INSTITUTO DE TECNOLOGÍA QUÍMICA

Anode performance based on high temperature proton conducting electrolysers and a multitube module construction

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idhea

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Electra

CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

UNIVERSITAT POLITÈCNICA DE VALÈNCIA

Outline

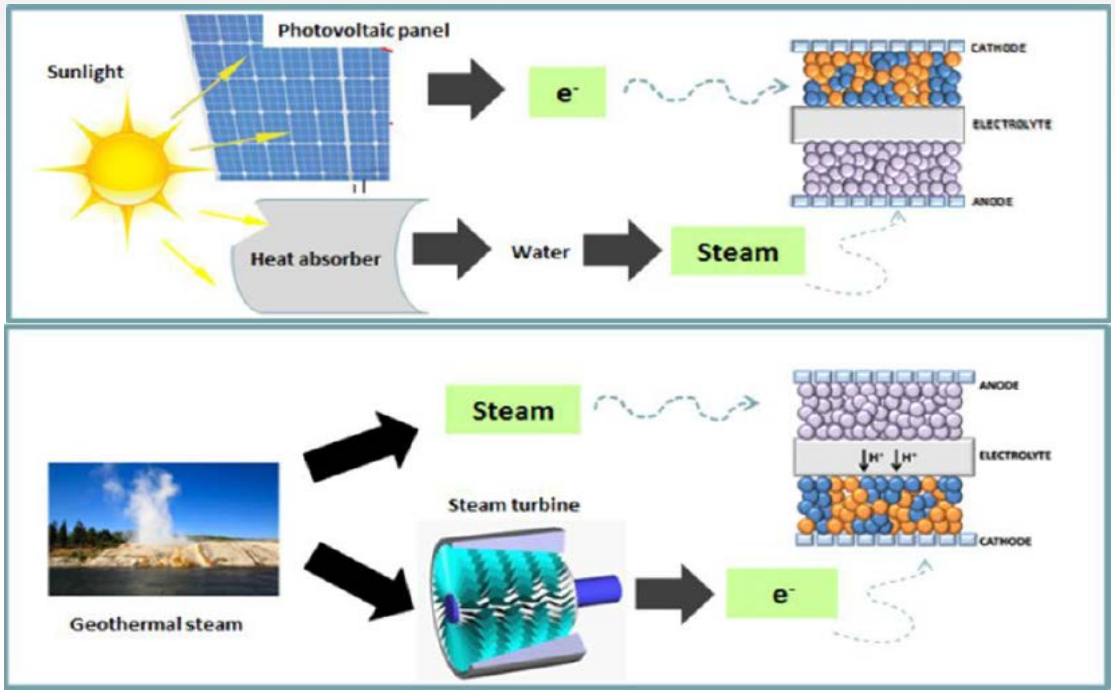
- ✓ Introduction
- ✓ Installation of the high pressure set-up
- ✓ Compatibility and stability tests of the selected anode material
  - Under 3 bars air + H_2O (75% steam) at 700 °C for 72 h
- ✓ Symmetrical cells EIS:
  - LSM/BCZY27 (50/50 and 60/40 vol.%)
    - Study by changing pH_2O , pO_2 and p_T
    - Infiltrations (Pr-Ce, Pr, Ce, Zr)
- ✓ Multitube module design
- ✓ Conclusions

Introduction

Electra

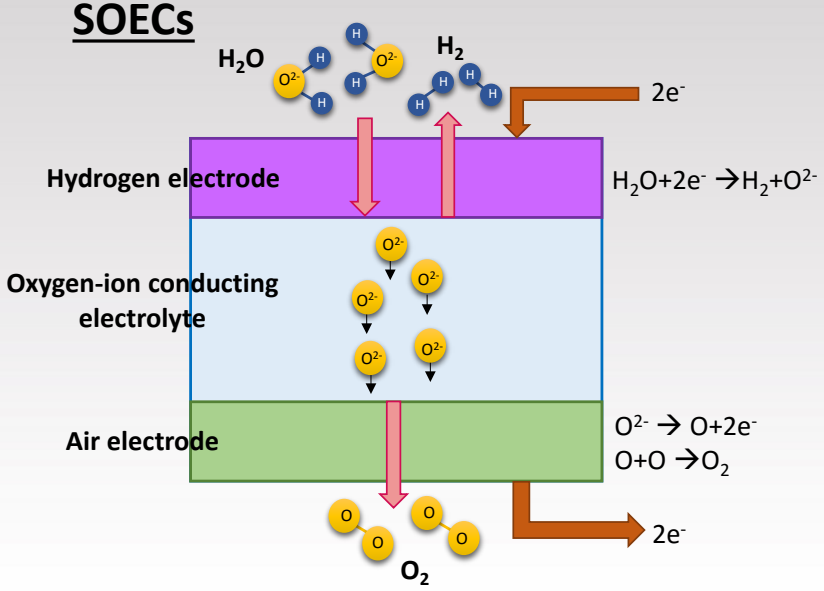
Introduction

- The ELECTRA project:
  - Scalable fabrication of tubular HTE cells with proton conducting electrolytes for production of H_2 from steam and renewable sources (solar, wind, geothermal, etc.)



Introduction

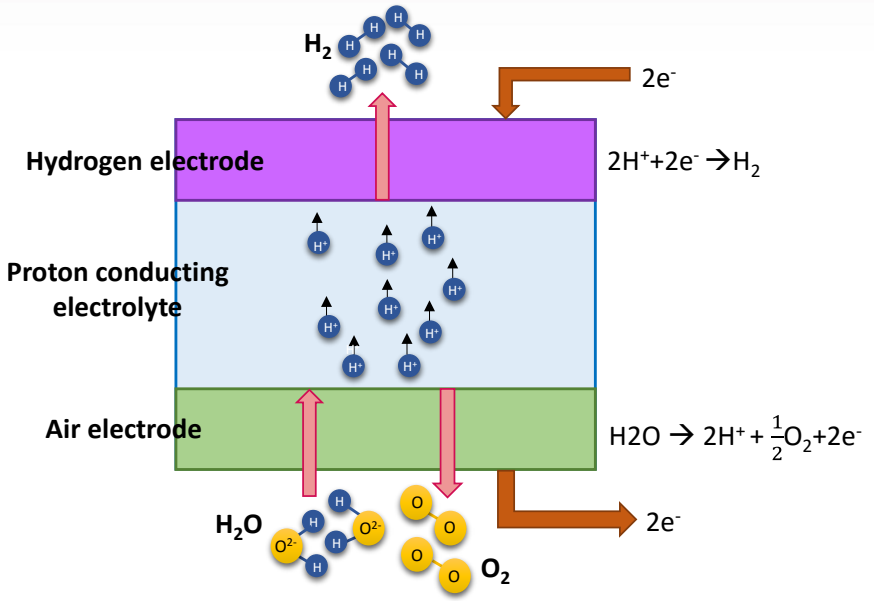
SOECs



- Utilise steam and heat procedures ✓
- Produce wet H_2 ✗
- Delamination of anode ✗
- High operation temperatures (>800 °C) ✗
- Technology more investigated ✓

PCECs

- Utilise steam and heat procedures ✓
- Produce dry H_2 directly ✓
- No anode delamination ✓
- Low operation temperatures (<700 °C) ✓
- Technology less investigated ✗
- Materials still in development ✗

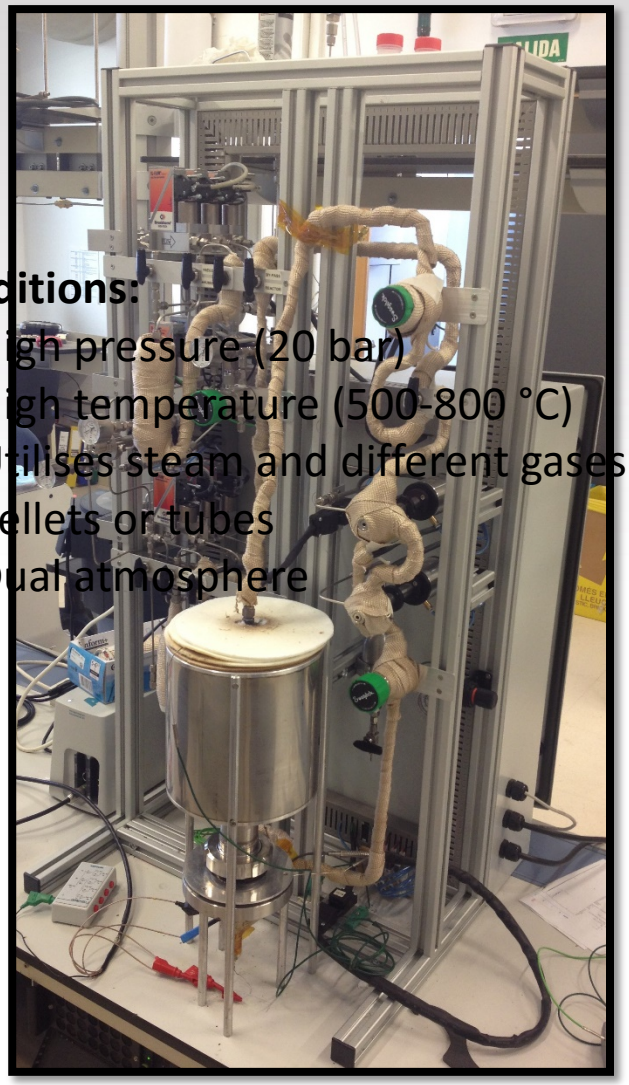


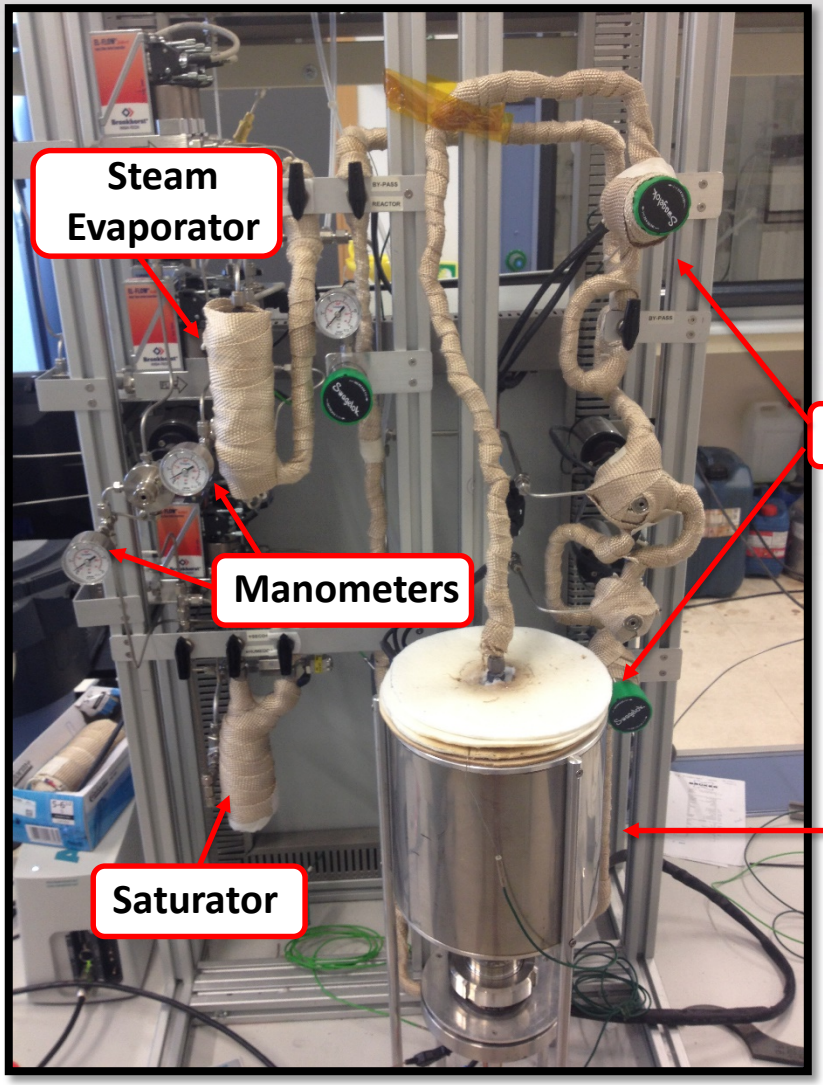
Installation of the high pressure set up

Installation of the high pressure set up

Conditions:

- High pressure (20 bar)
- High temperature (500-800 °C)
- Utilises steam and different gases
- Pellets or tubes
- Dual atmosphere



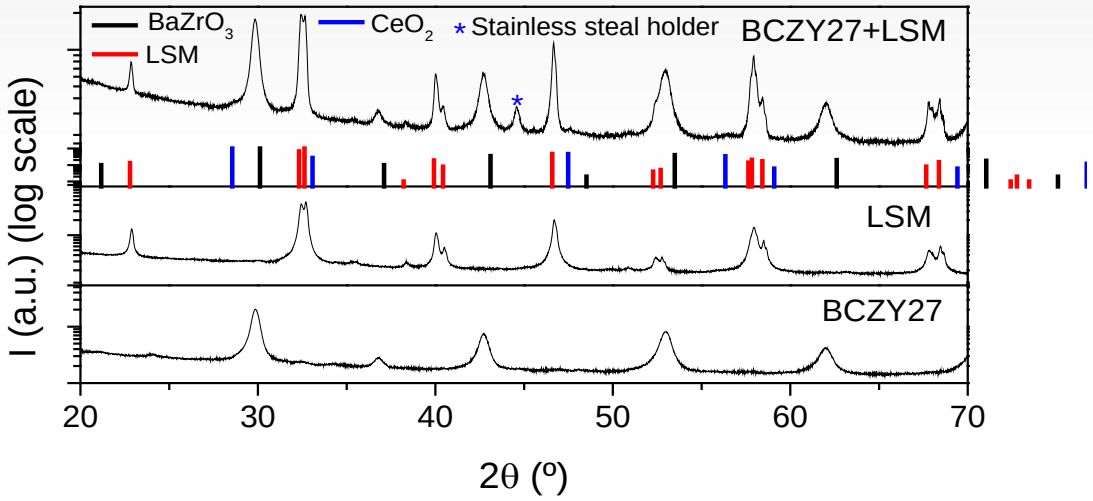


Compatibility and stability tests of the selected anode material

Compatibility tests with BCZY27

Electrolyte material	Possible Steam Electrode material	Testing T, t (dry)
BCZY27: $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_3$	LSM: $La_{0.8}Sr_{0.2}MnO_3$	1100 °C/5 h

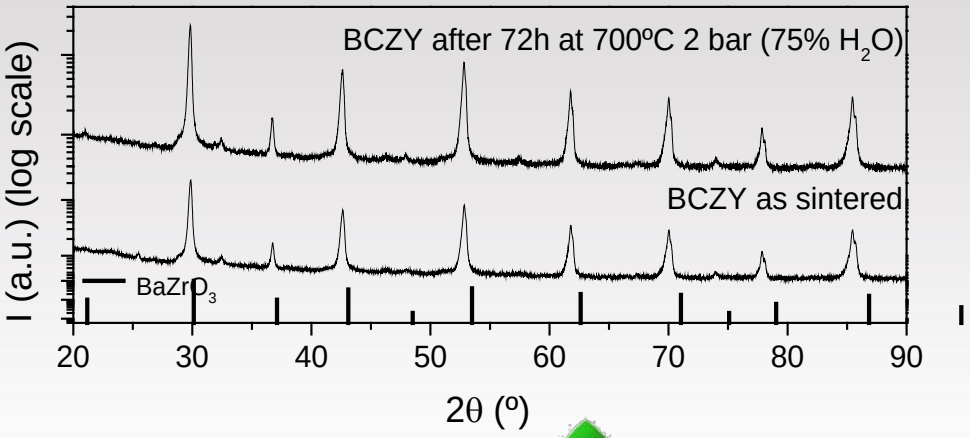
LSM: $La_{0.8}Sr_{0.2}MnO_3$

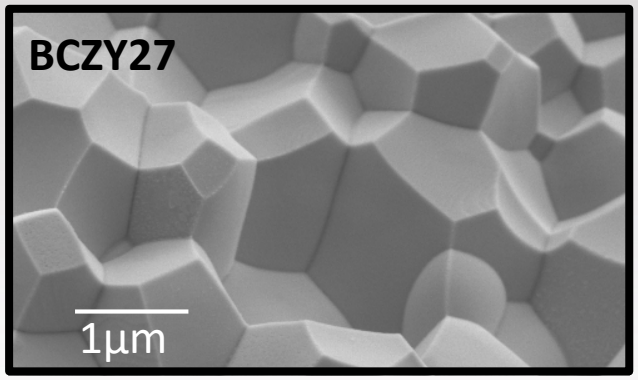


CeO_2 segregation also observed in BCZY27 after long times or higher sintering T

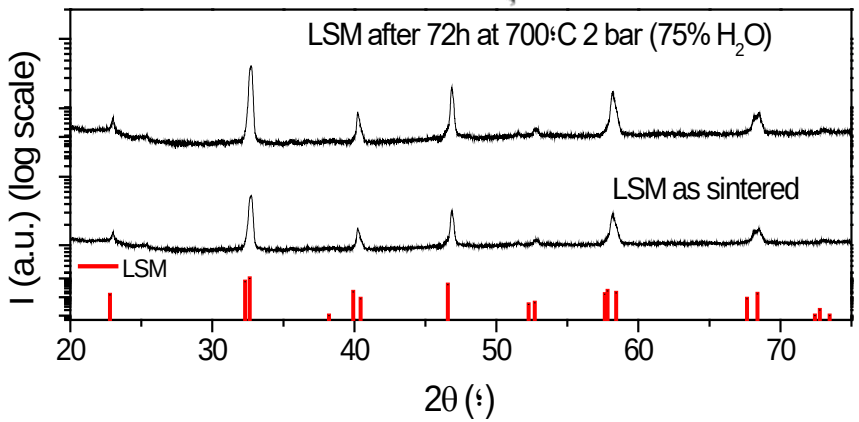
Stability tests under operating conditions

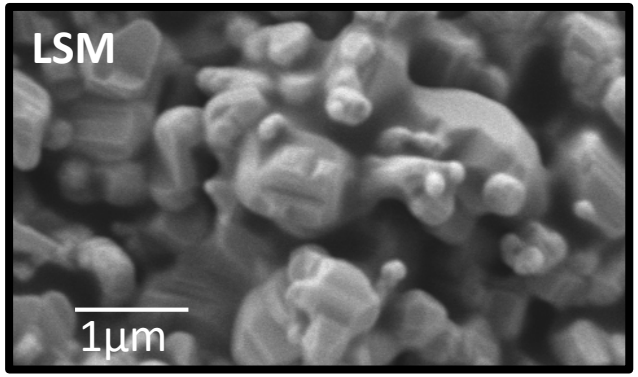
BCZY: $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_3$





LSM: $La_{0.8}Sr_{0.2}MnO_3$





3 bar air + H_2O (75% steam) at 700 °C for 72 h

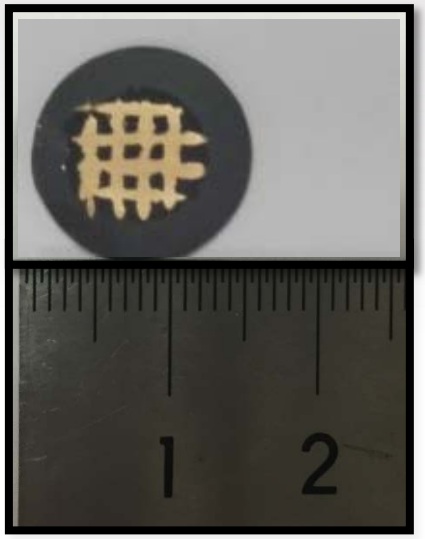
Symmetrical cells EIS

Symmetrical cells EIS

- **LSM/BCZY27**
  - ✓ Infiltrations:

1. Pr – Ce (50 % vol.) [2M] 850 °C/2h
2. Pr [2M] 850 °C/2h
3. Ce[2M] 850 °C/2h
4. Zr [2M] 850 °C/2h

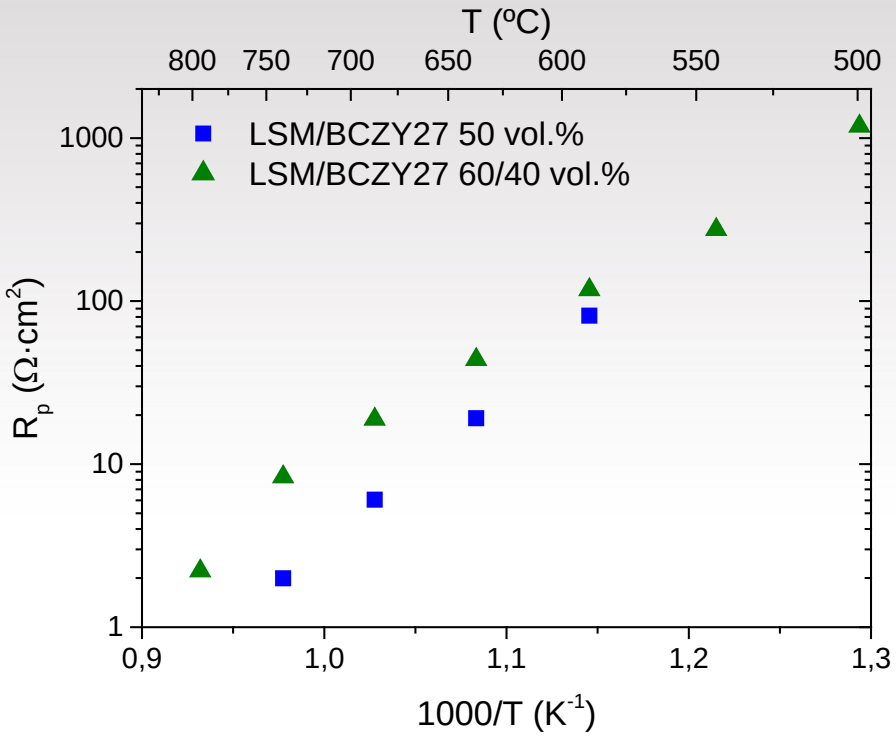
Electrolyte: BCZY27
Electrode: LSM/BCZY27 50 vol. %
Current collector: Au

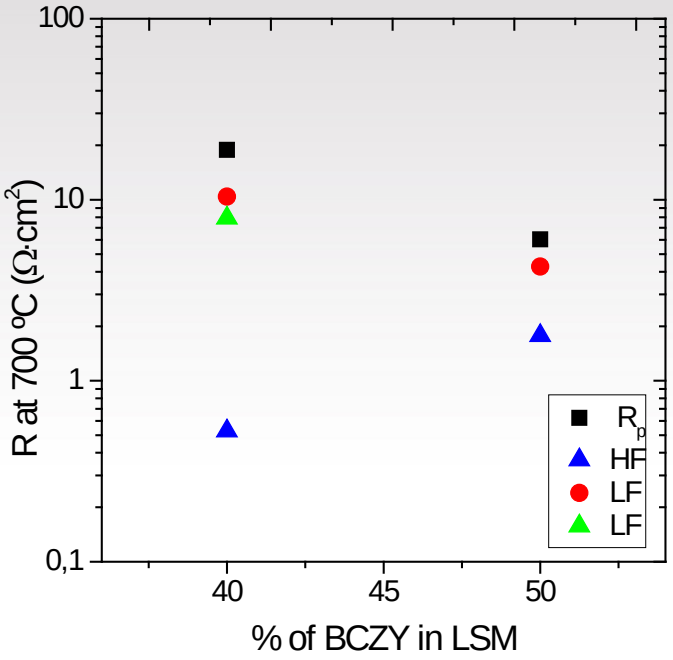


$Ø_{electrolyte}$ = 14 mm
$Ø_{electrode}$ = 9 mm
Thickness = 1.6 mm

Symmetrical cells EIS

LSM/BCZY composite

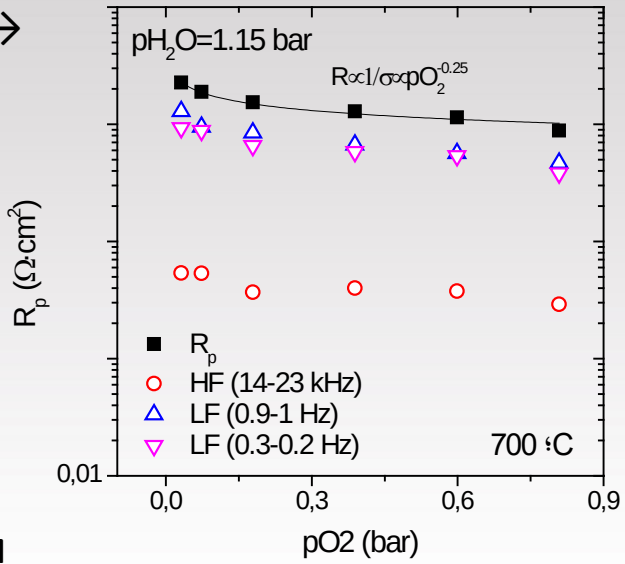


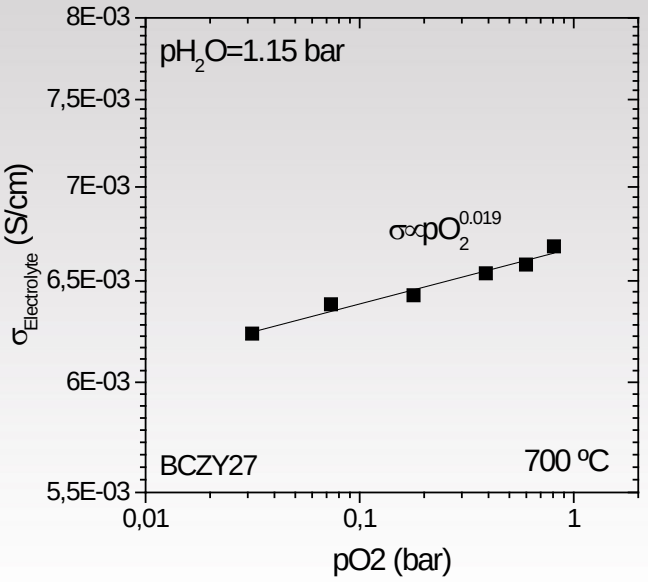


Conditions:
Total P= 3 bar
Steam 75%
3 days

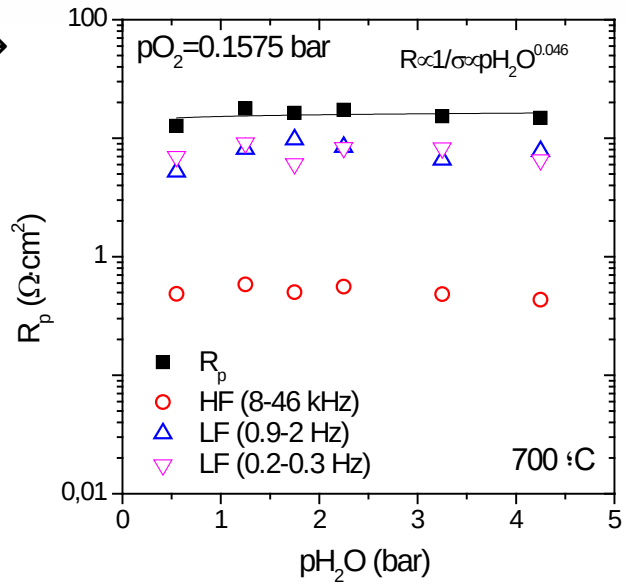
LSM/BCZY study by changing steam pressure, pO_2 and p_T

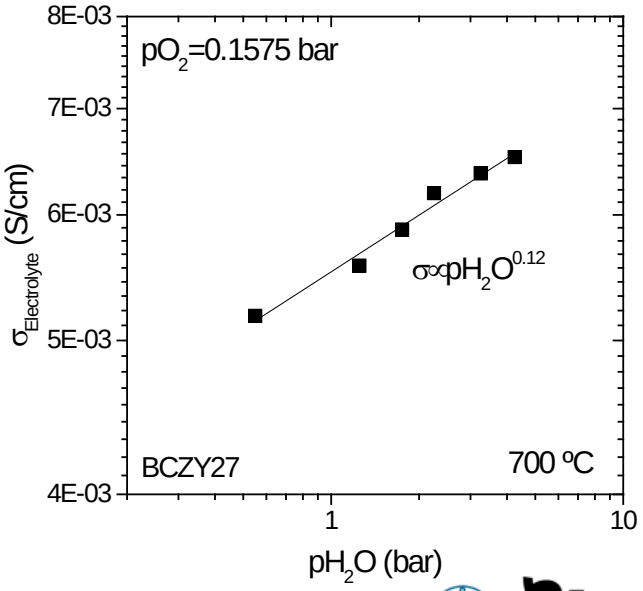
a) $pH_2O \rightarrow$
$pO_2 \nearrow$
$p_t \nearrow$





b) $pH_2O \nearrow$
$pO_2 \rightarrow$
$p_t \nearrow$

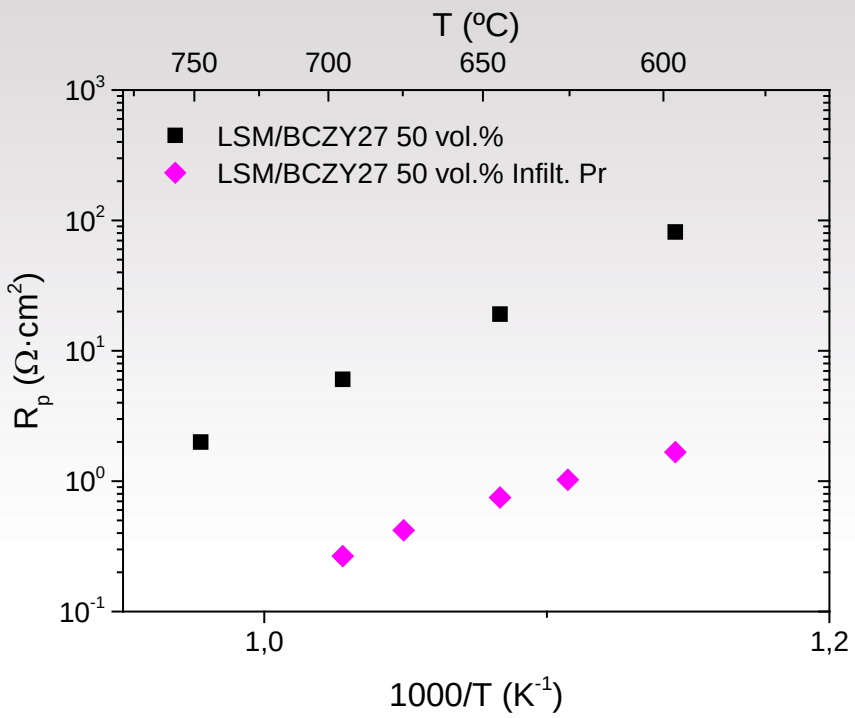




Infiltrations in LSM/BCZY

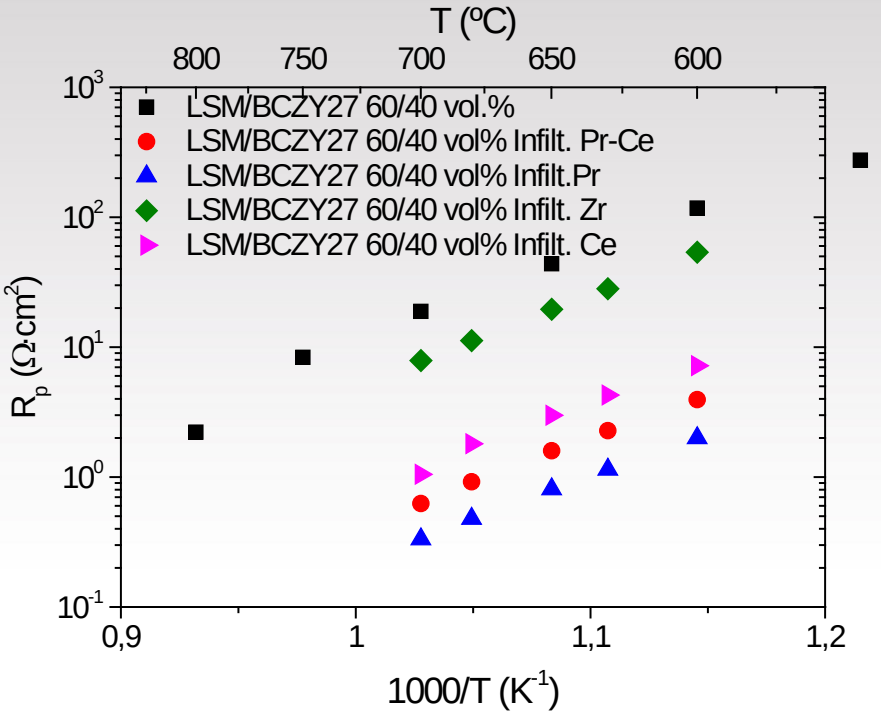
Symmetrical cells LSM/BCZY - Infiltrations

LSM/BCZY 50 vol. %



Infiltration Pr
Rp = 0.27 Ω·cm² at 700 °C

LSM/BCZY 60/40 vol. %



Infiltration Pr-Ce
Rp = 0.64 Ω·cm² at 700 °C

Infiltration Pr
Rp = 0.33 Ω·cm² at 700 °C

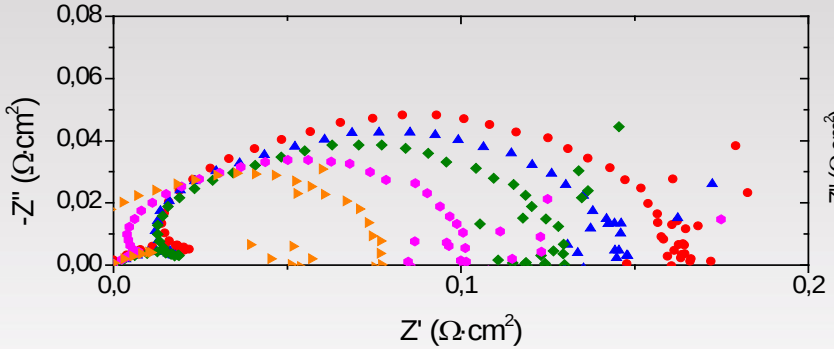
Infiltration Ce
Rp = 1.04 Ω·cm² at 700 °C

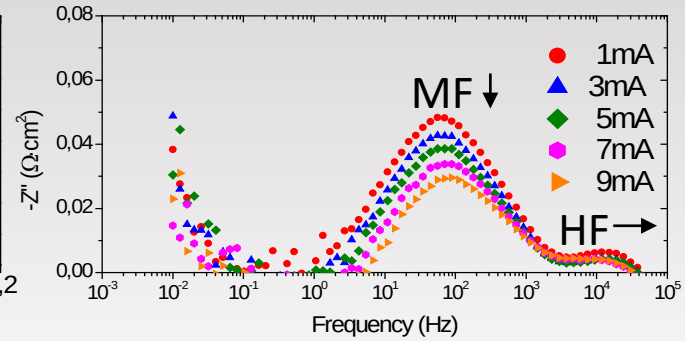
Infiltration Zr
Rp = 7.88 Ω·cm² at 700 °C

Conditions:
Total P= 3 bar
Steam 75%
T = 700 °C

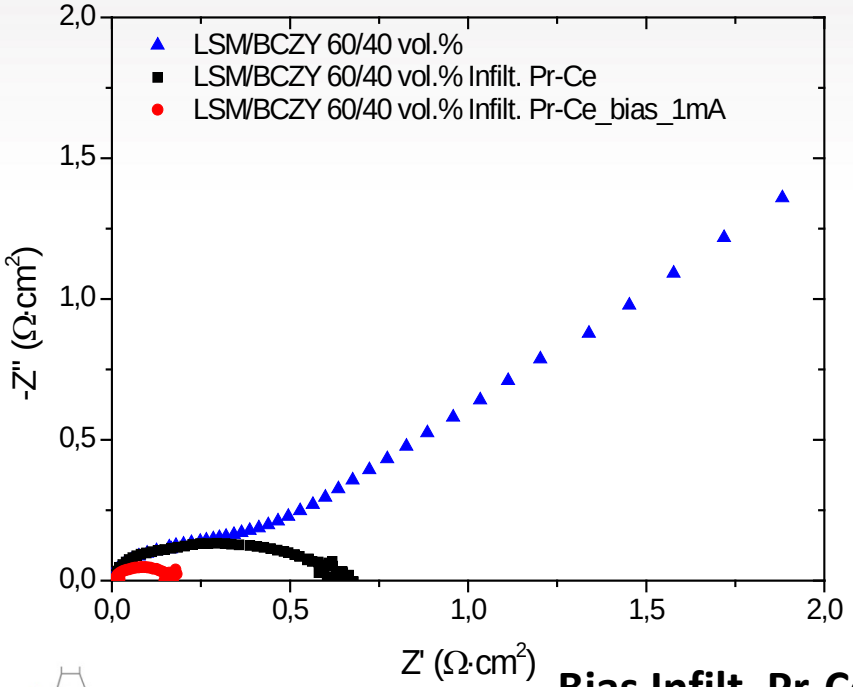
Bias – Infiltrations in LSM/BCZY 60/40 vol. %

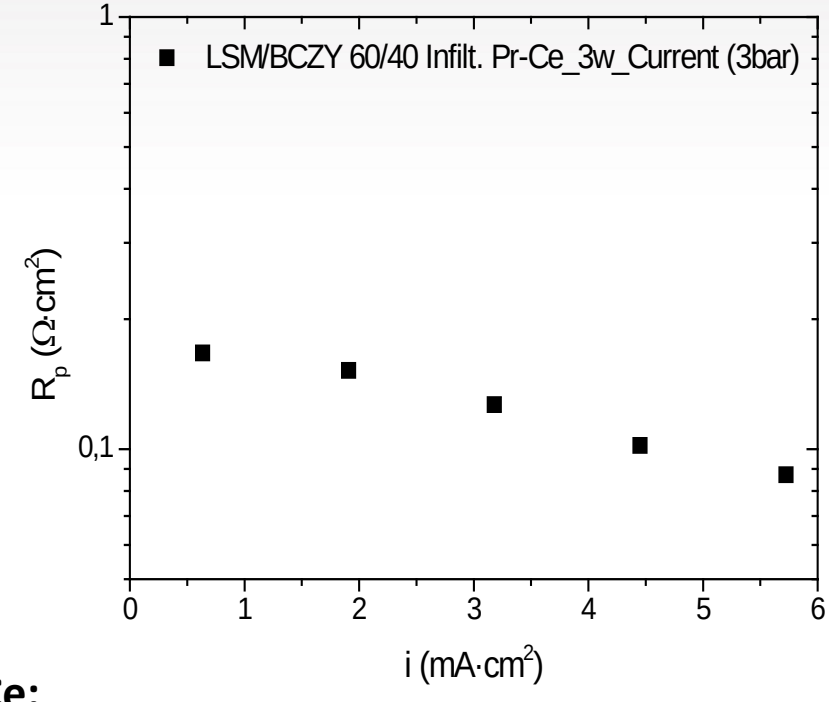
Infiltration Pr-Ce 850 °C in LSM/BCZY 60/40 vol. %





Conditions:
Total P= 3 bar
Steam 75%
T = 700 °C





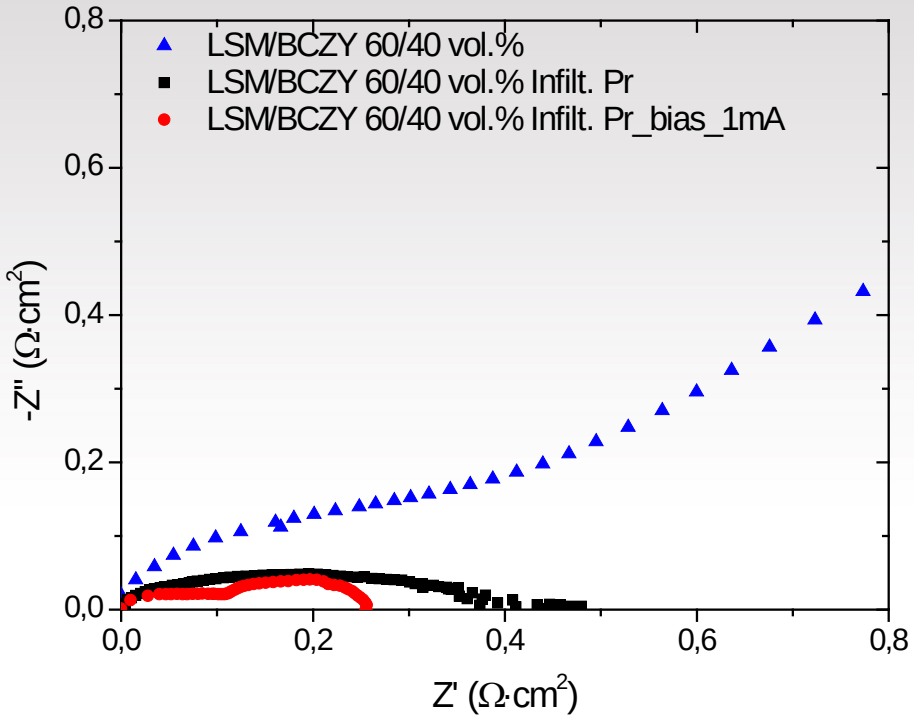
Bias Infilt. Pr-Ce:

i = 0.63 mA/cm² → Rp = 0.17 Ω·cm²

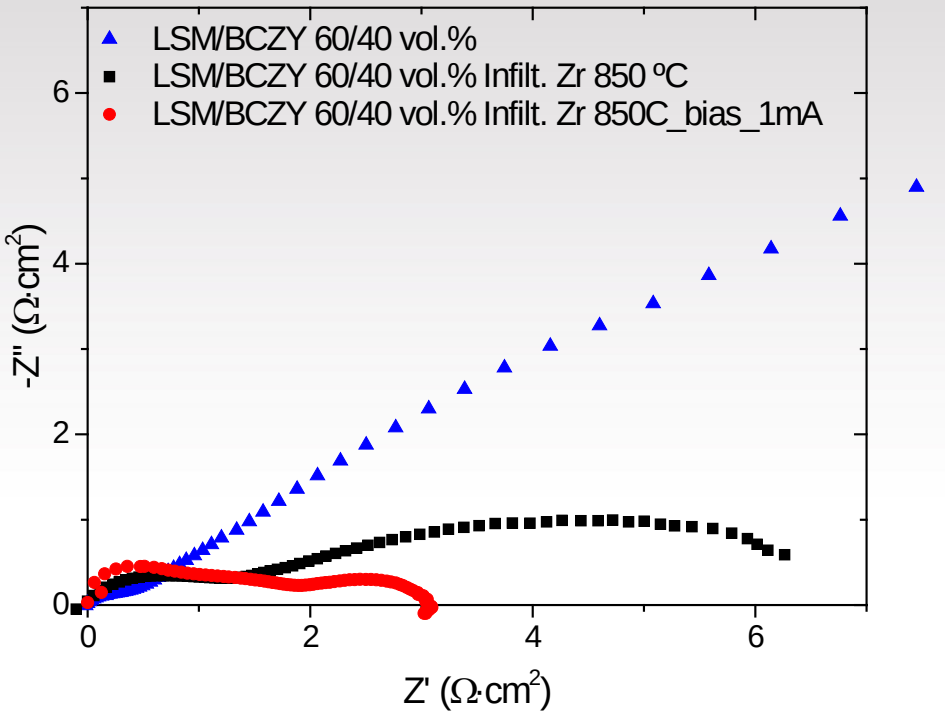
i = 5.7 mA/cm² → Rp = 0.087 Ω·cm²

Bias – Infiltrations in LSM/BCZY 60/40 vol. %

Infiltration Pr 850 °C in LSM/BCZY



Infiltration Zr 850 °C in LSM/BCZY



Bias Infilt. Pr:

i = 0.63 mA/cm² → Rp = 0.27 Ω·cm²

i = 3.2 mA/cm² → Rp = 0.18 Ω·cm²

Bias Infilt. Zr:

i = 0.63 mA/cm² → Rp = 2.53 Ω·cm²

i = 6.99 mA/cm² → Rp = 1.01 Ω·cm²

Conditions:

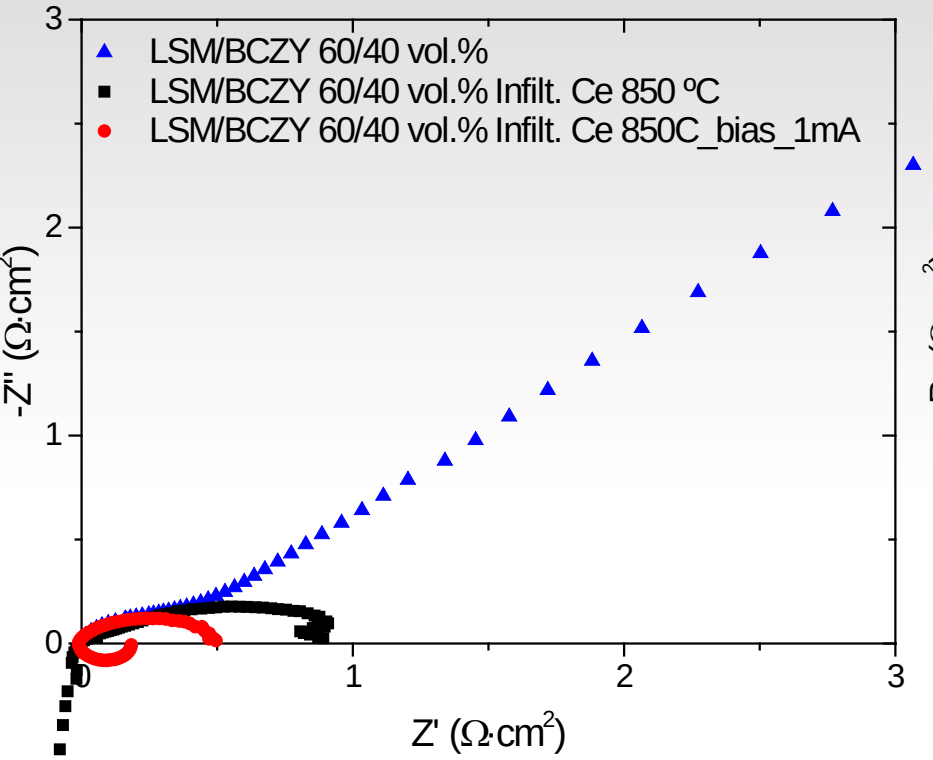
Total P= 3 bar

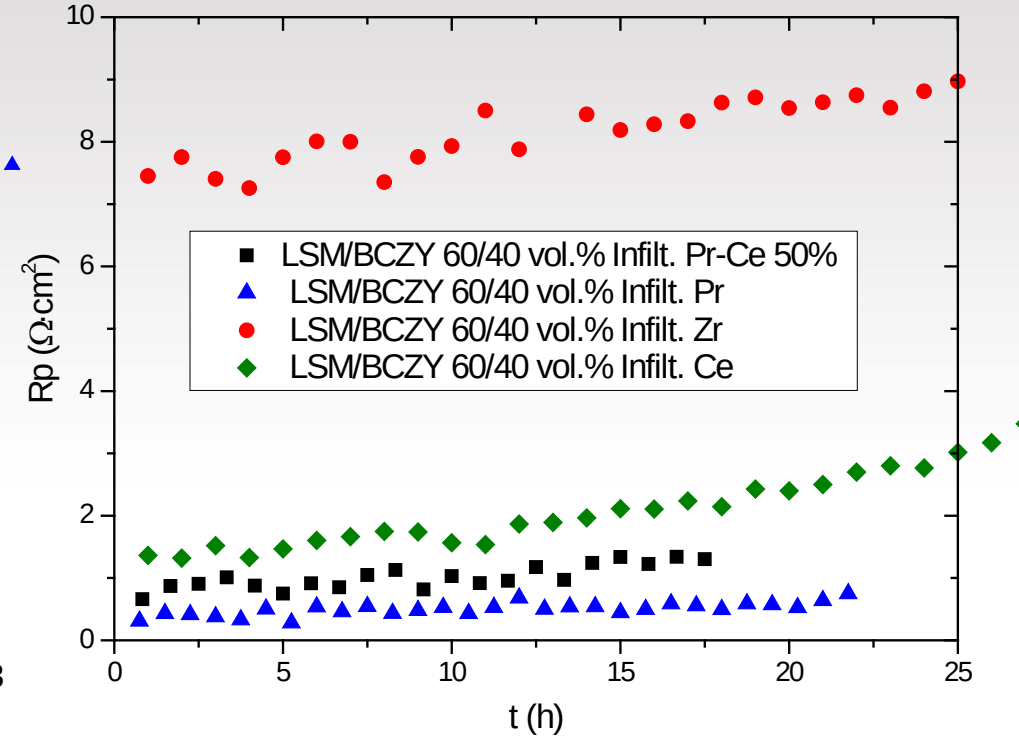
Steam 75%

T = 700 °C

Bias – Infiltrations in LSM/BCZY 60/40 vol. %

Infiltration Ce 850 °C in LSM/BCZY





Bias Infilt. Ce:

i = 0.63 mA/cm² → Rp = 0.54 Ω·cm²

i = 5.72 mA/cm² → Rp = 0.05 Ω·cm²

Conditions:

Total P= 3 bar

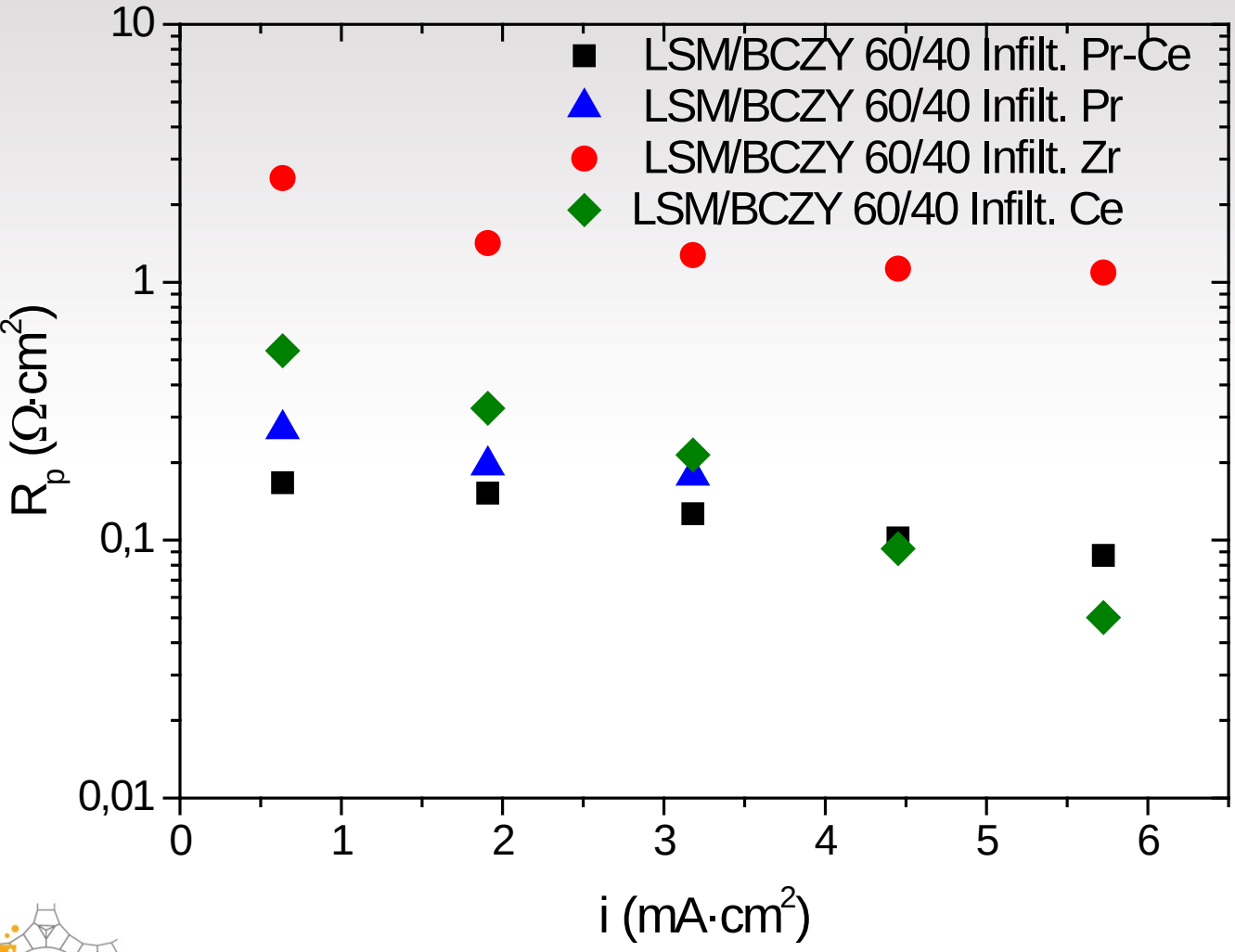
Steam 75%

T = 700 °C

Good stability!

Comparative infiltrations

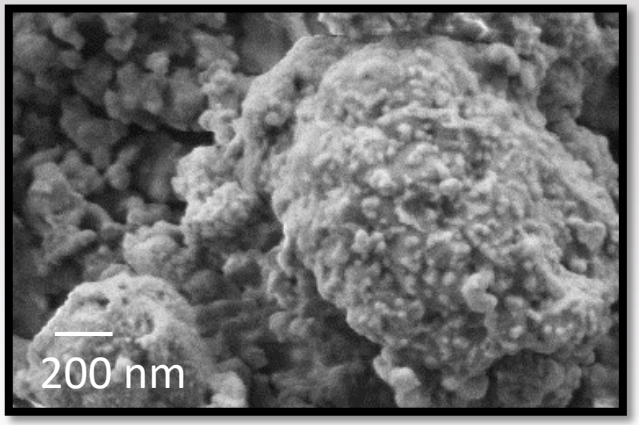
Infiltrations in LSM/BCZY 60/40 vol. %



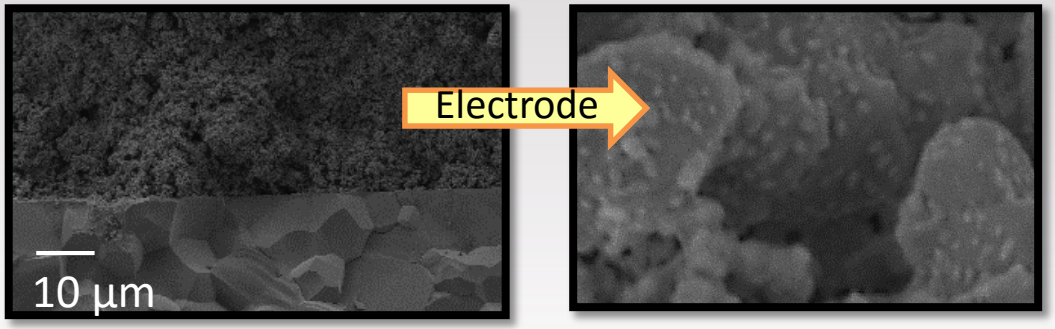
Conditions:
Total P= 3 bar
Steam 75%
T = 700 °C

SEM micrographs of LSM/BCZY 60/40 % vol. infiltrated with Pr-Ce 50% (850 °C)

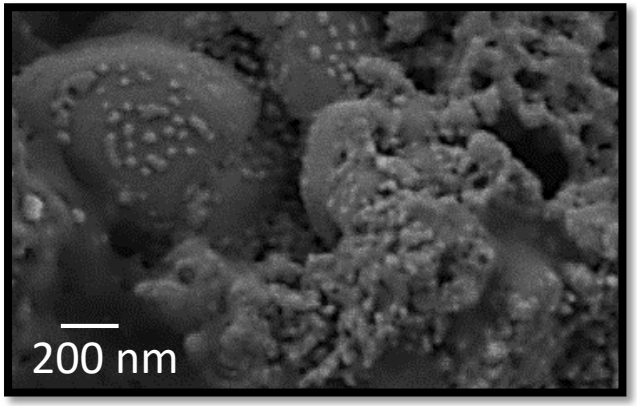
Powder 850 °C

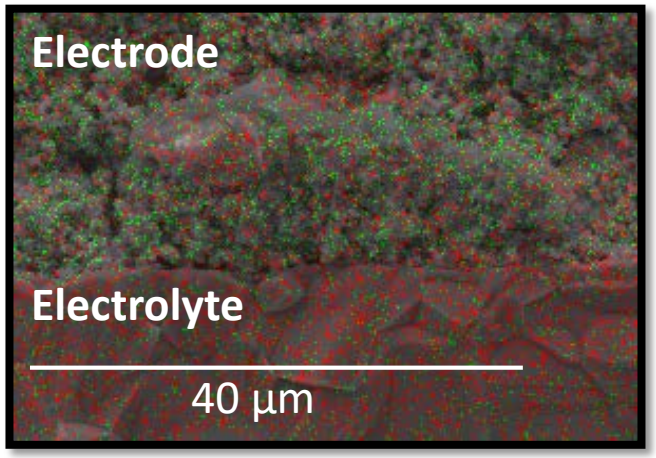


Fresh sample as a layer



Electrode after operating conditions





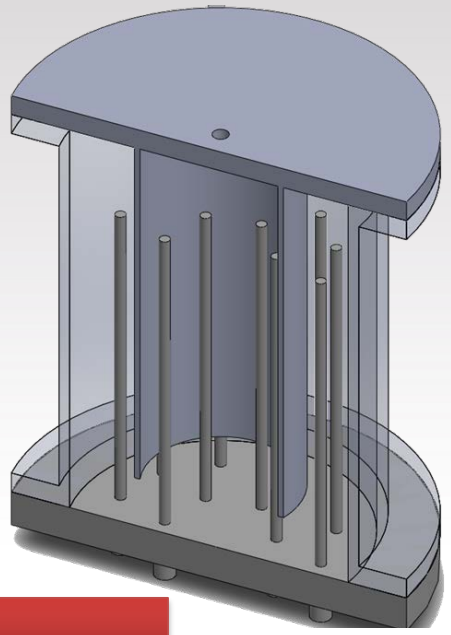
- Ce
- Pr

Good infiltration

Multitube module

Multitube module

Multitube module achieves stable operation for H_2O electrolysis with H_2 production of 250 L_n/h using 1kW of power

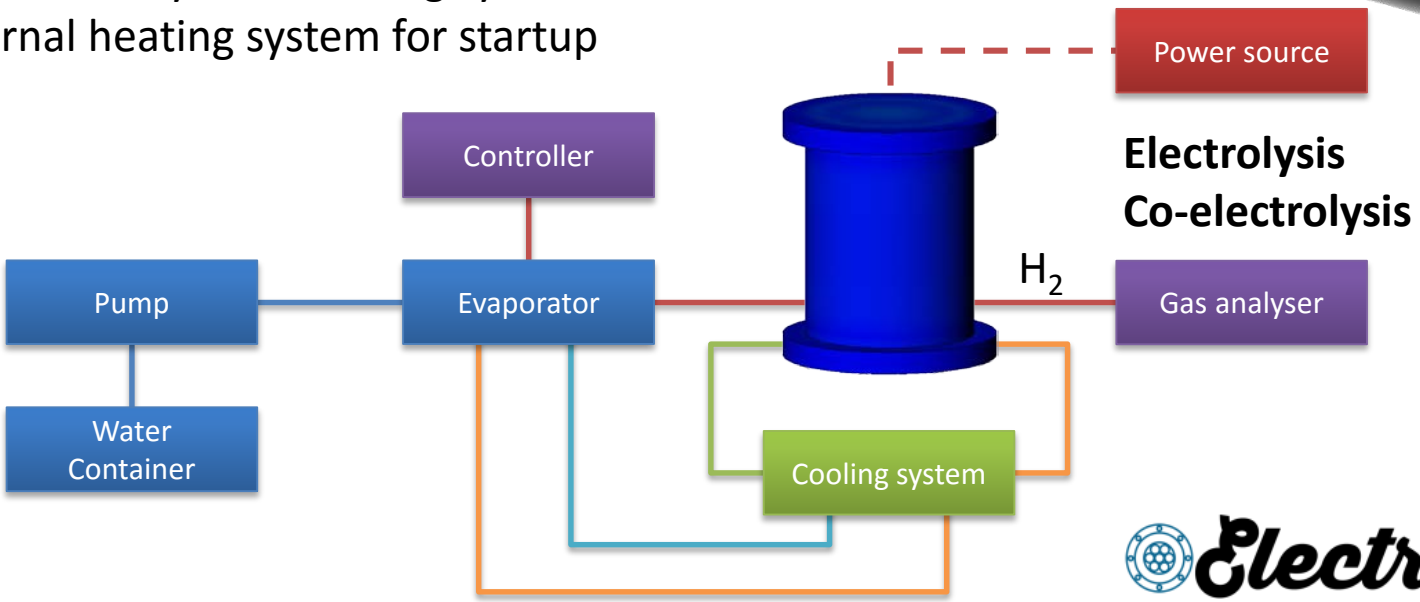


Working conditions:

- Temperature: 700 °C
- Pressure:
  - ✓ Total: 50 bar
  - ✓ Steam: 10 bar
- Steam temperature: 250-300°C

Temperature management system:

- Cooling system allows applying low temperature gaskets
- Heat recovery from cooling system
- External heating system for startup



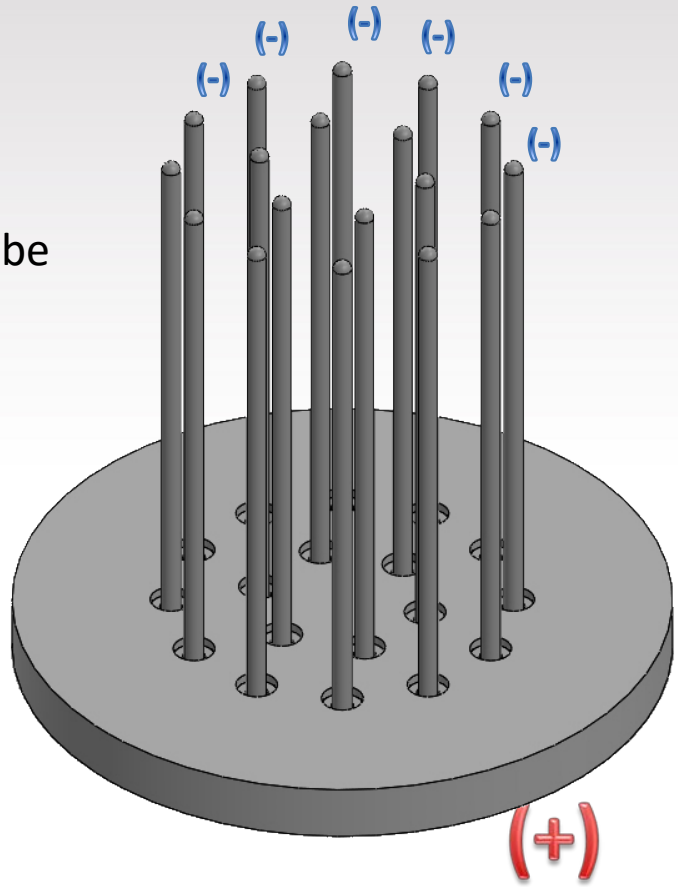
Multitube module

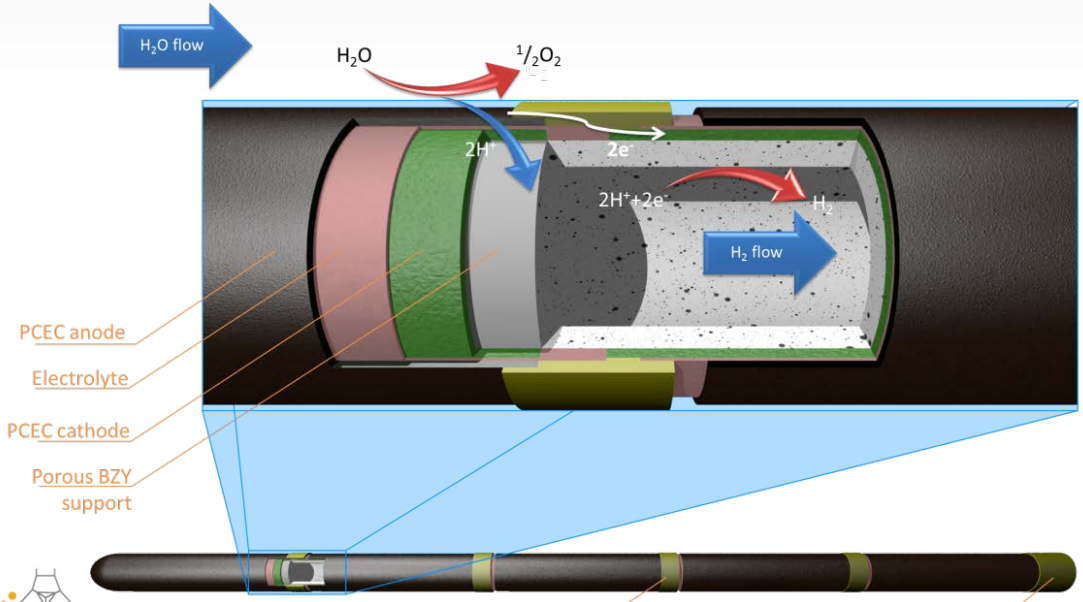
Tube materials

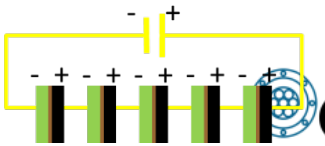
- Anode: LSM/BCZY or BGLC/BCZY (UiO)
- Cathode: Ni-BCZY cermet
- Electrolyte: BCZY

Electrical energy management system:

- Positive (+) current contact shared by all tubes
- Negative (-) current contacts independent for each tube
- One tube consists of 5 segments connected in series



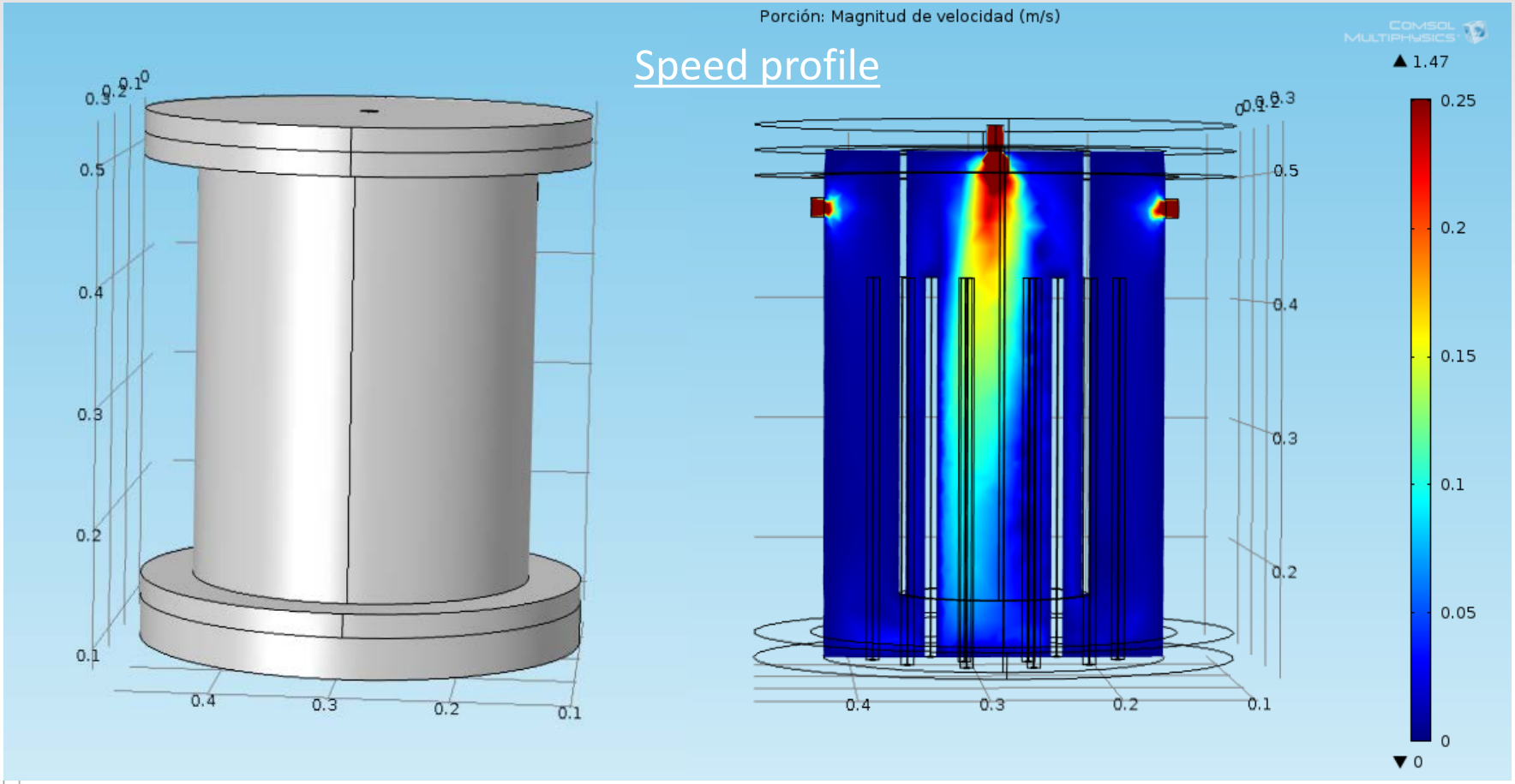




Multitube module

Geometry optimisation:

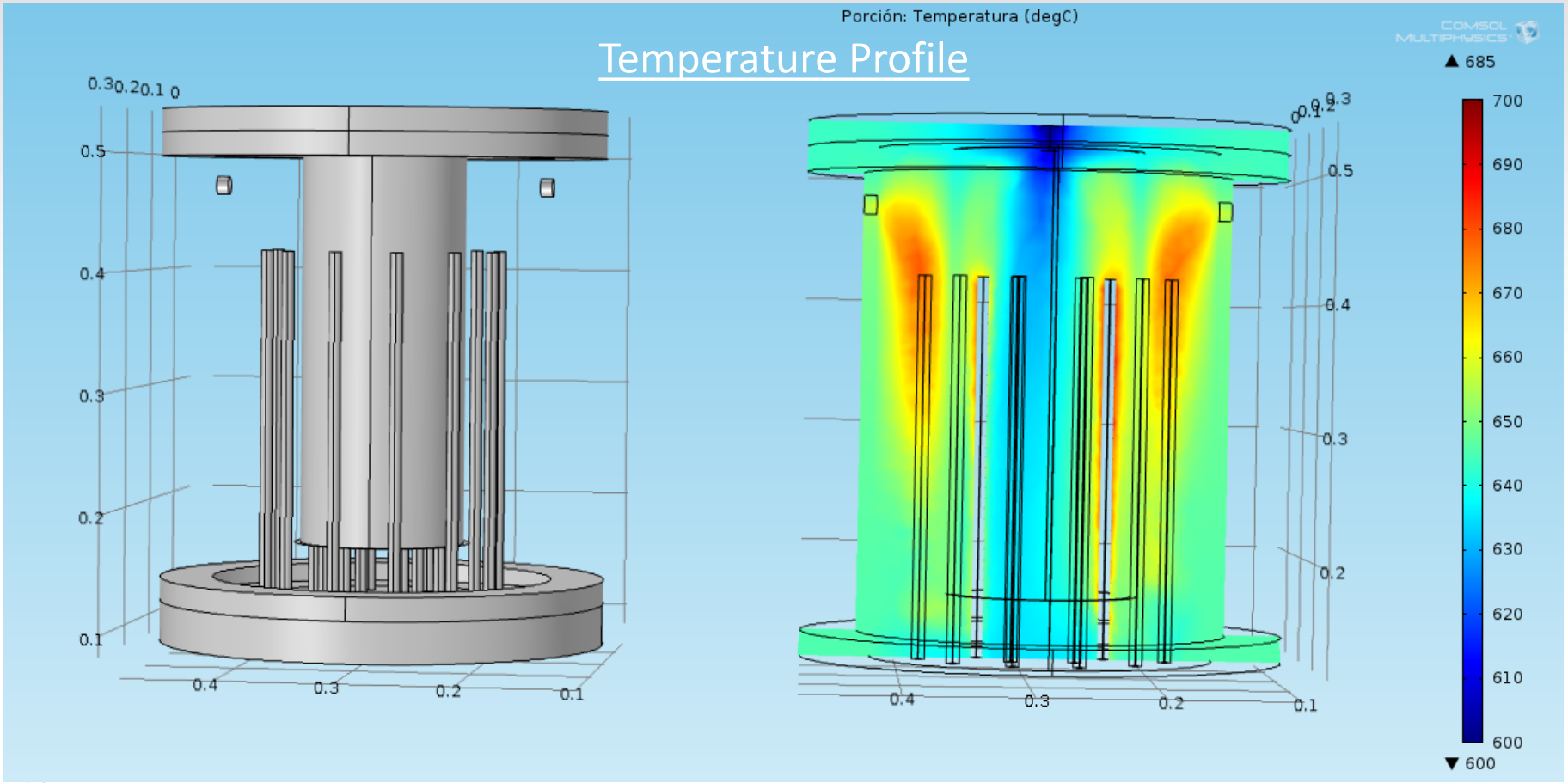
- Mechanical analysis (strength, thermal resistance)
- Fluid dynamics simulation (temperature profile and speed flow)



Multitube module

Geometry optimisation:

- Mechanical analysis (strength, thermal resistance)
- Fluid dynamics simulation (temperature profile and speed flow)

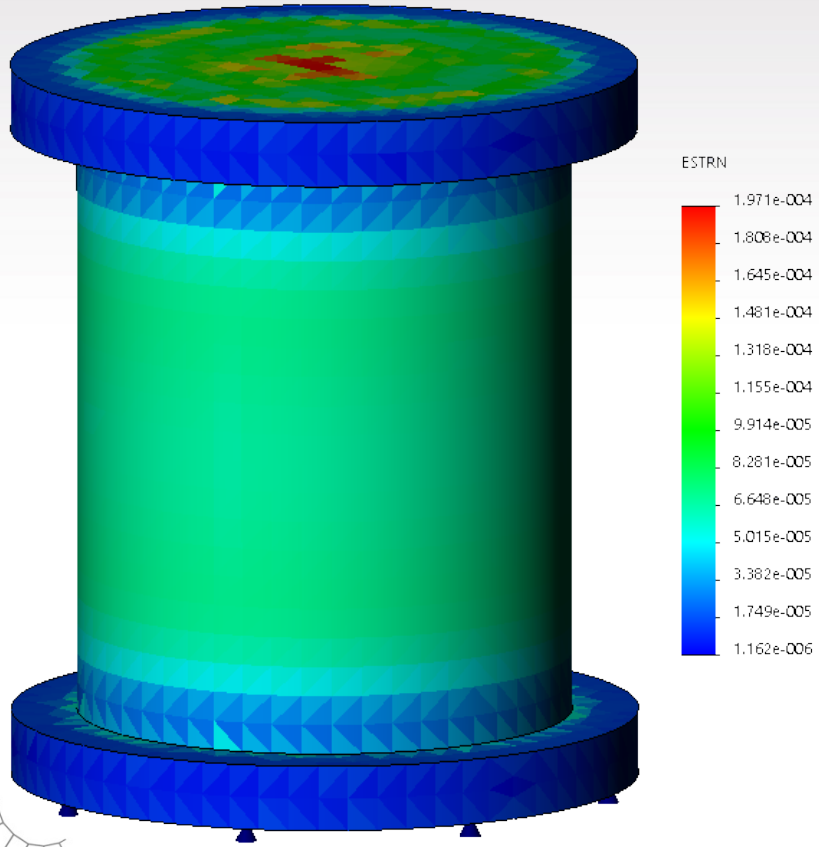


Multitube module

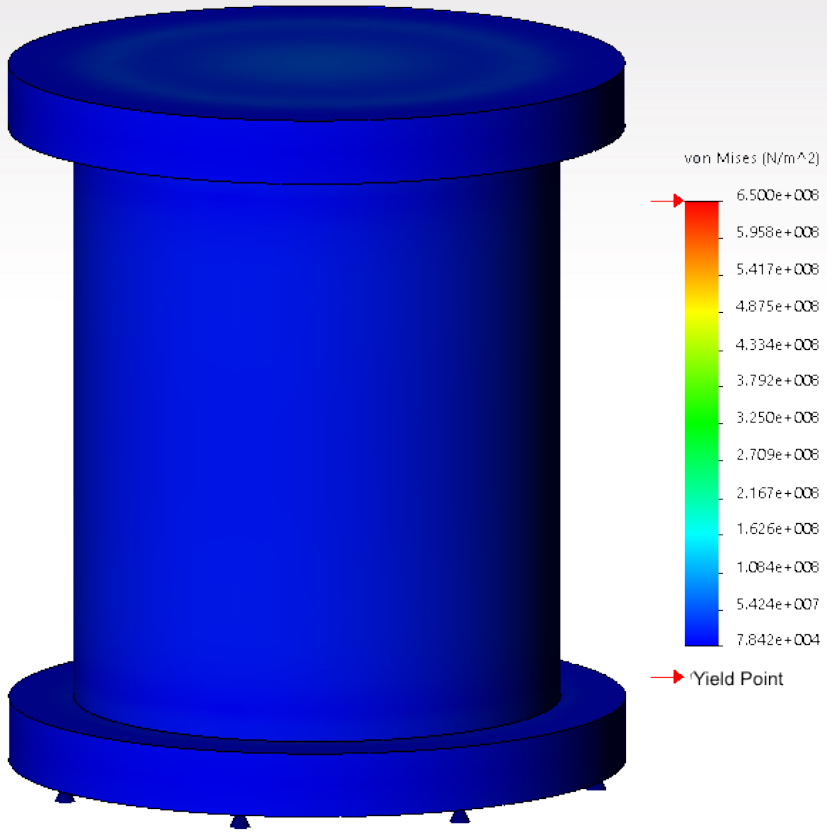
Geometry optimisation:

- Mechanical analysis (strength, thermal resistance)
- Fluid dynamics simulation (temperature profile and speed flow)

Displacement



Stress



Conclusions

- A thorough study by changing the measurement conditions (steam, pO_2 and total pressures)
- LSM/BCZY27 50/50 vol. % infiltrated with Pr shows the lower electrode Rp (700 °C)
- LSM/BCZY27 60/40 vol. % infiltrated with Pr-Ce and Ce show the lower electrode Rp when a current is applied (700 °C)
- Construction of a multitube module which allows efficient **electrolysis** of water and **co-electrolysis** of steam and CO_2 mixtures to obtain hydrocarbons

Acknowledgements

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My colleagues at ITQ/ELECTRA:

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Thank you for your attention

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