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Proton Conducting ceramic Cells: Status and Prospects

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Project Manager in Fuel Cell

Outline

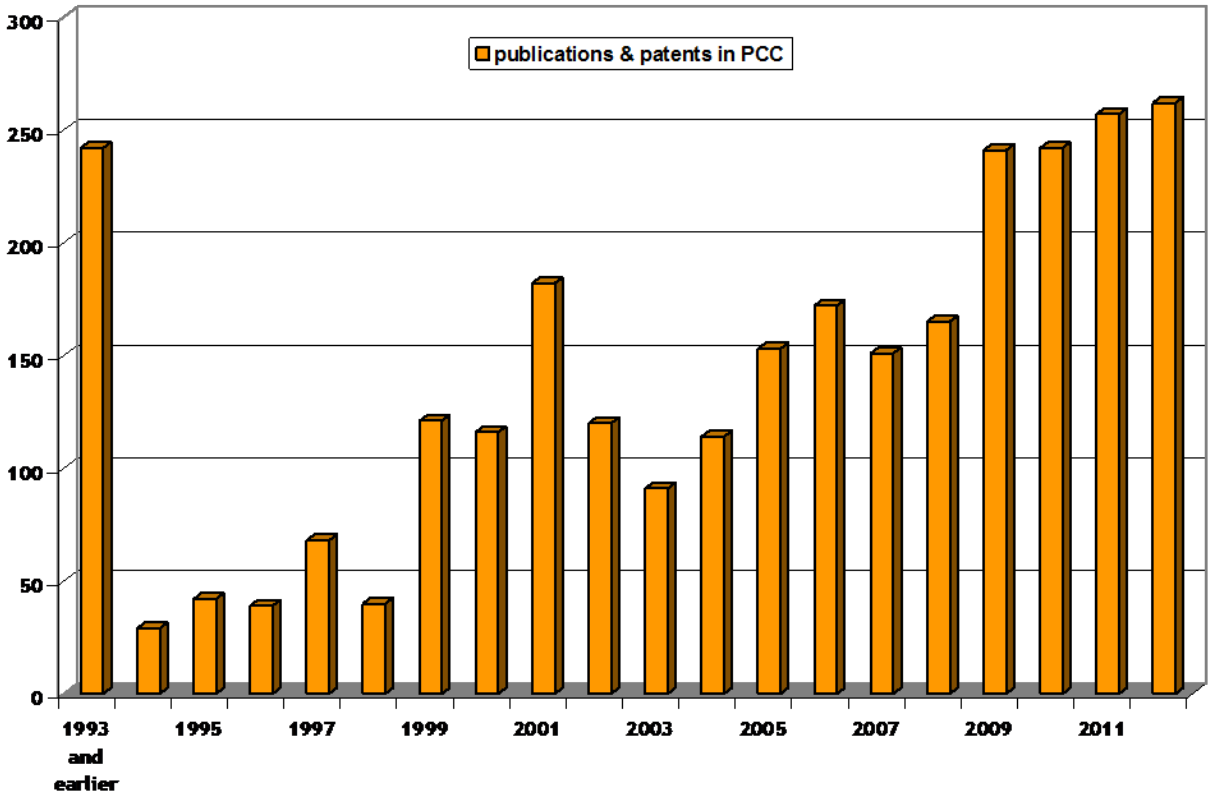
- Introduction
- Materials and processes
- Scale-up processes
- Performance and durability
- Conclusion and prospects

Outline

- Introduction
  - Research overview
  - Context & roadmap: case in fuel cell
- Materials and processes
- Scale-up processes
- Performance and reliability
- Conclusion and prospects

Introduction: PCC research in the literature...

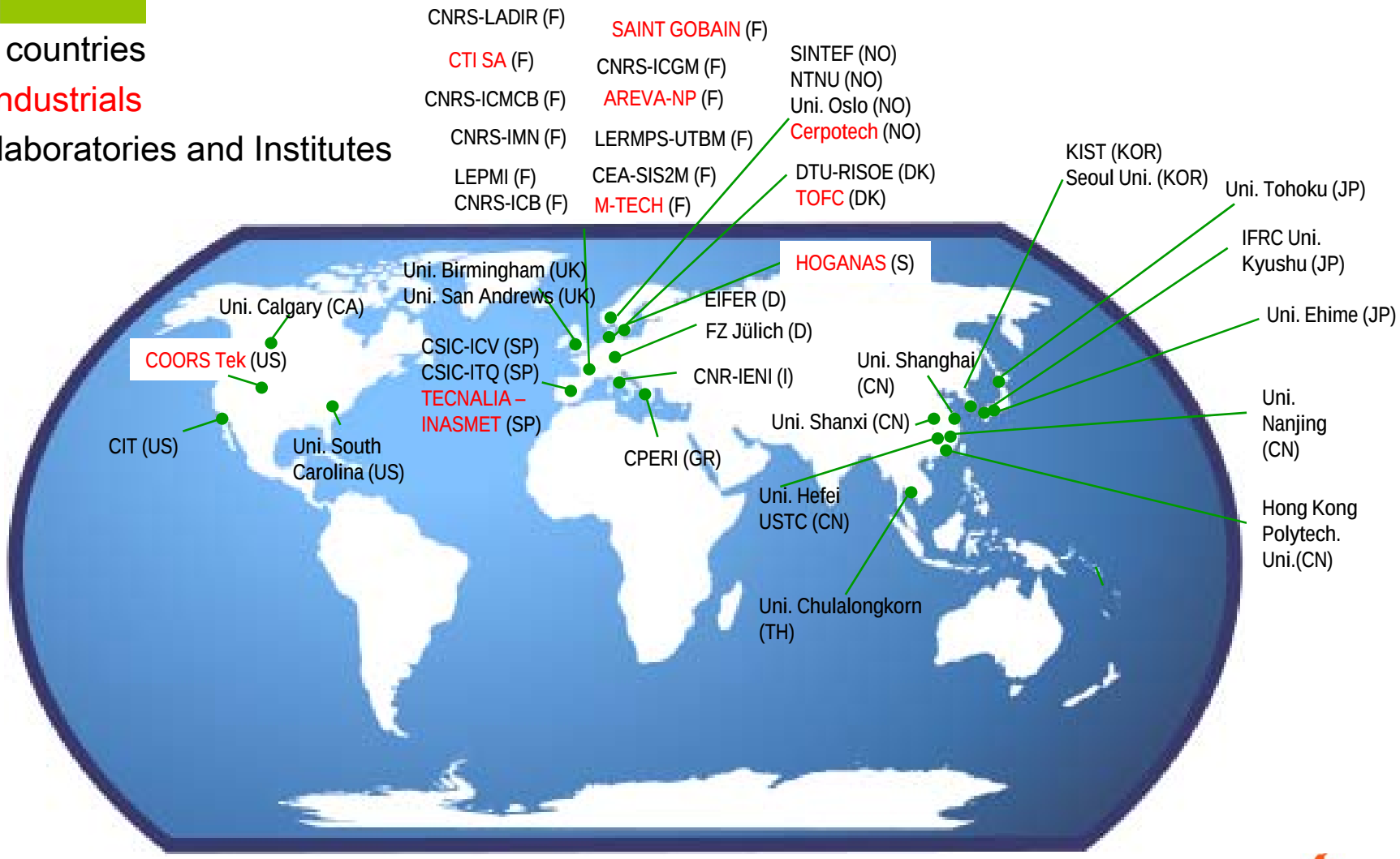
- More and more interests...
  - Better understanding of proton diffusion phenomena through the material
  - Optimization of intrinsic properties of materials and cell manufacturing (mechanical strength, performances)
  - Diversity of applications
    - Fuel cell
    - Hydrogen pumping
    - Ammonia synthesis
    - electrolysis



**source science direct*
Keyword: proton conducting ceramic fuel cell

Introduction: PCC research mapping*...

- > 15 countries
- > 9 industrials
- >30 laboratories and Institutes

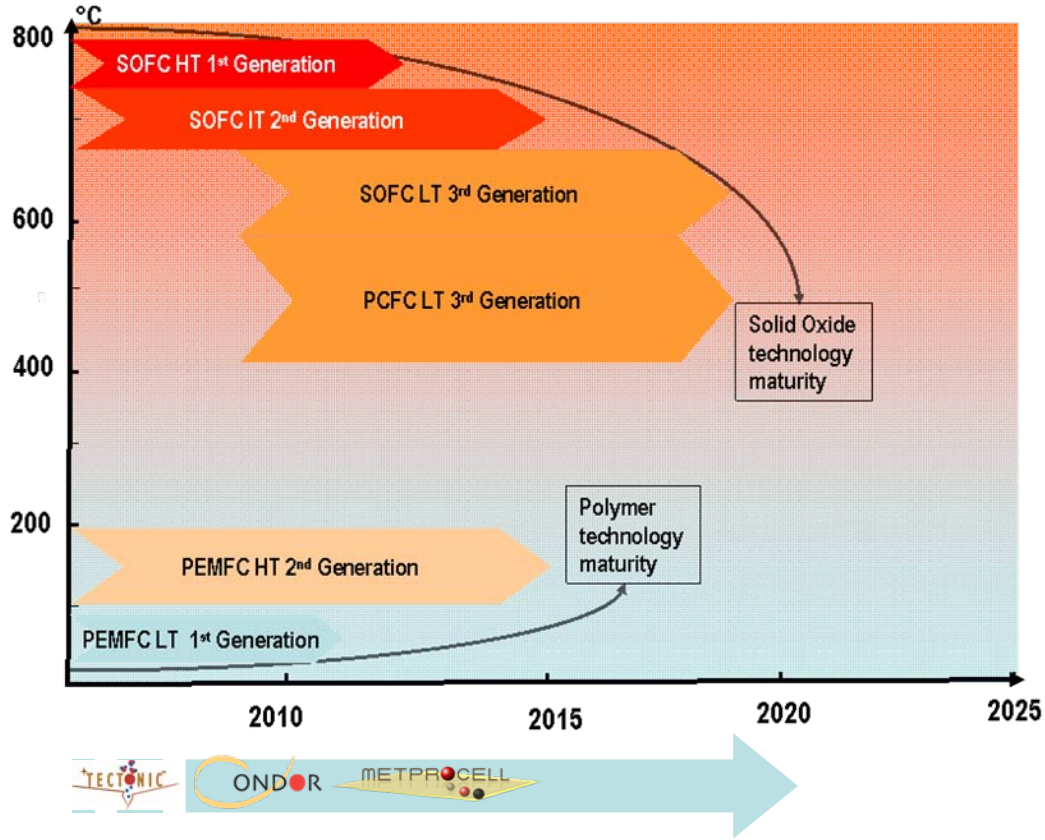


*List non exhaustive

Introduction: PCC in Fuel cell: Context & roadmap

- Assessment of PCFC technology as electrochemical devices vs. other FC technologies (SOFC, PEMFC)
  - Simplification of reforming step (vs. PEMFC)
  - (Potentially) use of common metalic Materials (reduction of cost) (vs. SOFC)
  - (Potentially) better stability under dynamic/thermal cycles (vs. SOFC)
  - (Potentially) better energetic efficency (no dilution of fuel @anode side) (vs. SOFC)
  - Better diffusion kinetics of H+ elements (vs. O2-)

- Opening market target: beginning 2020
  - Competition with LT SOFC technology



Outline

- Introduction
- Materials and processes
  - Criteria and status
  - Strategic approach
  - Nanopowder synthesis method
- Scaling-up
- Performance and reliability
- Conclusion and prospects

Materials and processes: the ideal PCC…

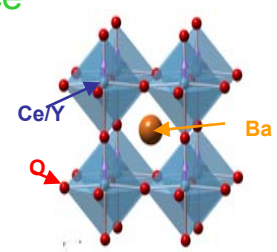
- Operating domain in PCFC research: 500 -700°C
  - >600°C : competition with IT-SOFC (2nd generation) and now LT-SOFC (3rd generation)
  - <600°C: non mature domain

600°C	Anode	Electrolyte	Cathode
Chemical stability	H_2/ H_2O	Air / H_2 / H_2O	Air / H_2O
CO_2/CO tolerance	yes	yes	yes
Ionic/protonic conductivity	> 10^{-2} S·cm^{-1}	> 10^{-2} S·cm^{-1}	> 10^{-2} S·cm^{-1}
Electronic conductivity	>1000 S·cm^{-1}	~ 0 S·cm^{-1}	>100 S·cm^{-1}
ASR	< 0.15 Ω.·cm²	< 0.15 Ω·cm²	< 0.15 Ω·cm²
Catalytic activity	yes	no	yes
Mechanical properties	Porous ~50% 300-800µm Thick	Dense >95% 10-30µm Thick	Porous ~30% 20-40µm Thick
Industrial aspects	Easy and not costly synthesis & manufacturing processes		

- Electrolyte materials
  - Perovskite type $AM_yX_{(1-y)}O_{3-\delta}$ (with A=Ba, Sr, M=Ce, Zr, Ta et X=Y, Yb, In)
    - **$BaCe_{0.9}Y_{0.1}O_{3-\delta}$ (BCY10)**
    - $BaCe_{0.7}In_{0.3}O_{3-\delta}$ (BCI)
    - **$BaCe_{0,8}\ Zr_{0,1}\ Y_{0,1}\ O_{3-\delta}$ (BCZY)**
  - Other perovskites:
    - Ba $(Ce_{0,6}\ Y_{0.3}\ Nb_{0,1})O_{3-\delta}$ (BCNY)
    - $La_{6-y}WO_{12-\delta}$ (LWO)
    - …
- Anode materials
  - Corresponding cermet (NiO-El)
- Cathode materials
  - Commonly SOFC materials
    - LSM, LSCF, **BSCF, Ln_2NiO_4**
  - others:
    - Cobalt-containing perovskite-type materials
      - $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ – $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SSC – SDC) (Sun et al. 2011)
    - …

Materials and processes: strategic approach

- Starting point: Perovskite BCY based materials as electrolyte
  - Need of thin and dense electrolyte with high mechanical strength and high performance stability
    - Reduction of electrolyte resistance
    - Use of nanopowder to enhance
      - Ionic grain boundary conductivity
      - The gastightness
    - Insertion of new doping elements (Zr, Zn...) (better CO2 tolerance, lower sintering temperature...)

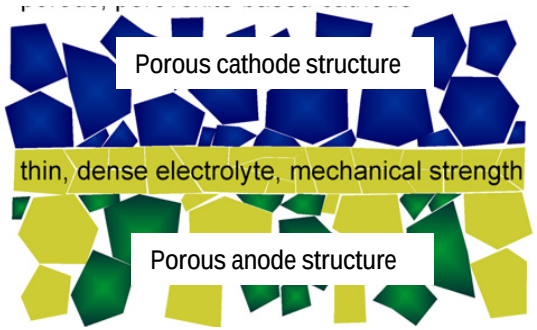


- Need of optimal microstructure and composition of the porous electrode for :
  - A good catalyst activity
  - To match TEC of materials
  - To improve adhesion between components
    - Use of Nanostructured electrode to get
      - High electro catalytic activity
      - Large TPB

Advanced MIEC cathodes

Composite approach

Advanced electrolyte materials



Optimization of intrinsic properties of baseline materials

Multi layer anode cermet

EIFER Materials and processes: nanopowder synthesis

- Flash Combustion method
  - Effective method used for the production of more than 1000 fine complex oxide powders
  - A self-sustained reaction of metal nitrates and different fuels
- Advantages
  - The liquid state allows mixing the reactants on the molecular level permitting uniform formulation
  - The high reaction temperature ensures high product purity and crystallinity
  - Short process duration promotes synthesis of nano-size powders with high specific surface area

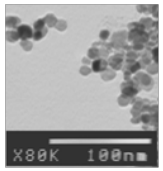
Nitrates + H_2O + Glycine

↓

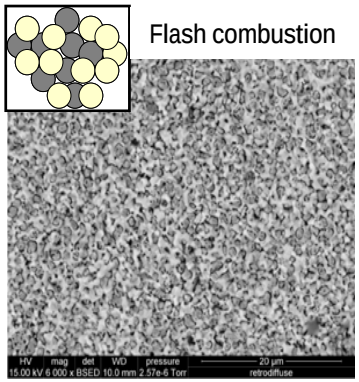
Dehydration @200 ° C

↓

Ignition/Combustion 600° C

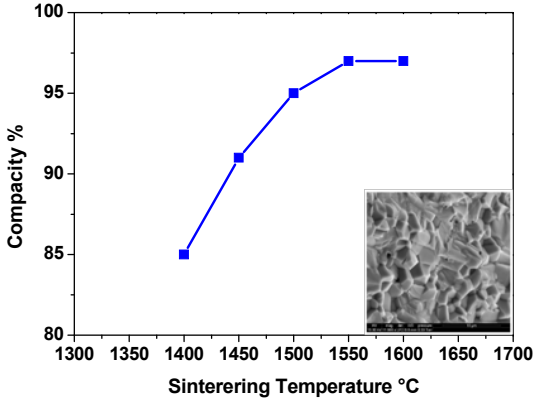


Anode layer



Homogenous distribution
Fine microstructure, large TPB

Electrolyte layer



Better sinterability
Higher apparent density (ex BZY)

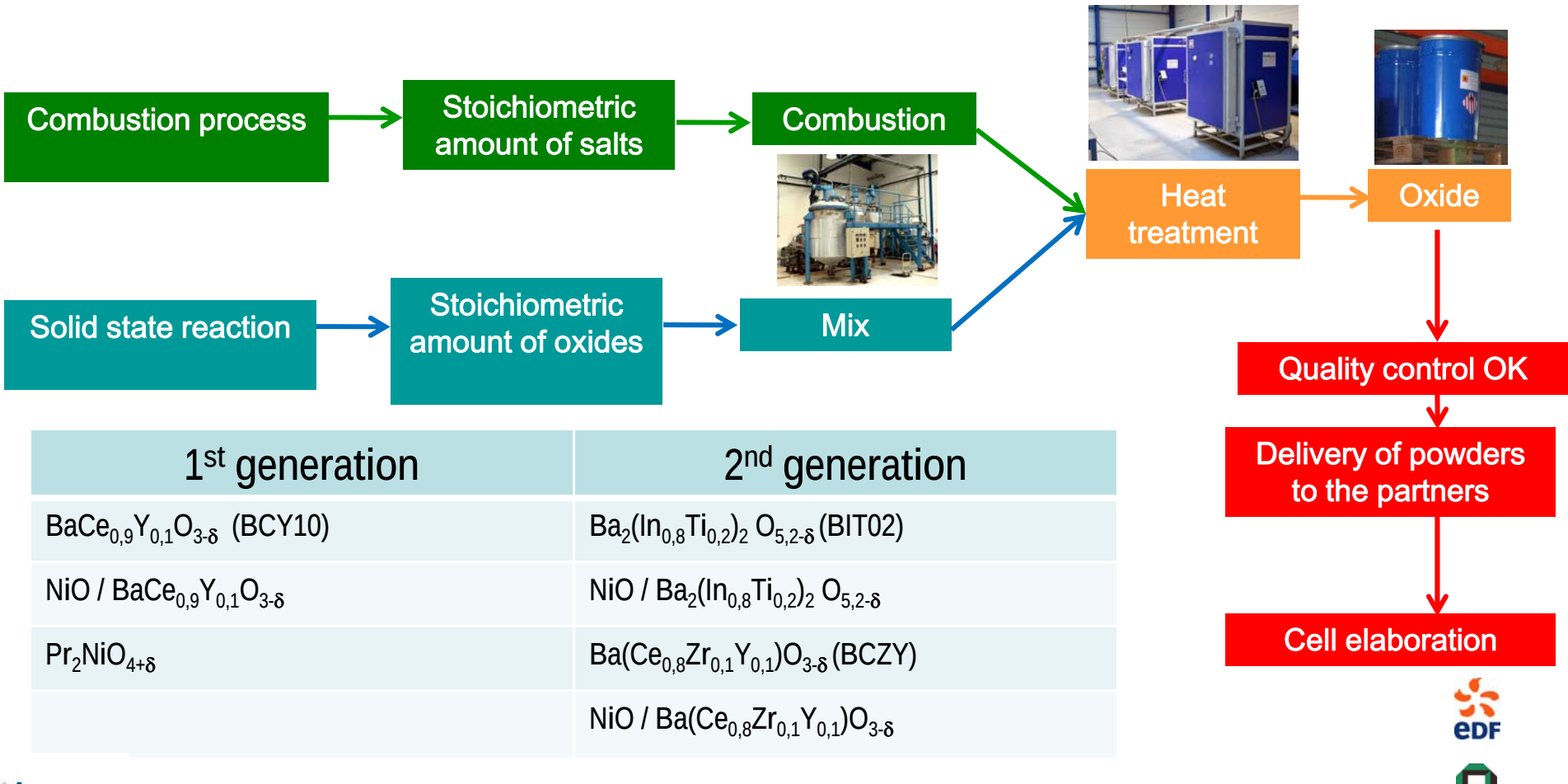
G. Taillades, M. Marrony et al., « New synthesis of nanopowders of proton conducting material. A route to densified proton ceramics » J. Solid State Chemistry (2009) 790-98.
G. Taillades et al., « Chemically Stable Electrolytes and Advanced Electrode Architectures for Efficient PCFC » ECS Transactions (2011) 805-11.
G. Taillades et al., « Engineering of porosity, microstructure and electrical properties of Ni-BCY cermet fuel cell electrodes by gelled starch porogen processing» Microporous and Mesoporous Materials (2011) 26-31.

Outline

- Introduction
- Materials and processes
- Scaling-up
  - Powder synthesis: the first level of maturity system
  - Cell manufacturing: the second level of maturity system...
- Performance and reliability
- Conclusion and prospects

Scaling-up step 1: powder synthesis

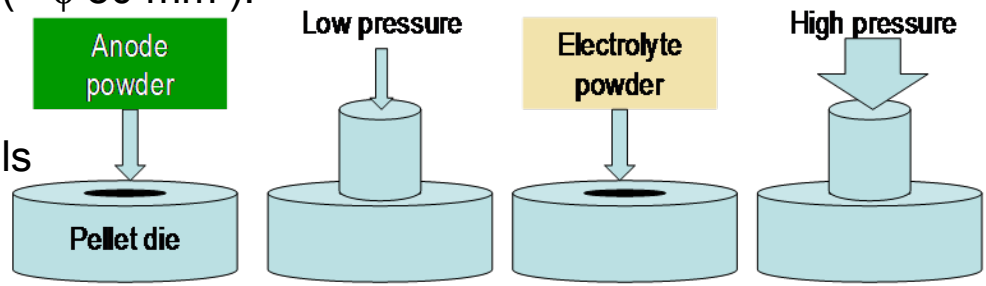
- Validation of the up-scaling step for lab powder synthesis process:
  - Combustion and solid state reaction
  - Good quality and reproducibility (>1 kg)



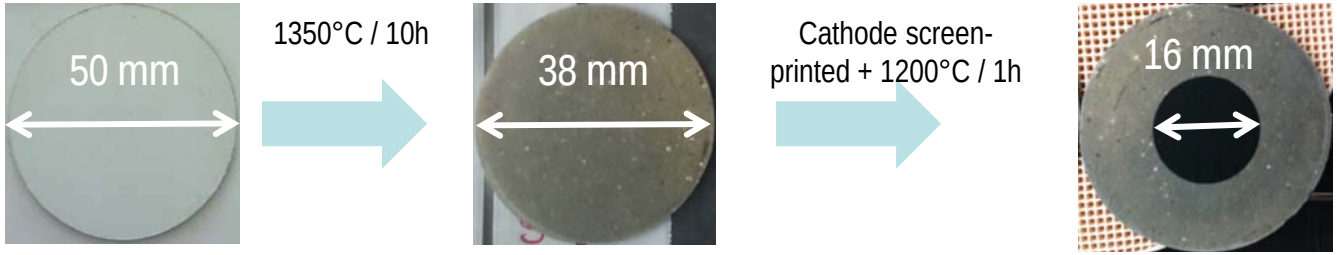
1st generation	2nd generation
$BaCe_{0,9}Y_{0,1}O_{3-\delta}$ (BCY10)	$Ba_2(In_{0,8}Ti_{0,2})_2\ O_{5,2-\delta}$ (BIT02)
NiO / $BaCe_{0,9}Y_{0,1}O_{3-\delta}$	NiO / $Ba_2(In_{0,8}Ti_{0,2})_2\ O_{5,2-\delta}$
$Pr_2NiO_{4+\delta}$	$Ba(Ce_{0,8}Zr_{0,1}Y_{0,1})O_{3-\delta}$ (BCZY)
	NiO / $Ba(Ce_{0,8}Zr_{0,1}Y_{0,1})O_{3-\delta}$

Scaling-up step 2: Anode Supported cell manufacturing (1)

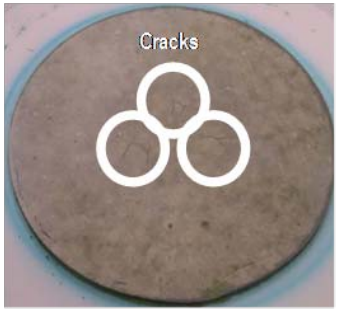
- Target: elaboration of cells at industrial level (> ϕ 80 mm):
  - Easy and industrial methods
  - Low manufacturing cost
- Evaluation of co-pressing method for half-cells (commonly used in the literature)



Half-cell



- ϕ 25 mm ☺ ➔ ϕ 40 mm ☺ ➔ ϕ 80 mm ☹
  - Difficulty with feasibility & reproducibility for bigger cells
    - Co-pressing method can not be easily used for mass production
    - Introduction of wet chemical routes



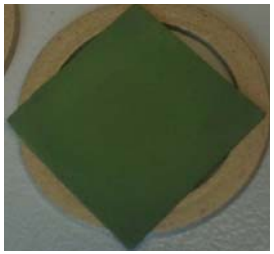
GENERATION 1

Dailly J., Marrony M. et al, under manuscript

Scaling-up step 2: Anode Supported Cell manufacturing (2)

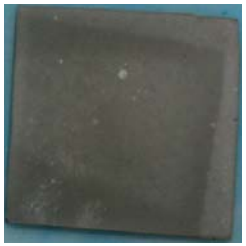
Anode	Electrolyte
Pressing	Tape-casting, screen-printing, slip-casting
Tape-casting	

Tape-casting NiO/BCY10

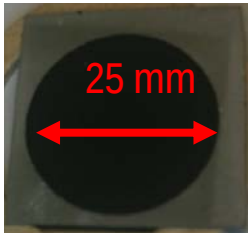


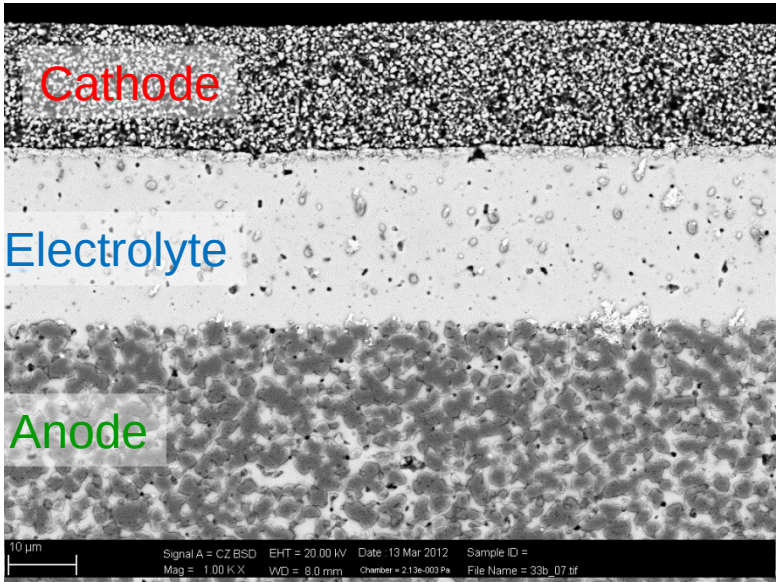
Screen-printing BCY10

Co-sintering 1400°C / 10h



Screen-printing , PrN, BSCF, $Nd_2NiO_{4+\delta}$ 1200°C / 1h





Before reduction	Thickness	Porosity
Anode	430 µm	2% (☹)
Electrolyte	25 µm	3% (☺)
Cathode	17 µm	30% (☺)

GENERATION 2: preliminary results…

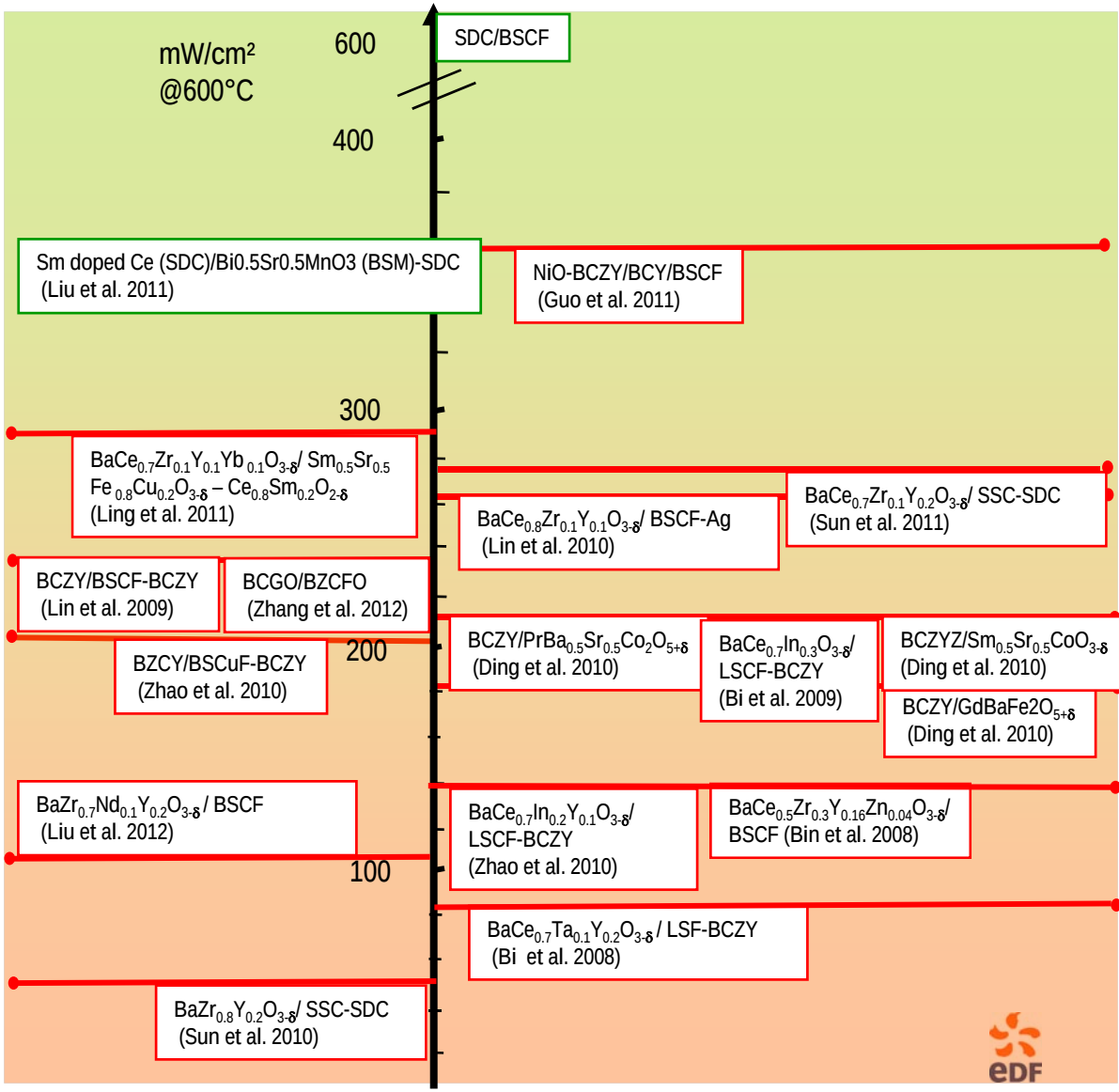
Outline

- Introduction
- Materials and processes
- Scale-up processes
- Performance and durability
- Conclusion and prospects

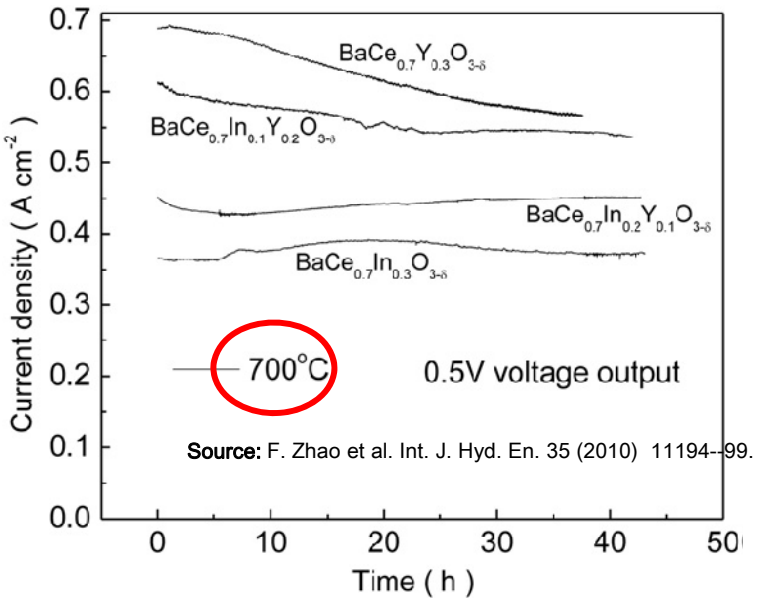
Performance and reliability: status (1)

- Actual average cell performance:
  - 100 - 250 mW/cm²@600°C
  - Cell diameter below 10 mm ☹
  - BCZY and BCY based cells
  - Many cathode/electrolyte couples

- Targeted cell Performances:
  - >400 mW/cm², 600°C
    - ➢ …LT-SOFC > 500 mW/cm², 600°C



Performance and reliability : status (2)

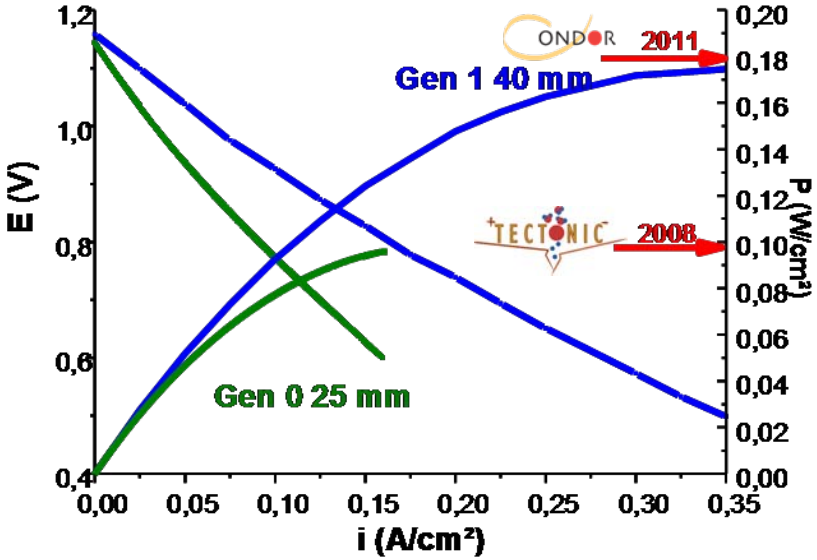


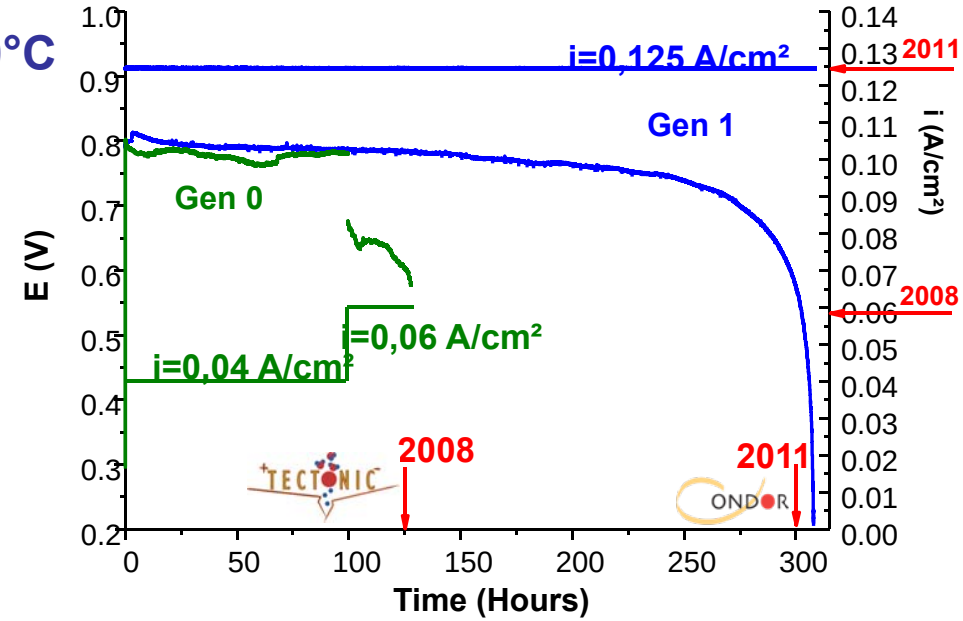
Source: F. Zhao et al. Int. J. Hyd. En. 35 (2010) 11194--99.

Cell	Operating conditions	Degradation rate (mV/h)	Lifetime (h)
NiO-BZCY/ BZCY/BSCuF-BCZY (Zhao et al. 2010)	@0.2 W/cm², 600°C	<-0.05	40
NiO-BCI30/ BCI30/LSCF-BCI30 (Bi et al. 2009)	@OCV, 600°C	<-0.05	110
TECTONIC	@OCV, 600°C	-1	>800

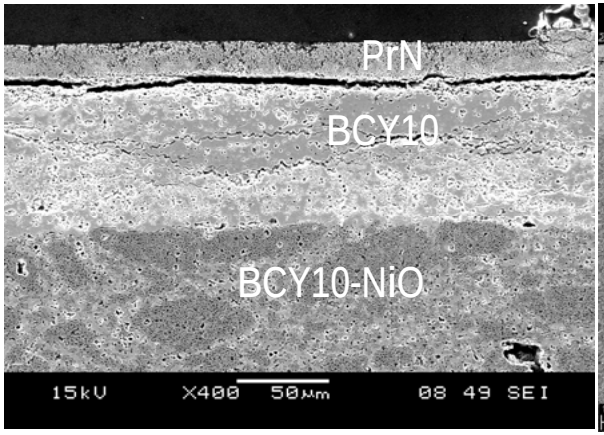
- Cell Reliability target
  - Few thousand hours under static mode (@0.7-0.8V)
  - >100 dynamic cycles
- Lifetime tests in PCFC:
  - No real data in the literature :
    - **Few tens hours... @700°C!!!**

Performance and durability: BCY10/PrN based cell

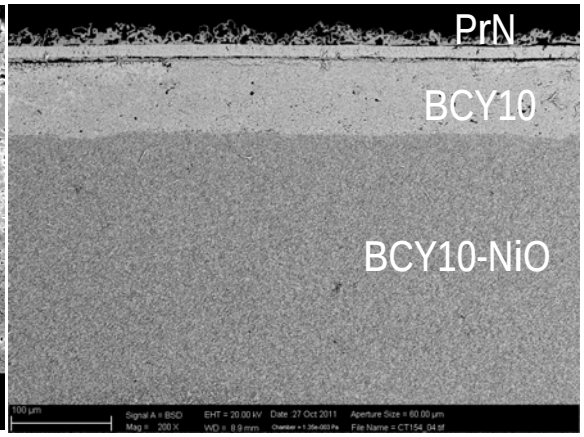




Gen O



Gen 1



- Cell performance and reliability improved
  - 180 mW/cm², 600°C
  - >250h
- SEM/EDX analysis
  - Electrolyte layer:
    - Porosity and quality improved
    - Thickness to be reduced (< 20 µm)
  - Anode layer
    - Better homogenity
- Cathode Layer:
  - High reactivity PrN / BCY
  - Delamination effect

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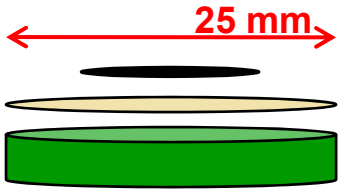
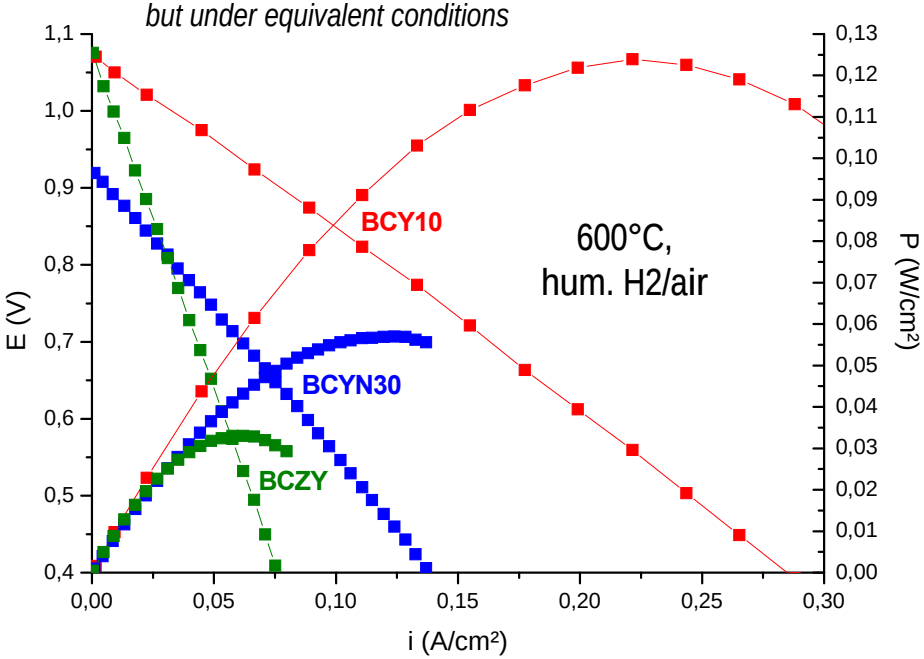
Performance and durability : advanced substitued perovskite based cell

$Ba(Ce_{0,9}Y_{0,1})O_{3-d}$ ➔BCY10
$Ba(Ce_{0,8}Zr_{0,1}Y_{0,1})O_{3-d}$ ➔BCZY
$Ba(Ce_{0,6}Y_{0,3}Nb_{0,1})O_{3-d}$ ➔BCYN30

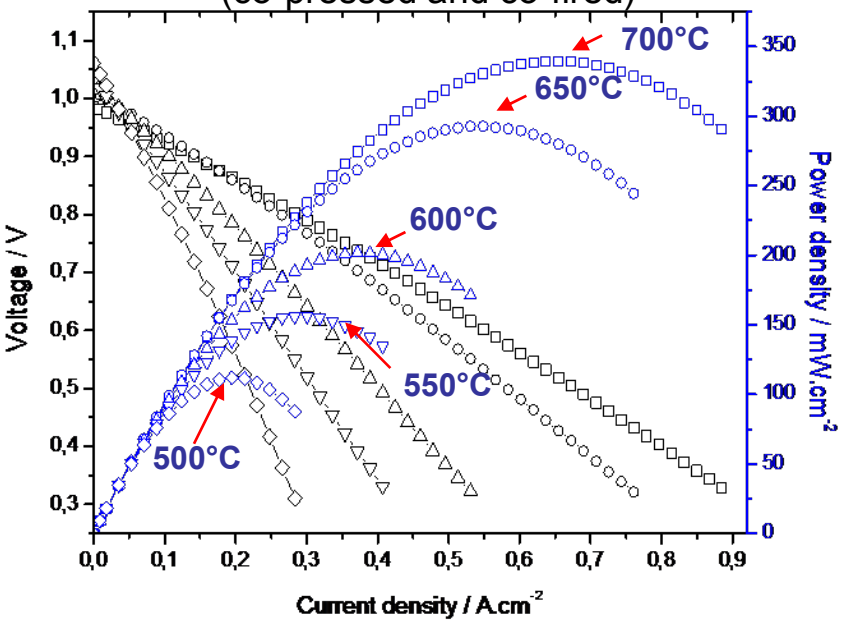


BSCF or BSCF/BCY (Screen Printed and fired) (20 µm)
Electrolyte (30 µm)
Cermet (1 mm)
(co-pressed and co-fired)

**Results obtained on non-optimised cells but under equivalent conditions*



Influence of material electrolyte (NiO-electrolyte / electrolyte/BSCF) on cell performance

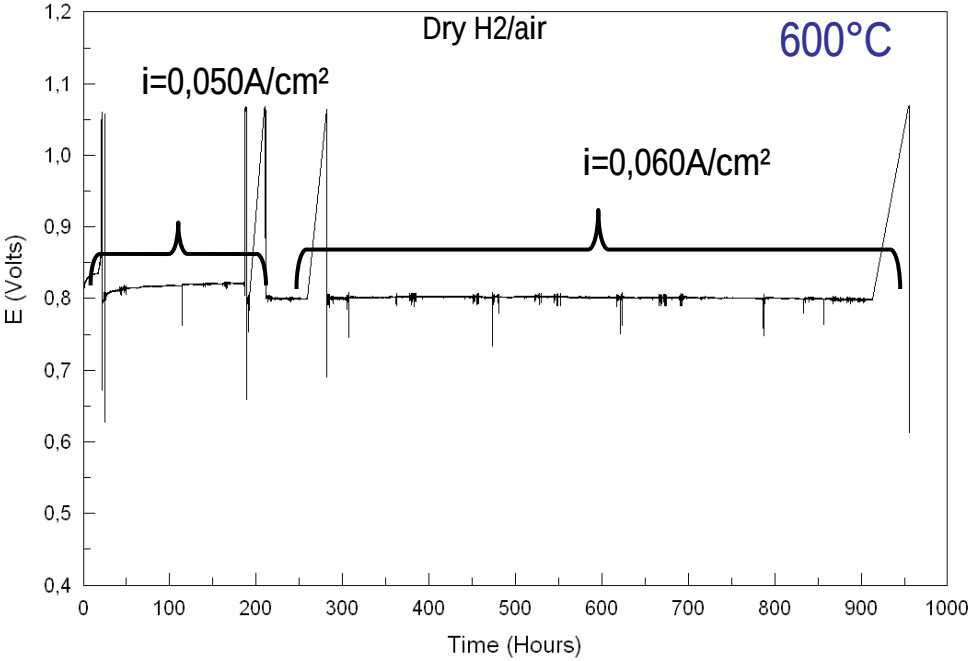


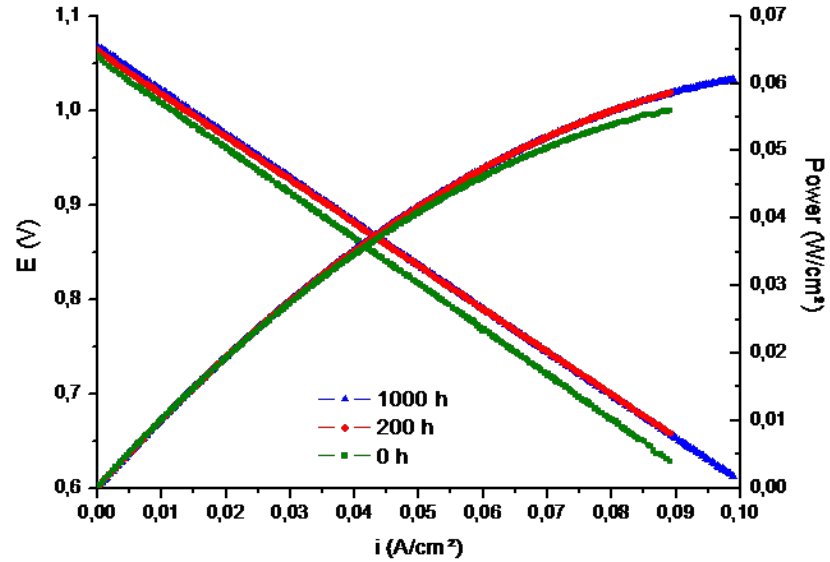
Influence of composite approach (NiO-BCY / BCY /BSCF-BCY) on cell performance vs. temperature operation

- Electrolyte based PCFC cell :
  - BCY >BCYN > BCZY
- P= 125 mW/cm², 600°C without composite,
- P = 200 mW/cm², 600°C with composite
  - Case of BSCF

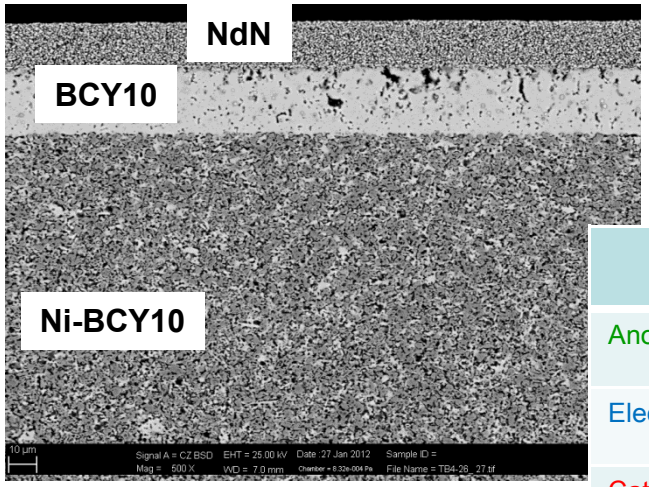
Performance and reliability: BCY stable?

Endurance test @0.8V: NiO-BCY/BCY/NdN made by wet chemical routes





IV curves of NiO-BCY/BCY/NdN cell vs. time (h)



	Thickness (µm)	Porosity After test
Anode	430	2% → 18%
Electrolyte	25	3% → 10%
Cathode	17	30% → 25%

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- Performance to be optimized
  - 1000h @0.8V without degradation!☺
  - Pmax=60 mW/cm² ☹...
  - ... but OCV > 1 V ☺, even after 1000h!
- SEM/EDX observations
  - No diffusion of elements through layers ☺
  - Slight increase of porosity of electrolyte ☹
    - Because power density is nearly constant with time, the properties of BCY is not the parameter key of degradation...
      - Cathode interface layer to be optimized (protective coating interface?)

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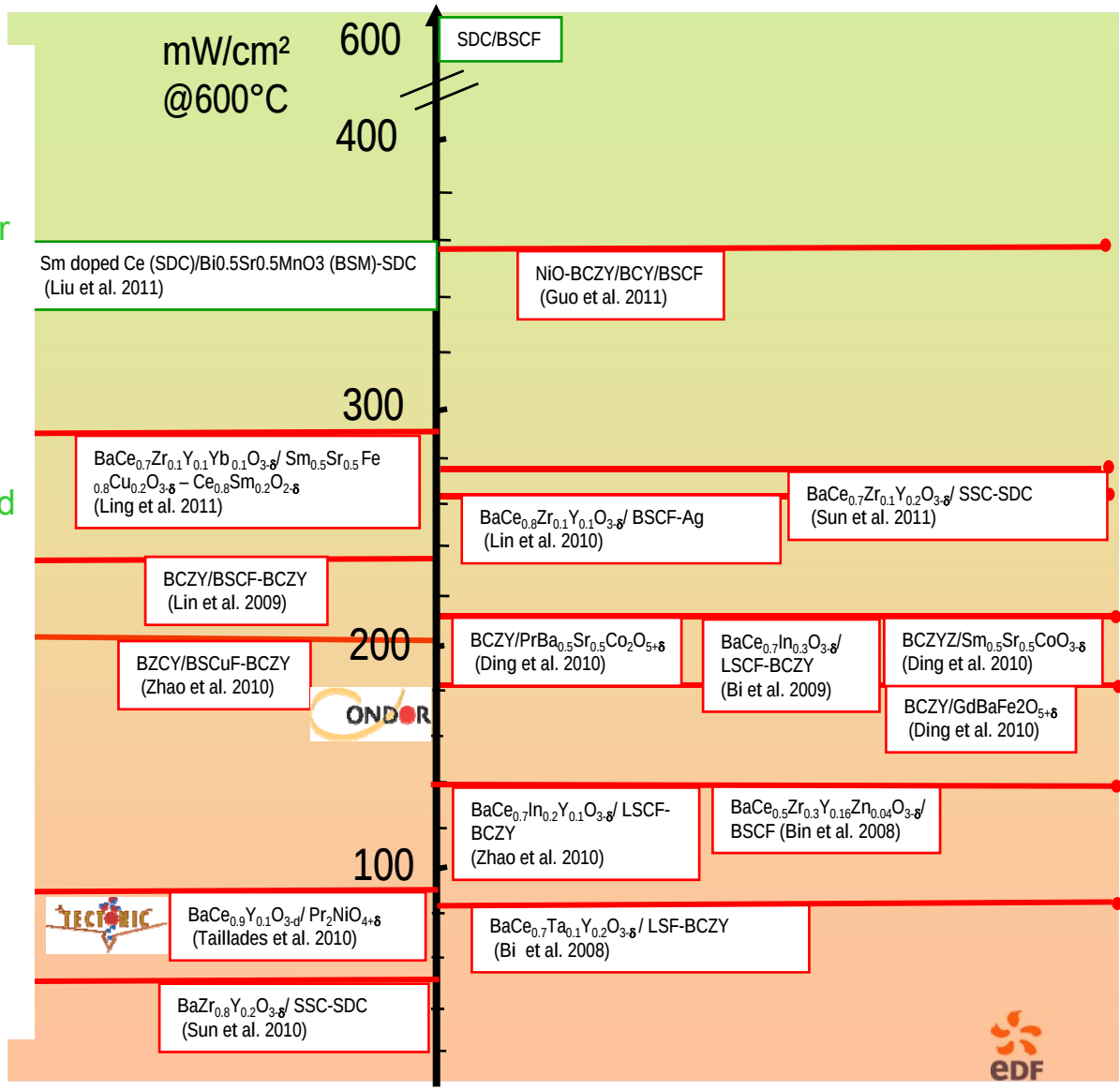
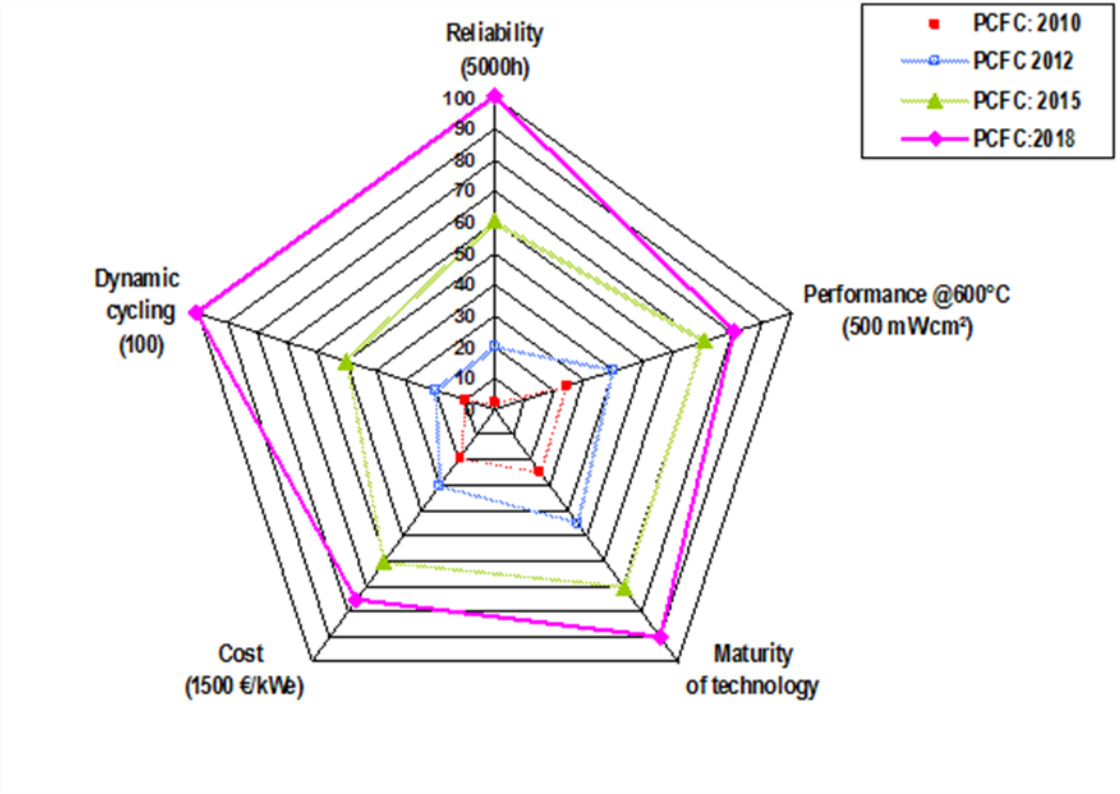
Conclusions

- Promising technology in fuel cell but not enough mature materials and processes used
  - Research activity growthing up for the 10 last years
- Materials & processes
  - Validation of the scale up of material synthesis
  - Cell manufacturing to be improved
    - Wet chemical routes
- Cell Performances
  - Actually : ~200 mW/cm², 600°C
    - BCY based cell
    - In the literarure: 350 mW/cm², 600°C
  - To be reached :
    - >400-500 mW/cm², 600°C…
    - …vs. LT-SOFC > 500 mW/cm², 600°C
- Cell reliability
  - >1000h with BCY based cell without any degradation



Prospects (1)

- In order to reduce technological bottlenecks...
  - Towards « Nafion® » or YSZ references
    - Understanding of proton diffusion mechanisms through materials
    - Innovative materials
  - Towards the best couple electrolyte/cathode
    - Better compatibility (TEC, chemical reactivity…)
      - Composite system?
  - Towards the best microstructure
    - Composition gradient
    - Innovative materials : MIEC (H+/e) for both cathode and anode layers
  - Towards the best operating conditions
    - Standard criteria
    - Vs. Application profile



METPROCELL

tecnalia Inspiring Business

Marion Technologie

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cnrs dépasser les frontières

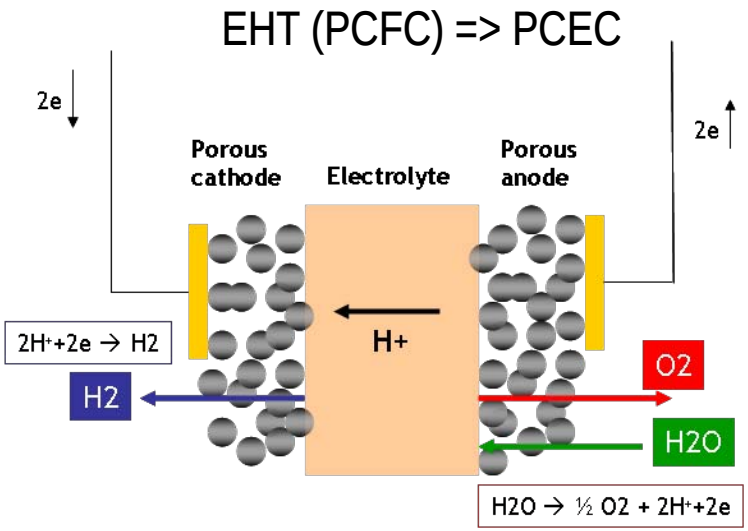
CerPoTech Ceramic Powder Technology

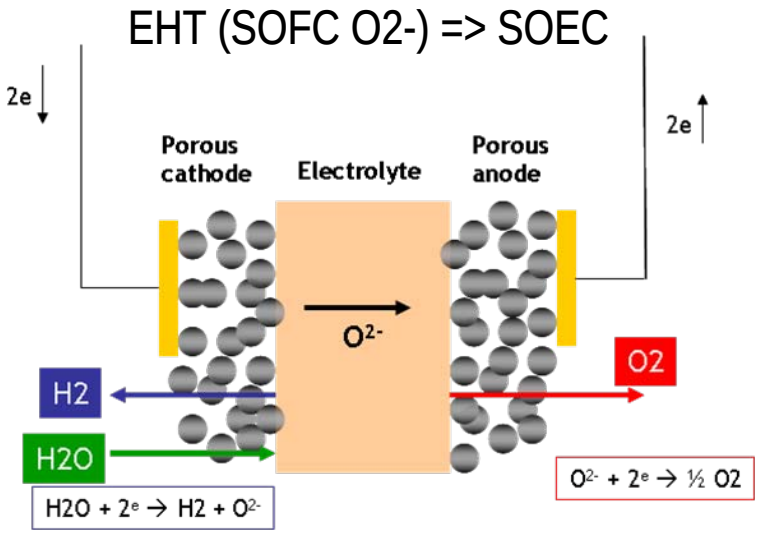
EDF

TOPSOE FUEL CELL RETHINKING ENERGY

Risø DTU National Laboratory for Sustainable Energy

Prospects (2)





- Opening to electrolysis @ intermediate temperature (500-700°C): energy storage via H2
  - ☹ PO2 ↑ @ H2 side by shifting SOFC/SOEC modes
  - ☺ PO2 ↑ @ O2 side by shifting PCFC/PCEC modes
    - High produced H2 quality
    - Better stability of material properties (Ni elements especially)
    - Reversibility concept more acceptable
- … but poor state of the art
  - 2-3 recent scientist articles

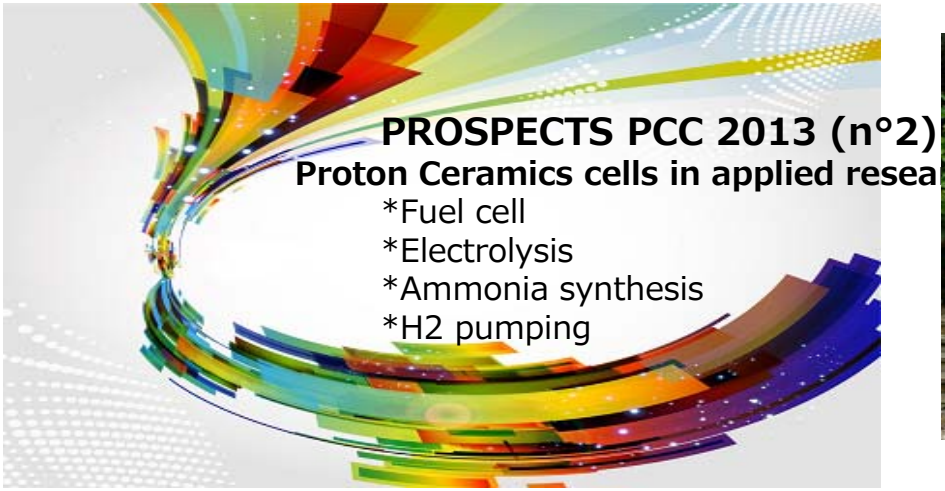
Acknowledgments and informations…

CONDOR team…

Financial supports…

More information on PCFC results : www.pcfc-condor.org
www.metprocell.eu

EVENT in 2013 in Montpellier (France) → 1st announcement come soon…

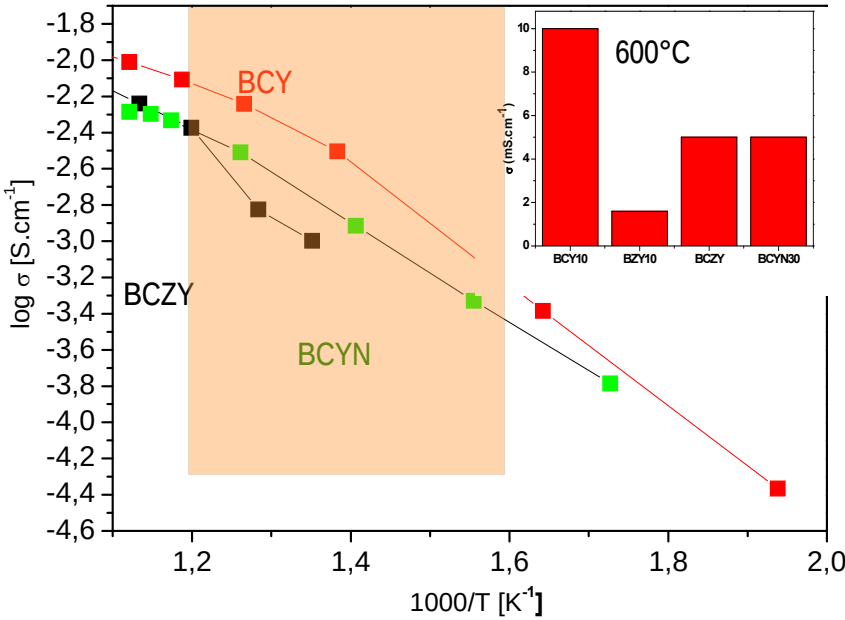


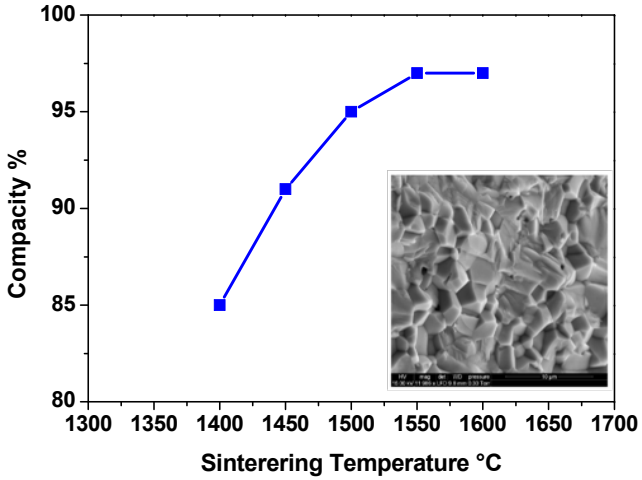
Thank you for your attention!

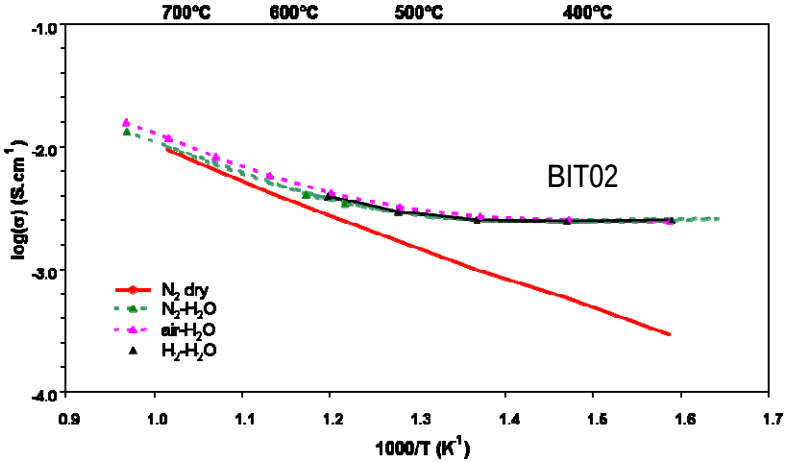
EIFER Materials and processes: electrolytes (1)

- Substitued Perovskites and derivates
  - Generation 1:
    - $BaCe_{0,9}\ Y_{0,1}\ O_{3-d}$ (BCY10)
      - BCY10: s(H+) = 1-10 mS/cm, 400-600°C
    - $BaZr_{0,9}\ Y_{0,1}\ O_{3-d}$ (BZY10)
  - Generation 2:
    - Ba $(Ce_{0,6}\ Y_{0.3}\ Nb_{0,1})O_{3-d}$ (BCYN)
    - $BaCe_{0,8}\ Zr_{0,1}\ Y_{0,1}\ O_{3-d}$ (BCZY)
    - $Ba_2In_{2-x}Ti_x\ O_{5+d}$ (avec x=0.2) (BIT02)
- Nanopowdered approach
  - High sinterability
  - high apparent density
    - Ex: BZY10: sintering temperature 200°C lower than those described in the literature (ref: 1700°C)

Conductivity measurements vs. T(°C) [Ar/H2, H2O 3%]







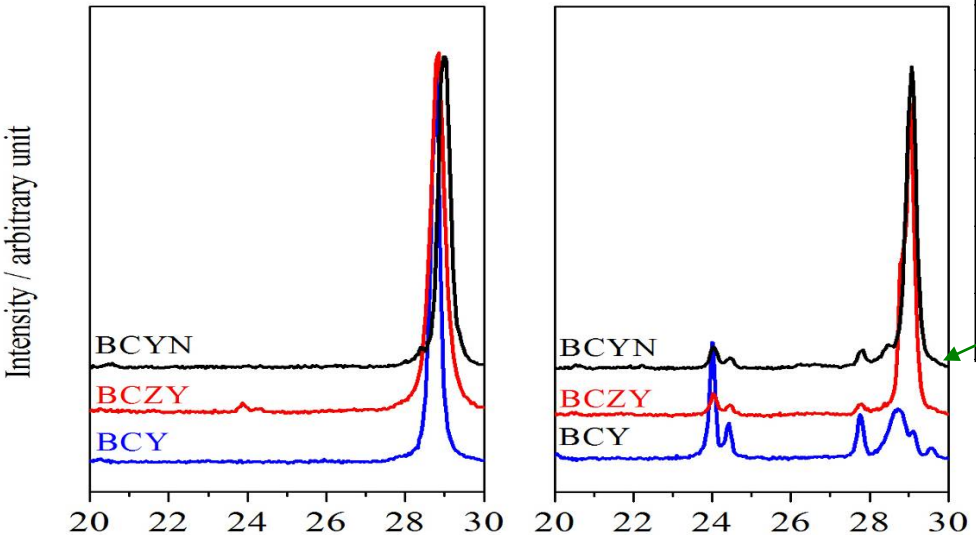
G. Taillades et al., « Chemically Stable Electrolytes and Advanced Electrode Architectures for Efficient PCFC » ECS Transactions (2011) 805-11.

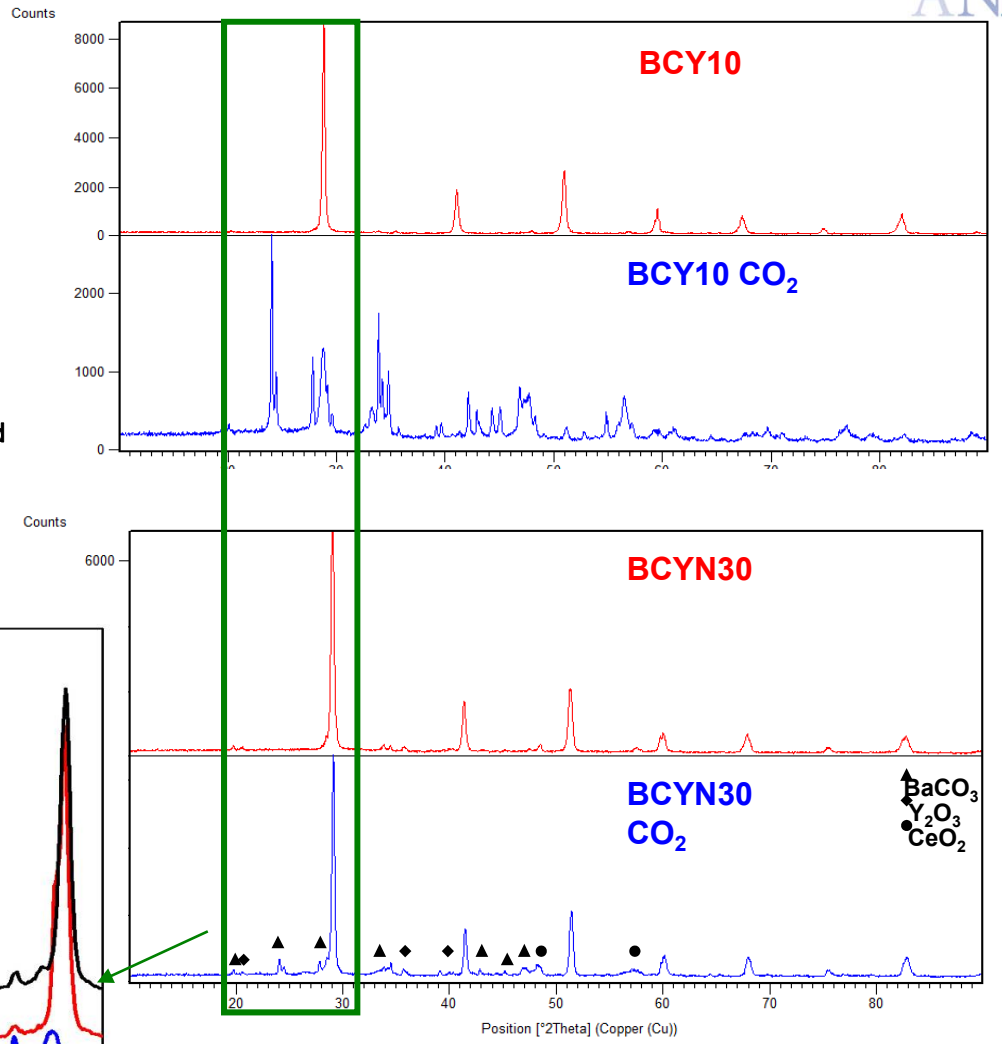
O. Joubert et al., « Water incorporation and proton conductivity in titanium substitued barium indate » J. Power Sources (2010) 1136-41.

Materials and processes: electrolytes (2)

4% CO_2/He 700°C/10h

- Substitued Perovskites
  - Reactivity ranking
    - ➢ BCYN30 > BCZY >> BCY
      - Powder level ☹
      - **Dense material : reactivity less pronounced**
        - » Kinetics effect

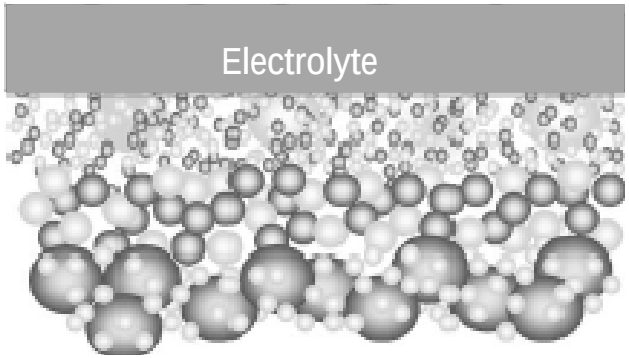


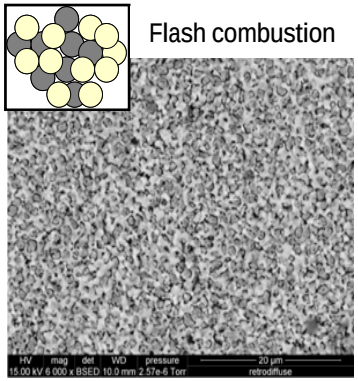


G. Taillades et al., « Chemically Stable Electrolytes and Advanced Electrode Architectures for Efficient PCFC » ECS Transactions (2011) 805-11.

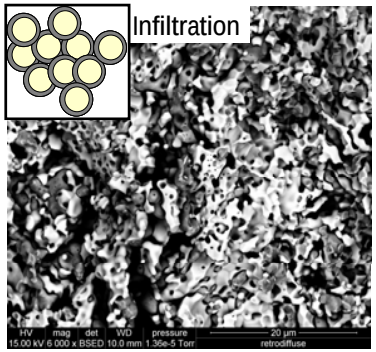
EIFER Materials and processes: anode cermet (1)

- Characteristics of the support
  - Mechanical strength
  - Gas permeability (~ 40 % porosity)
  - Total conductivity higher than 100 mS/cm
- Structuration of Functional layer
  - Fine microstructure, large TPB
- Control of microstructure (porosity) vs. synthesis methods
  - Flash combustion
  - Infiltration
  - Physical mixture
  - Gelling starch as porogen

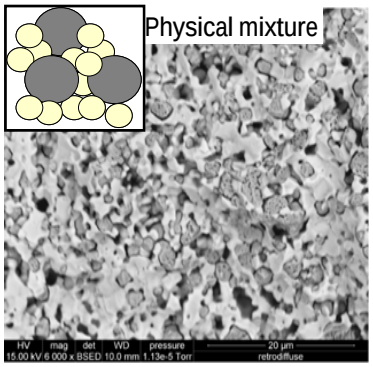




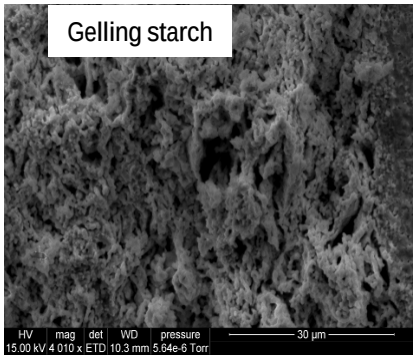
Homogenous distribution



Interpenetrated networks



Larger NiO domains
Distribution lower

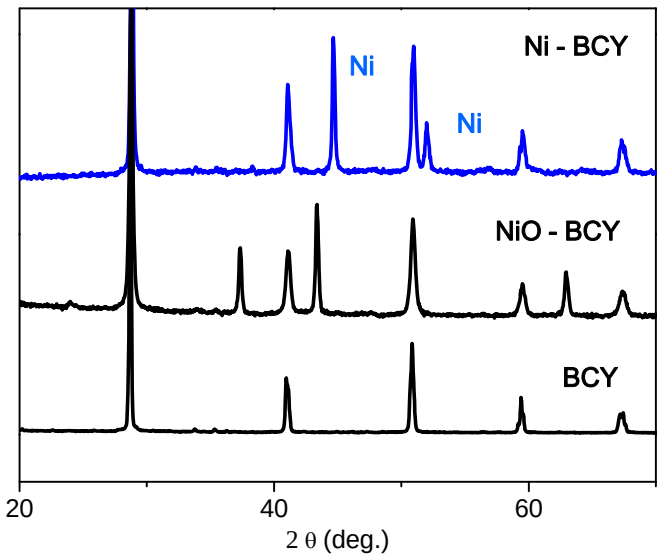


Uniform open porosity

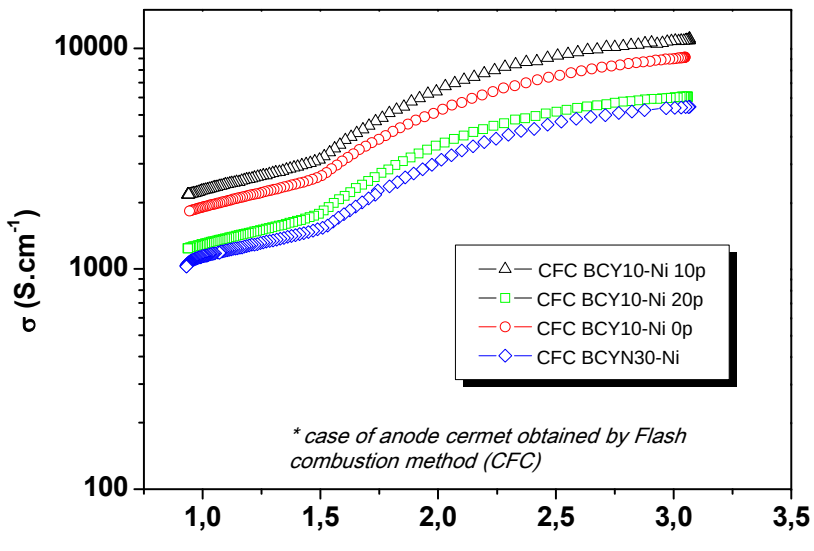
G. Taillades et al., « Engineering of porosity, microstructure and electrical properties of Ni-BCY cermet fuel cell electrodes by gelled starch porogen processing» Microporous and Mesoporous Materials (2011) 26-31.

EIFER Materials and processes: anode cermet (2)

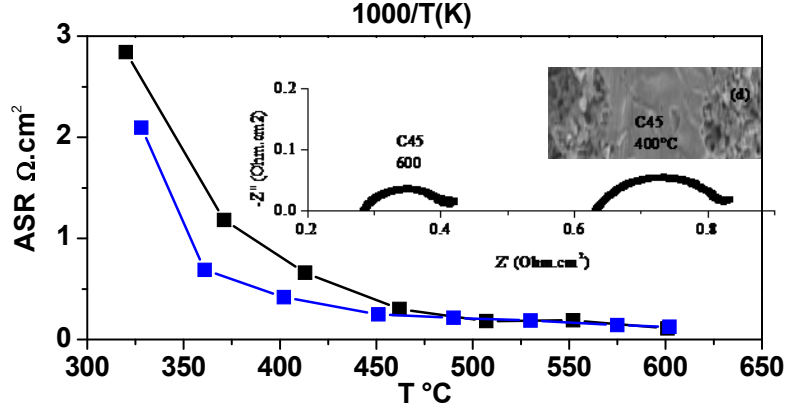
- Pure Ni-BCY cermet after reduction @ 700°C



- Metallic behavior, percolation of the Ni phase
- σ > 1000 S/cm, @ 600°C attributed to high homogeneity



- EIS on symmetrical cell (anode/electrolyte/anode)
  - Low polarisation ASR ≈ 0.1 Ω cm² @ 600°C for any synthesis methods



G. Taillades et al., « Engineering of porosity, microstructure and electrical properties of Ni-BCY cermet fuel cell electrodes by gelled starch porogen processing» Microporous and Mesoporous Materials (2011) 26-31.

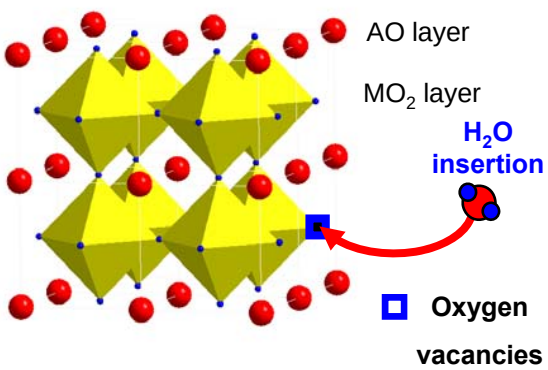
EIFER Materials and processes: Cathode (1)

- Cathode materials
  - Water insertion abilities in oxides materials
  - 3 structural types

$$A_xB_yO_z + \frac{n}{2}H_2O \rightarrow A_xB_yO_{z-\frac{n}{2}}(OH)_n$$

Perovskites

$A_{1-x}A'_xM_{1-x}M'_xO_{3-\delta}$

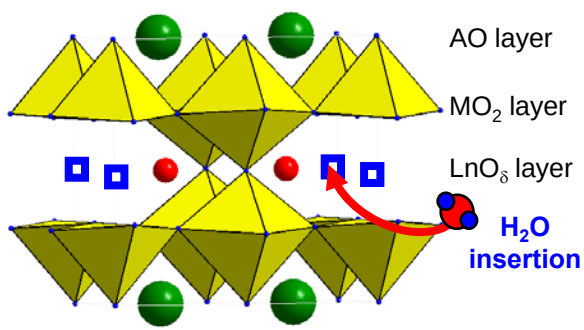


$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$

Double Perovskites

$LnBaM_2O_{5+\delta}$



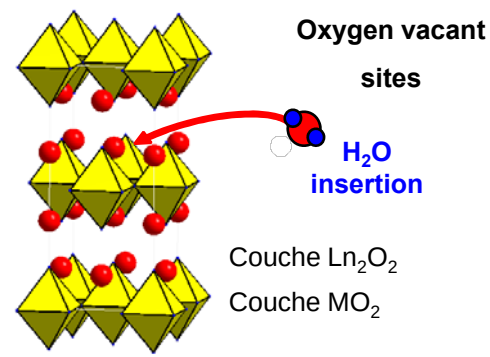
$GdBaCo_2O_{5+\delta}$

$NdBaCo_2O_{5+\delta}$

$PrBaCo_2O_{5+\delta}$

Ruddlesden-Popper

$Ln_2MO_{4+\delta}$



$La_2NiO_{4+\delta}$

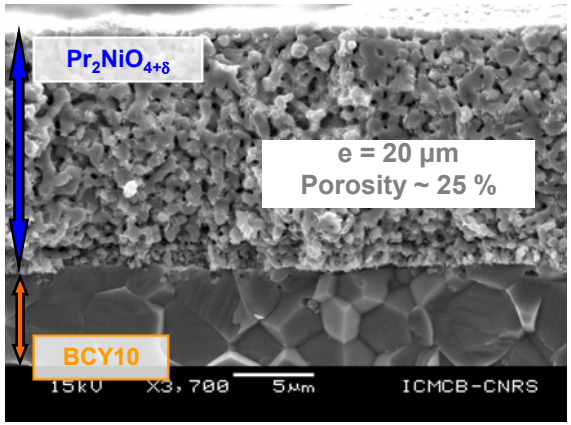
$Nd_2NiO_{4+\delta}$

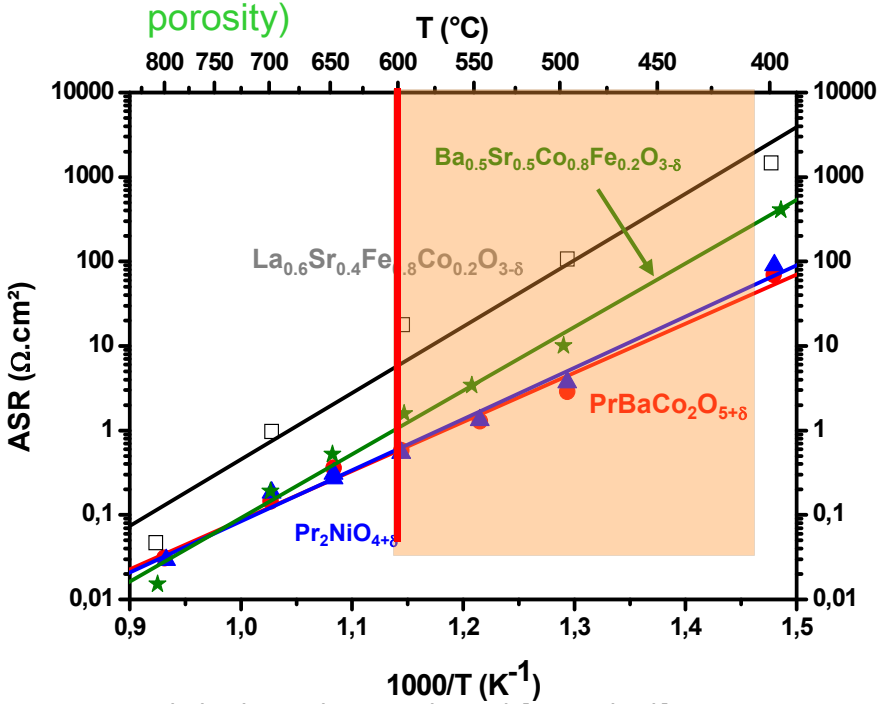
$Pr_2NiO_{4+\delta}$

F. Mauvy, M. Marrony et al., « Hydration properties and rate determing steps of the oxygen reduction reaction of perovskite-related oxides as H+-SOFC cathodes» J. Electrochem. Soc. (2012) B683-694.

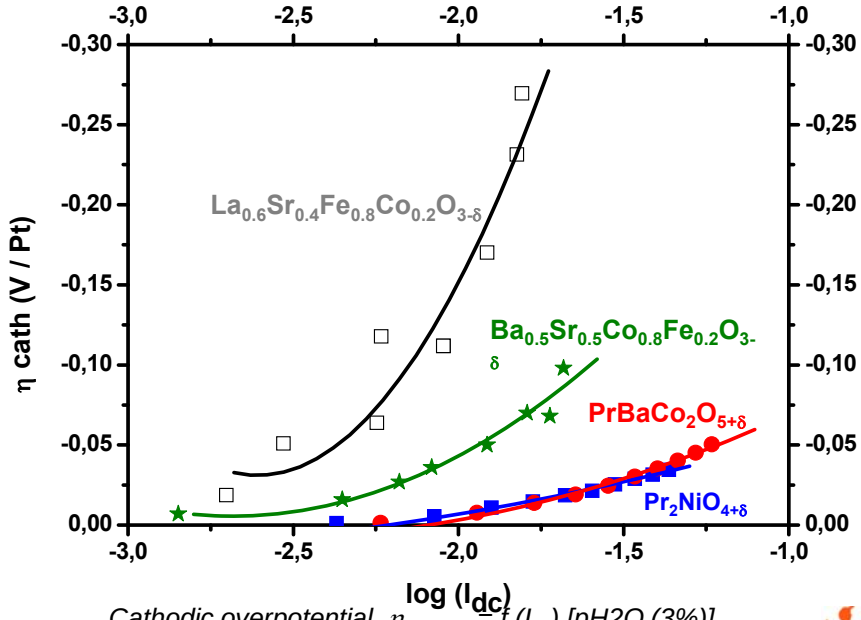
EIFER Materials and processes: Cathode (2)

- Electrochemical measurements
  - Symmetric electrode/electrolyte/electrode half cells
    - Preparation of dense $BaCe_{0.9}Y_{0.1}O_{3-d}$ electrolyte pellets
    - Electrode ink (particle size < 1 mm) screen printed
    - Electrode layer sintered between 1000 and 1200 °C
  - Electrode layers with controlled microstructure (thickness and porosity)





Polarization resistances (I_{dc} = 0) [pH2O (3%)]



Cathodic overpotential $\eta_{cathodic} = f(I_{dc})$ [pH2O (3%)]

- Pr_2NiO_{4+d} and $PrBaCo_2O_{5+\delta}$ (ASR ≈ 0.4 Ω cm² @ 600°C / $\eta_{cathode}$ ~ 0.025 V / Pt à 600°C pour Idc = 50mA/cm²
- BSCF (ASR ≈ 1Ω cm² @ 600°C) appear as the most promising cathode materials for H⁺-SOFC

F. Mauvy, M. Marrony et al., « Hydration properties and rate determing steps of the oxygen reduction reaction of perovskite-related oxides as H⁺-SOFC cathodes» J. Electrochem. Soc. (2012) B683-694.