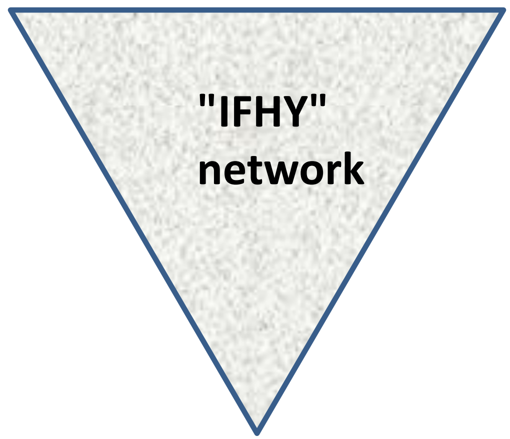
# Hydrogen in France:

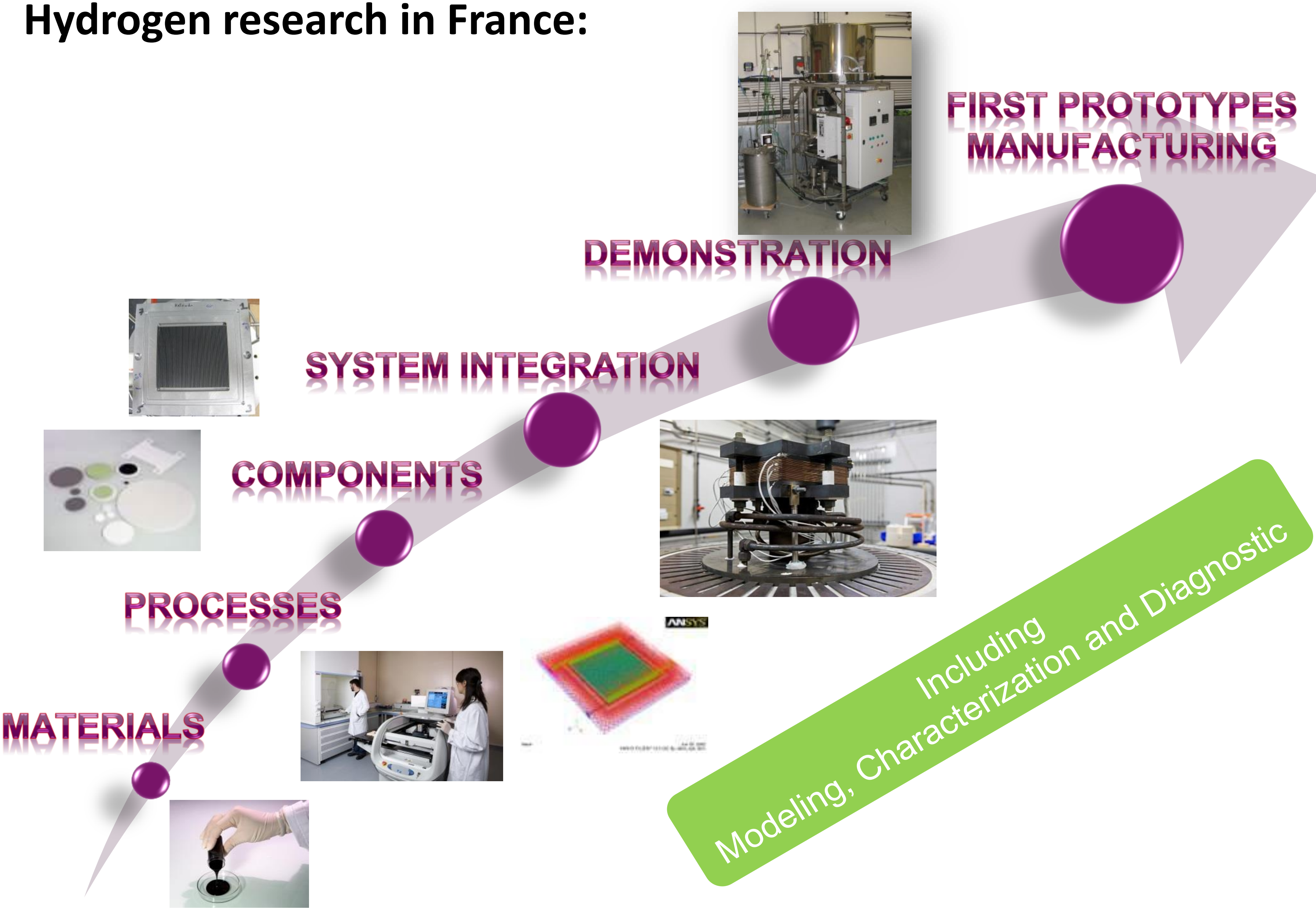



**& Universities**

**Industries**

Prof. Olivier Joubert
olivier.joubert@cnrs-imn.fr
www.gdr-hyspac.cnrs.fr

# Hydrogen research in France:



# HySPàC

Head : Prof. Olivier Joubert
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French academic research grouping on Hydrogen

**HySPaC**: « Hydrogen. Systems. Fuel Cells » **A Structuring « academic » research operation (started in 2001 !)**

**- 250 researchers**
**- 4 topics (Low and High temperature FC and E, Hydrogen Production (not E) and Storage, FC and E Systems)**
**- Scientific shared production (/year) : 50 papers, 25 PhD, 5 patents,**

**Objectives**:

- Promote scientific workshops & networking
- Ensure a permanent updated state-of-the-art
- Establish realistic scientific objectives for French research centers
- Build consortia for applying to national or international programs


**Members**
- 77 CNRS teams
- 10 CEA teams
- industries

**Competences**
- Materials,
- shaping,
- caraterisations : Electrochemistry, Mecanical, thermal, performance
- modelisation…

HySPàC

# Topic: **Hydrogen storage**

## Scientific & Technical Challenges

- Hydrogen production methods with low $CO_2$ fingerprint
- Hydrogen purification by selective membranes
- Materials for solid-state hydrogen storage
- Development of storage tanks
- Coupling of storage tanks to fuel cells systems

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# HySPàC Hydrogen storage: novel hydride materials

## Light B–H and B–N–H compounds for energy

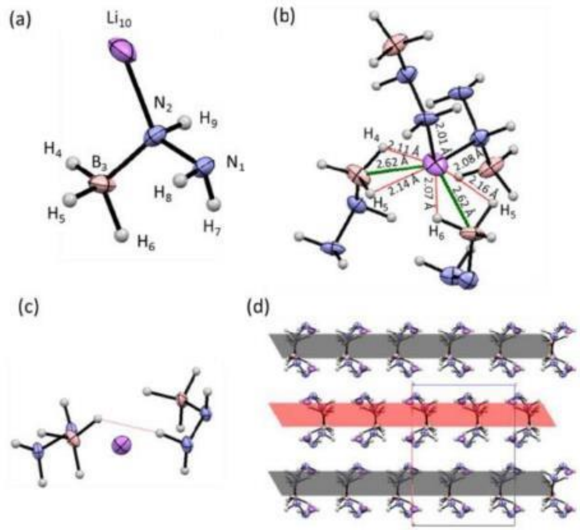
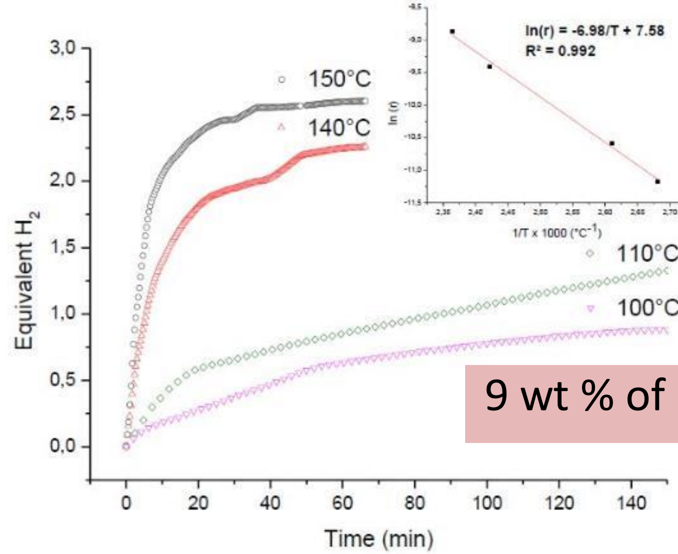



**Figure 4.** Crystal structure of β-LiHB with detailed view of: (a) the asymmetric unit with labels; (b) the coordination of $Li^+$; (c) the intermolecular $H^{\delta+}\cdots H^{\delta-}$ dihydrogen bond according to the Klooster et al.'s definition[20] ($H_4\cdots H_7$ = 2.25 Å, $B_3$–$H_4\cdots H_7$ = 106.8° and $N_1$–$H_7\cdots H_4$ = 171.2°); and (d) the representation of the parallel plans on which the $H^{\delta+}\cdots H^{\delta-}$ network extend.




9 wt % of $H_2$

**Figure 6.** Volumetric measurements under isothermal treatment at 100, 110, 140 and 150°C of β-LiHB. The inset figure is the Arrhenius plot for the determination of the apparent activation energy from the data of the volumetric measurements.

*Our focus*: B–H and B–N–H materials, from chemical hydrogen storage materials to liquid-state fuel of fuel cell, via energetic materials…

Chem. Mater. 26 (2014) 3249

umit.demirci@um2.fr

HySPàC

# Hydrogen storage: energy management

## Fuel Cells, $H_2$, Renewable Energy Management

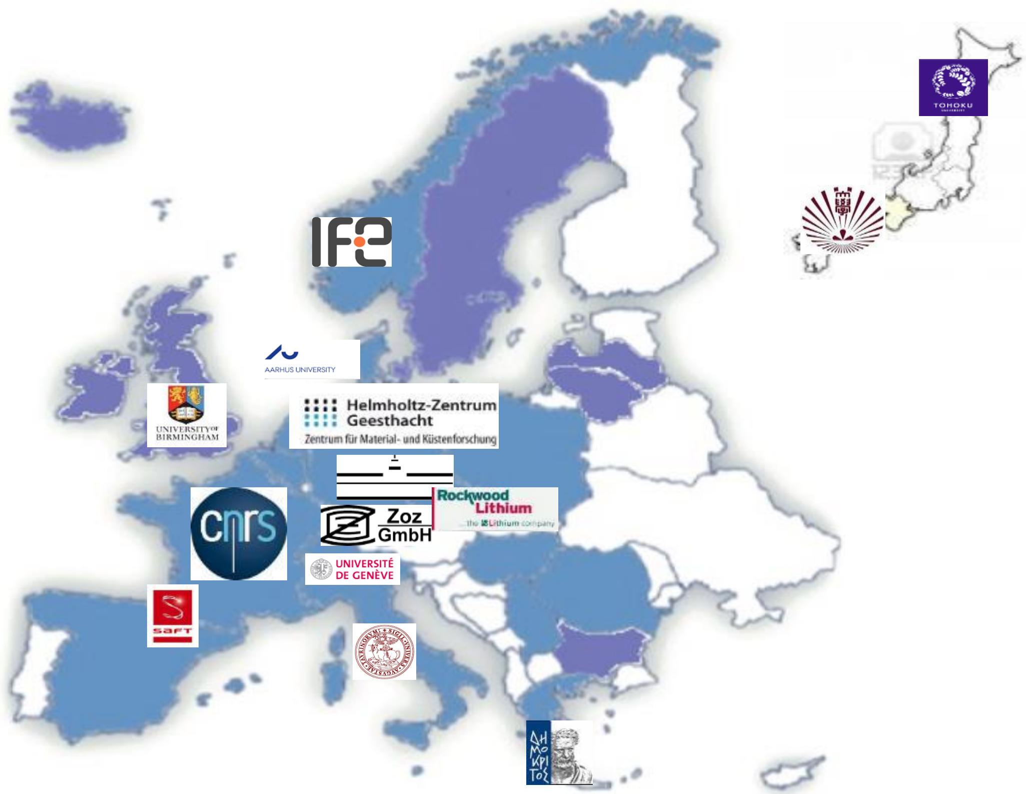
## Example of a R&D program

SEVENTH FRAMEWORK PROGRAMME

MARIE CURIE ACTIONS

### the ECOSTORE project (2013-2017)

*ITN Marie Curie Action: 4 M€*




**Novel Complex Metal Hydrides for Efficient and Compact Storage of Renewable Energy a Hydrogen and Electricity**

13 European laboratories and industries
2 Japanese labs


latroche@icmpe.cnrs.fr

# HySPàC Hydrogen storage: system integration

## Stand-alone relay station

### $H_2$ storage by pressurized gas


**type-IV tanks**
**5 $kgH_2$, 30 bar**

**Modular all-in one energy station ensuring continuous seasonal autonomy**

Collaborative project RHYTA (2015-2018)

CASSIDIAN femto-st PowiDian UFC MAHYTEC UNION EUROPEENNE L'Europe s'engage en Franche-Comté

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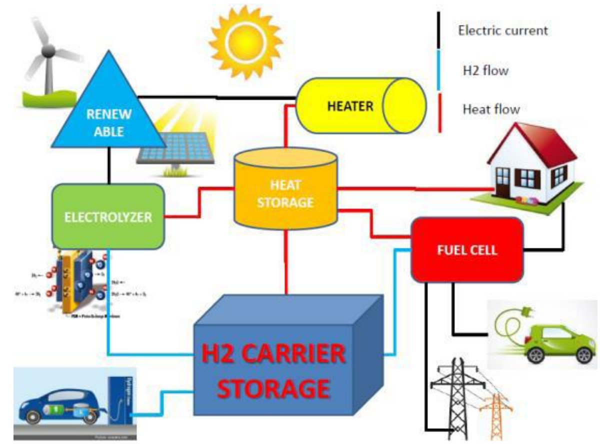
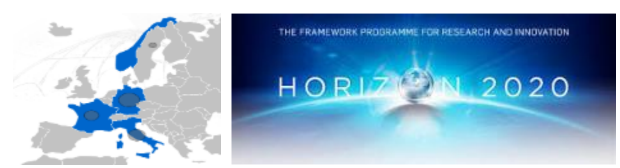
## Stationary storage

### $H_2$ storage in metal hydrides




**$TiFeH_2$ and PCM materials for the storage of renewable energy**
**50 $kgH_2$, 2 bar**

HyCARE project (2019-2021)




cnrs Helmholtz-Zentrum Geesthacht Zentrum für Material- und Küstenforschung engie IFE

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# HySPàC Fuel Cells and electrolysers

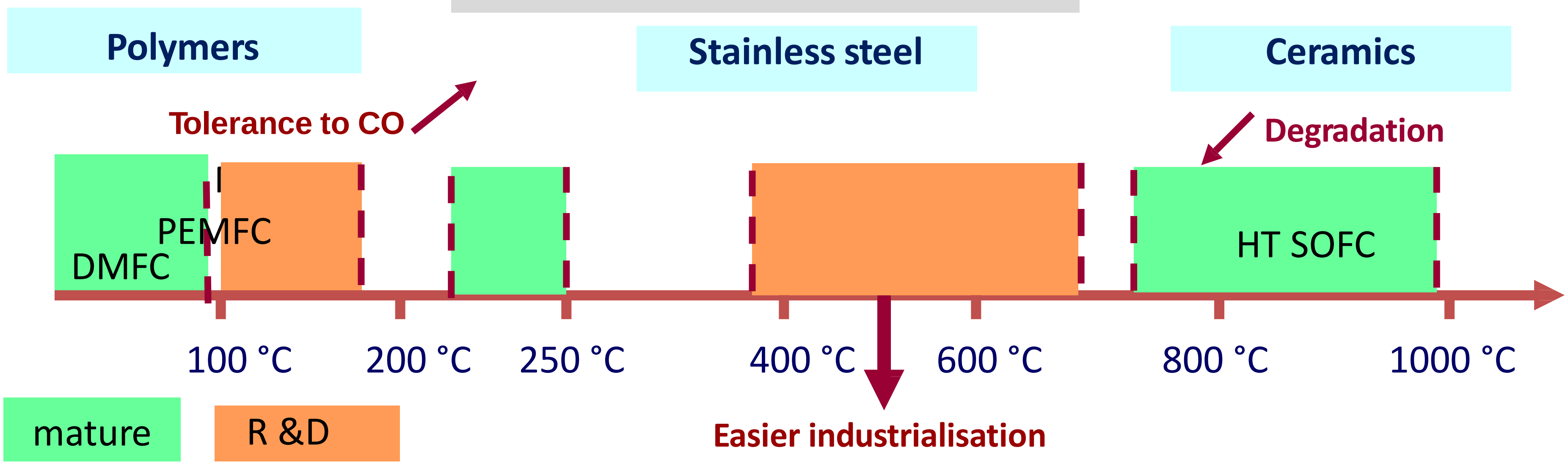
## Scientific & Technical Challenges

**Expensive membranes**
**Need of Pt catalyst**
Complex Reforming
at low T (no CO)
**Water management**,
Hydration of gases /
Limited cogeneration

Low cost fabrication processes (metallic materials)
Easier thermal cycling
Simple reforming

**BUT Need of materials for Electrolytes and Electrodes**

**Expensive interconnects**
**(ceramics or alloys)**
Difficulty of thermal cycling
Too long starting time
**Degradation of electrodes**
**at high temperature**
Sealing problems. Lifetime

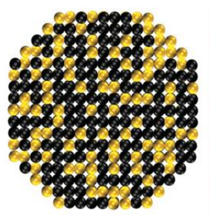


# Topic: **PEM (Catalysts)**

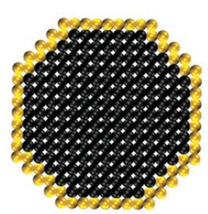
Christophe.coutanceau@univ-poitiers.fr

**Development of synthesis methods for active, selective and stable catalysts for the ORR and the oxidation of small molecules with energetic interest**

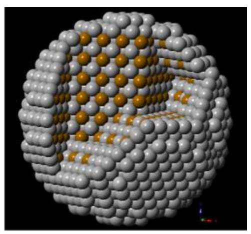
## PGM-based Catalysts



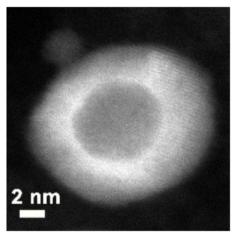
alloys



Core-shell

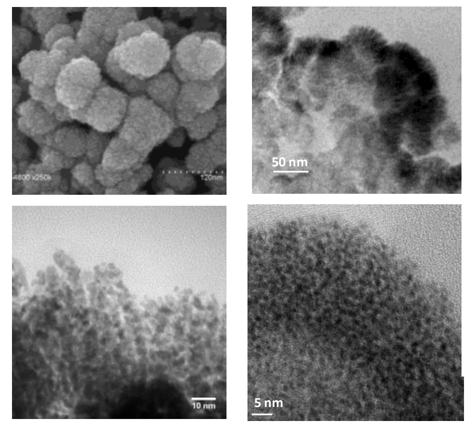


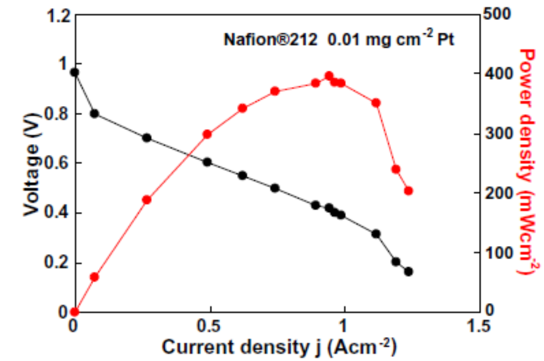
intermetallic




"Hollow" Pt NPs

## New electrode architecture

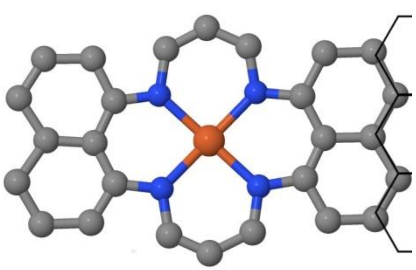


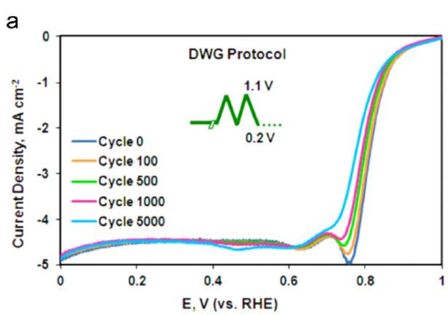



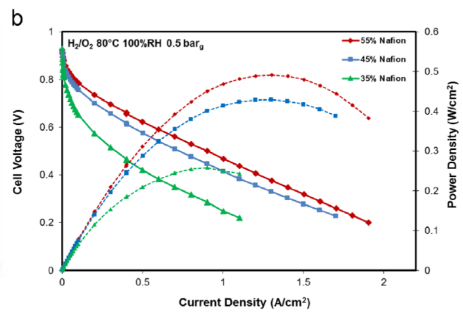

**0.02 $mg_{Pt}$ $cm^{-2}$; 0.4 W $cm^{-2}$ = > 20 $kW_e$ /$g_{Pt}$**

M. Cavarroc, et al. Electrochem. Comm. 11 (2009) 859–861 ;
P. Brault et al. ChemSusChem 6 (2013) 1168-1171.

## No-PGM based catalysts

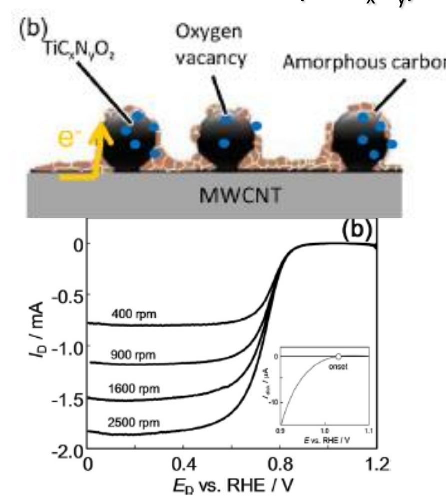





F. Jaouen et al., GDR HySPàC, Poitiers, 2014 ; A. Serov et al., Nano Energy (2015) 16, 293–300.

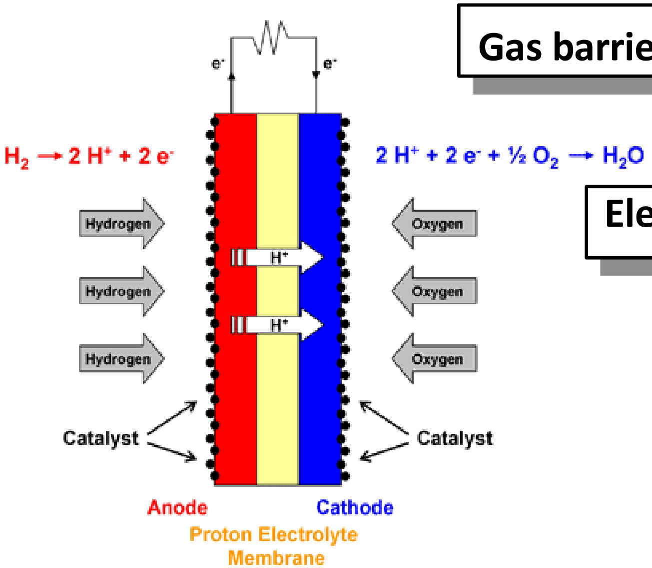
Titanium carbonitride($TiCN_xO_y$)

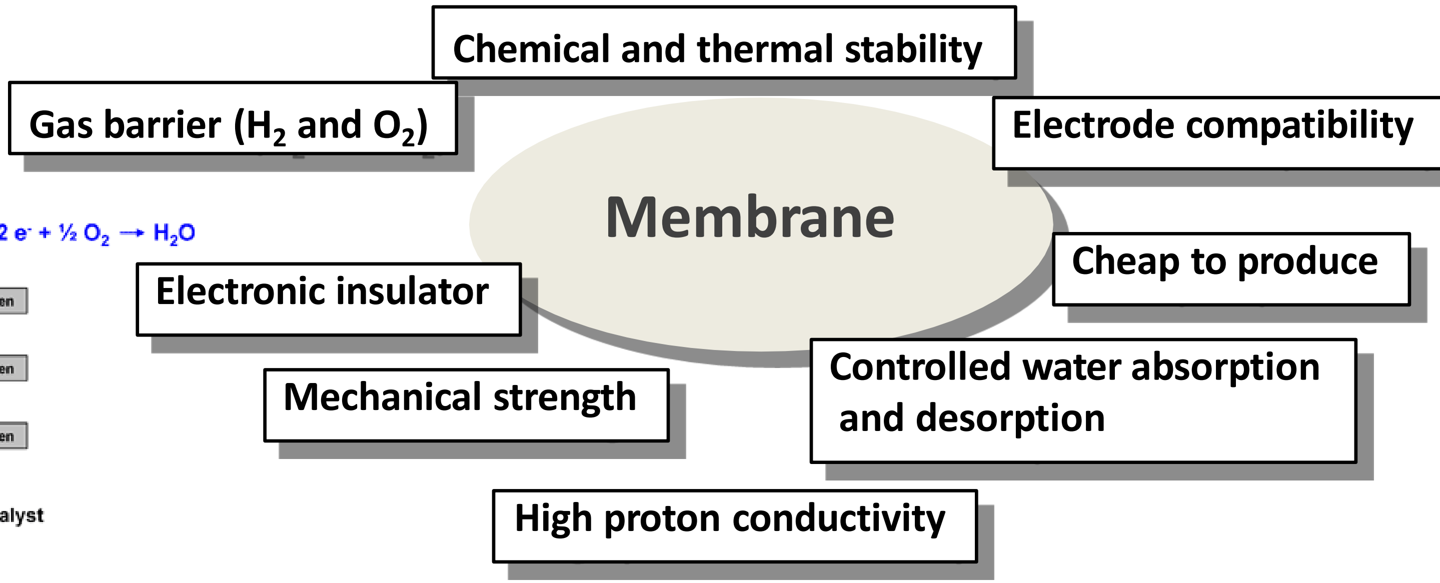



T Hayashi et al., Electrochim.Acta 209 (2016) 1–6

# HySPàC PEM (Membranes)

## Fuel Cells, $H_2$, Renewable Energy Management




➔ Develop alternative membranes to PFSA membrane: low cost and with good thermo-mechanical strength, conductivity in a large window of T ( 0 < T > 120°C) and low RH

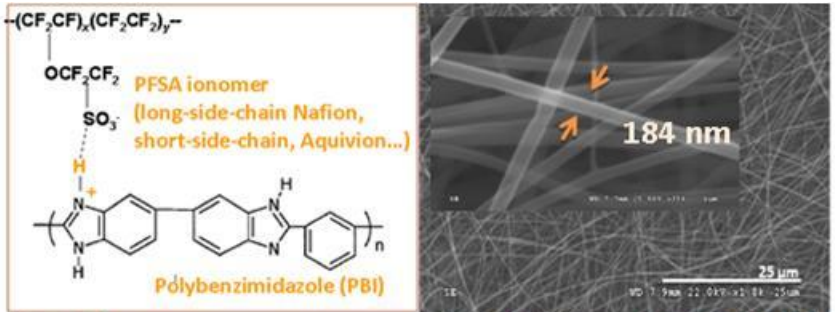
➔ Increase the operation temperature of PEMFC at more than 120°C at low RH or in anhydrous conditions

➔ Study/Enhance the durability of MEA

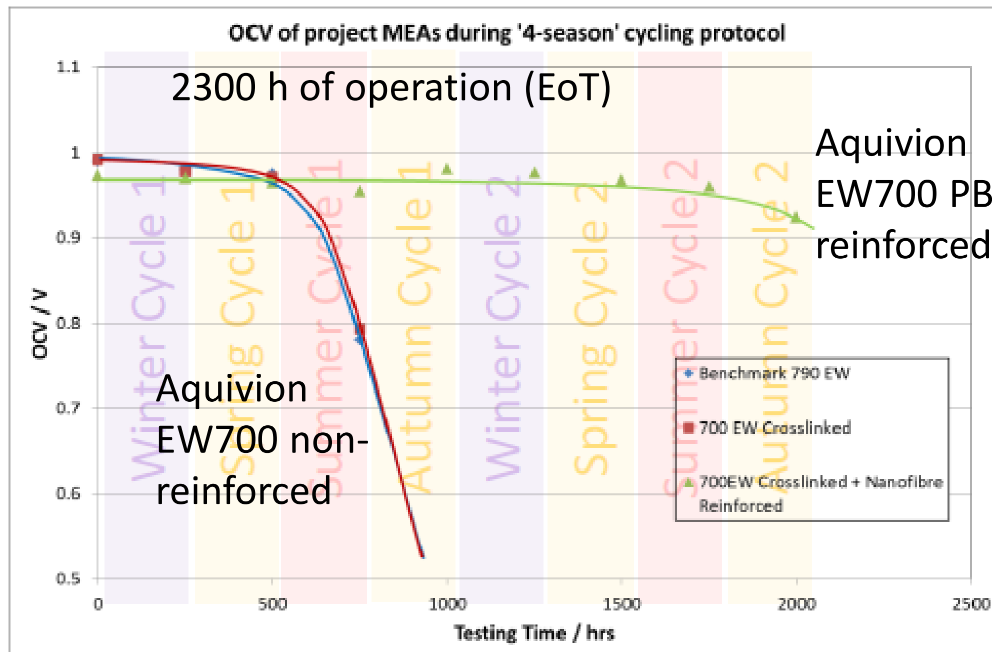
# HySPàC PEM (Membranes)

## Robust Membrane Development

ICGM Département de Chimie du Solide et de la Matière Divisée AIME




- Composite membranes PFSA/nanofibres (with PBI)
- **Separation of the two functions: structural (reinforce) and transport (ionomer)**
- **"ionic Reticulation"** good interface between materials
- Stack "arc-en-ciel" 9 cells, 50 cm$^2$, 80 °C, 30% RH.


**Scaling up of reinforced membrane**

FCH JU MAESTRO and VOLUMETRIQ Projects

Deborah.Jones@univ-montp2.fr

# HySPàC Topic: SOFC/SOEC

## scientific and technological Hurdles

### MEA:

**New materials for SOFC and SOEC**

- **Electrolytes** : composites, proton conductors (stability vs conductivity), modélisation (DFT,…) vs performance
- **Electrodes** : MIEC (particularly ionic conductivity $10^{-2}$S/cm), stability (vs $CO_2$), decreasing polarization resistance (microstructure, catalyst)
- **interconnectors** (more and more important / metal supported cell) : solving the problem of oxidation during the design of the cell, using precursors to synthesize interconnects, how to limit the Cr diffusion (development of protecting layer).
- **sealings** : glass type new materials to improve stability, self-healing

### Half and Complete cells:

- Using **industrials shaping methods**
- **New diagnostic tools** (electrochemical tools)
- Cost reducing: reducing the number of heating steps

### Tests, durability (vs impureties):

- improving the performance by adding diffusion barrier or by modifying the composition
- **modelisation** (degradation mecanism)

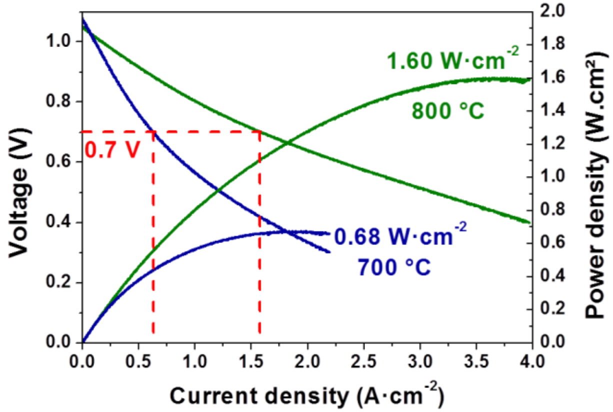
HySPàC

# Topic: SOFC/SOEC

## Innovative oxygen and impregnated electrodes

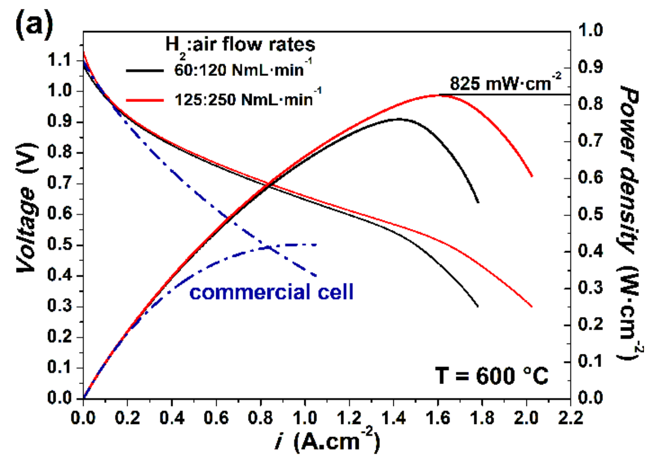
icmcb institut de chimie de la matière condensée de bordeaux

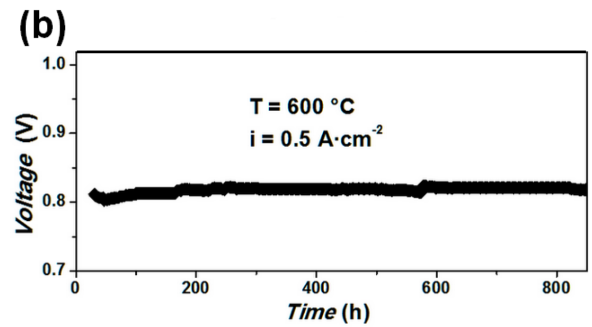
### 1) Ni-YSZ//YSZ//GDC//$Pr_4Ni_3O_{10+\delta}$
### *Screen-printed electrodes*




**Power density**
**At 800 °C: 1.6 W.cm⁻²**

### 2) Porous CGO *impregnated by $Pr_6O_{11}$*
### Benchmark with commercial cell (600°C)




### 3) Innovative cells

1) ***Shaping of a porous/dense/porous support using the same electrolyte***

2) ***Infiltration of solutions => preparation of electrodes at moderate T°***

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"$Pr_4Ni_3O_{11}$ : a new promising oxygen electrode for SOFC"
V. Vibhu, J.M. Bassat et al, J. Power Sources 314 (2016) 1-10

"An innovative efficient oxygen electrode for SOFC: $Pr_6O_{11}$ infiltrated into Gd-doped ceria backbone"
C. Nicollet, J.M. Bassat et al, Int. Journal of Hydrogen Energy 41 (34) (2016) 15538-15544)

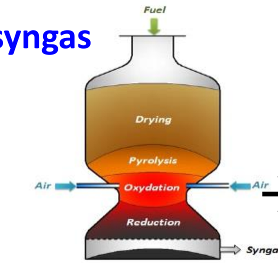
# HySPàC Topic: SOFC/SOEC

## TEST: Electrochemical diagnosis

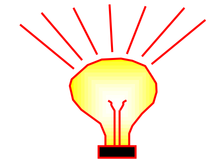
**VALORPAC and Roxsolidcell *** Projects

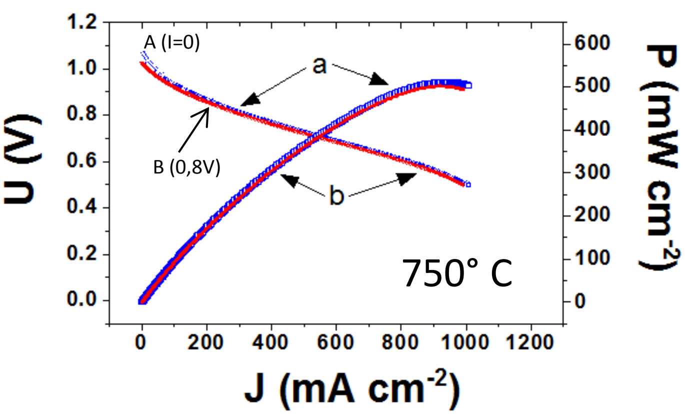
**Using SOFC with syngas**

→ Gazifier



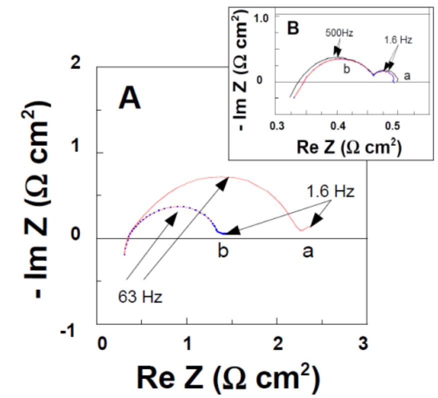

→ SOFC






(a) $H_2$ 20% - CO 20% - $CO_2$ 10% - $N_2$ 50% : 482 mW $cm^{-2}$

(b) $H_2$ 17% - $CH_4$ 3% - CO 20% - $CO_2$ 10% - $N_2$ 50% : 502 mW $cm^{-2}$




Impedance diagrams →

*Electrodes :*

*80% of ASR at OCV, 30% at 0.8V*

– *of power density values due to reforming reaction: $CH_4 + H_2O \rightarrow CO + 3H_2$*


"Effects of carbon monoxide, carbon dioxide, and methane on Nickel/Yttria-stabilized Zirconia-based Solid Oxide Fuel Cells performance for direct coupling with a gasifier" M. Lebreton. B. Delanoue . E. Baron F. Ricoul A. Kerihuel A. Subrenat, O. Joubert, A. Le Gal La Salle, *International Journal of Hydrogen Energy*, 40 (32), 10231-10241 (2015)



* ADEME-TITEC Program

** Eurostar RoxSolidCell project



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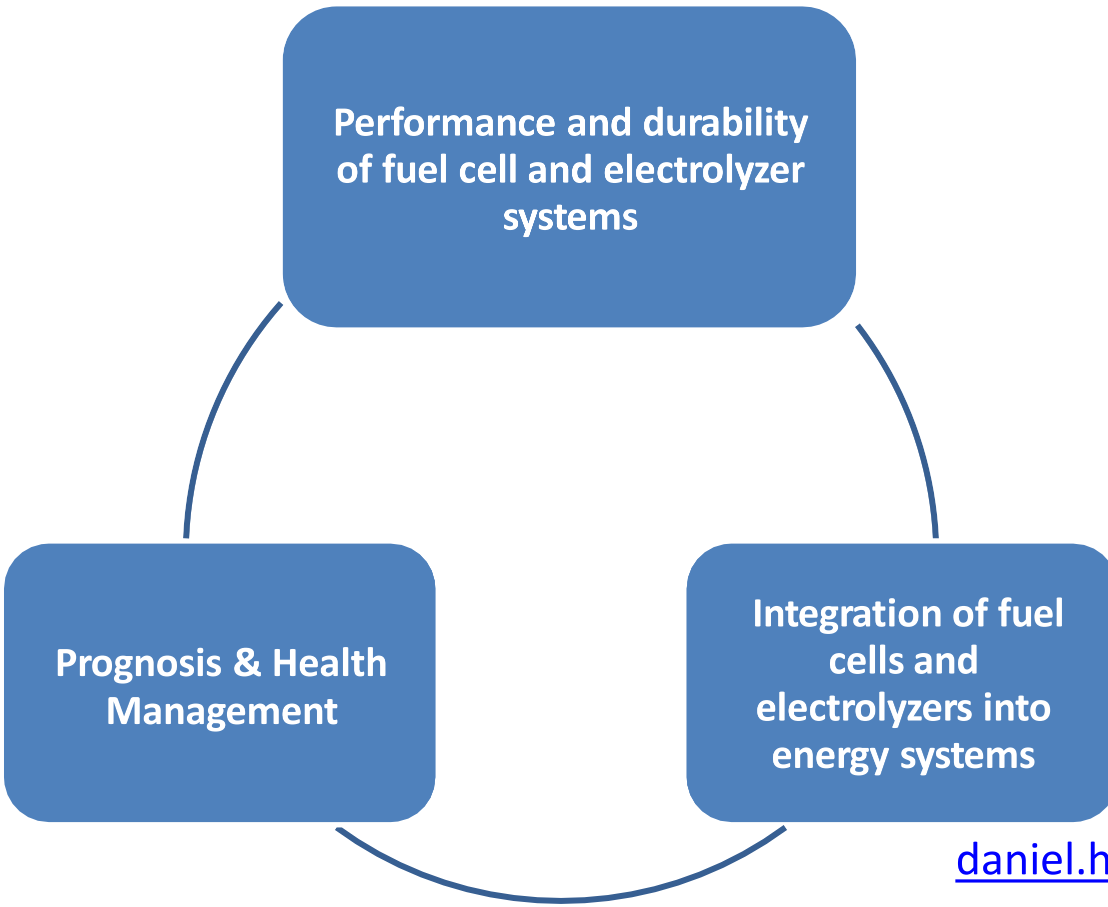
HySPàC

# Topic: **FC systems**

## Multi-flow energy systems based on fuel cells and electrolyzers

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HySPàC FC Systems

Systems : Assessment in real world

# Mobypost EU project – Main project objectives

- Taking care of postmen requirements
- Design an optimized hybrid FC powertrain
- Energy flow supervision
- Coupling with renewables (PV panels)
- Hydrogen production & storage on-site
- 1st French FCV fleet (10 vehicles, 2 H2/PV stations) testing in constrained environment (temperature, power demand)

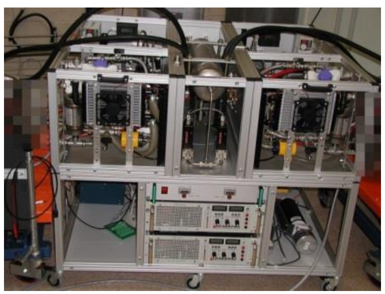
# Key numbers

- **2** demonstration territories in B-FC region
- **2** years experimental trial
- **8** European partners
- **10** FC vehicles
- **920** MM work
- **1682** postal routes covered
- **2017** (demonstration ended in…)

# HySPàC FC Systems

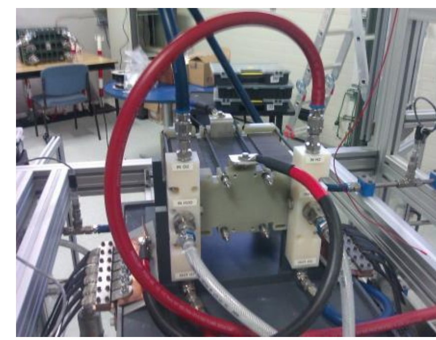
## FC LAB (Belfort)

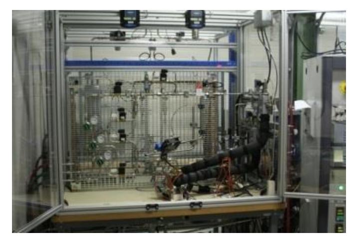
- 60 permanent staff
- Facilities area > 1000 m²
- **Land transport** applications
- Stationary applications
- Test up to 100kW



## Laplace (Toulouse)

- 13 permanent staff
- Facilities area: 250m²
- **Aircraft** applications
- Stationary applications
- Test up to 10kW





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**Thank you for your attention**

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