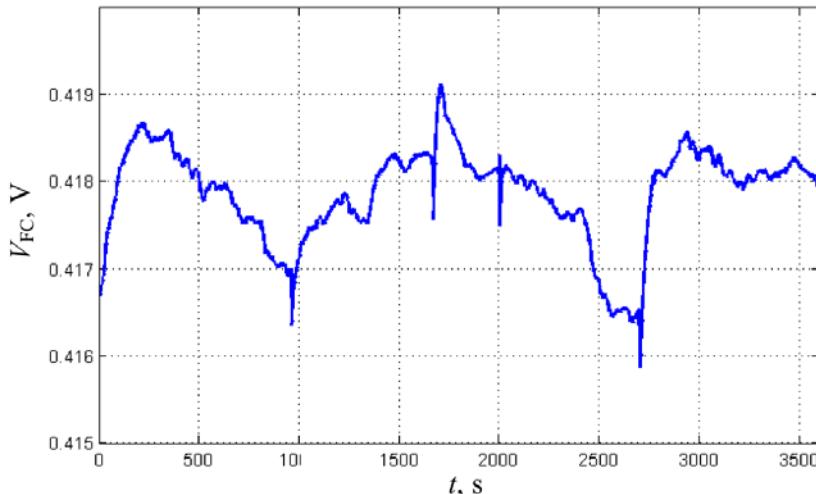


→ 1 Franco-Algerian cosupervision Thesis : R. Maizia (2017)

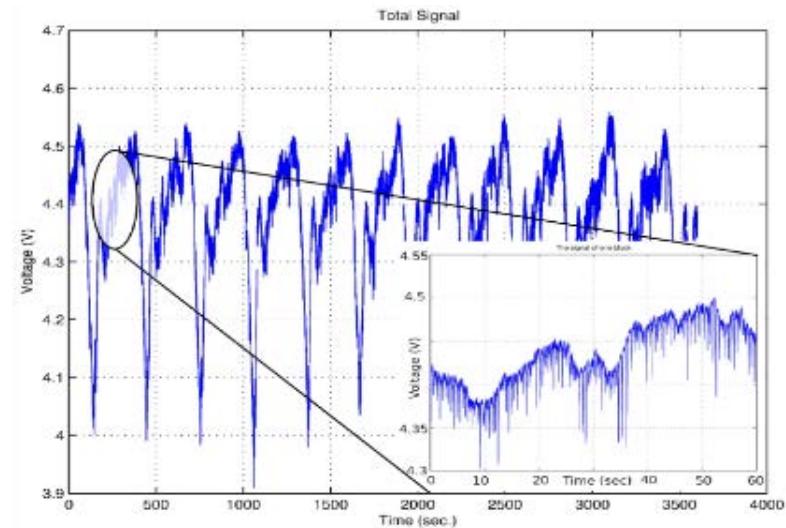
- Kazan National Research Technical University (Russia)



- Durability, Diagnostics & Prognostics of fuel cell systems



Denisov 2011 - One cell system (25W)



Adiutantov 2015 – Stack system 8kW

→ 2 Franco-Russian cosupervision Thesis : E. Denisov (2012) & N. Adiutantov (2016)

→ 1 International Exploratory Cnrs Project (Pics – 2010)

→ 1 French ANR Project (Propice 2013 – Femto Belfort)

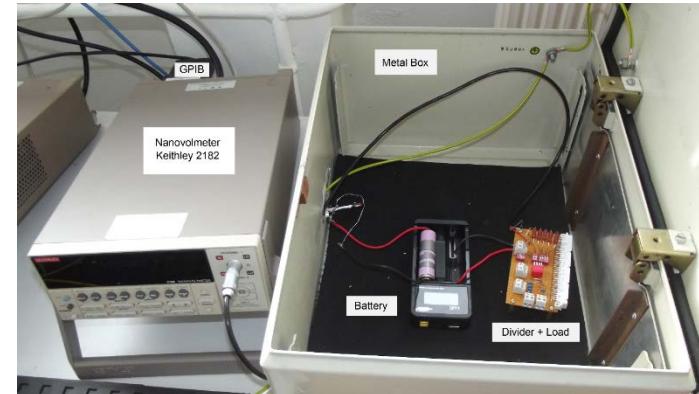
Electrochemical Noise = stochastic fluctuations of voltage (or current)

generated by mechanical and/or chemical degradations (cracks, dissolution, gas bubble formation,...)

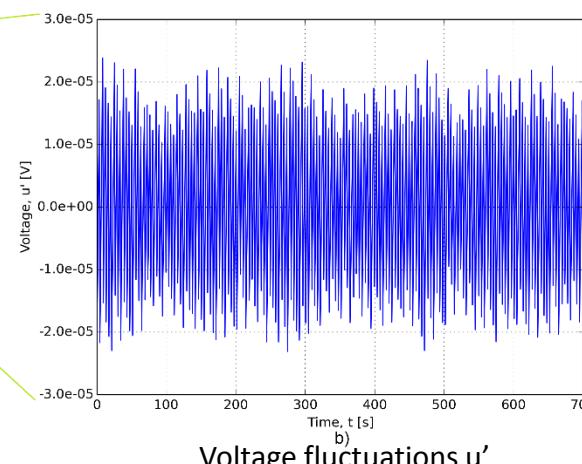
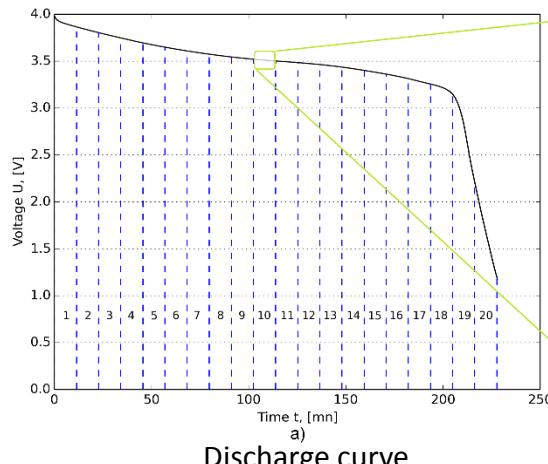
Why use EN? Non intrusive method (*compare to impedance spectroscopy or current interruption*)

Battery Applications : → Safety (prevent battery explosion)

→ Generate descriptors for diagnostics & pronostics



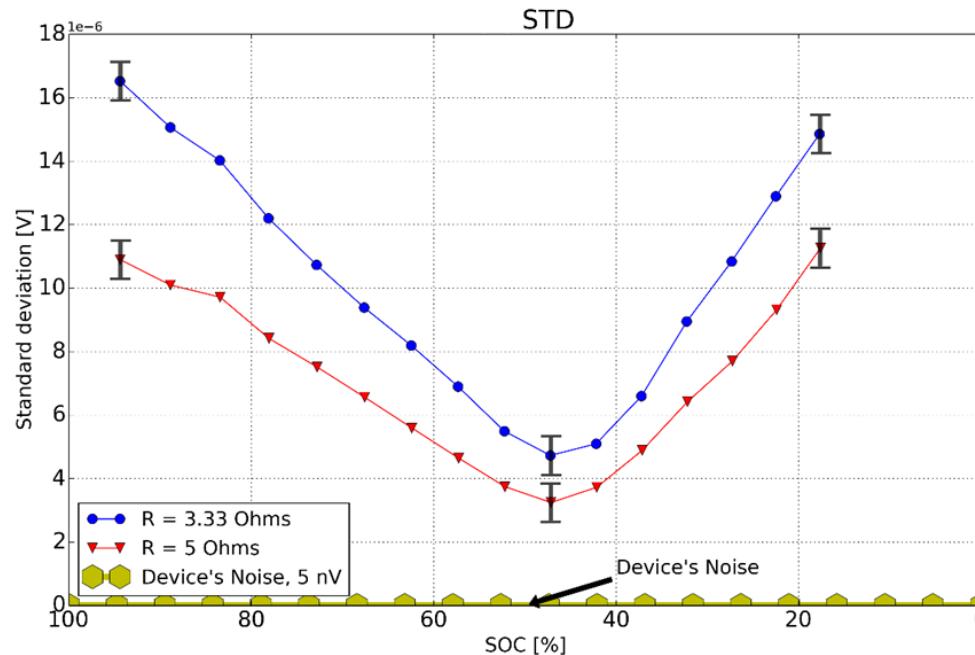
Voltage measurements in commercial ICR 18650 Lithium ion battery
Non stationary signal



$$u' = U - \bar{U}$$

Piece-Wise-Polynomial method
to calculate \bar{U}

Standard deviation of u' with State-of-charge (SOC)



V-shape curve

- Minimum of $3.5 \mu\text{V}$ for 5.5Ω load
- Minimum of $5 \mu\text{V}$ for 3.3Ω load
around 45% of SOC

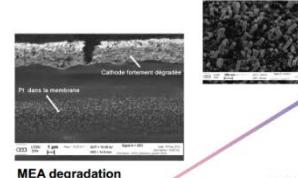
- New and innovative metrologies & systems (*Sensors, Reactor & Cells Designs*)
- Modelling (*Multiphysics, Multiscales, Modular, Predictive*)
- Applications (*Energy storage, Mobility, Green chemistry*)



Nano-characterisation

characterisation equipments

Surface analysis, Ions beams, Microscopes, X ray diffraction, Sample preparation



Modeling
From nanoparticles to systems

Multi-scales

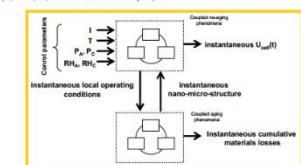
Physical macroscopic values

(T, HR, P, current density...)

Modular

(fluidics, catalyst, degradation, pollutants...)

Predictive tool



Acknowledgements

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Pr. C. Coutanceau



Frumkin Institute

Dr. D. Bograchev

PhD. R. Maizia



Dr. H. Dib



Pr. S. Grigoriev



Thank you for your attention