MINES ParisTech

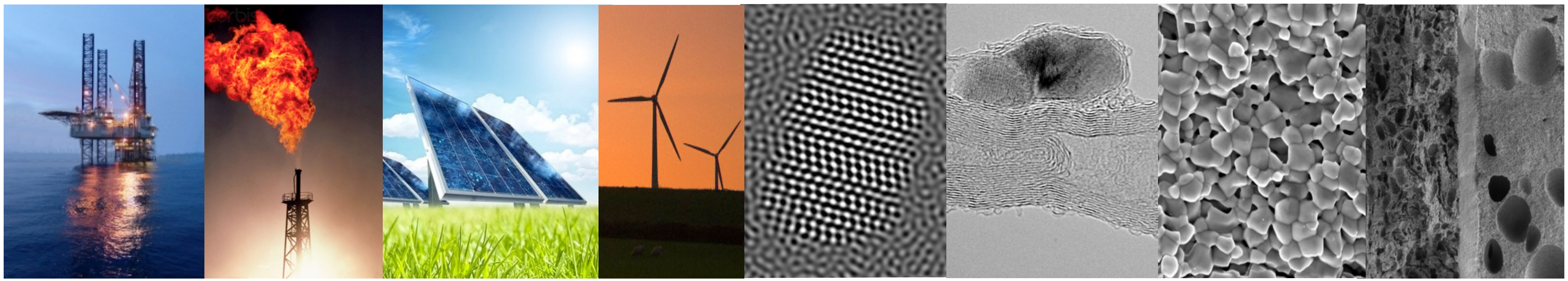
PSL RESEARCH UNIVERSITY PARIS

Les Piles à Combustible au Centre des Matériaux

CENTRE DES MATERIAUX
P.M FOURT

ARMINES

Pôle SIP – 15 décembre 2017



Piles à Combustible

- contexte
- état des lieux
- prochaines étapes

Piles à Combustible

Contexte

1. considérations générales
2. historique PAC au laboratoire
3. cœur de pile et polarisation

1- Considerations at the national level on the energy of the future

- **Energy policy:** not very visible and not very continuous, conflicting national objectives
- **energy transition plan**: focused on the fight against global warming, development of renewable energies (ER) and energy saving
- Must be accompanied by a **long-term policy** and a **global technical and economic analysis**; but difficult to predict (eg a sharp decrease in the cost of renewable energies was not anticipated, what about the storage of electricity, what about the decarbonation of transport?), therefore difficult to invest
- **Storage**: solutions depend on the frequency of demand: if sub-day = batteries; if week = hydraulic; if above = hydrogen. But costly solutions and difficult to integrate massively
- The **development of large-scale ER** requires technological leaps on storage
- Short- and medium-term **energy mix** can not be composed solely of REs; in France, nuclear power will be part of it

1- Considerations at the International level on the energy of the future

- **global context** (growth in Asia and Africa, urbanization, economy) implies an increasing demand for energy, which will be ensured by fossil materials (coal in China and africa)
- **energy policy at the least cost**, for economic competitiveness: focus on R&D, storage, cost reduction in nuclear
- **lack of consistency** in energy decision-making at national and European levels
- **Difficult access to market of electrical ER networks**; local production runs counter to the principle of equal prices and access to the territory (variations in prices accepted for oil, not for electricity)

1- Ruptures and priorities on energy production and storage

- **Batteries** : from Li-ion to Na-ion
- **PV** : maintain efforts on 2nd-generation panels, multilayers, down conversion layers, antireflectivity, bi-modules, colored-filtered cells…
- **Hydrogen**: ***storage*** in the form of hydrides and/or divided matter and/or in microporous matter, high pressure vessels; ***production*** via high temperature electrolysis and use in Fuel Cells (France well placed), but requires defining a real and coherent industrial strategy and pursuing R&D efforts without erratic and conflicting decisions (continuity in calls, non-discouraging success rates, support for academic initiatives, sweeping the entire TRL scale, etc.)
- **Nuclear** : sector to be restructured including the fuel cycle, expansion of the catalog of reactors, small modular reactors for small territories and/or operation of small reactors in battery
- **Management of industries with high CO_2 emissions** : techniques for decarbonisation, storage, sequestration, synthetic fuels, require an economic model (CO2 prices that are currently too low)

2- Historique PAC au laboratoire

Thèses de doctorat
Olivier Sanséau (thèse ENSMP, 2002)
Arnaud Grosjean (thèse ENSMP, 2004)
Julien Hafsaoui (thèse ENSMP, 2009)
Rémi Costa (thèse ENSMP, 2009)
Jackie Milhans (thèse GaTech/ENSMP, 2010)
Joao Abreu (thèse Science et Entreprise, ENSMP, 2011)
Maya Geagea (thèse ENSMP, 2017)
David Masson (thèse ENSMP, 2015)
Rossen Tchakalov (thèse ENSMP, 2020)

DUT, autres
Léo Lagrost (DUT Mesures Physiques, IUTLille, 2011)
Nicolas Rousseau (1^e année de thèse ENSMP, 2007)
Claire Pilot (matériaux Ingénieur, CFA Union,
PolyTech Paris-Sud, Université Paris-Sud)
Guillaume Ciesco (Technicien Supérieur AFPA, 2017)

DEA, master(e)
Caroline Curfs (DEA ENSI-Caen, 1998)
Arnaud Grosjean (DEA ENSMP-INSTN, 2001)
Matthieu Caruel (Mastère-2 MSE, 2007)
Ali Laddada (Mastère Pro-2, UEVE, 2007)
Nicolas Wegrzyn (Master II, ENSMSE, 2012)
Meng Xu (Master II, MAGIS, 2014)
Jian Ouyang (Master II, ICARE, 2015)
Joyce Kuoh-Moukouri (Master II, MAGIS)
Yang Zhang (Master II, ICARE, 2016)
Tang Shi (Master II, ICARE, 2016)
Ismahan Hachemi (Master II, MET INSTN, 2017)
Tiankai Lan (Master II, ICARE, 2017)
Yuting Lei (Master II, ICARE, 2017)

Post-Doc
André-Pierre ABELARD (LASIPS)

Professeur invité
Gilles Caboche (1 stage, Univ. Bourgogne)

Stagiaires étrangers
Alessio Bassano (stage PhD, CNR-Gênes, 2008)
Dennis Soysal (stage de PhD, DLR-Univ. Stuttgart, 2009)
Wenlu Li (Master ICARE, Huazong University of Science
and Technology, Wuhan, Chine, 2012)
Blagoy Burdin (enseignant-chercheur, IEES, BAS, 2016)

2- Historique PAC au laboratoire

1995

SOFC :
- Coulage
- Filter pressing
- Mat. cathode

1998

SOFC :
- Coulage
- Co-frittage
- cathode

2004

SOFC :
- Coulage aqueux
- Interfaces
- Propriétés électriques

2009

PCFC :
- Coulage
- Interfaces
- Propriétés électriques
- Déformation en frittage
- vieillissement

2009

Membrane H2:
- Coulage et co-frittage
- catalyseur
- Reformage du méthane

2010

Joints étanchéité SOFC :
- frittage
- modélisation

PAC à conduction mixte:
- PoC
- Sérigraphie
- Co-frittage
- Modélisation
- Mousse de Ni

2010

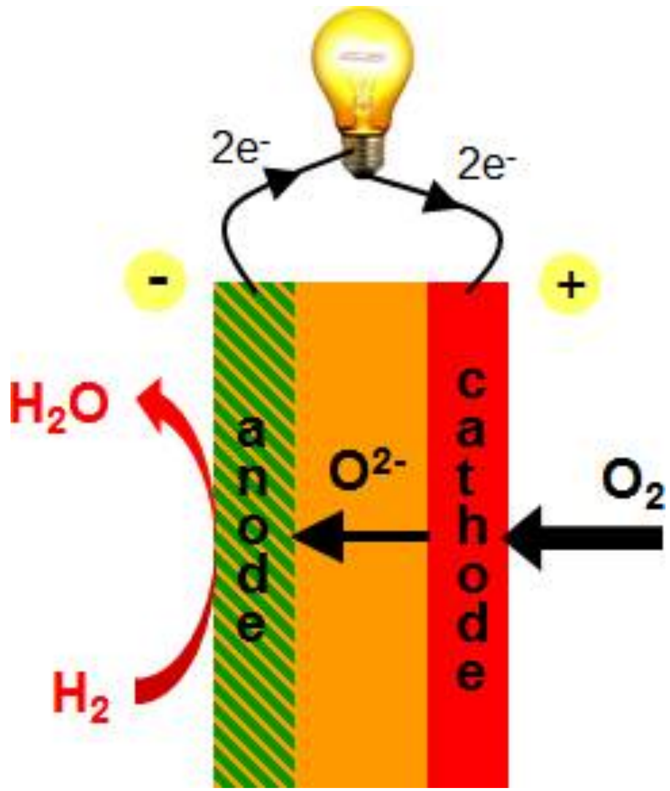
SOFC metal support
PAC à conduction mixte:
- Co-frittage
- design
- Catalyseurs
- Mousse métallique

2015

2017

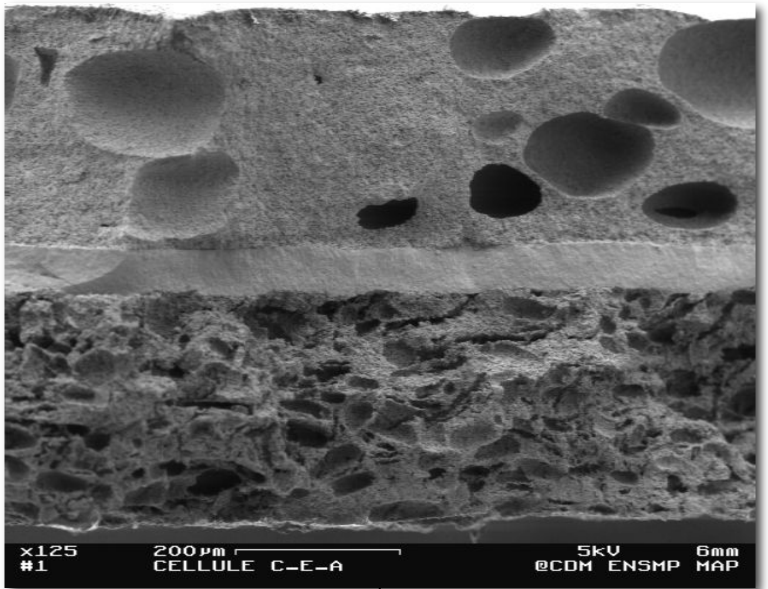
SOFC + PAC conduction mixte:
- Architecturation Interfaces
- Propriétés électriques
- Catalyseurs
- Design

3- Cœur de pile et polarisation



3- Cœur de pile et polarisation

SOFC: made of ceramics



Cathode: LSM

Electrolyte: YSZ

Anode: YSZ + Ni

Understanding of ceramics processing and sintering

-Control of the electrodes porosity
-Percolation
-Full density for the electrolyte
-Bonding different materials
-Quasi 2D component (t ± 0.5mm, ≈ ± 10cm)

$$H = U + pV$$

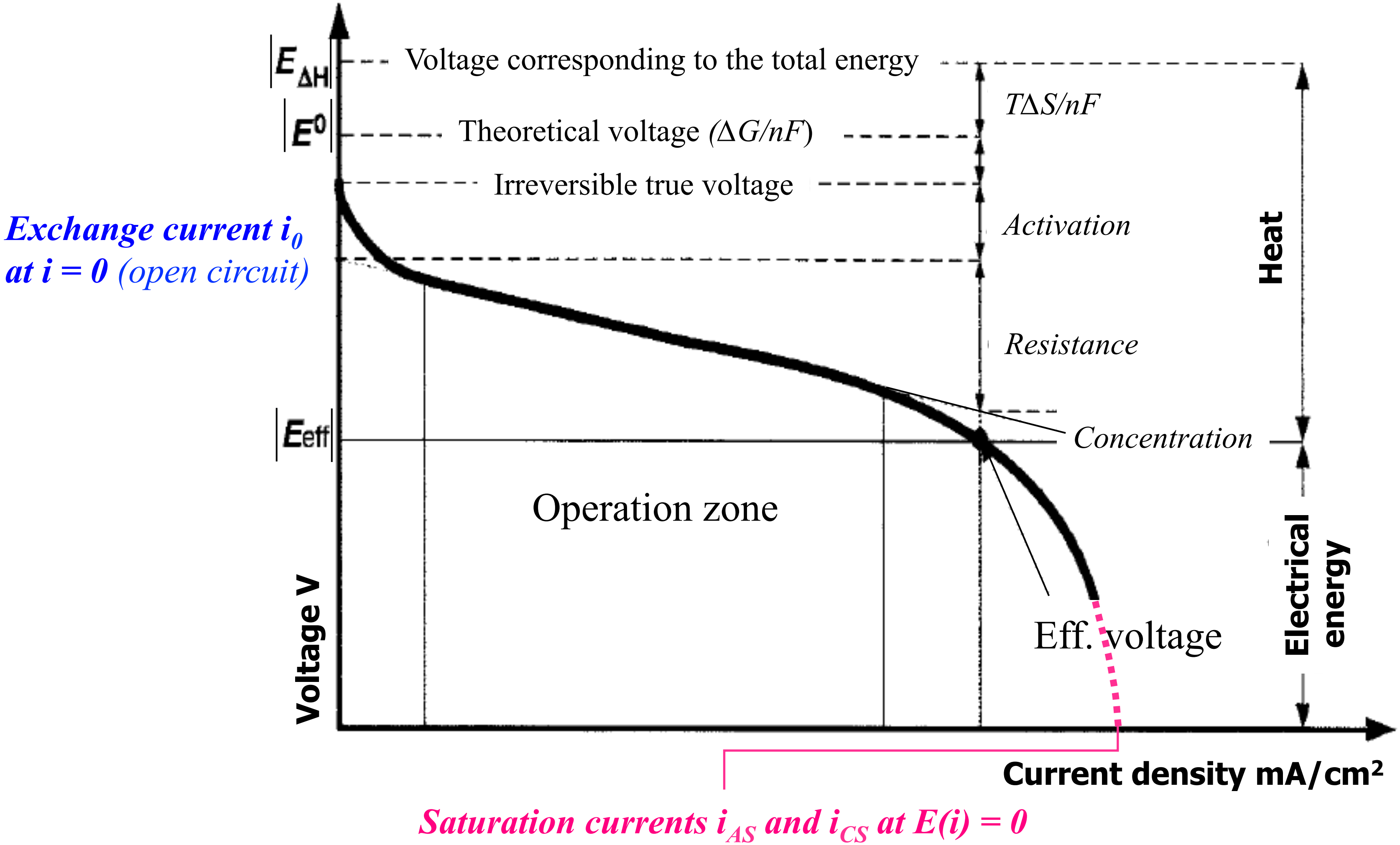
$$G = H - TS$$

Electrochemical reaction

$$\Delta G = -n.F.E = \Delta H - T\Delta S$$

$$E = \frac{\Delta G}{-n.F} = \frac{\Delta H}{-n.F} - T\frac{\Delta S}{-n.F}$$

$$\frac{\Delta H}{n.F} = \frac{\Delta G}{n.F} + T\frac{\Delta S}{n.F}$$



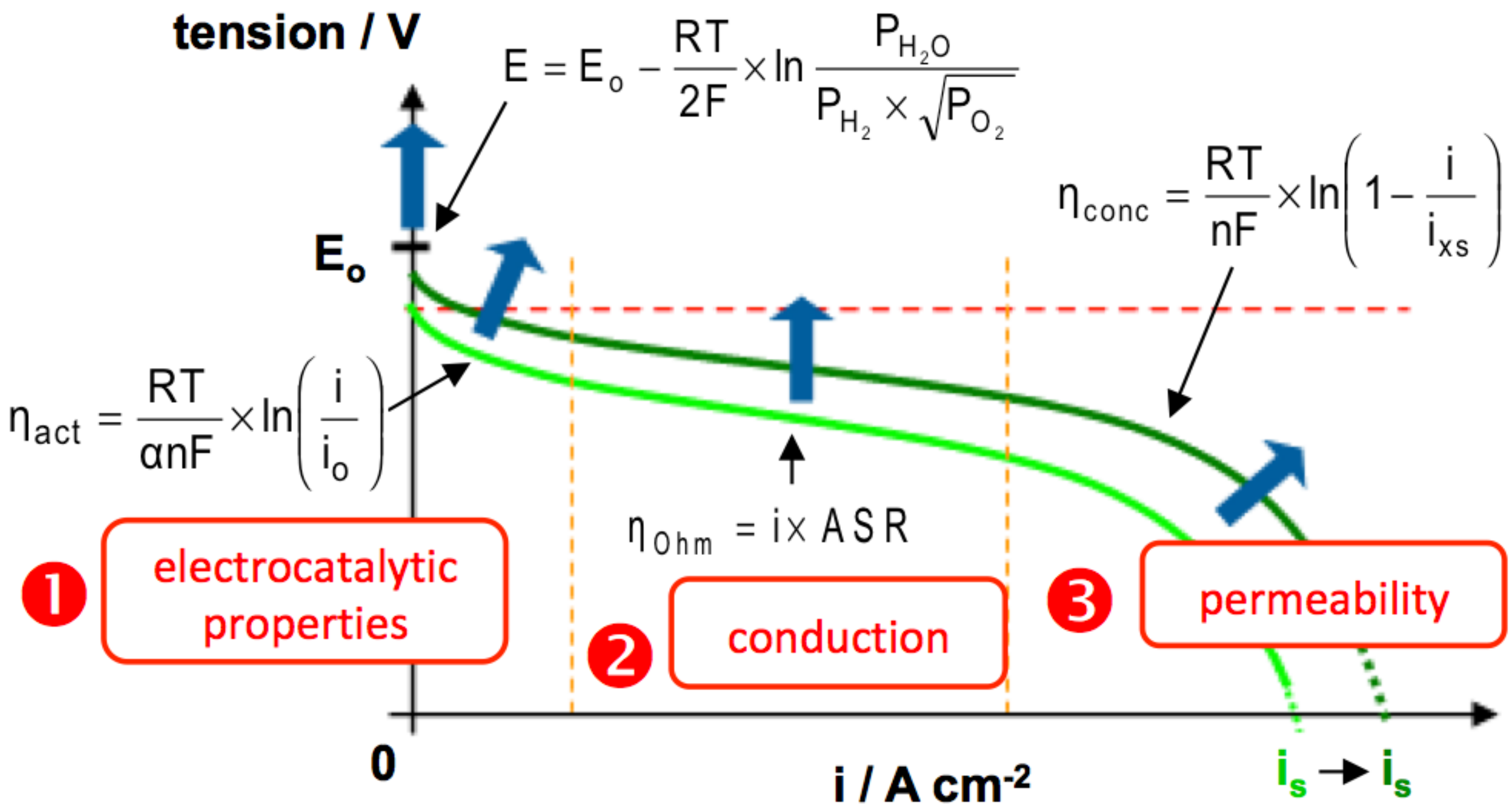
$$E_C = E_0 - iR_i - \eta_{act} - \eta_{conc}$$

Piles à Combustible

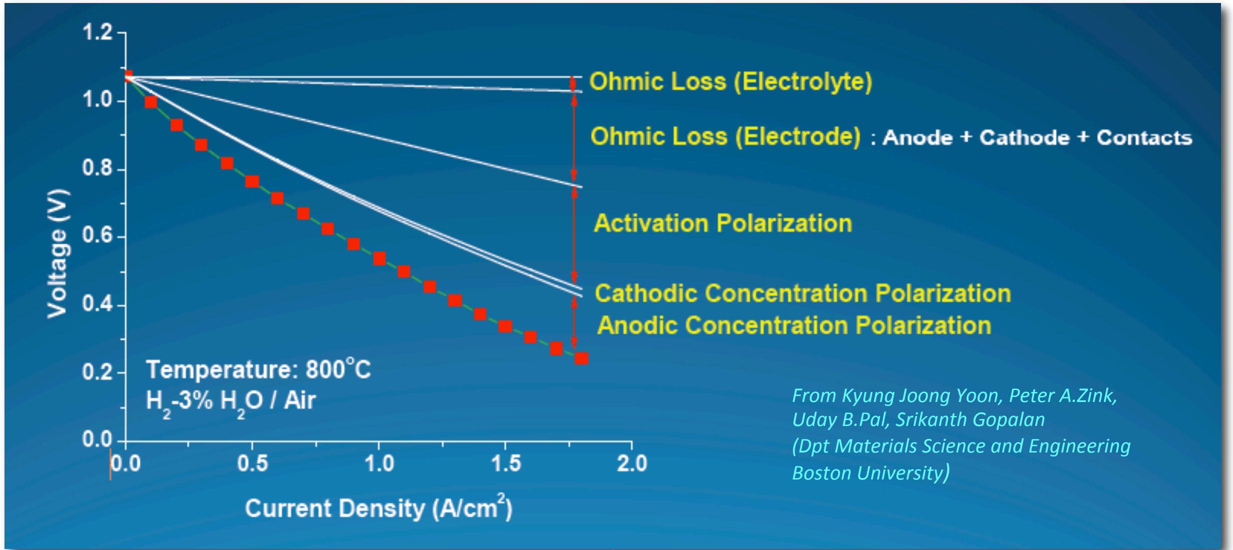
Etat des Lieux

1. voies d'optimisation
2. travaux et résultats
3. les difficultés

1- Voies d'optimisation



1- Voies d'optimisation



Increase of performances

- *change of materials with better σ*
- *microstructure**
- *geometry, design**
- *interface architecture**
- *operation conditions*
- *catalysts**
- *change in conduction type**
- *change of concept**

SOFC → **PCFC** → **IDEAl-Cell**

$$E_C = E_0 - iR_i - \eta_{act} - \eta_{conc}$$

$$E_C = E_0 - iR_i - \frac{RT}{F}\ln\left\{\frac{1}{2}\left[\left(\frac{i}{i_0}\right) + \sqrt{\left(\frac{i}{i_0}\right)^2 + 4}\right]\right\} + \frac{RT}{4F}\ln\left(1 - \frac{i}{i_{CS}}\right) + \frac{RT}{2F}\ln\left(1 - \frac{i}{i_{AS}}\right) - \frac{RT}{2F}\ln\left(1 + \frac{P^0_{H_2} i}{P^0_{H_2O} i_{AS}}\right)$$

OCV

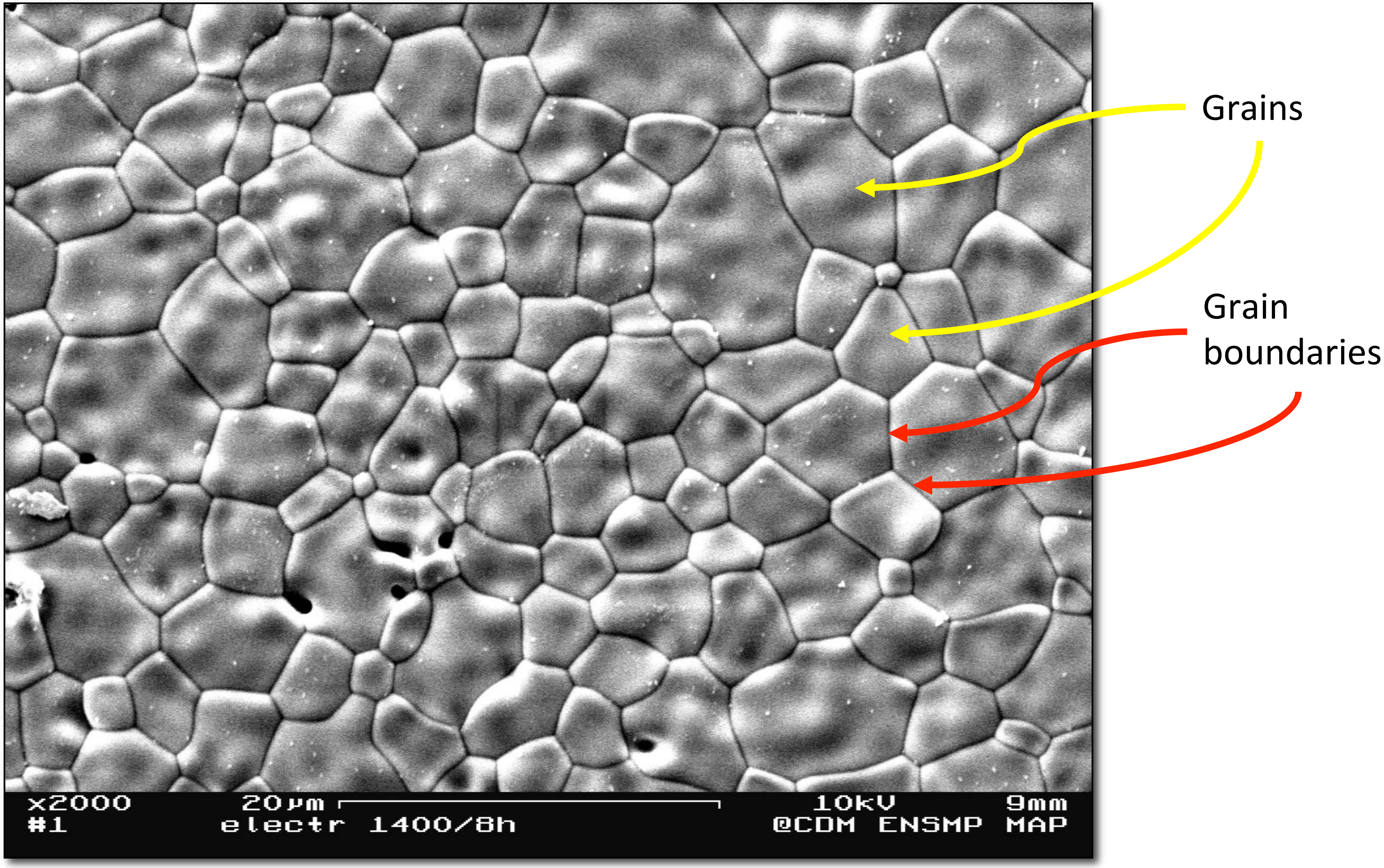
Ohmic Polarization

Activation Polarization

Concentration Polarization cathode

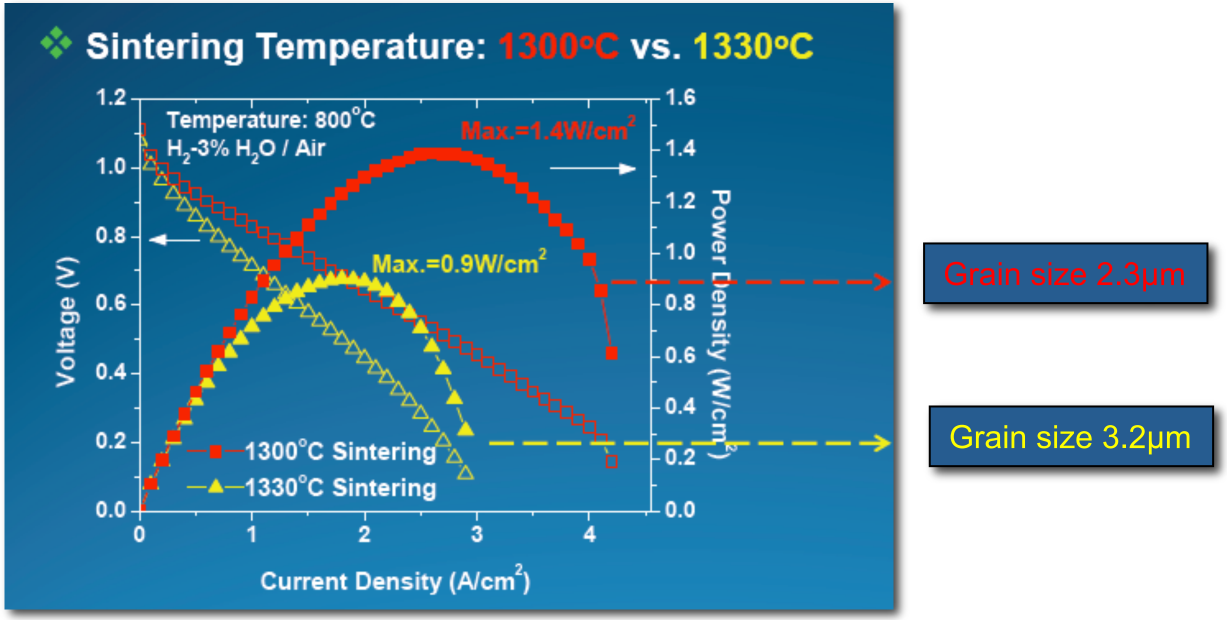
Concentration Polarization anode

1- Voies d'optimisation : microstructure



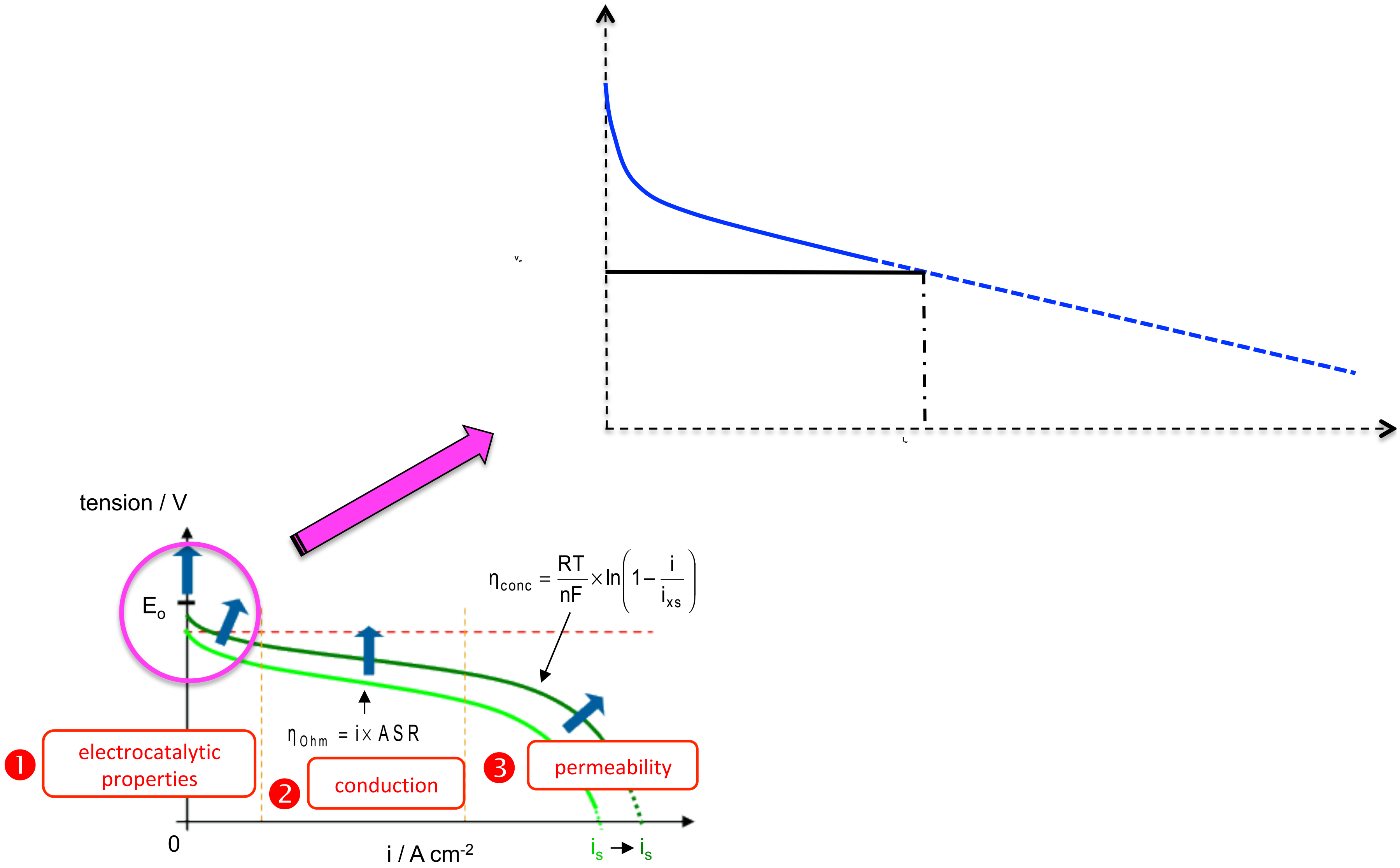
Typical microstructure of Zirconia (ZrO_2) used for electrolyte in a SOFC

1- Voies d’optimisation : microstructure

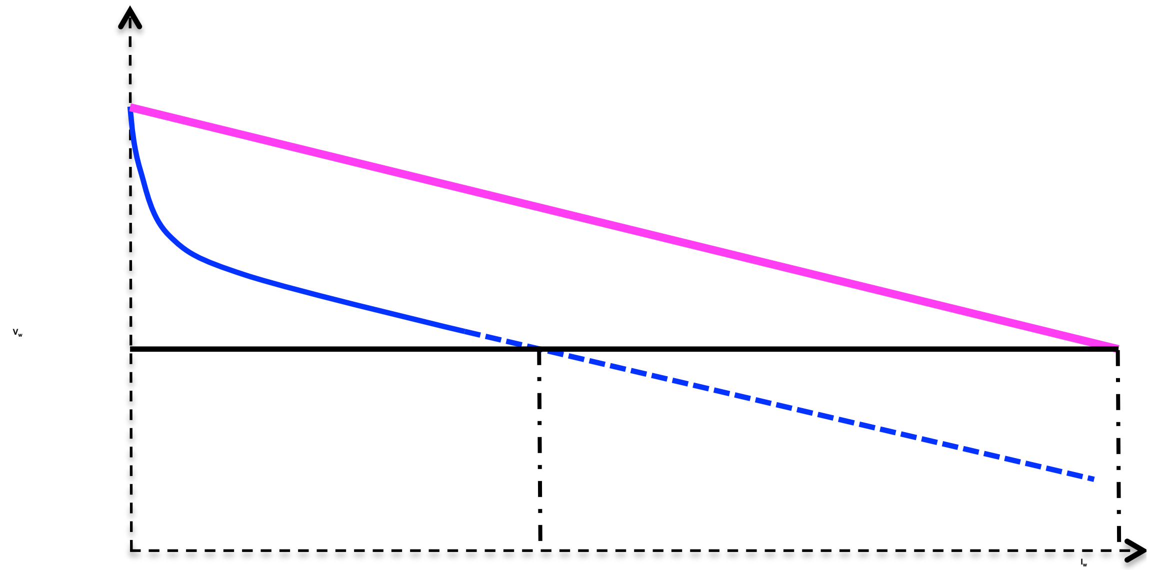


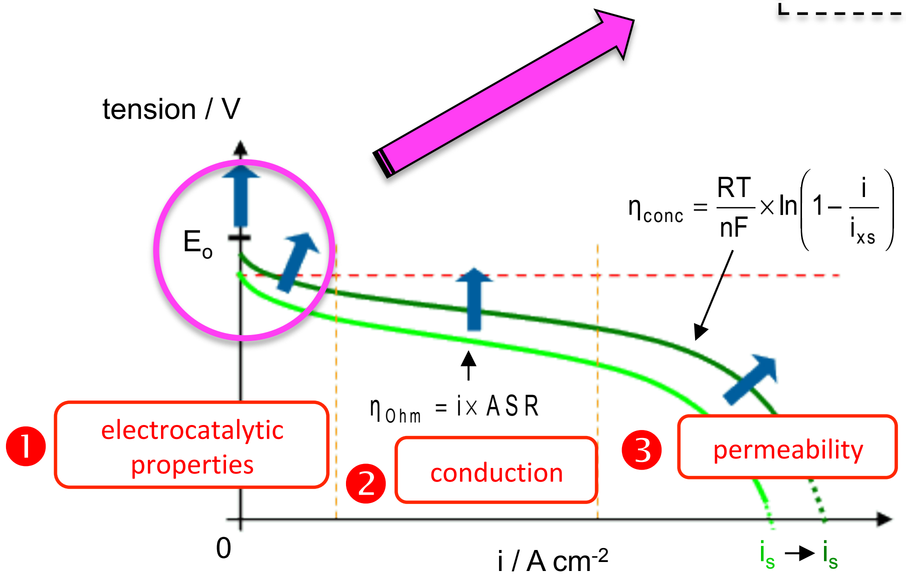
From Kyung Joong Yoon, Peter A.Zink, Uday B.Pal, Srikanth Gopalan (Dpt Materials Science and Engineering Boston University)

1- Voies d'optimisation : activation



1- Voies d'optimisation : activation





- Corrugation des interfaces
- Impregnation par un catalyseur
- Augmentation de L_{TPB} / S_{TPB}

2- Travaux et Résultats : activation

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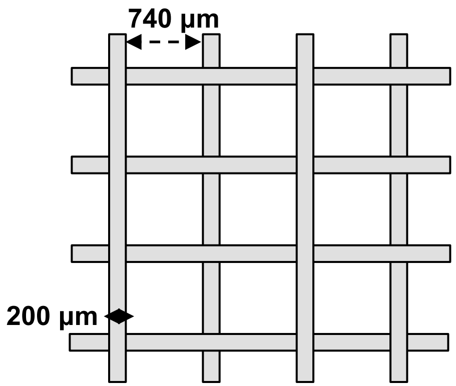
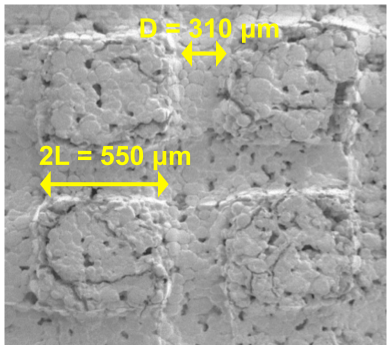
- **Architecturation of the self-supported anode by cold stamping**

Grid

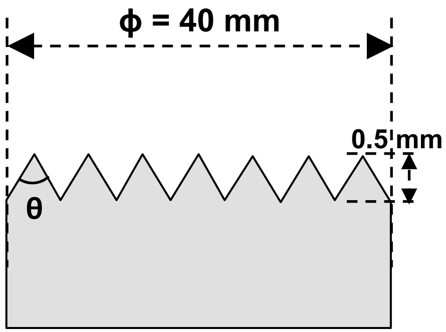


λ = ??

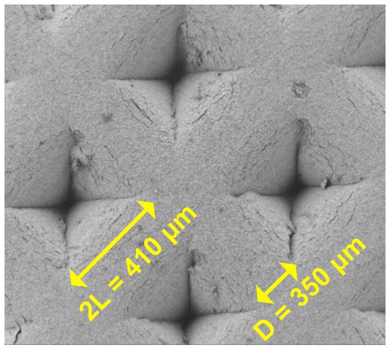


Self-supported anode
H = 65 µm

Pyramid (θ = 45°)

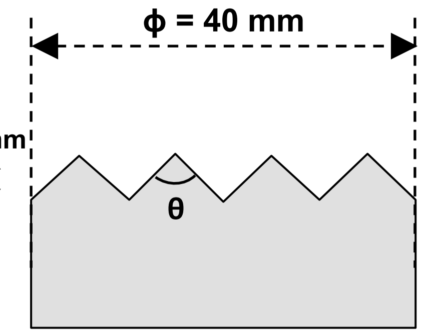


λ = ??

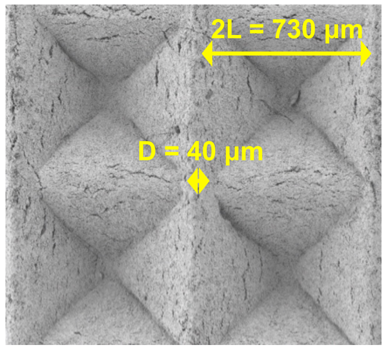


Self-supported anode
H = 140 µm

Pyramid (θ = 90°)

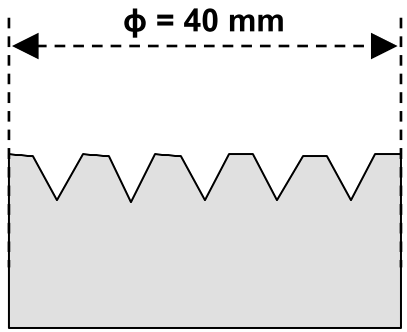


λ = ??

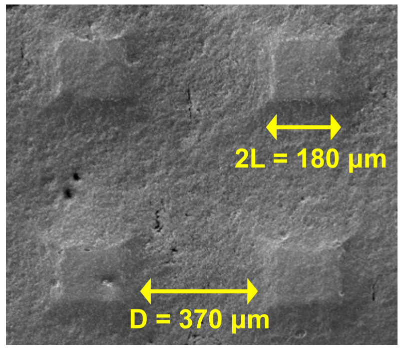


Self-supported anode
H = 130 µm

Truncated pyramid



λ = ??



Self-supported anode
H = 50 µm

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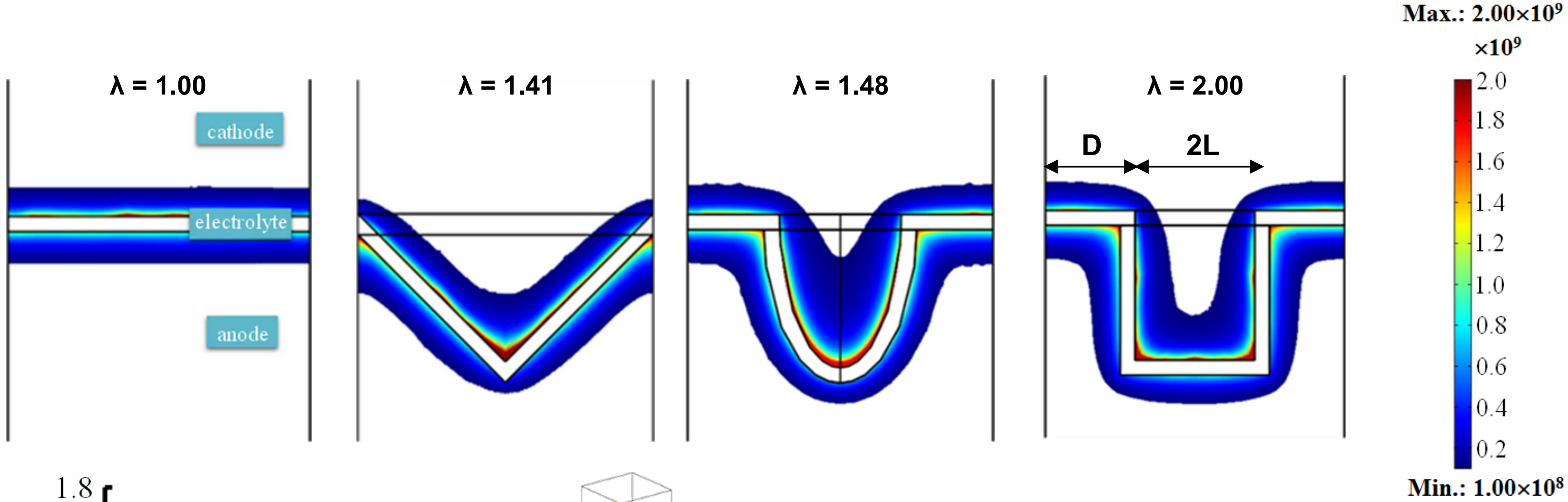
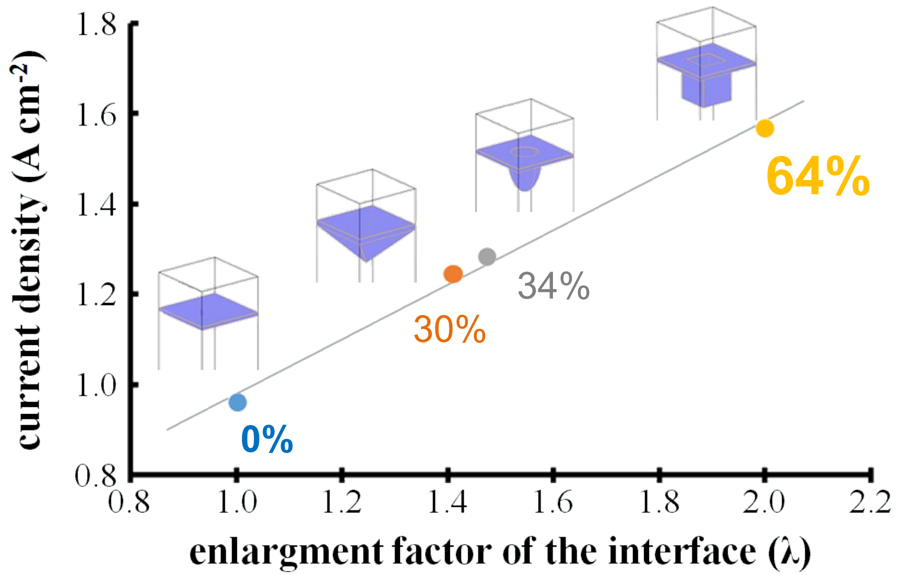
- **Effect of pattern geometry on the distribution of exchange currents**





→ *i_V varies essentially at the vicinity of the interface*

→ *minima and maxima of i_V in convex and concave regions*

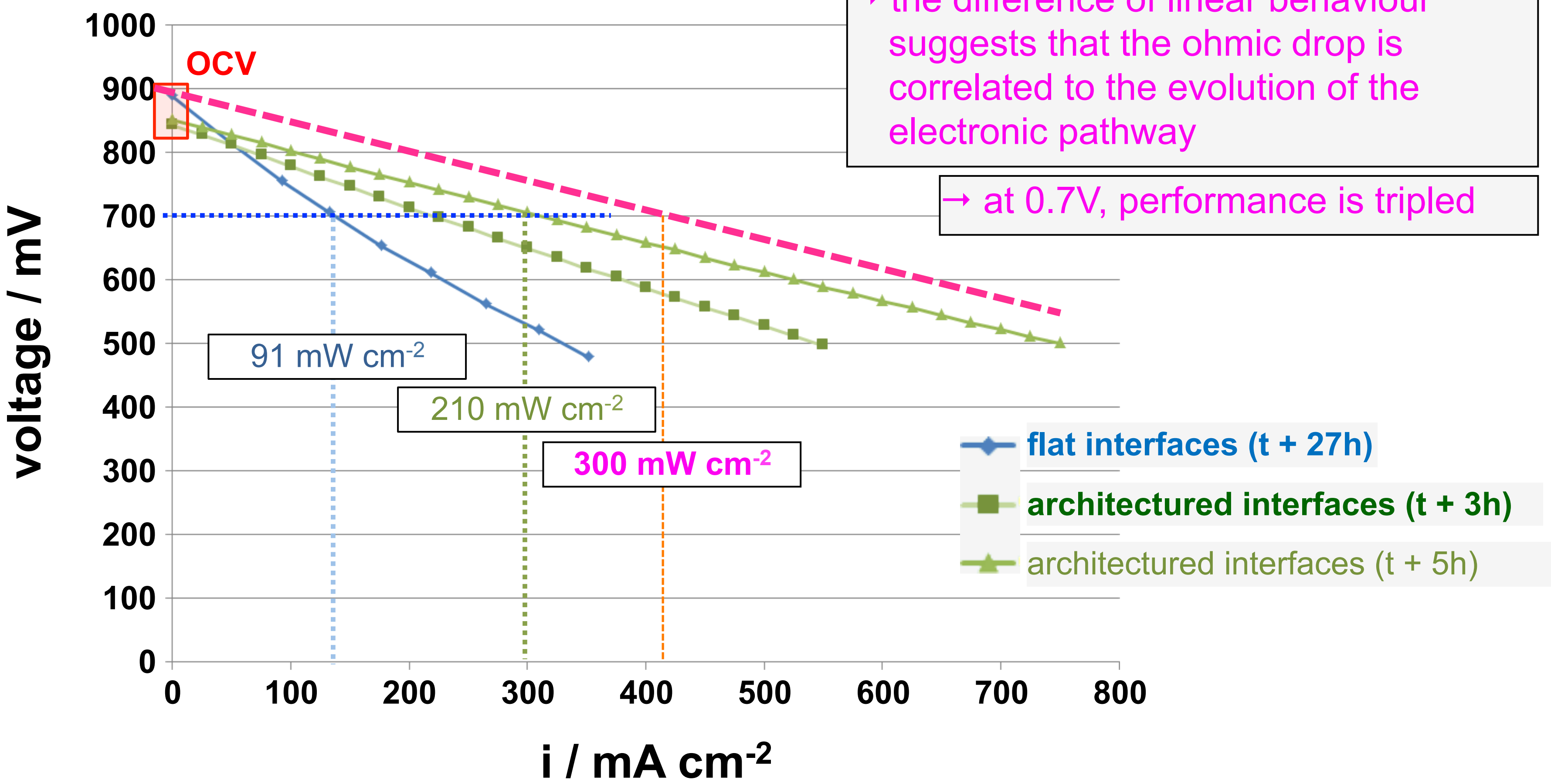
→ *D and L should be chosen so as to confine the electrode material ($2L >> t_{electrolyte}$)*

- **i/v characteric curves : flat vs. architectured interfaces**

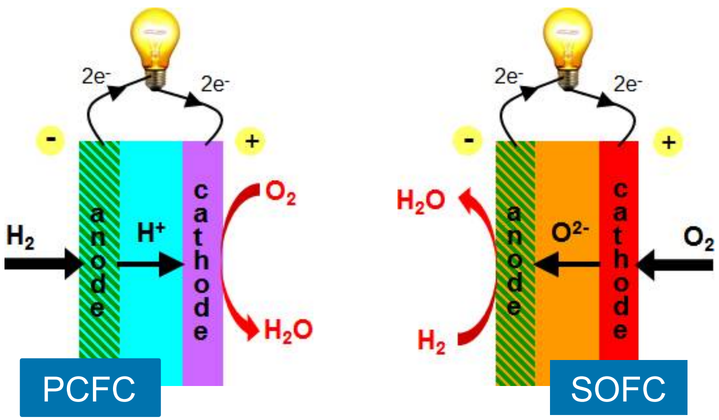
→ $(\eta_{act})_{a,c}$ are negligible with regard to (η_{res})

→ the difference of linear behaviour suggests that the ohmic drop is correlated to the evolution of the electronic pathway

→ at 0.7V, performance is tripled



2- Travaux et Résultats : nouveau concept



Limitations

- Formation de H_2O à l'une des électrodes
- **Température de fonctionnement élevée**

⬇

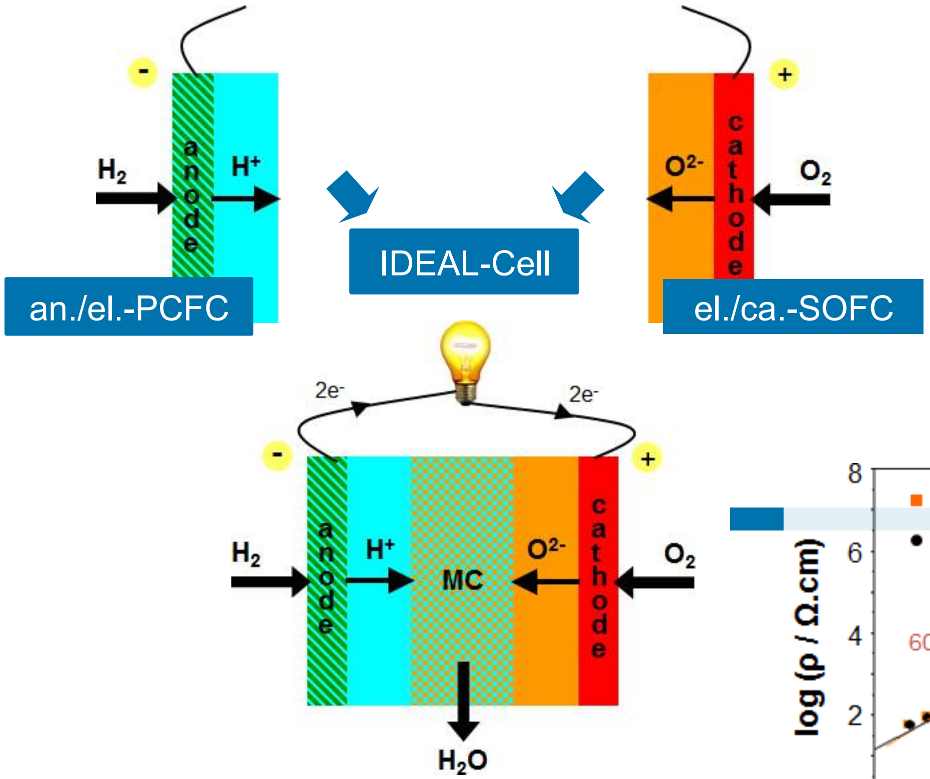
Conséquences

- **Perte d'efficacité**
- **Dégradation accélérée**

⬇

Durabilité ??

2- Travaux et Résultats : nouveau concept

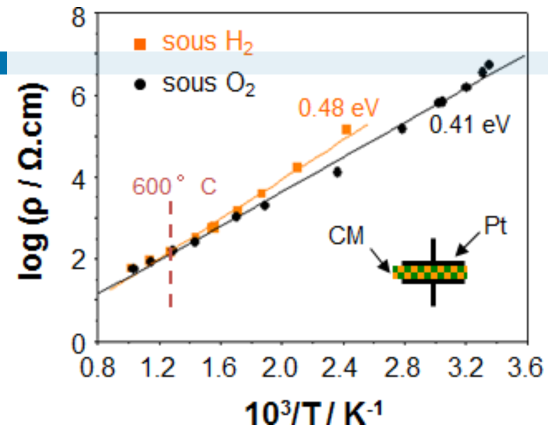


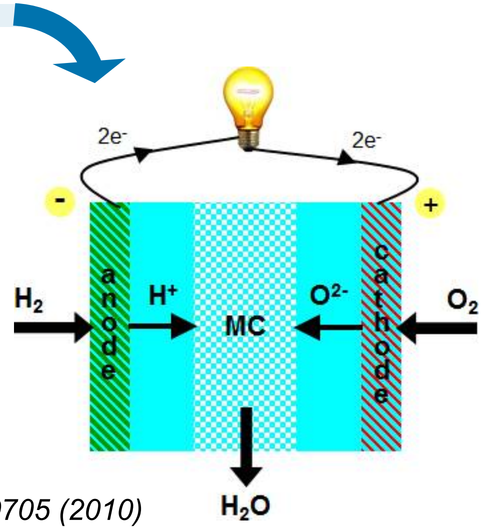
Saut technologique

- pas d'eau aux électrodes (↘ η_{act}, ↘ η_{conc}, et ↘ corrosion)
- possibilité d'appliquer une pression de gaz aux électrodes

Dispositif « Monolithique »

- intégration d'un conducteur mixte (nouveau mécanisme)
- ↘ tortuosité de la phase solide
- segments triples → surfaces triples
- mise en forme simplifiée

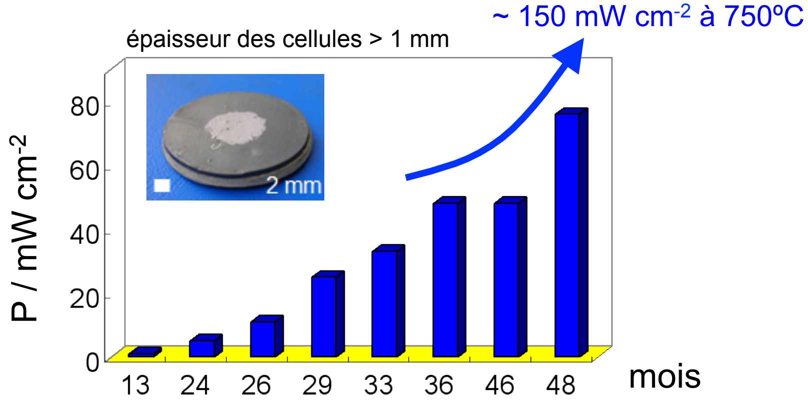




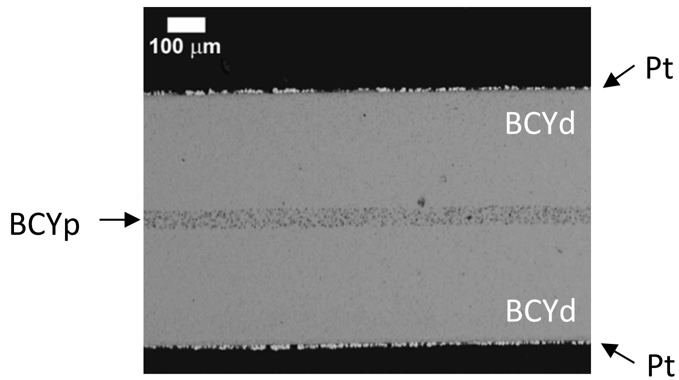
Brevet d'invention N°1060705 (2010)
Déposants : ARMINES

2- Travaux et Résultats : nouveau concept

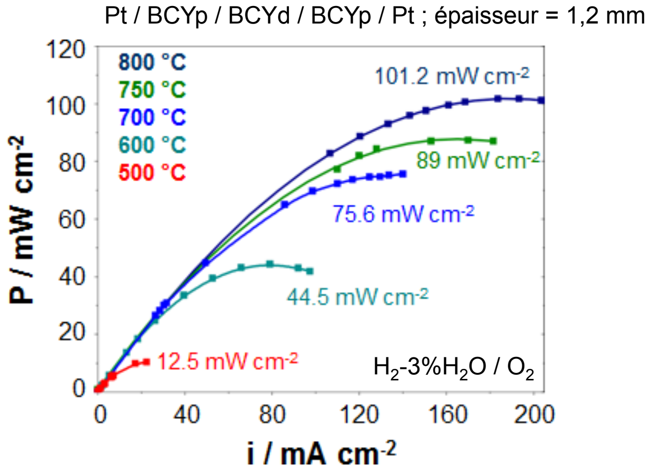
Performances : m-IDEAL-Cell



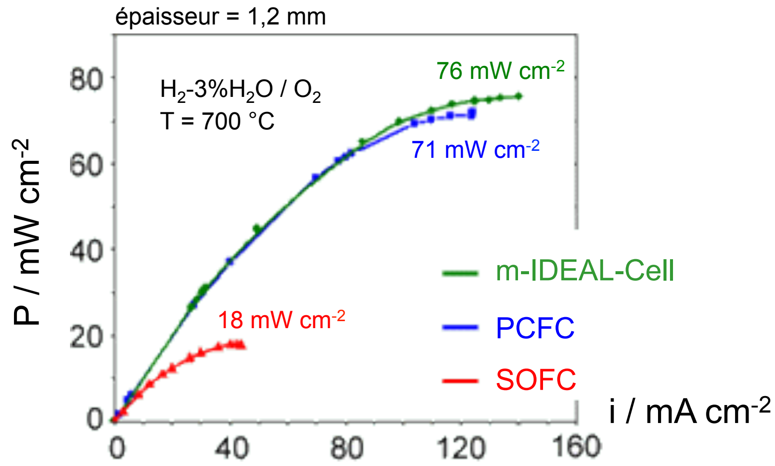
m-IDEAL-Cell : coulage en bande



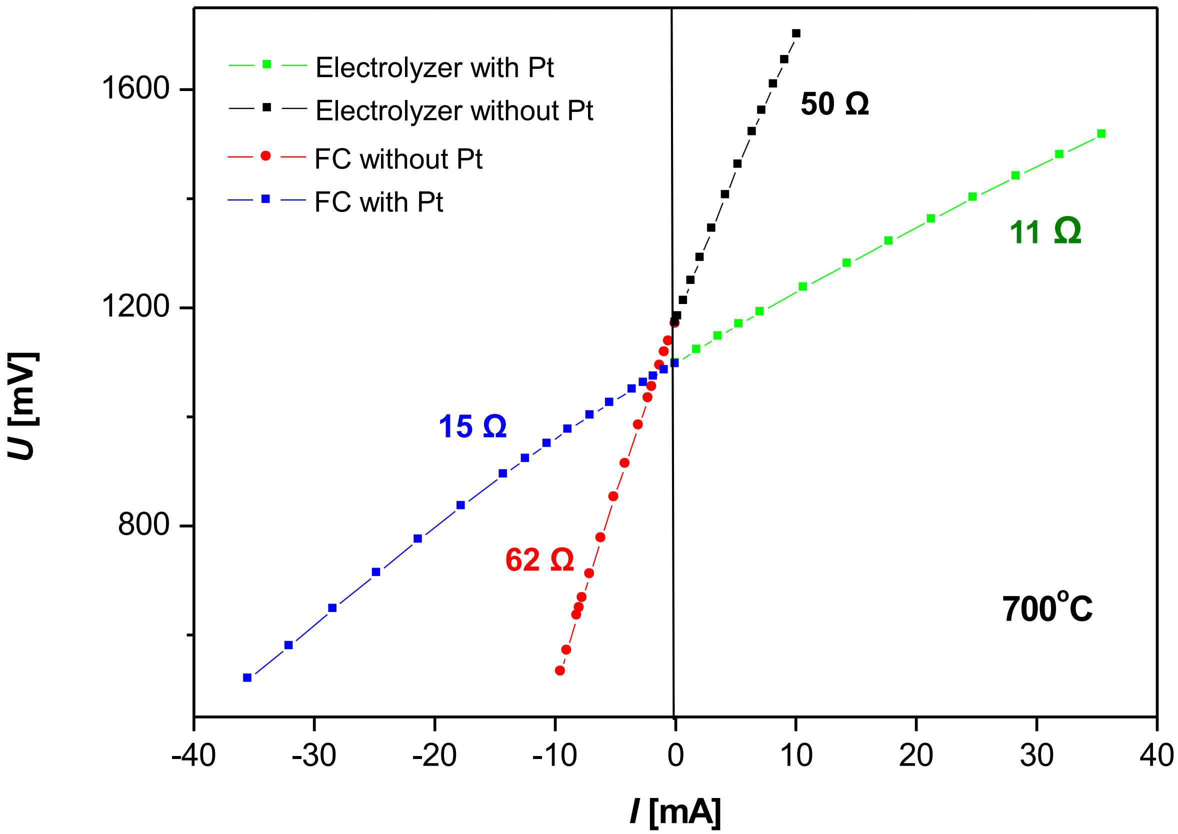
- **prédiction : 0,9 W cm⁻² (↘ épaisseurs)**



Performances vs. SOFC & PCFC



2- Travaux et Résultats : activation + nouveau concept

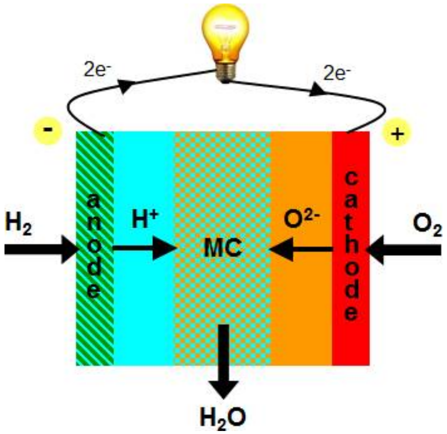


Ω / 5 in HTE mode
Ω / 4 in FC mode

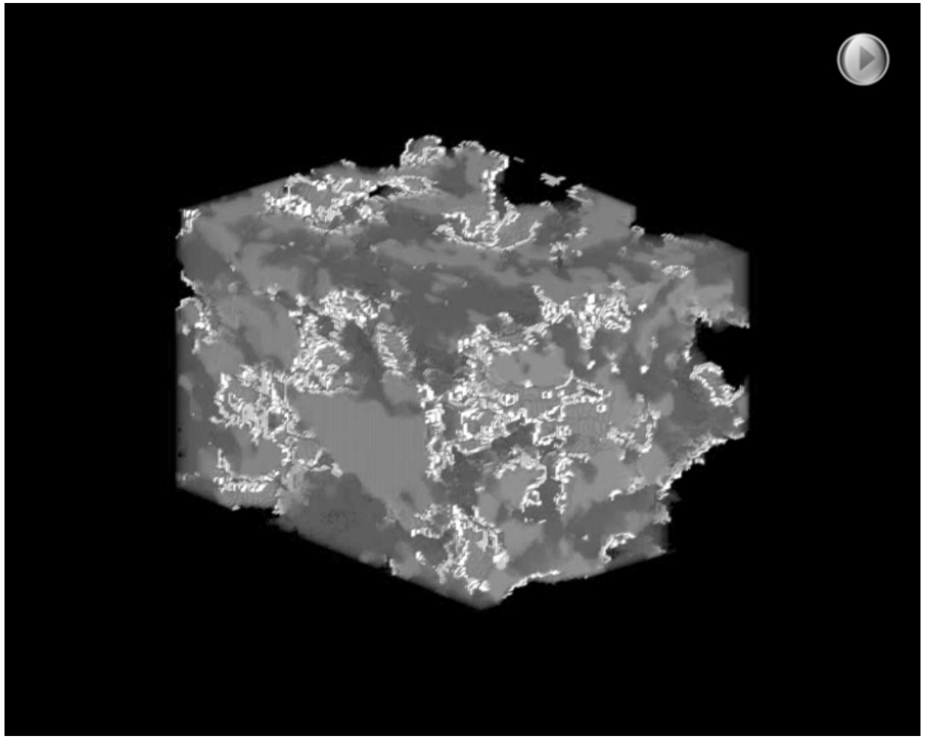
Non optimized millimeter thick dmFC operated in the SOFC mode of in the SOEC mode, with a Central Membrane impregnated with Pt nanoparticles or not, at 700°C

SOFC mode gases:
Sample with Pt - H_2 = 84 mL/min; N_2 = 0; Air = 108 mL/min;
Sample without Pt - H_2 = 74 mL/min; N_2 = 0; Air = 133 mL/min;

2- Travaux et Résultats : activation + nouveau concept



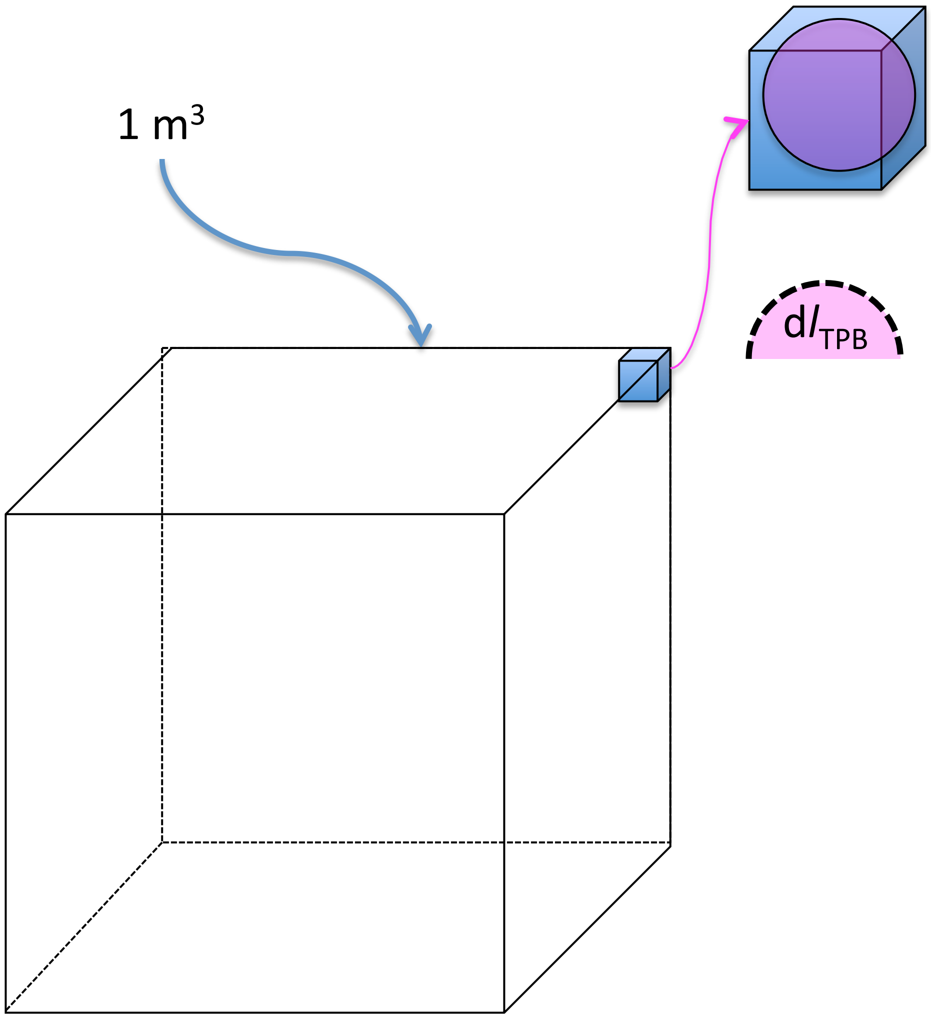
- Porosité
- Percolation x, y, z
- Tortuosité x, y, z
- Conductivité effective
- Segments triples (TPB) actifs



→ permeability (Blake-Kozeny relation) : $K = \frac{d_p^2}{72\tau} \times \frac{\varepsilon^3}{(1-\varepsilon)^2}$

→ kinetics of the reactions at the electrodes (Butler-Volmer relation) : $i_V = i_{TPB} \times \ell_{TPB} \left[\exp\left(\frac{\alpha_a nF}{RT} \eta_{act} \right) - \exp\left(-\frac{(1-\alpha_c) nF}{RT} \eta_{act} \right) \right]$

$$i_V = i_{TPB} \times \ell_{TPB} \left[\exp\left(\frac{\alpha_a nF}{RT} \eta_{act} \right) - \exp\left(-\frac{(1-\alpha_c) nF}{RT} \eta_{act} \right) \right]$$



- d = 2µm
- Number of grains in 1 m³ :
  $(1/2.10^{-6})^3 = 0.125 \times 10^{18}$
- Hypothesis dl_{TPB} = ½ circumference :
  π x 1µm = 3×10^{-6} m per grain
- Total length of TPB in 1 m³ :
  $0.125 \times 10^{18} \times 3 \times 10^{-6}$ m = 0.4×10^{12} m

About 3 times the Earth-Sun distance !!

- 1 mm³ : $l_{TPB} = 0.4 \times 10^3$ m
- Typical anode (200 µm x [π x 1 x 10^{-2}cm])
  60 mm³ : $l_{TPB} = 24 \times 10^3$ m

- modelling : $l_{TPB} = 1.8 \times 10^{12}$ m.m³
- ideal-cell$_{2011}$: $l_{TPB} = 0.6 \times 10^{12}$ m.m³

3- Difficultés

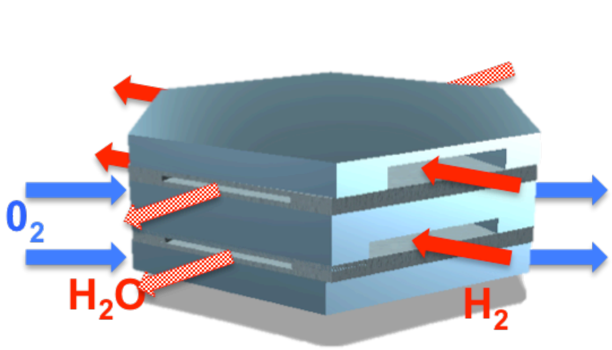
Piles à Combustible

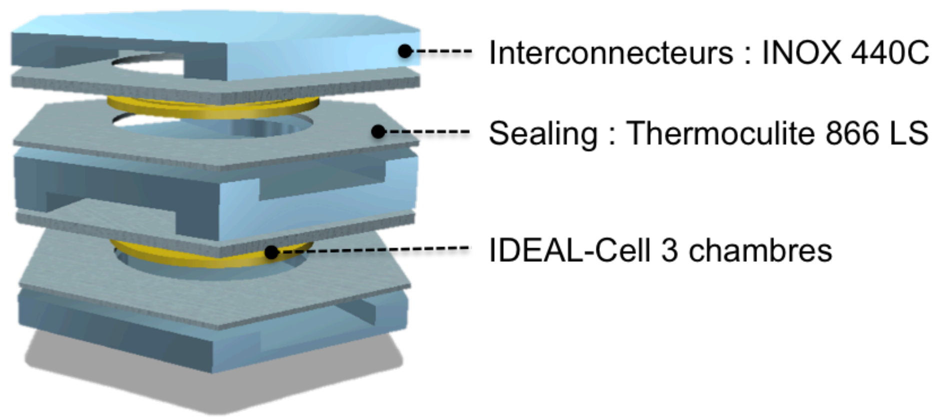
Prochaines étapes

1. le projet RIGEL
2. le consortium
3. déclinaisons

1- Le projet RIGEL

<u>Unité de base ”unit stack”</u>



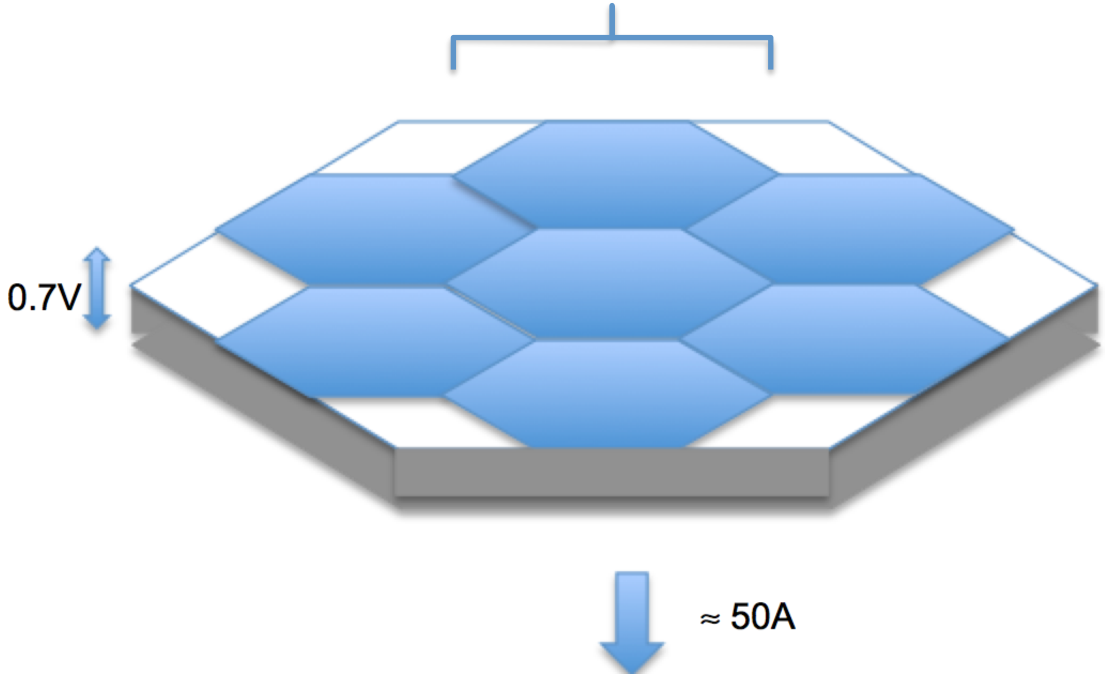


1- Le projet RIGEL

- Cellule unitaire (ex) :
20 cm^2; 300 mW/cm^2 à 0,7 V; 400 mA/cm^2

- cassette:
140 cm^2; 0,7 V; 50 to 55 A

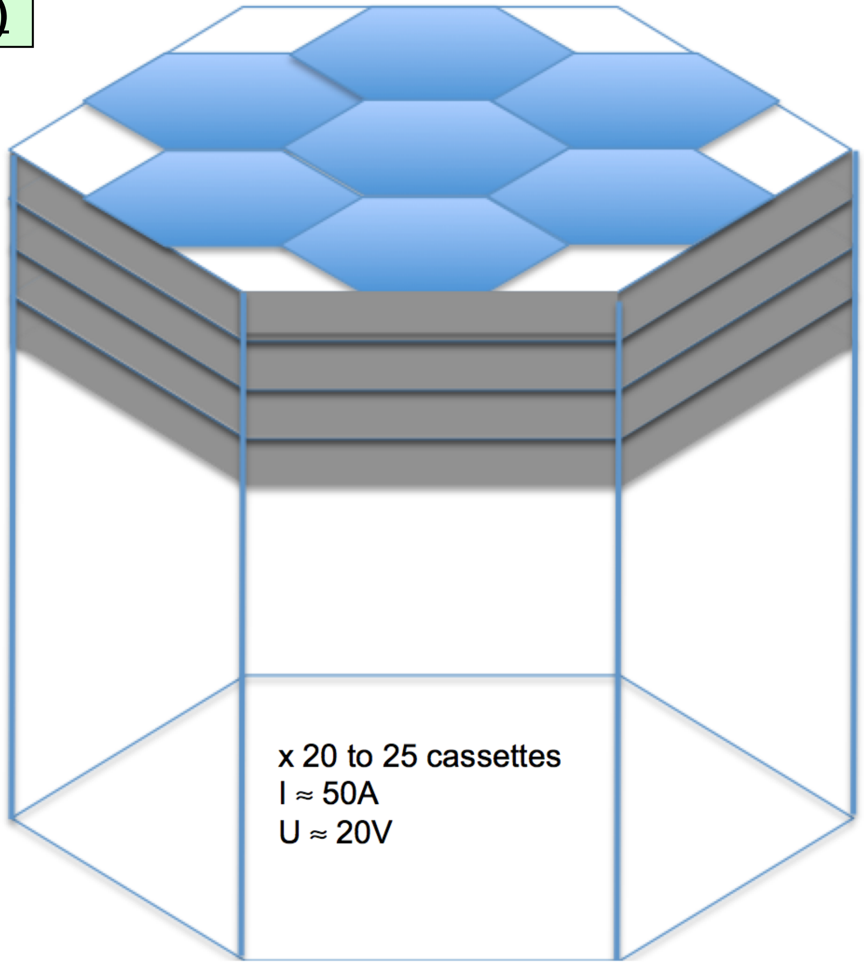
<u>Cassette intégrant 6 ou 7 "unit stacks"</u>



Extension horizontale augmente l'intensité
Extension verticale augmente le voltage

1- Le projet RIGEL

<u>1kW stack (50A, 20V)</u>



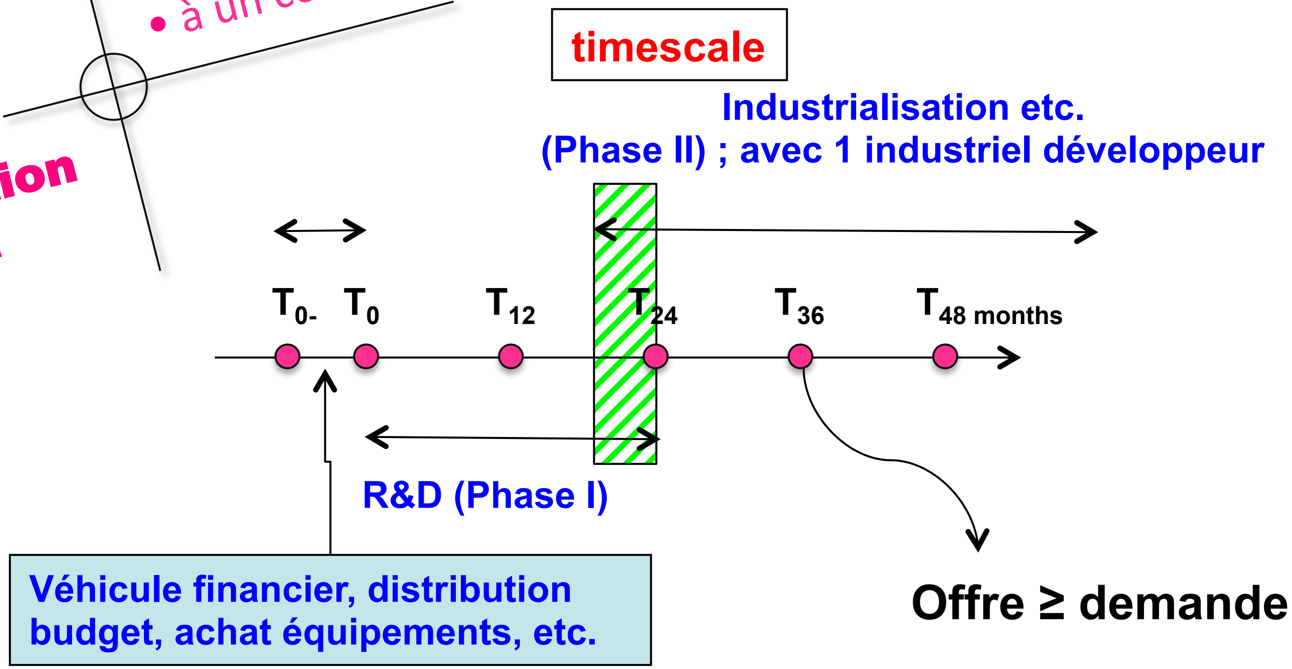
Bi-modularité

1- Le projet RIGEL

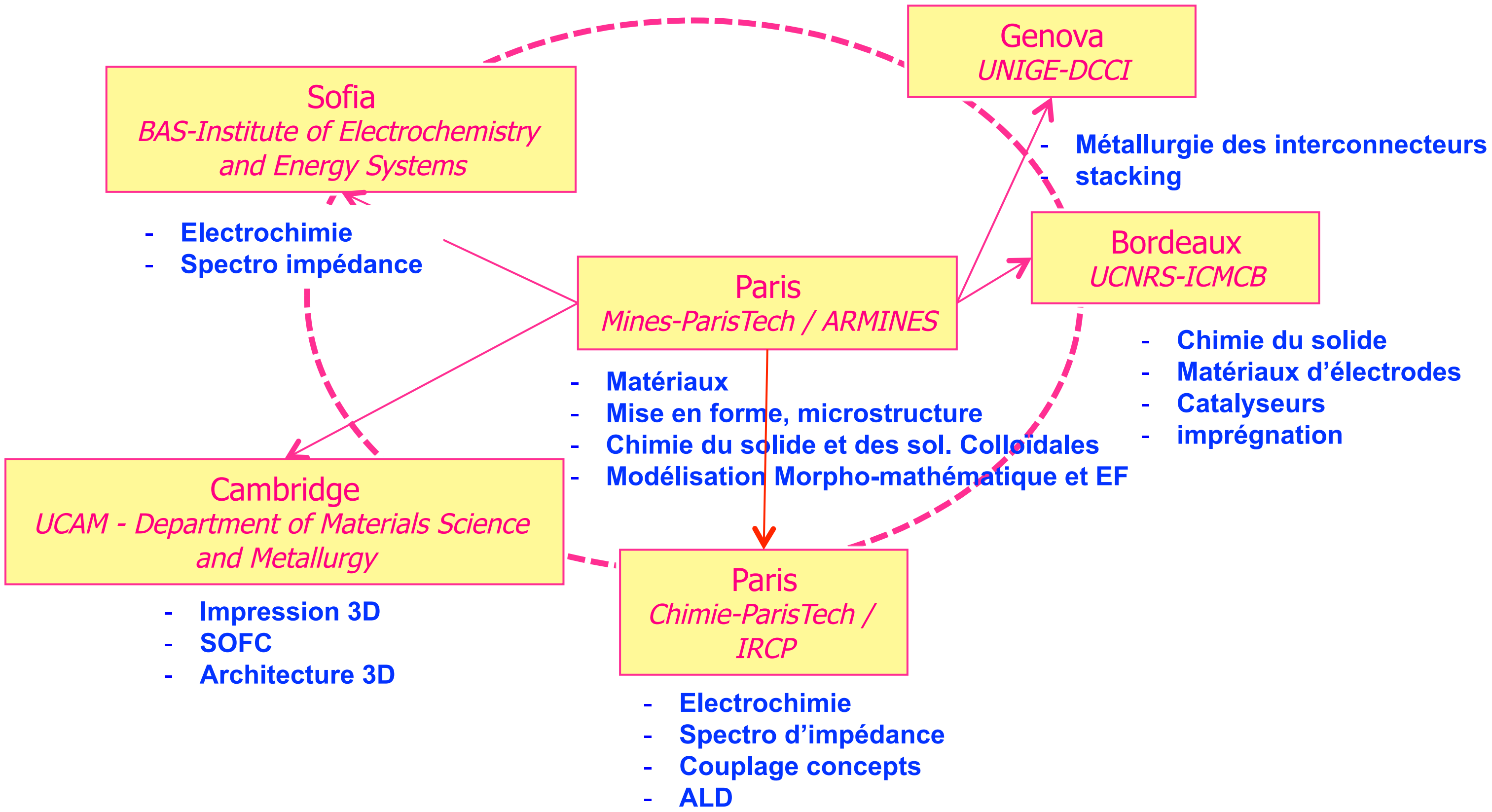
RIGEL-Stack

- prochaines étapes (stacking, stratégie,…)
  - réalisation d'un stack de 1kW (3 concepts)
  - testé, éléments de BoP, réversible
  - habilité à produire H_2
  - bi-modulaire (développement simplifié)
  - à un coût compétitif (Capex)

Organisation Du Projet

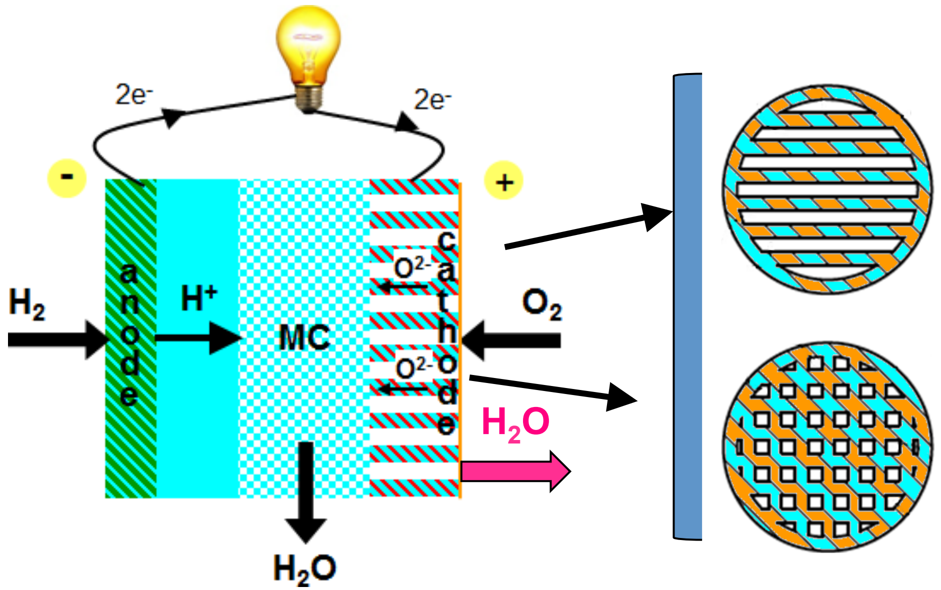


2- Le consortium



Brevet ARMINES N°1159969 – 2011

ZEBRA, un concept de pile à combustible à cathode avec canaux



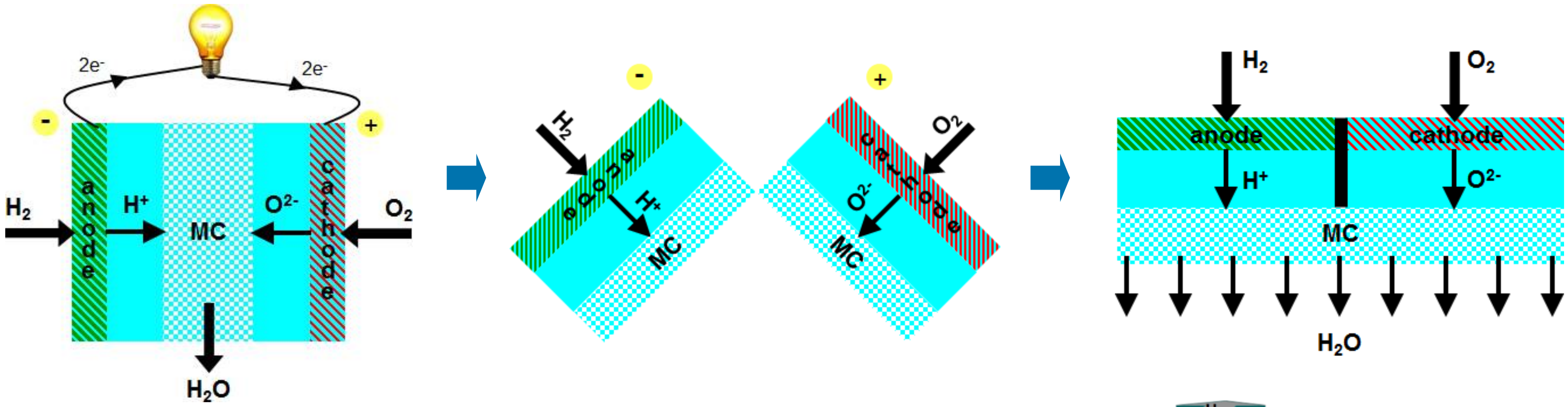
- design à 2 chambres séparées
- configuration idéale pour la production de H_2
- ↗ surface libre du côté cathodique
- 160 mW cm^{-2} pour des cellules d'épaisseurs ± 1 mm

Brevet d'invention N°1159969 (2011)
Déposants : ARMINES, IEES, CNR

		Pmax / mW cm^{-2} (air)				Pmax / mW cm^{-2} (O_2)			
		600°C	700°C	800°C	850°C	600°C	700°C	800°C	850°C
MC fine (~ 100 µm)	**Pt01 (1 mm)**	35	60	-	123	-	80	132	160
MC épaisse (~ 400 µm)	**Pt04 (1 mm)**	8	17	-	-	-	-	-	-
	ZEBRA (0,7 mm)	-	107	-	-	-	**156**	-	-

3- Déclisaisons de la Technologie Monolithique : le concept RIGEL 3D

RIGEL, un concept de PAC à conduction mixte par ions H^+ et O^{2-} réversible et durable pour couplage avec des RES



- design à 3 chambres séparées
- prédiction : ↘↘ η de la MC
- réversibilité optimale
- cellule « compacte », diamètre non limité
- mise en forme : impression 3D, procédés informatisables