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Reversibility approach based on proton conducting ceramic cells

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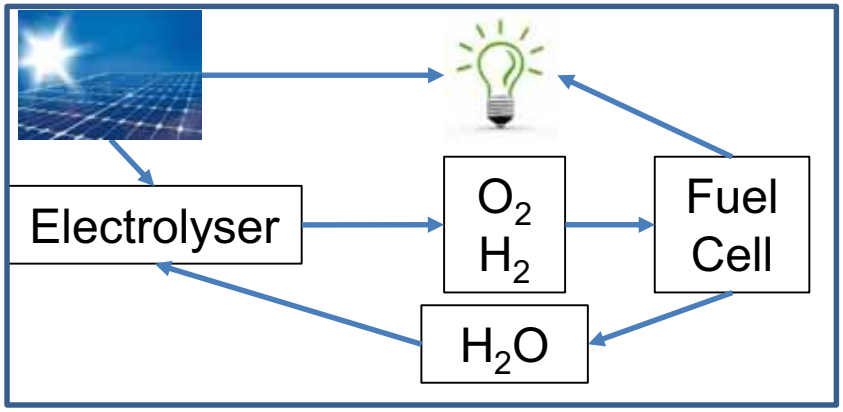
Introduction & Context

Introduction & Context

Actual topic ➔ management of use/storage of renewable energies

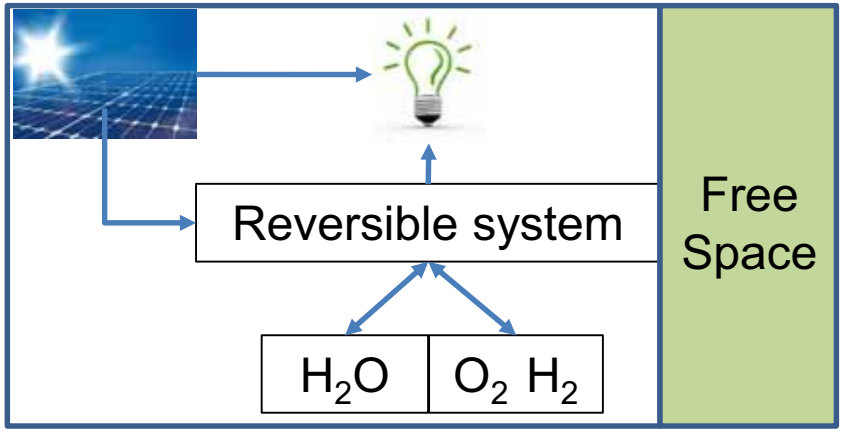
An efficient solution consists in the combination of a Fuel Cell and an Electrolyser.



➔ Need of two separate devices: a Fuel Cell and an electrolyser

Ex: Myrte project

http://myrte.univ-corse.fr



Reversible system: one device operating in both modes
➔ Lower price
➔ Higher compacity

Ex: Sunfire module

Fuel Cell Bull. 2 (2016)

Introduction & Context

Which technology for the reversiblity?

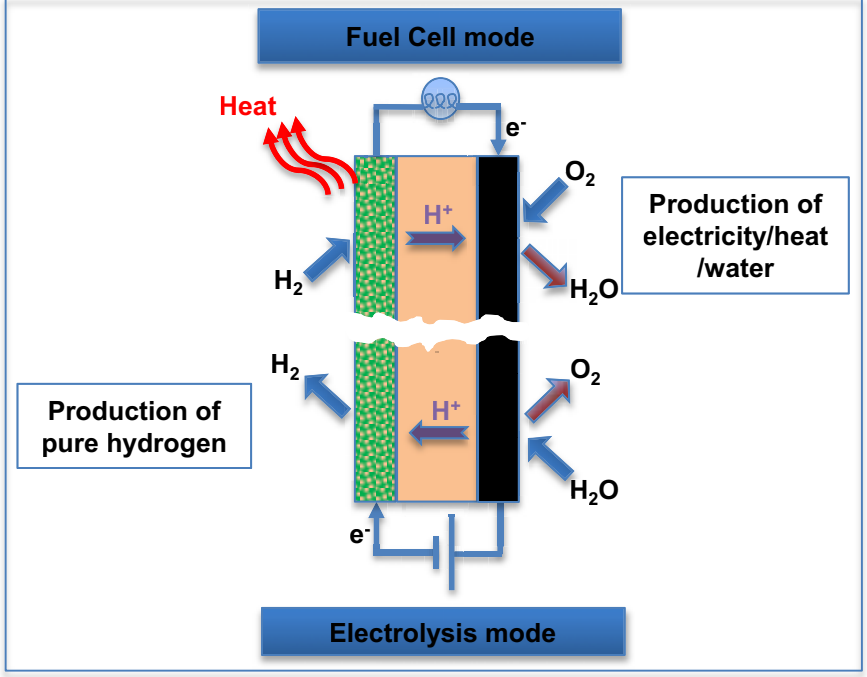
PEM and SOC-based systems at demo level but…

PEM
Accelerated ageing of catalysers
Problem with the management of water

SOC
High T°: Accelerated ageing of materials
Production of humidified fuel

PCC
Intermediate operating temperature
Production of pure hydrogen

Principle of a reversible protonic ceramic cell



Materials & Processing

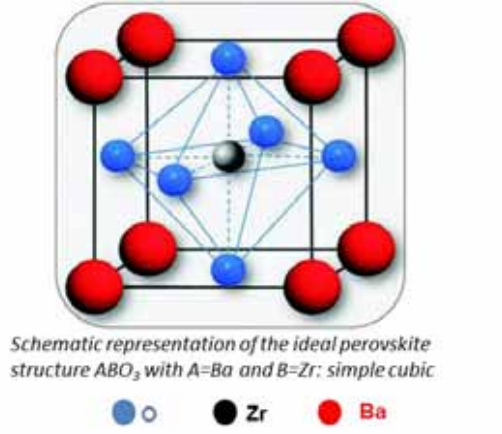
Materials

Choice of classical perovskite: (Ba, Ce)-based materials

Electrolyte

Compromise between the chemical (CO_2) tolerance of $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ and good conductivity of $BaCe_{0.9}Y_{0.1}O_{3-\delta}$

➔$BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ BCZY81 (+5%wt ZnO as sintering aid)

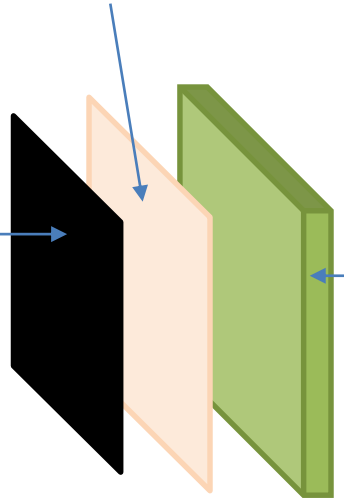


Schematic representation of the ideal perovskite structure ABO_3 with A=Ba and B=Zr: simple cubic

Bilayer air electrode

Composite BCZY81 / BSCF

+ $Ba_{0.5}Sr_{0.5}Co_{0,8}Fe_{0.2}O_{3-\delta}$



Hydrogen electrode

Cermet NiO-BCZY81 (60/40%wt)

Use of the electrolyte material into the electrodes to reduce mechanical stress and improve the chemical compatibility

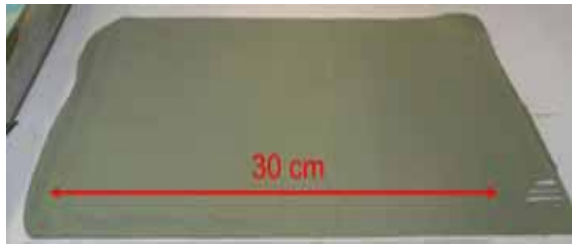
All these products can be manufactured by industrials at kg scale!

Processing

H_2 electrode-supported cells: planar configuration using industrial processes

Wet chemical routes: tape casting and screen printing ➔ easy to transfer and low cost

H_2 electrode slurry

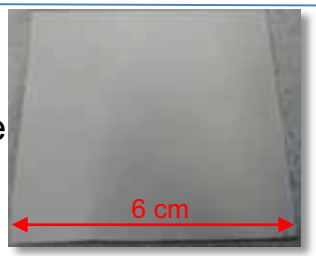


Casting of the slurry + drying step

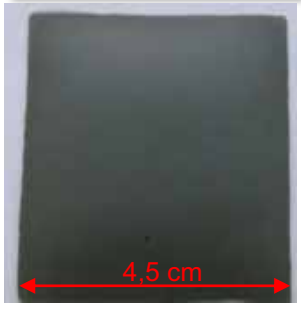
Crude samples are cut and pre-sintered (1100°C)

H_2 electrode substrate

Screen-printing of the electrolyte

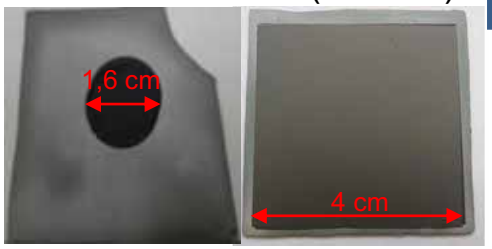


Co-sintering step at 1400°C (25% shrinkage)

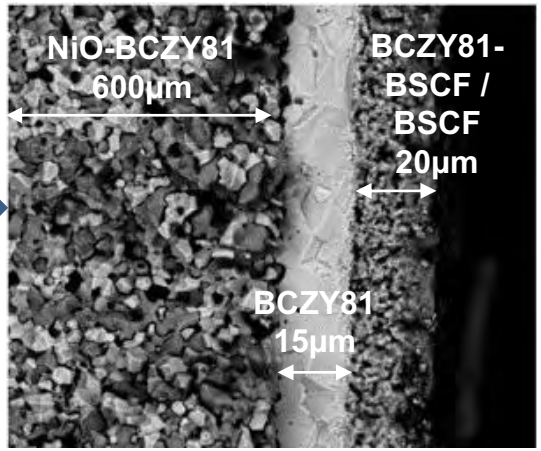


Manufacture of 20cm² PCC cells with desired microstructure

Screen-printing and firing of the air electrode (1100°C)



SEM analysis



M. Marrony, M. Ancelin, G. Lefèvre, J. Dailly, "Elaboration of intermediate size planar proton conducting solid oxide cell by wet chemical routes: A way to industrialization", Solid State Ionics, 275 (2015) 97-100.

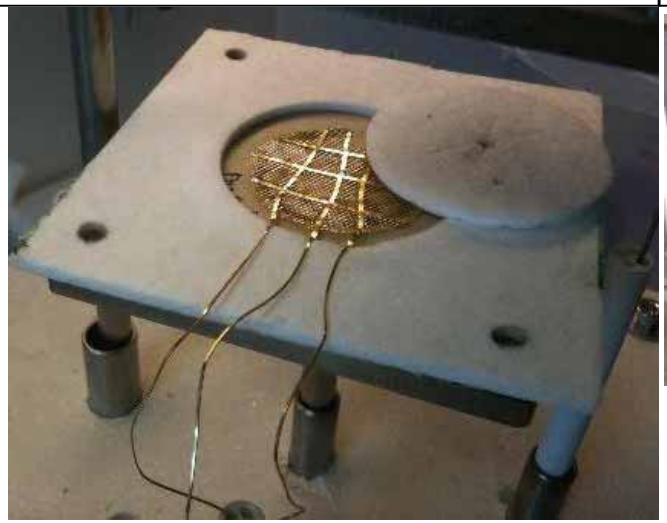
Reversibility & Reliability

Reversibility & Reliability

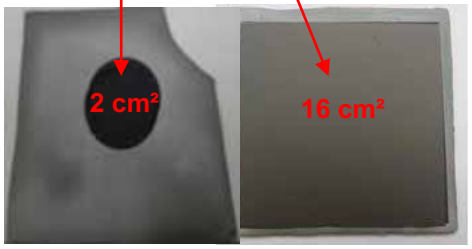
Experimental conditions

Test bench	Gases

Measurement performed in a non-sealed Fiaxell open flange test bench



Current collectors: gold grids ϕ2 and 10cm²



Compressed air from air laboratory Air compressor

Hydrogen produced in the lab PEM electrolyser

Gases are not humidified. (except air in electrolysis)

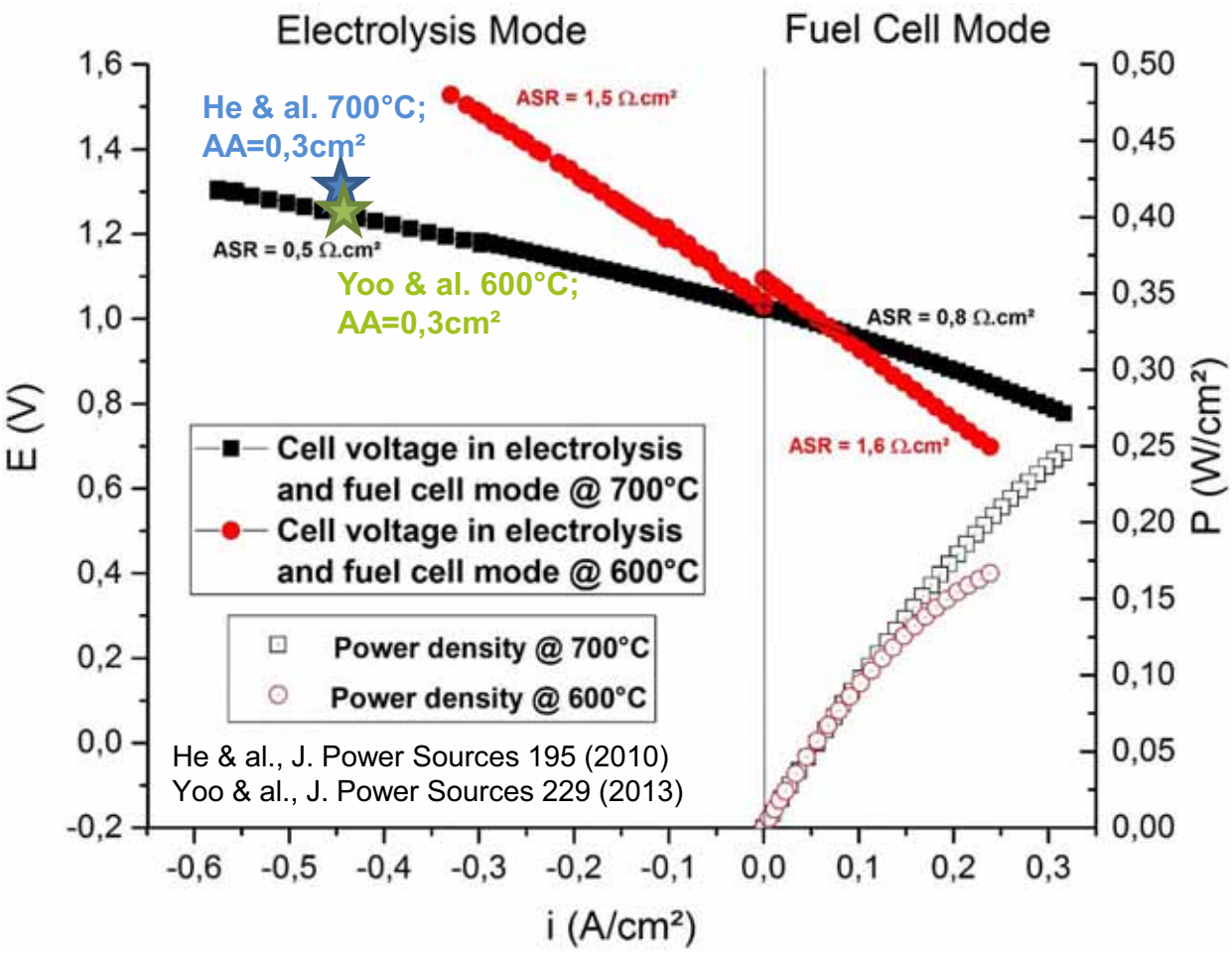
Reversibility & Reliability

Evaluation of performances

BSCF / BCZY-BSCF
BCZY
NiO-BCZY

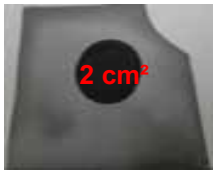
PCFC			
T (°C)	AA (cm²)	OCV (V)	P @ 0,8V (mW/cm²)
600	2	1,09	145
700	10	1,03	235

PCEC			
T (°C)	AA (cm²)	OCV (V)	i @ 1,2V (A/cm²)
600	2	1,04	-0,1
700	10	1,02	-0,35



Reversibility & Reliability

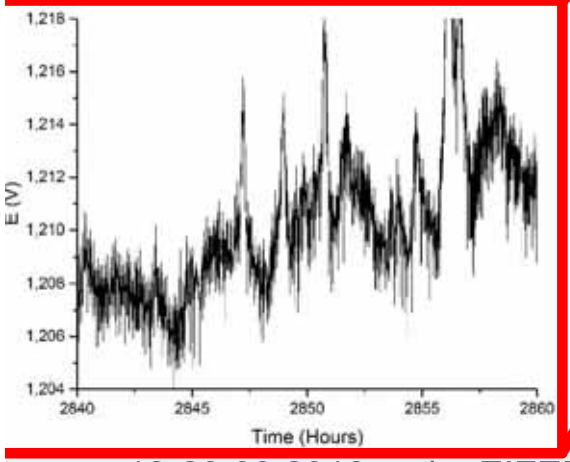
Reversibility at 600°C

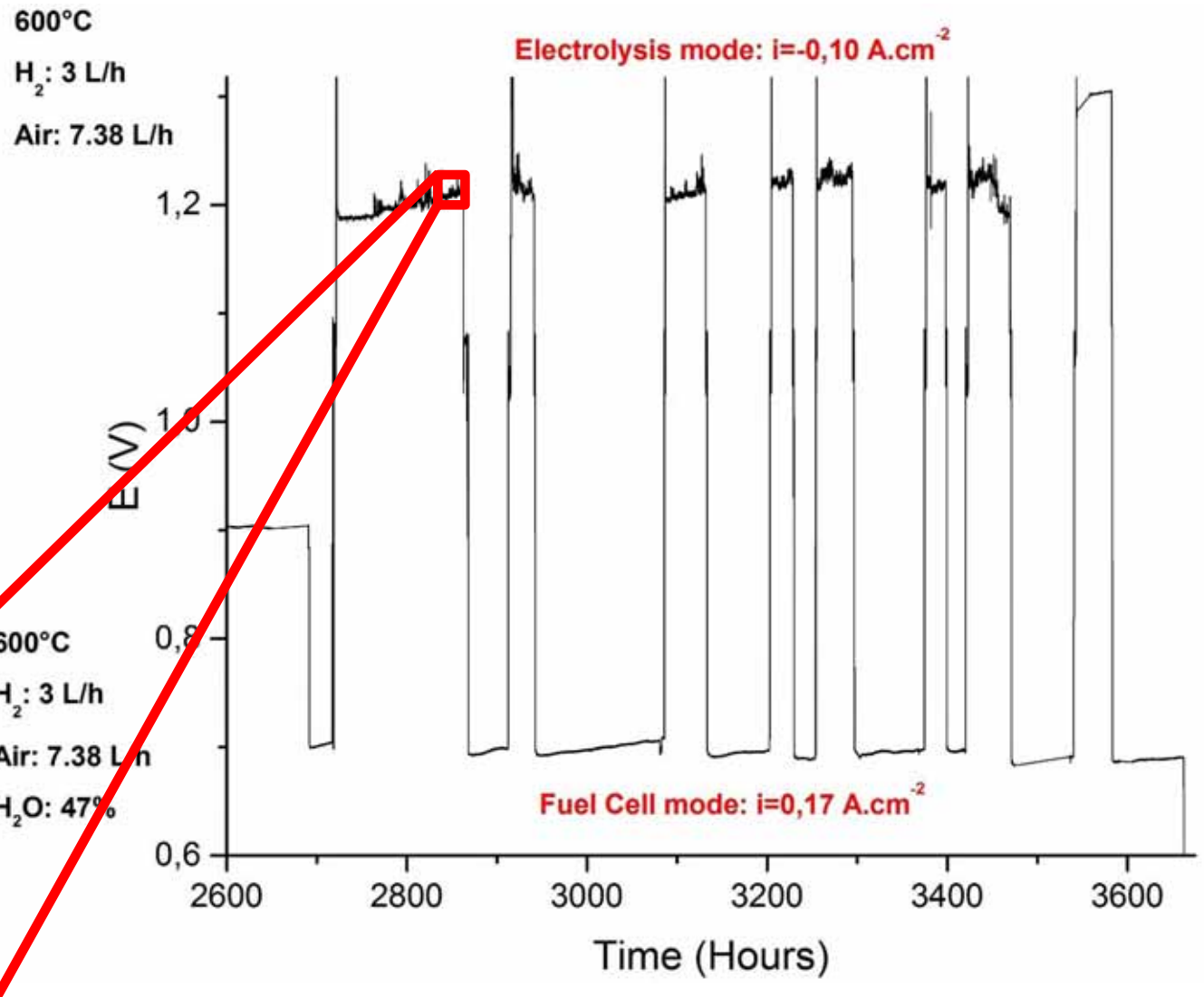


Non-optimized conditions

PCFC mode:	PCEC mode:
Air = 7,38 L/h	Air = 7,38 L/h
H_2 = 3 L/h	H_2 = 3 L/h
FE = 5%	SC = 3%

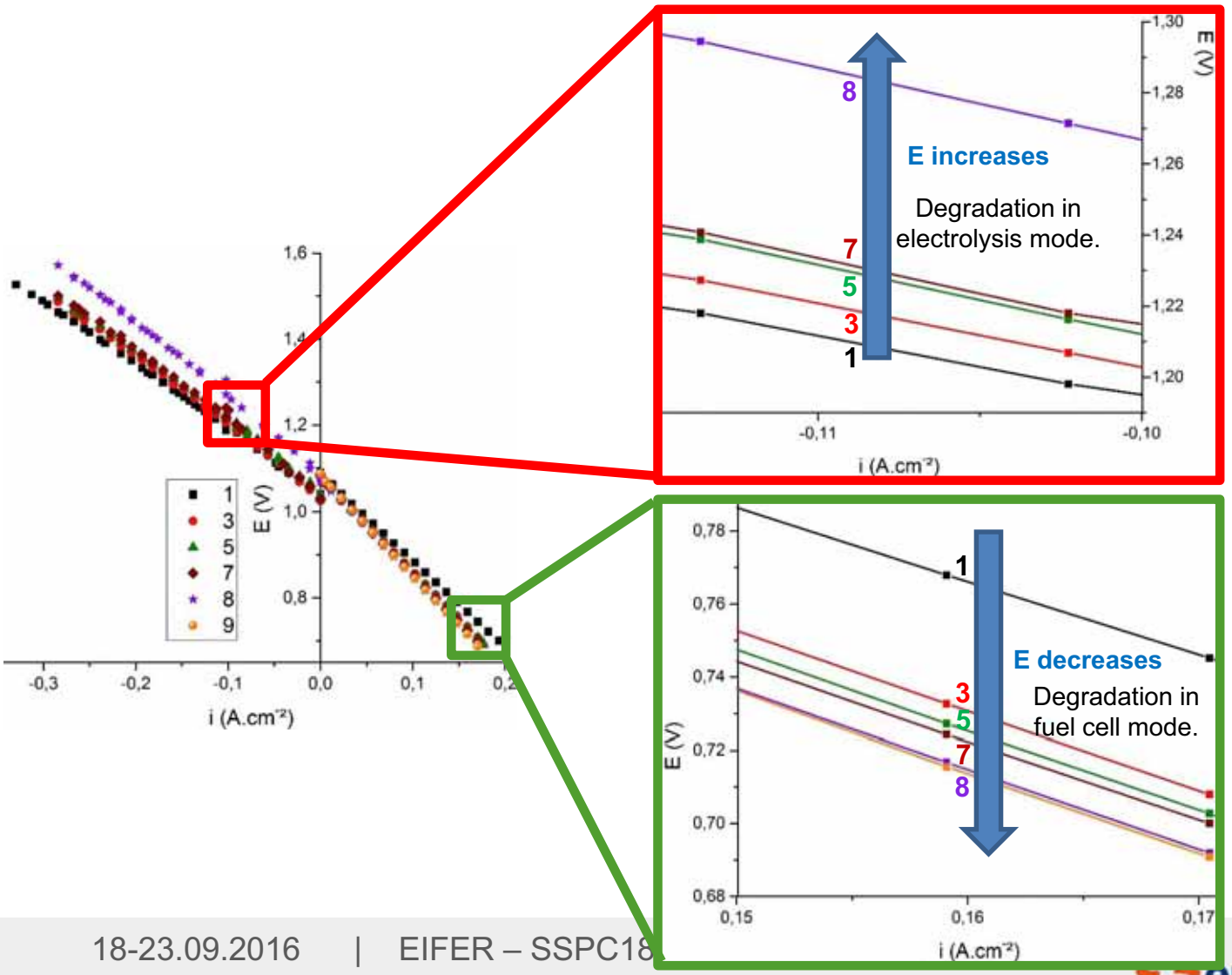
Perturbations in electrolysis mode: water supply not stable





Reversibility & Reliability

Reversibility at 600°C ➔ Comparison of IV-curves



Electrical degradation under both Electrolysis and Fuel Cell conditions
➔ Logical behaviour

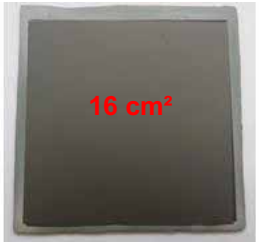
Voltage instability lead to high degradation rate:

➔ Optimisation of water supply
➔ Periodicity of cycles

Reversibility & Reliability

Reversibility at 700°C

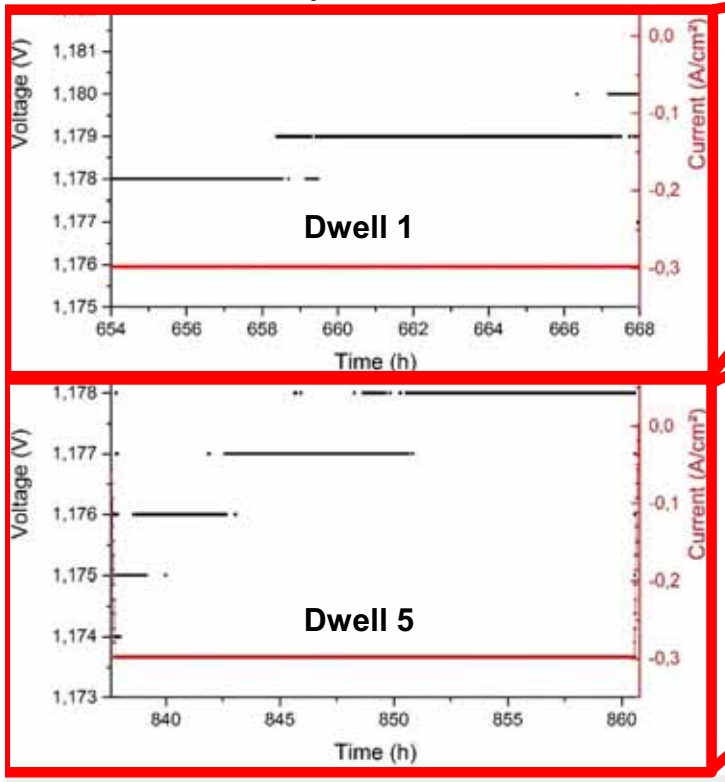
Each cycle ~ 20 hours
Total ~ 260 hours

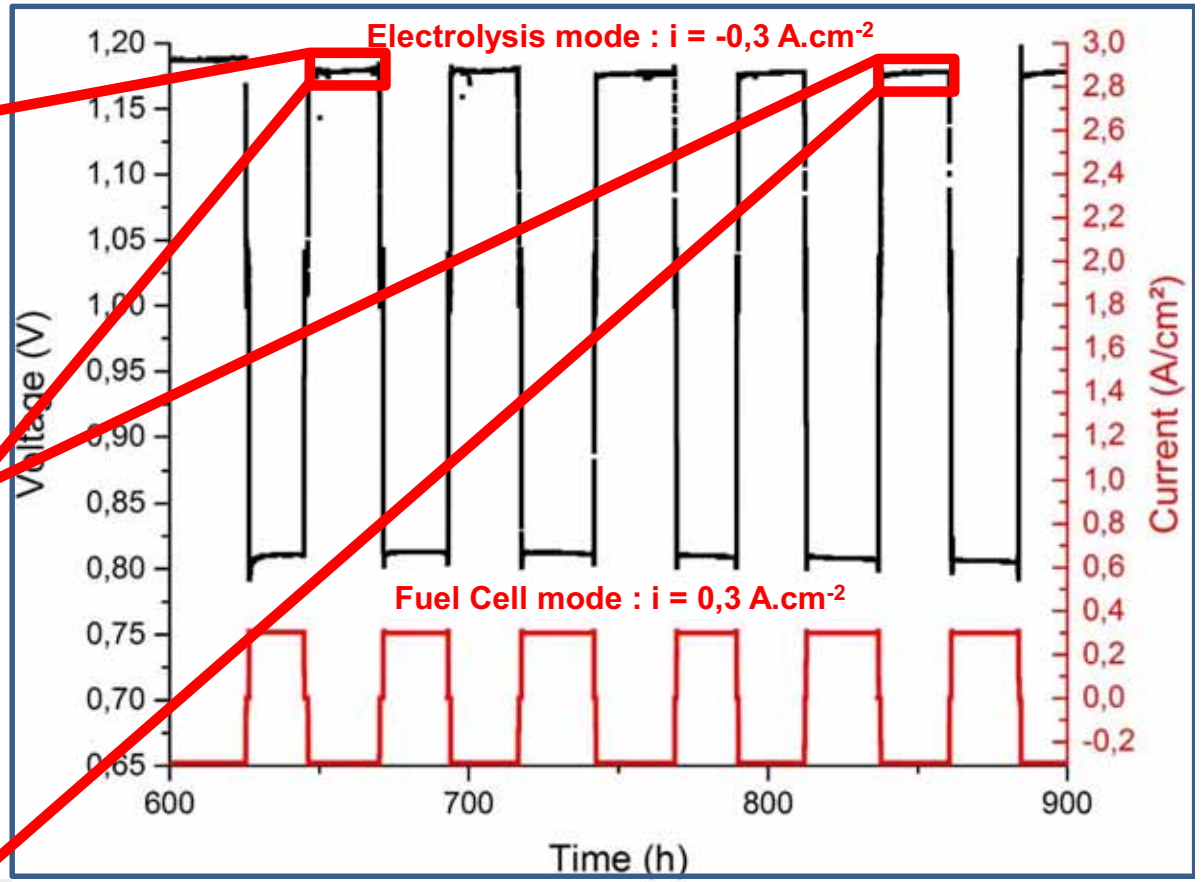


PCFC mode:
Air = 18,66 L/h
H_2 = 4,38 L/h
Fuel Efficiency= 30%

PCEC mode:
Air = 18,66 L/h; H_2O = 7%vol.
H_2 = 3 L/h
Steam conversion= 84%

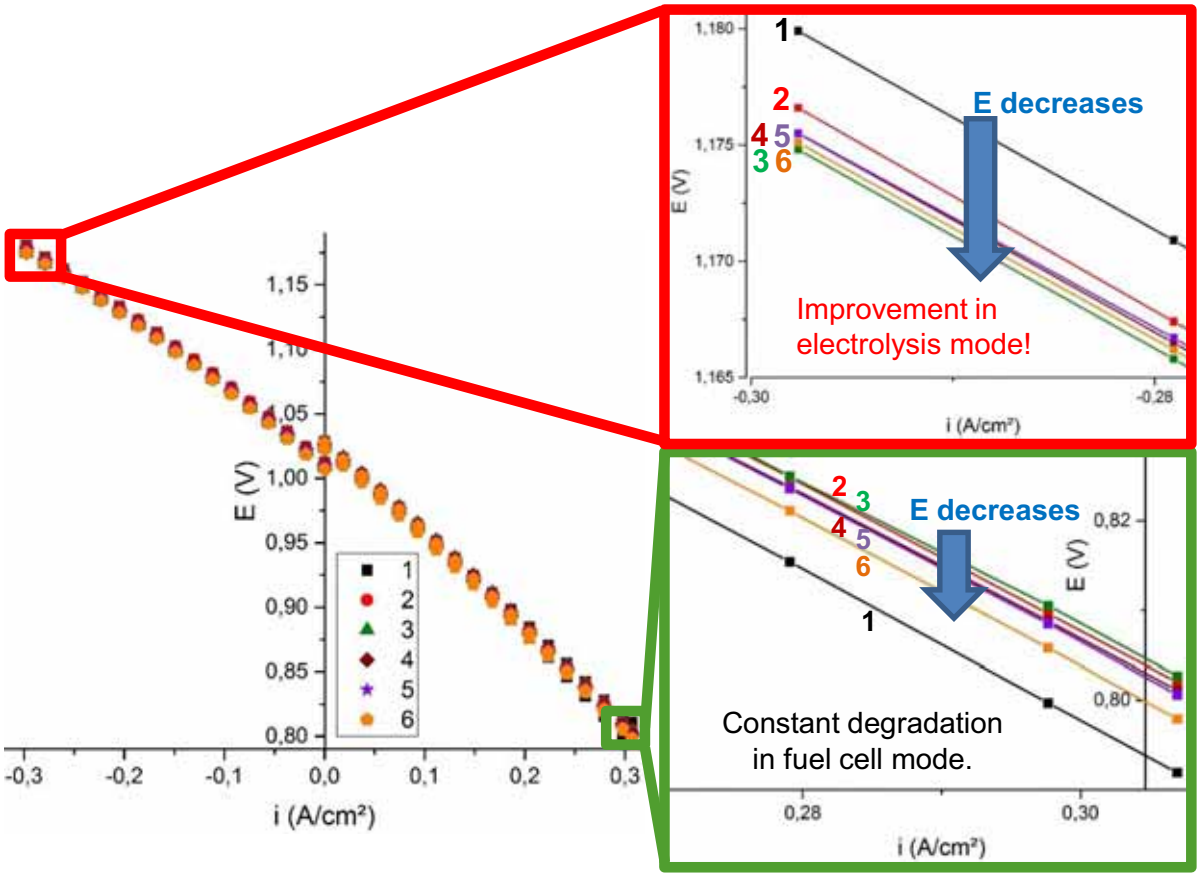
Improvement of the water supply: good stability of the voltage during the electrolysis dwells!

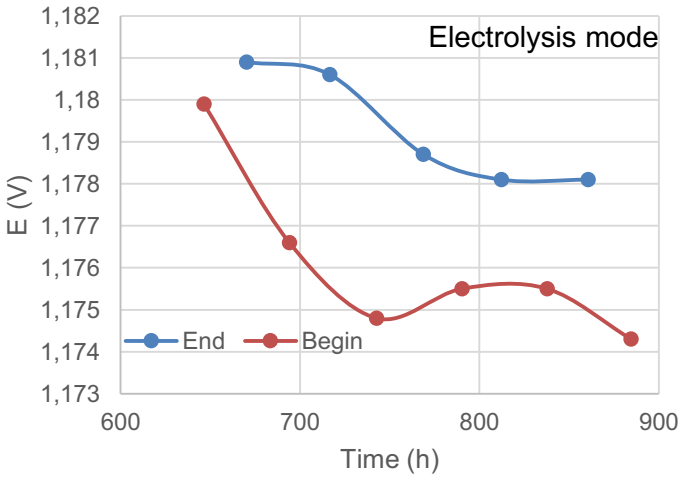




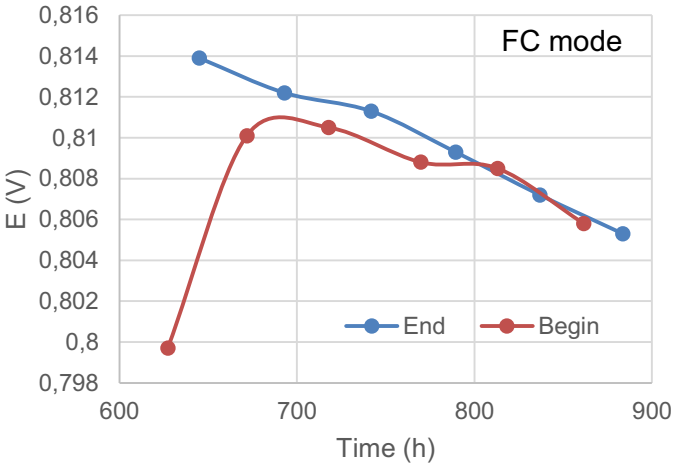
Reversibility & Reliability

Reversibility at 700°C ➔ Comparison of IV-curves





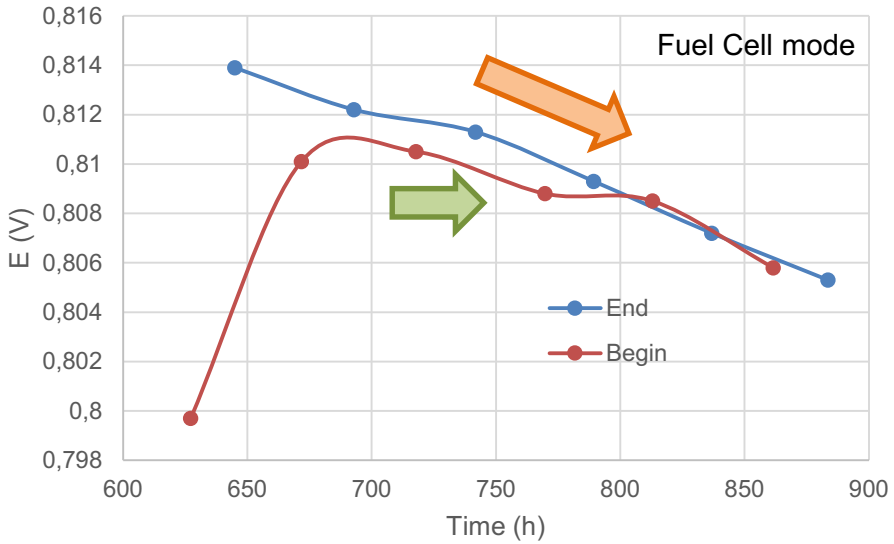
Different behaviours…

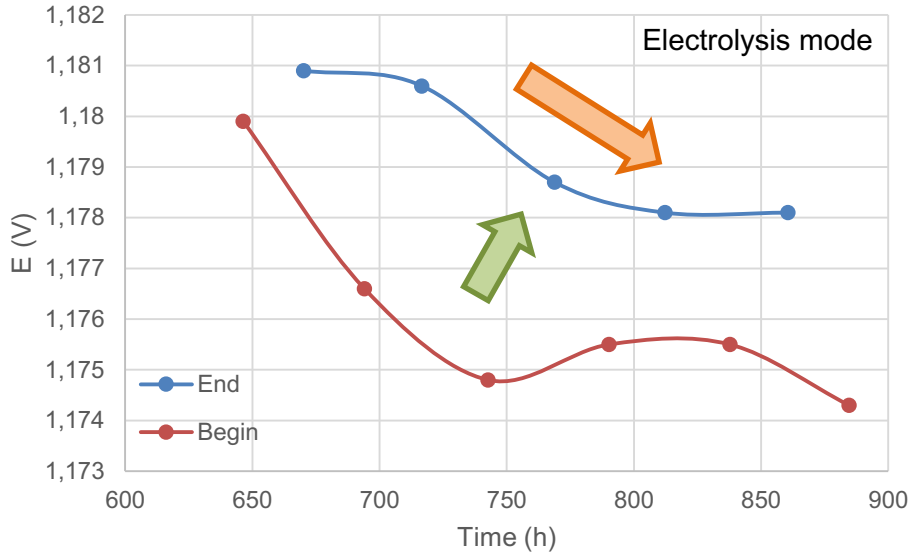


Reversibility & Reliability

Reversibility at 700°C ➔ Evolution of E (V)

Global evolution of E Evolution of E during the step





<u>PCFC mode:</u>

-Electrical degradation comes from the reversibility

<u>PCEC mode:</u>

-Electrical degradation comes from the galvanostatic period
-Kind of recovery between each cycle

Hypothesis: link with the amount of water?
➔High steam conversion: higher stress
➔Circulation of water vapor: microstructure
➔Stability of materials under polarization/RH

Reversibility & Reliability

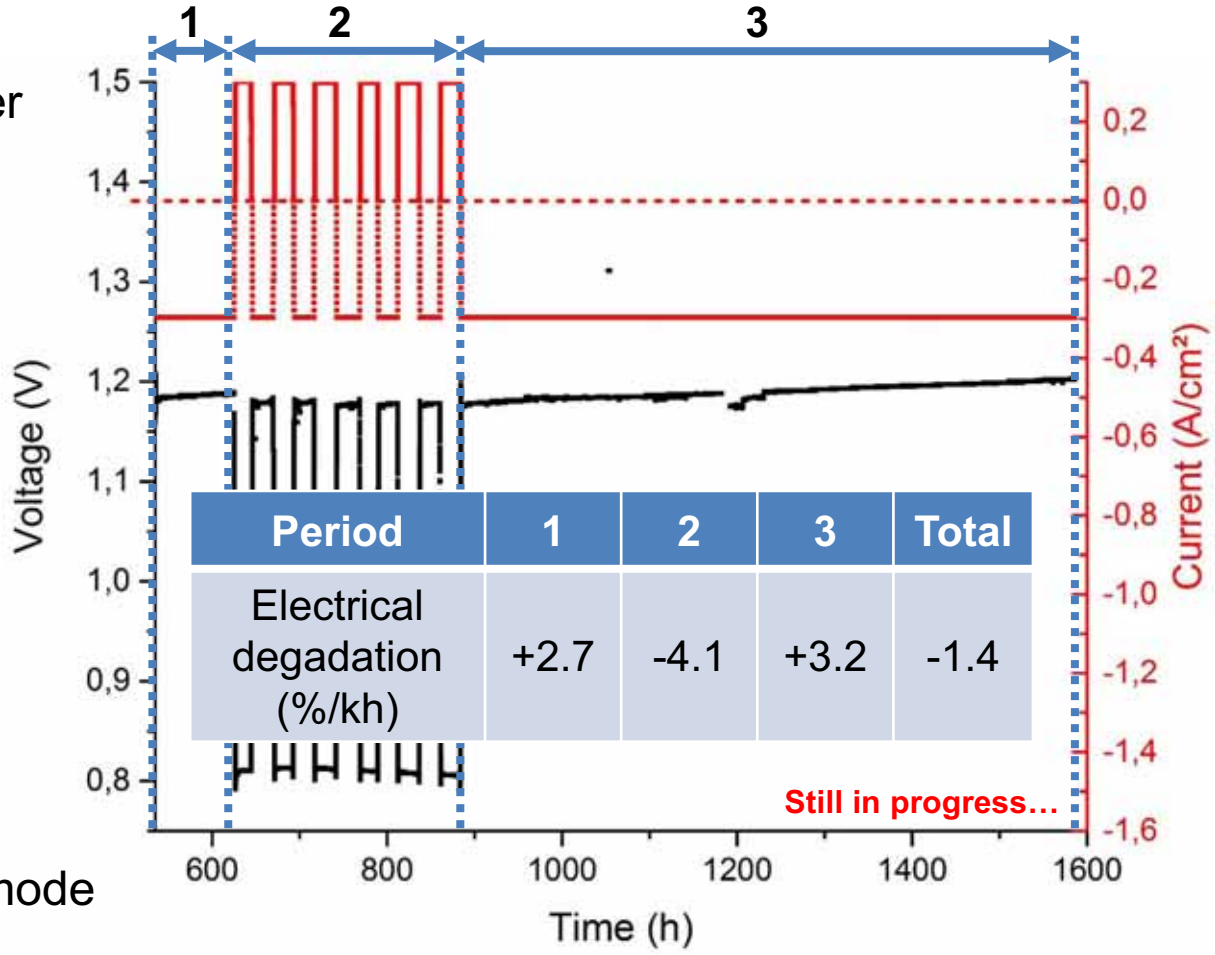
Reversibility at 700°C ➔ Impact on the cell behavior

Measurement of the electrical degradation before / under / after the reversibility period

➔Electrical degradation is higher under electrolysis-galvanostatic than under reversible condition

➔Correlation with previous conclusions: electrolysis-galvanostatic periods are harder for the cell

Insertion of period in Fuel Cell mode as recovery period…?



Period	1	2	3	Total
Electrical degadation (%/kh)	+2.7	-4.1	+3.2	-1.4

Conclusions & Prospects

Conclusions & Prospects

Conclusions

- Combination of well-known materials and processings: elaboration of good quality cells (20cm²)
- Good electrochemical performances: P=235mW/cm², E=0,8V @700°C
- Dynamic reversible concept with low electrical degradation -1.4%/kh
  - > Quality of water vapor is of great influence on the electrical degradation (voltage instability)
  - > Improvement of electrolysis-galvanostatic conditions

Prospects

Materials & Processing

- Advanced materials to improve the performances: $BaCe_{1-x-y}Z_x(Y,Yb)_yO_{3-\delta}$,$(Sm, Ba)_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$
- Up-scaling: improve the manufacture of 50 cm²-sized PCC: SSRS, nano-infiltration

Reversibility & Reliability

- Improve the stability under electrolysis/regenerative profile:
  - > Influence of water: steam conversion, microstructure, chemical stability under i/RH
- Impedance measurements to better understand the behaviour: focus on the air electrode side…
- Post-Mortem analysis: link between microstructure and electrical degradation

Thank you…

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