Development of proton ceramic electrolysers using tubular design

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High pressure PCE

- Pressurized dry H_2: 30 bars

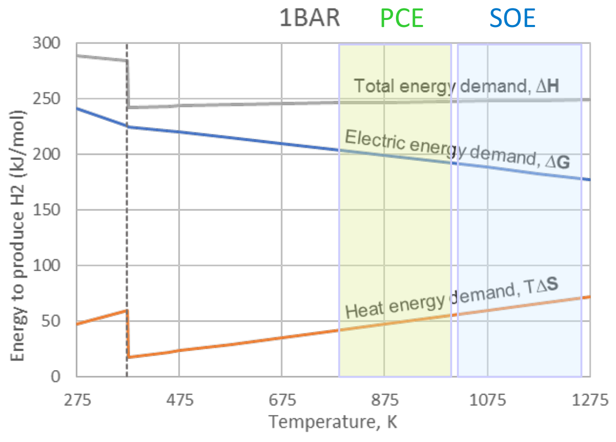
  Simpler system and lower cost of electrochemical compression

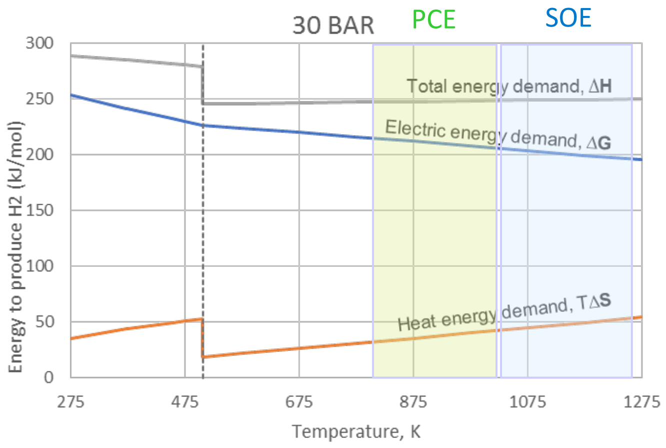
- pH_2 is balanced with pH_2O+pO_2

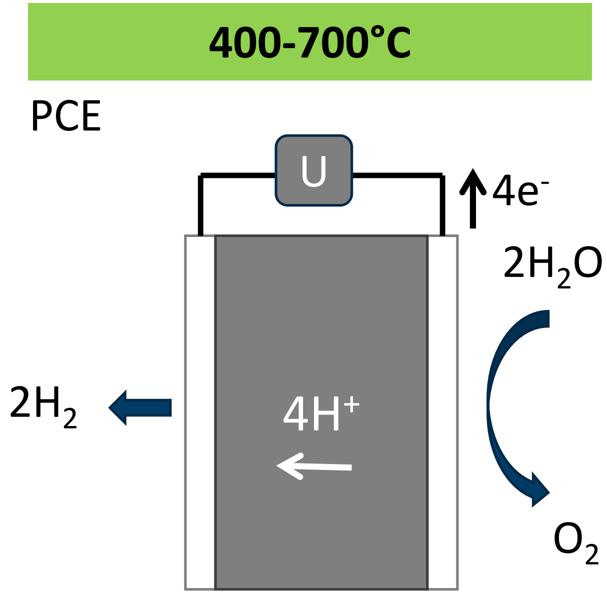
  No need to handle high pressure hot oxygen (as for SOE)

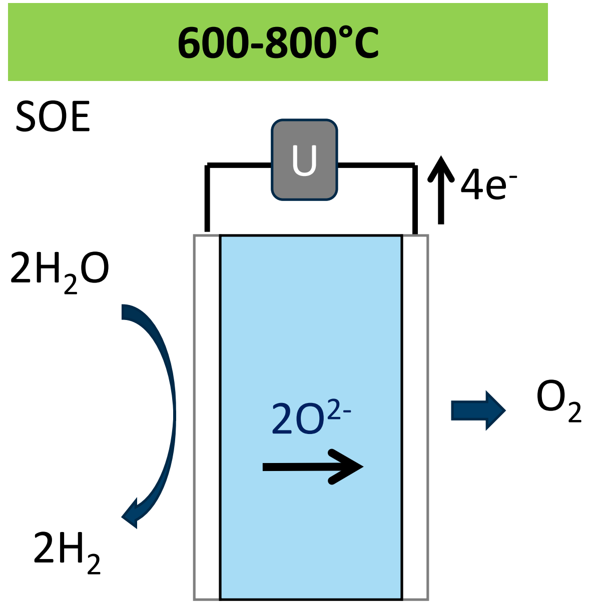
- Application at potentially intermediate T

  Potentially increased lifetime and more efficient coupling with renewables: Solar, geothermal plants (electricity, steam, heat)

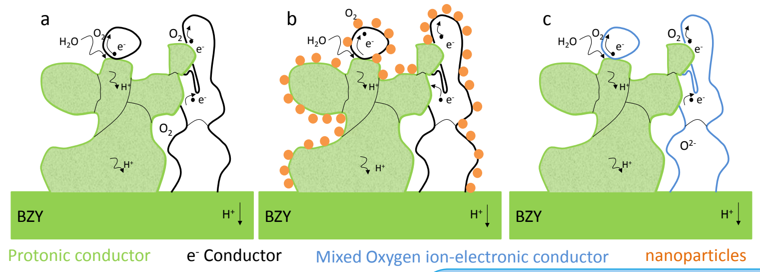








High temperature electrolysers with novel proton ceramic tubular modules (2014-2017)



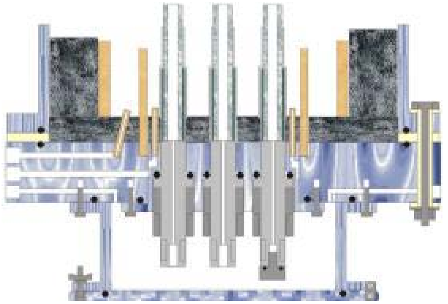
Development of tubular cathode supported electrolyte cell

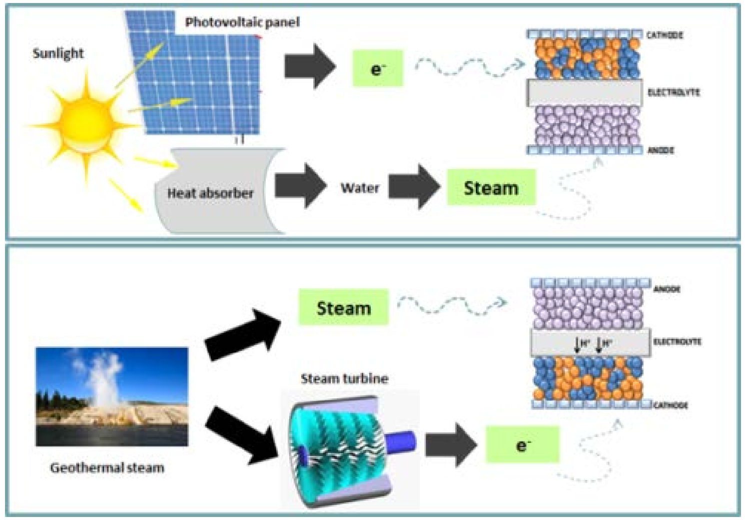
Development and optimization of anodes and current collection

Single tube module development and testing

Multi-tube module testing
Aim: 1kW demo

Process integration and evaluation



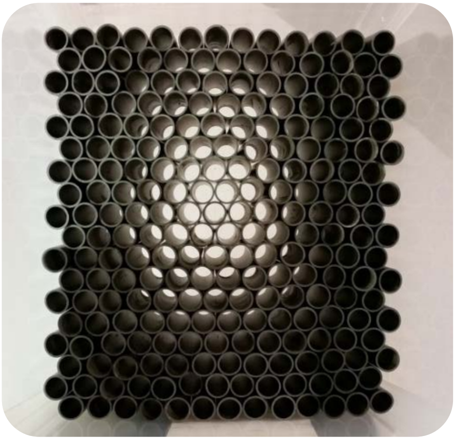


UiO : Universitetet i Oslo · SINTEF · CSIC · CoorsTek Membrane Sciences · ABENGOA HIDROGENO · Carbon Recycling International · Marion Technologie

PCE design

Tubular design to facilitate current collection

- Simpler sealing technology, lower sealing area
- Better stress distribution during transient conditions
- Module design enables to close off a tube / replace it



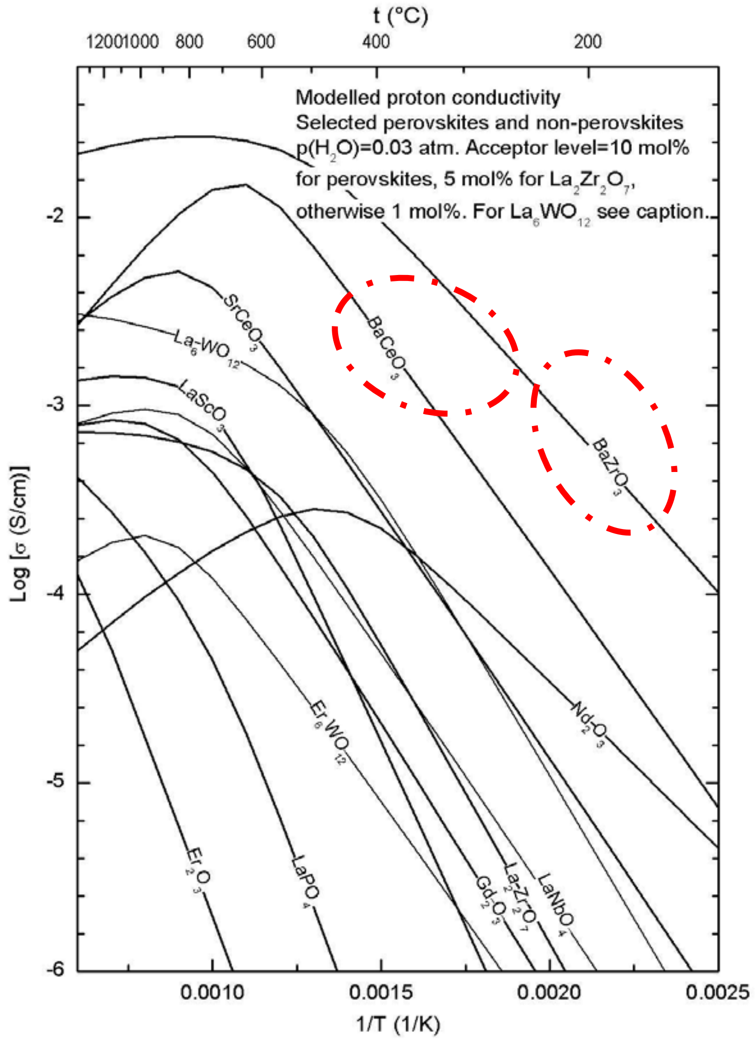
Mass scale processes for low cost production

- Water based extrusion
- Spray-coating and dip-coating
- Limited fabrication steps (in particular firing steps)

Materials: BZCY

- $BaZr_{1-x-y}Ce_xY_yO_{3-d}$
- 10-20% Y ; 10-20% Ce $BaZr_{1-x-y}Ce_xY_yO_{3-d}$
  - Ce improves sintering and gb conductivity compared to BZY ☺
  - Ce decreases stability compared to BZY 😐
- Grain growth increases specific grain boundary conductivity ☺
  - Not trivial to achieve large grains
- Sintering aids bring temperatures of BZY and BZCY to <1600°C ☺
  - NiO, ZnO, CuO, etc.

Solid state reactive sintering with Ni sintering aid



T. Norby, **"Proton conductivity in perovskite oxides"**, in "Perovskite oxides for solid oxide fuel cells", T. Ishihara, ed., Springer, 2009, ISBN 978-0-387-77707-8.

Manufacturing process of half-cells: pilot scale production

Paste preparation ($BaSO_4$, NiO, ZrO_2, Y_2O_3, CeO_2)

↓

Extrusion of 1 m long tube

↓

Drying, cutting to 40 cm

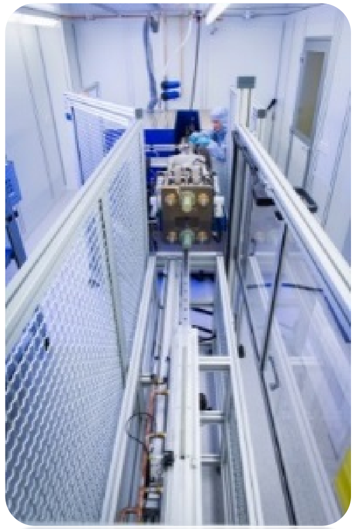
↓

Spray-coating with suspension of SSRS mixture

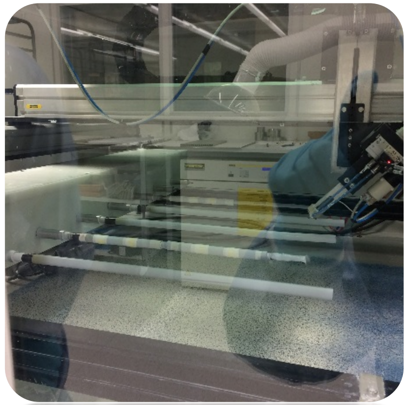
↓

Sintering

- Three processing steps
- One co-sintering step
- $BaSO_4$ instead of $BaCO_3$
- Lower CO_2 emissions
- Lower cost



Automatic 40 tons extruder with capping, cutting systems and air lifted conveyor belt



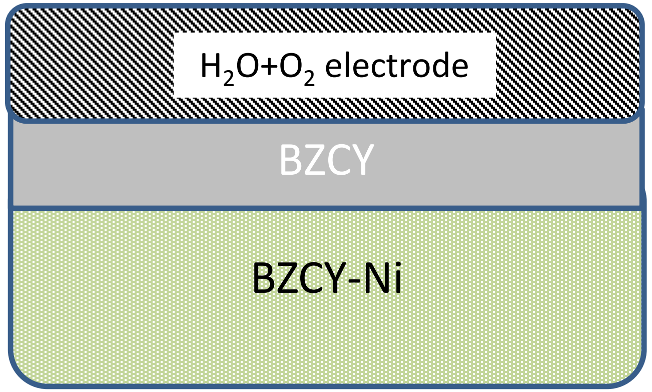
Automatic spray-coater for 40 cm long sample (batch of 6 samples)

CoorsTek Membrane Sciences

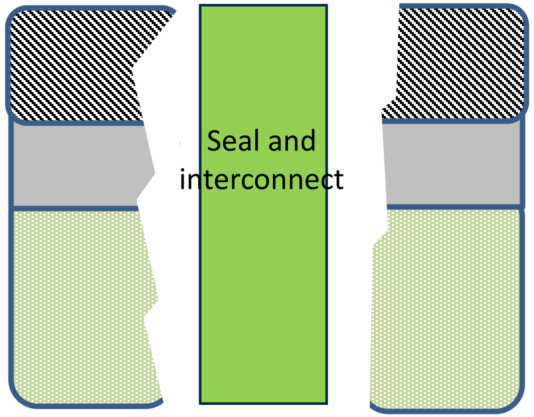
SINTEF

Cell designs for various concepts of current collection

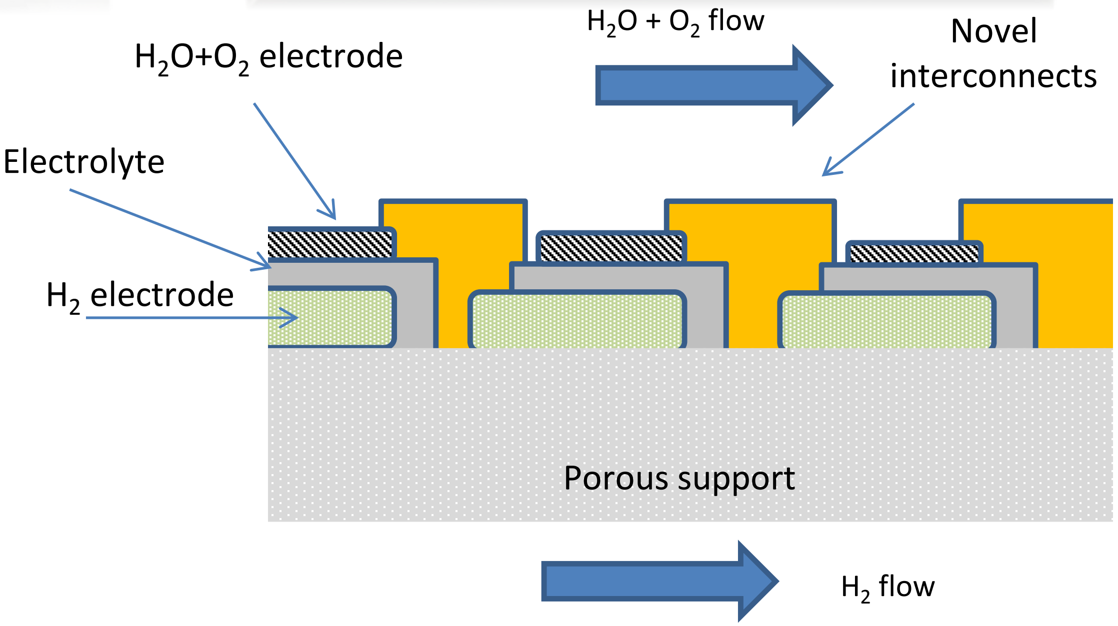
Single "segment"



Segmented-in-series cells by stacking

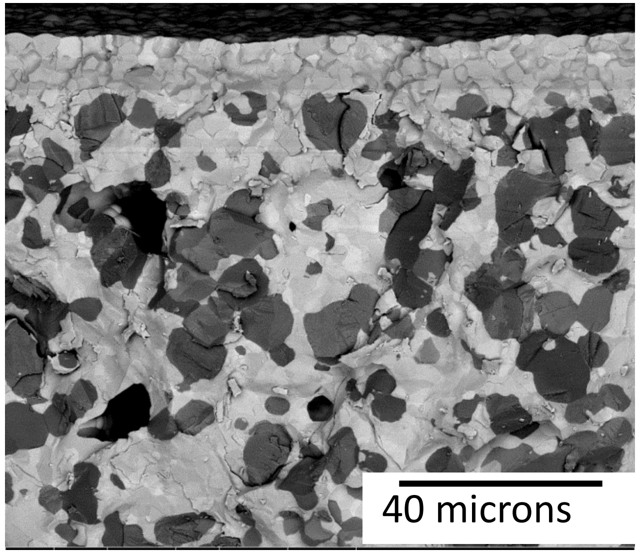


Segmented-in-series cells by printing



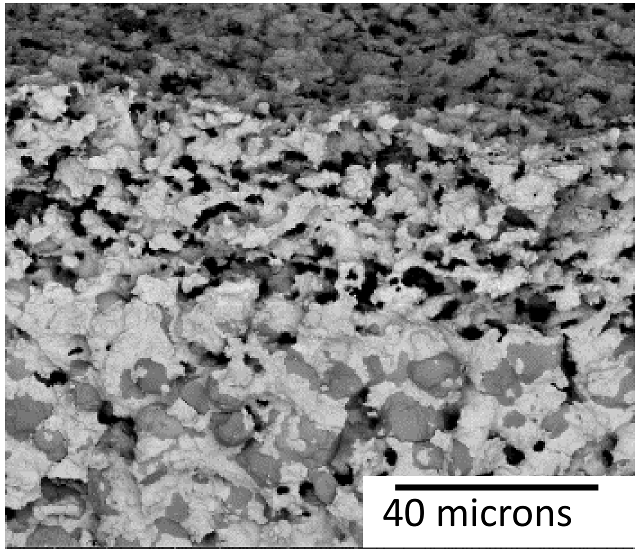
Various electrolytes: thickness 15-30 microns

BZCY72 // BZCY72-NiO



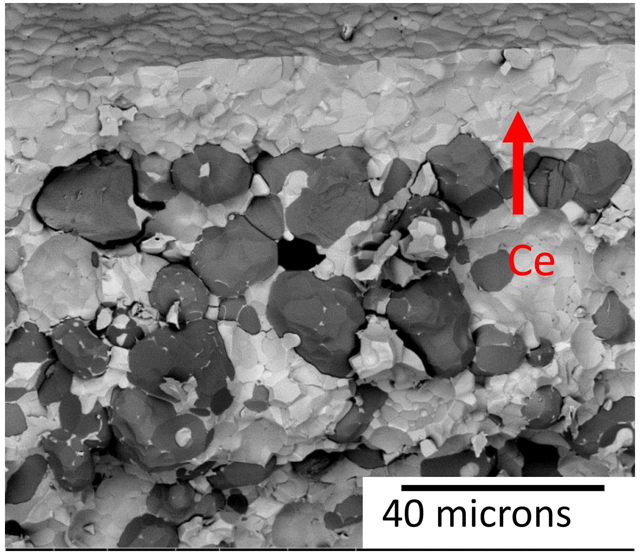
Dense electrolyte @
1550°C – 24h
1610°C – 6h

BZY10 // BZY10-NiO



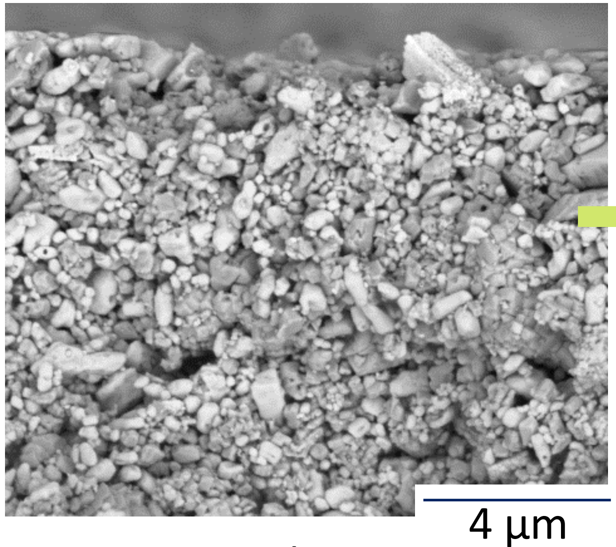
Porous electrolyte @
1550°C – 24h
1610°C – 6h
1650°C – 6h
1670°C – 6h

BZY10 // BZCY72-NiO → BZY10+2%Ce

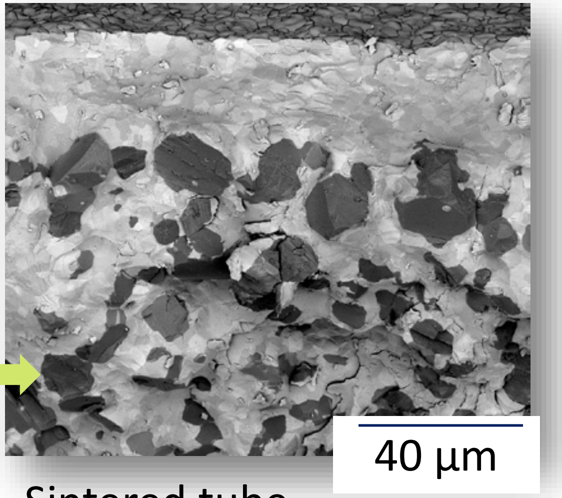


Dense electrolyte @
1550°C – 24 h
1610°C – 6 h

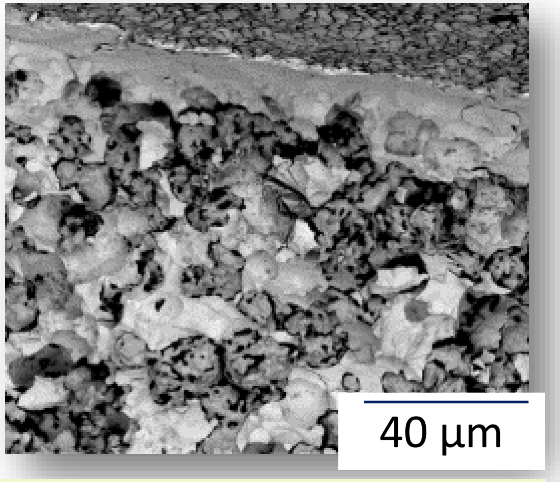
Half-cells before and after reduction



Green tube

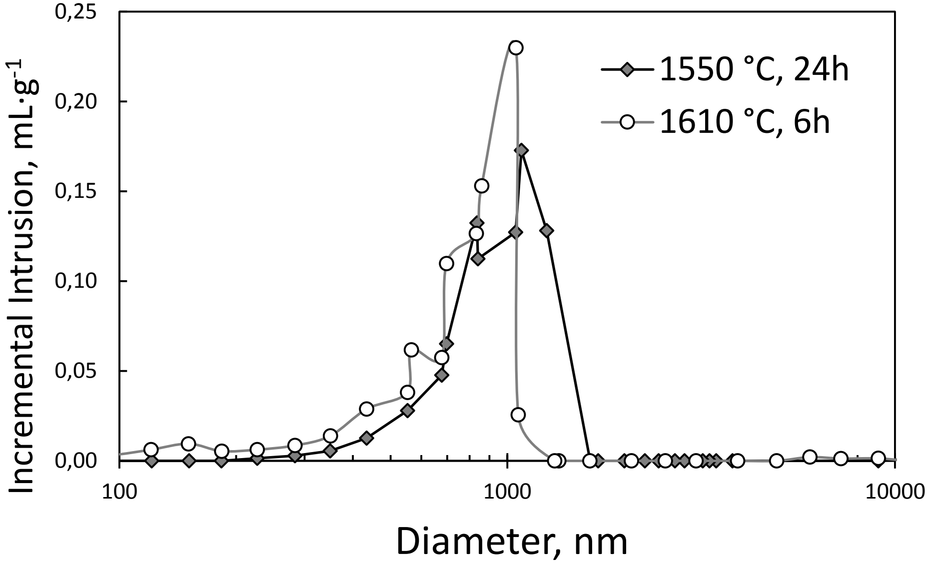


Sintered tube



Sintered reduced tube

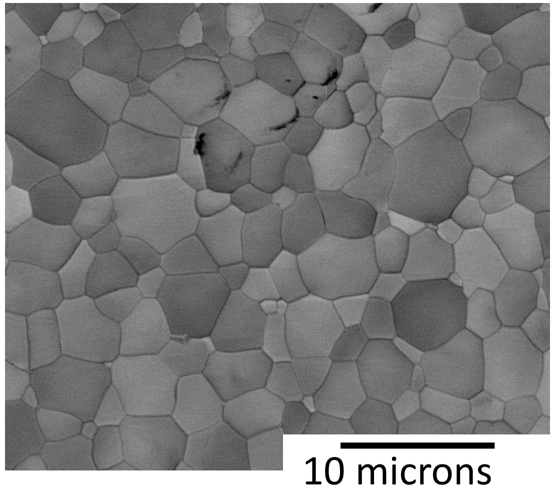
Hg-porosimetry



Between 27-32 vol% porosity (with 60 vol% Ni)

BZCY72 // BZCY72-NiO

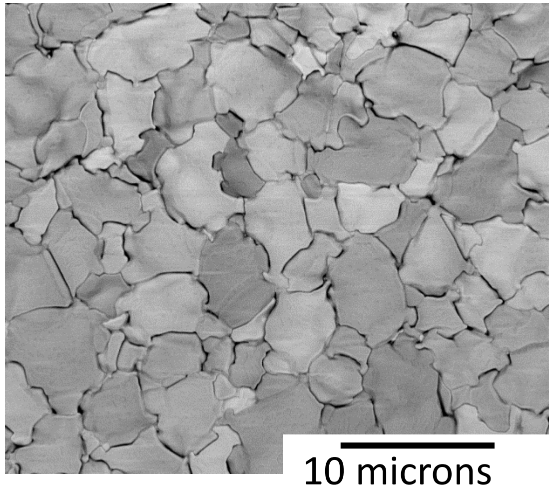
1550°C – 24h



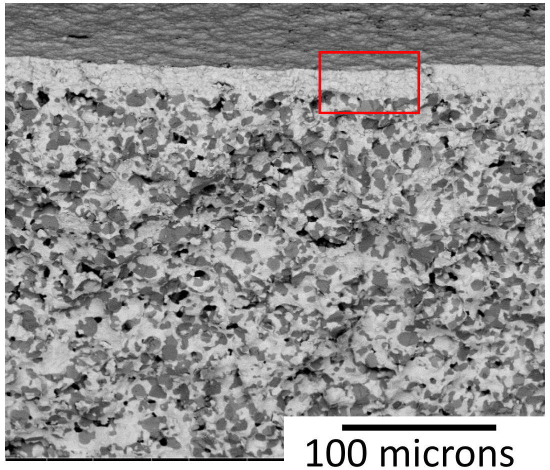
Grain size:
Large: 5 microns
Small: 2 microns

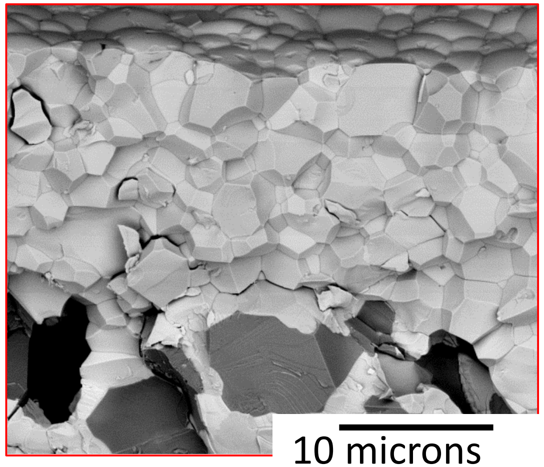
Grain growth

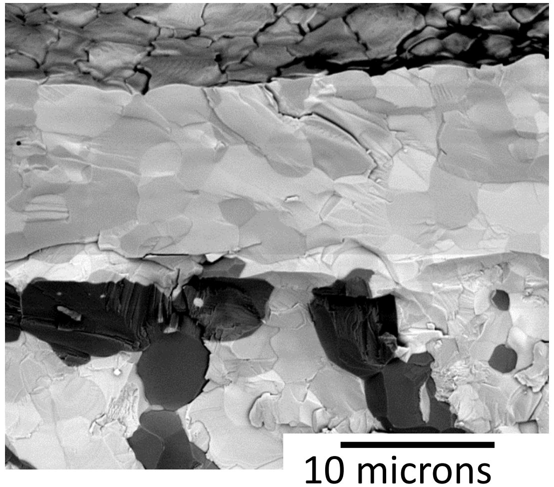
1610°C – 6h



Grain size:
5-10 microns







Electrodes

- Pre-selection of materials based:
  - Chemical compatibility with BZCY (powders mixture annealing)
  - Stability in high steam content of sintered pellets (3 bars air; Steam 75%; T = 700 °C)
- Impedance spectroscopy measurements
  - Performance
  - Manufacturability (adhesion/quality of interfaces)
- Requirements of overall integration of cells/seals in module

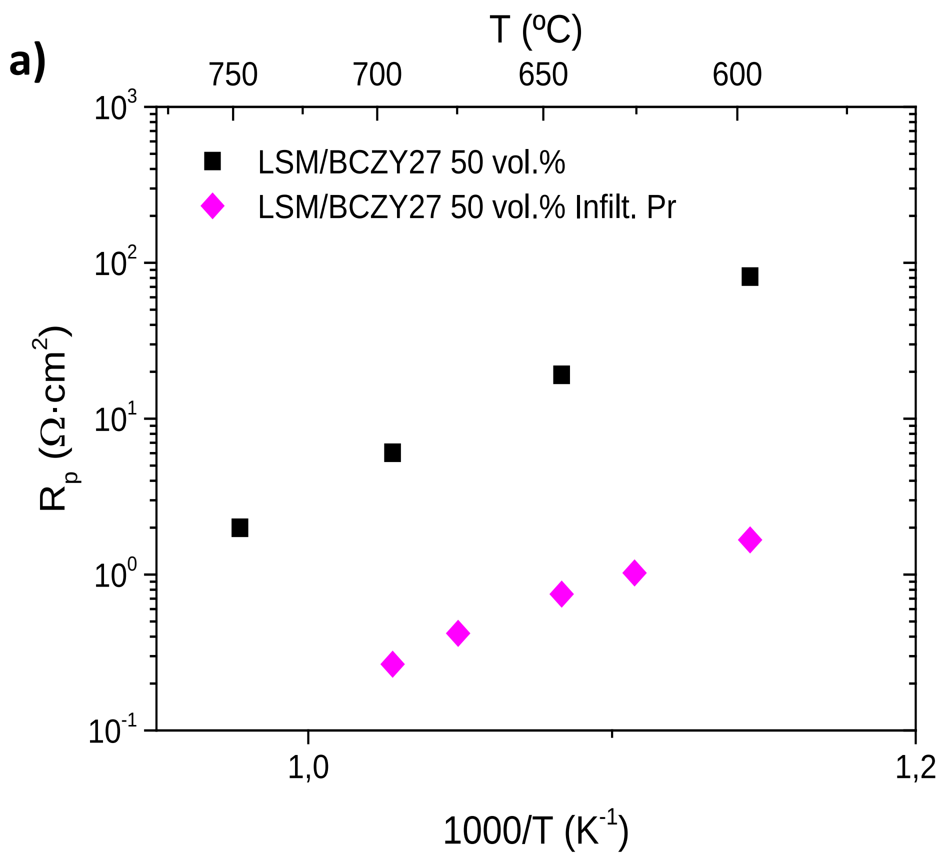
- LSM: $La_{0.8}Sr_{0.2}MnO_{3-\delta}$
- LNO: $La_2NiO_{4+\delta}$
- LSC: $La_{0.87}Sr_{0.13}CrO_{3-\delta}$
- BSCF: $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$
- LSCF: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$
- BGLC: $Ba_{1-x}La_xGd_{0.8}La_{0.2}Co_2O_{6-\delta}$

Symmetrical cells: LSM/BCZY + catalysts

Current collector: screen-printed Au grid
Electrolyte: 14 mm diameter
Electrode: 9 mm diameter

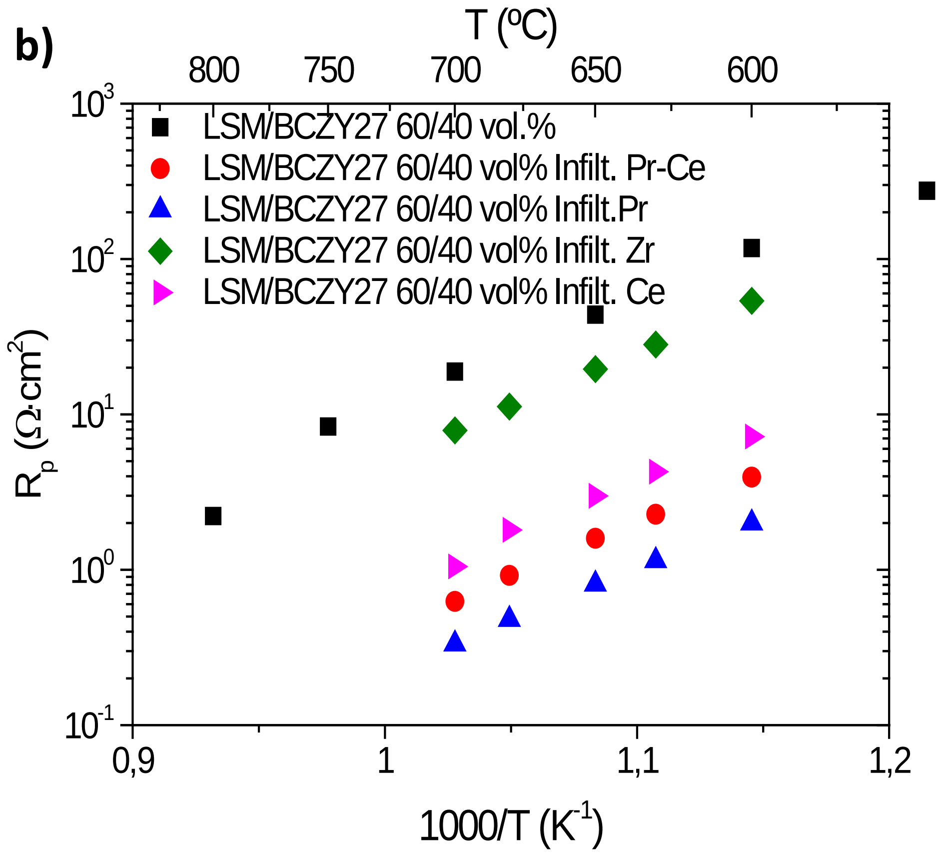
Conditions:
Total P= 3 bar
Steam 75%

LSM/BCZY 50 vol. %



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

LSM/BCZY 60/40 vol. %



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

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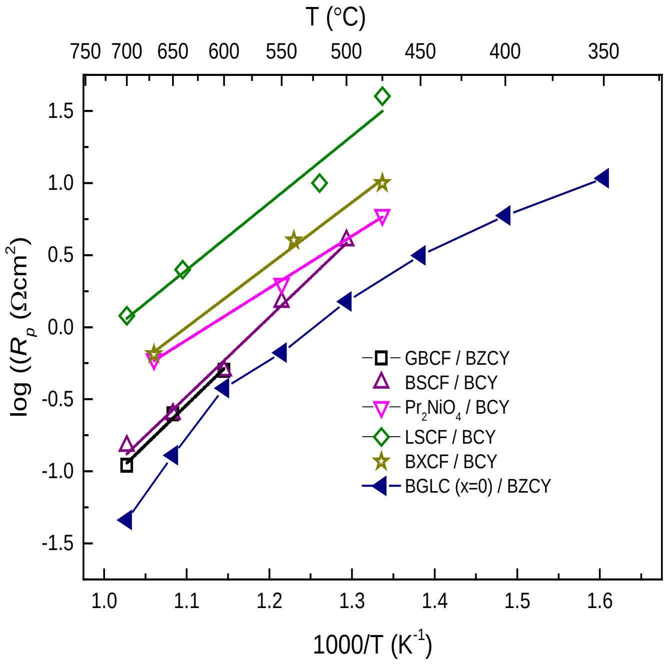
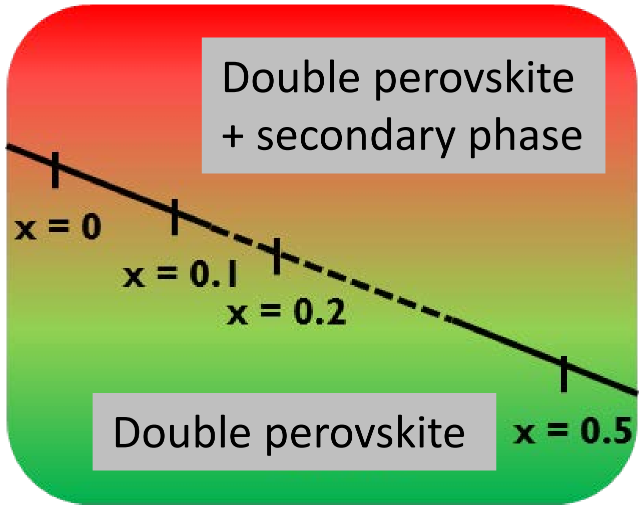
Symmetric cells: BGLC

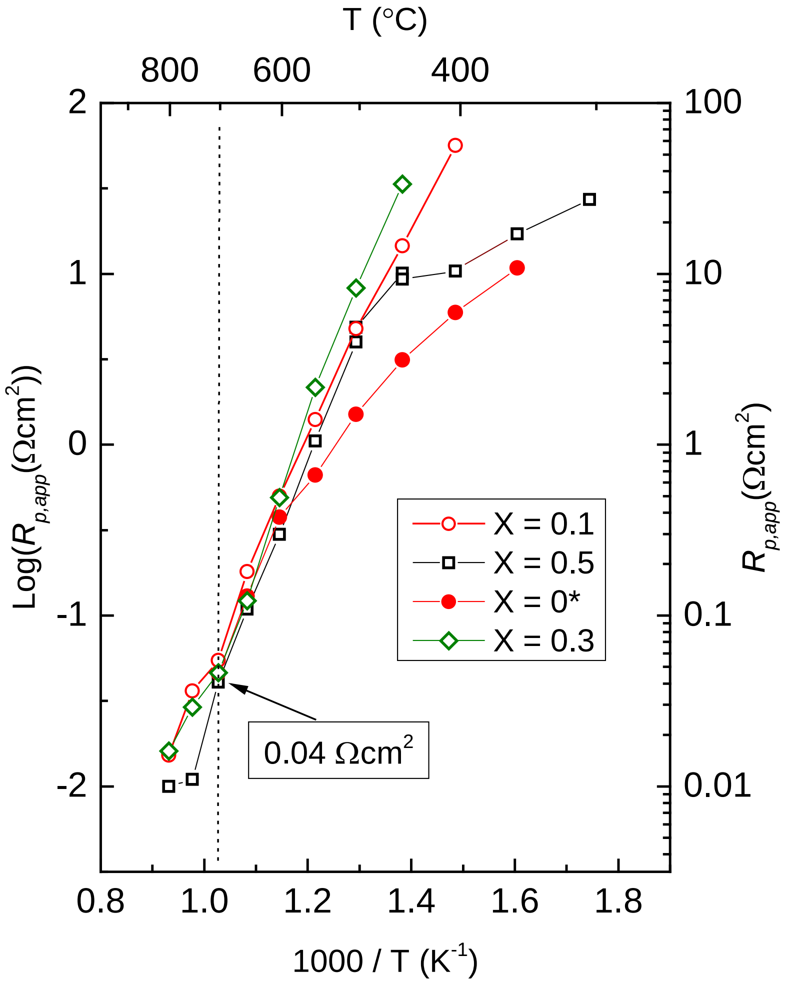


PROTON, MERANET

$Ba_{1-x}La_xGd_{0.8}La_{0.2}Co_2O_{6-\delta}$



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

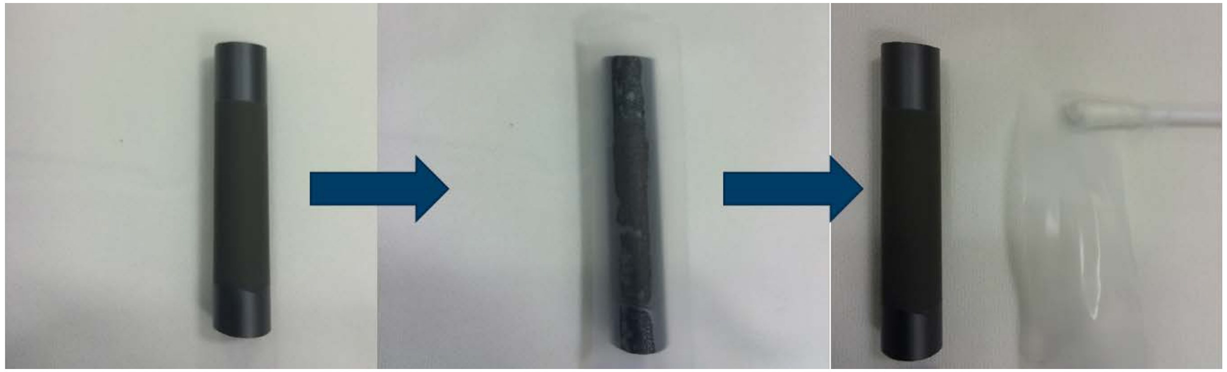


O06: "Hydration and structural properties of mixed conductor $Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$ (BGLC)" *R. Strandbakke*

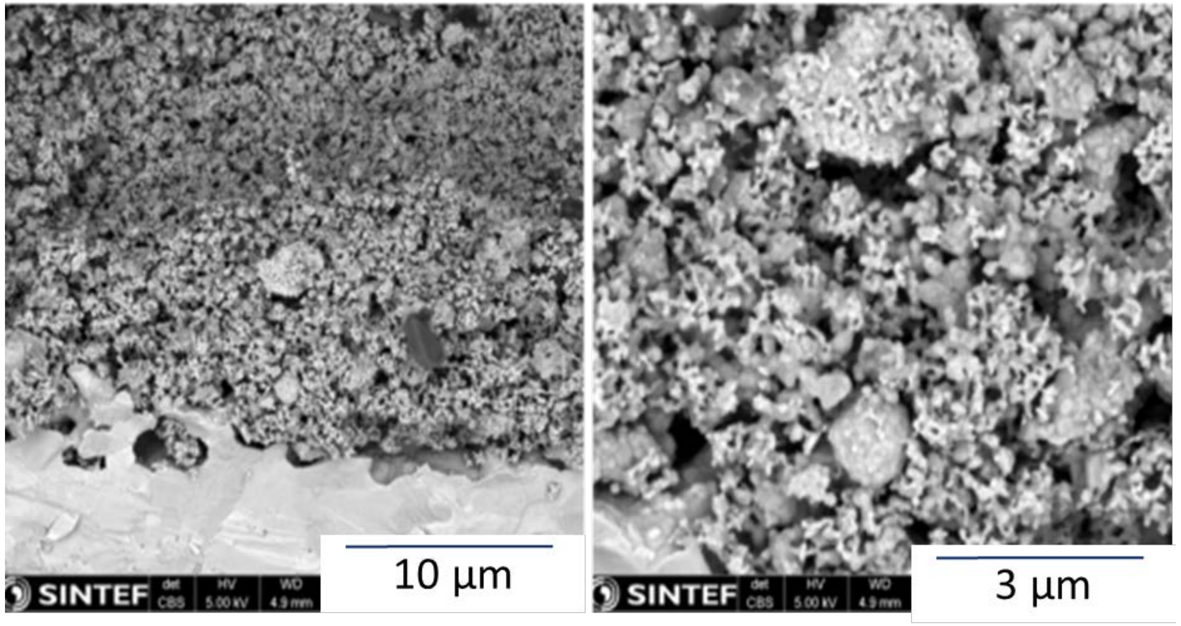
Manufacturing

- Manufacturing based on dip-coating/annealing using powders produced by Marion Technologies
- Dip-coating and drying in air
- Annealing in air

Tape-test

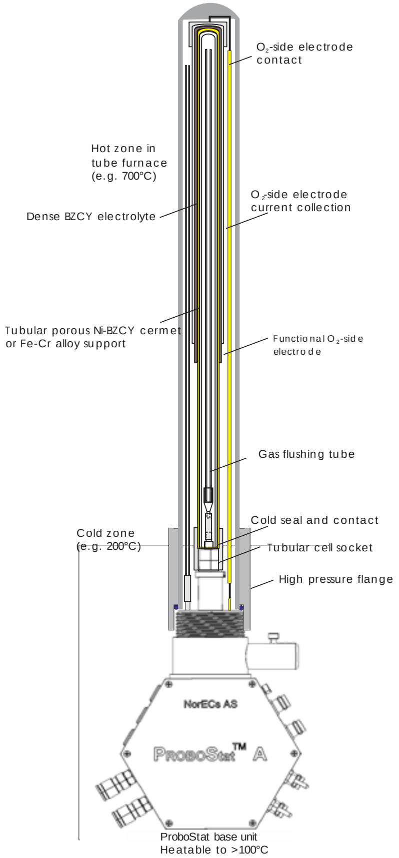


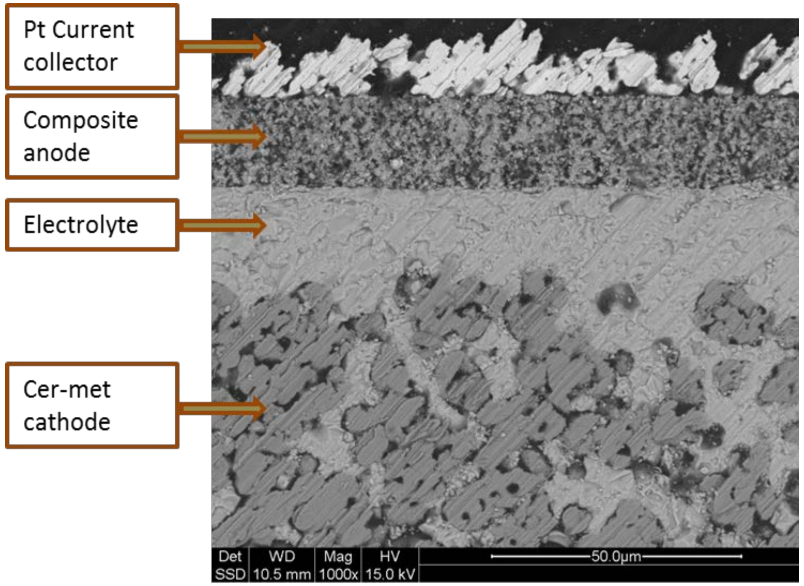
BZCY-LSM composite



Complete cells

- Testing in Probostat™
- Capped and sealed towards alumina riser
  - Sealing technology developed by CTMS
- In-situ reduction





BZCY - BGLC

Cell Area:
5- 11 cm^2

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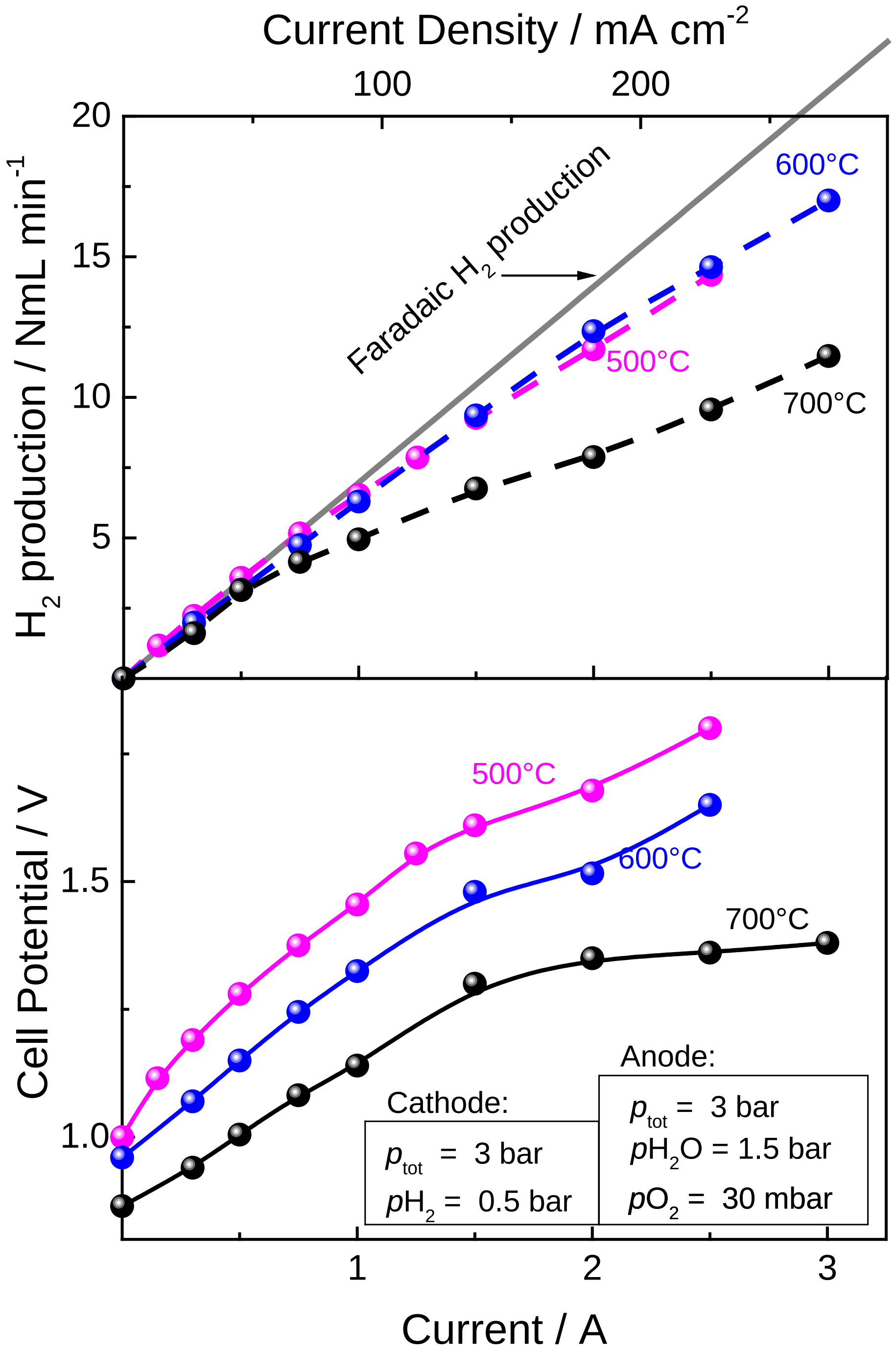
Hydrogen production

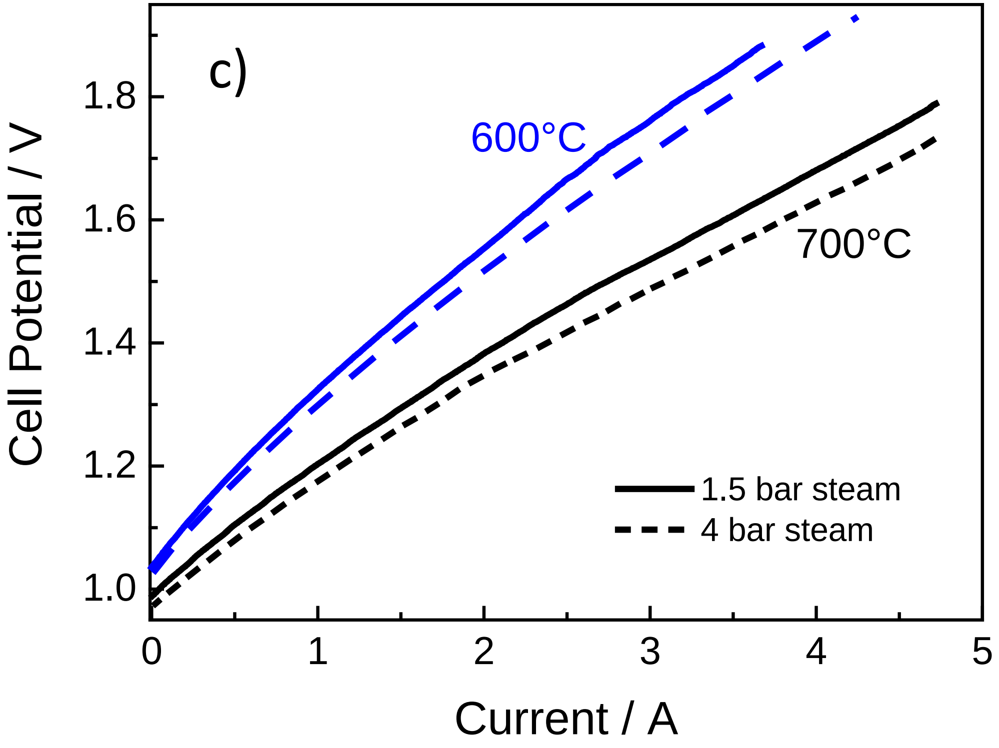
Cell	Anode	Current collector	Anode comp
2	BGLC-BZCY	Pt	x = 0.5

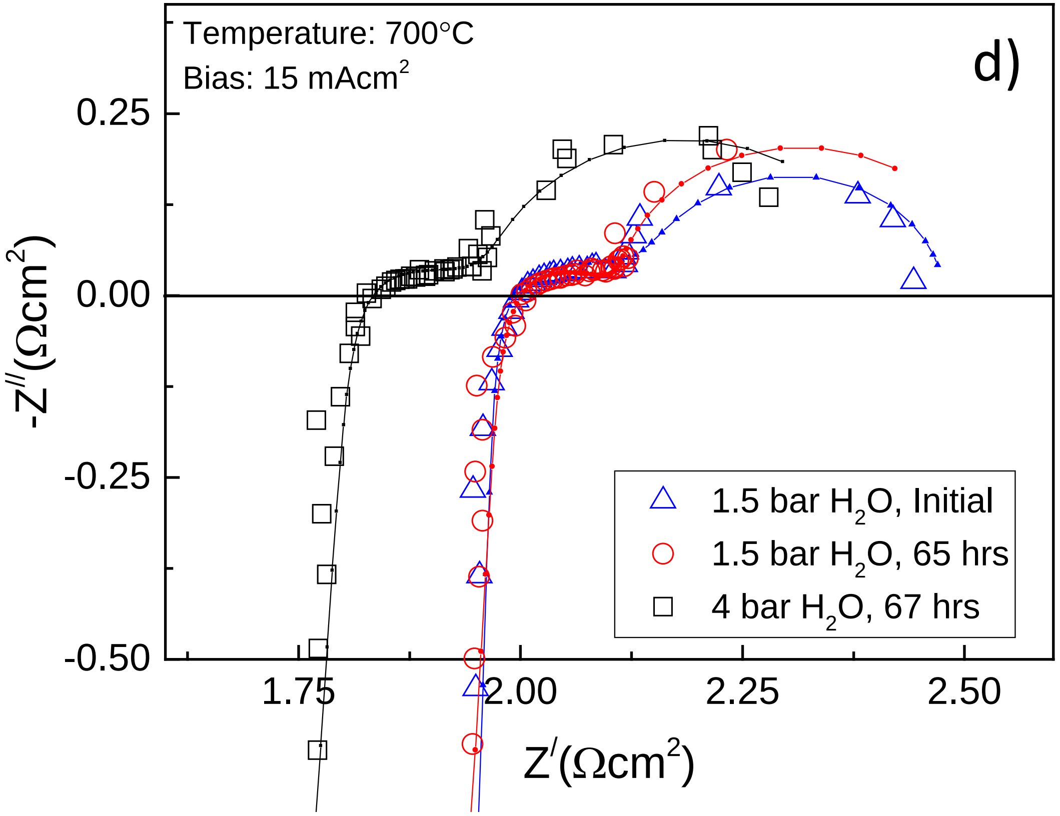
Conditions:
Total P= 3 bar
Cell Area: 11 cm^2



Effects of steam pressure

Cell	Anode	Current collector	Anode comp
2	BGLC-BZCY	Pt	x = 0.5





Development of 1kW reactor at CSIC

Working conditions:

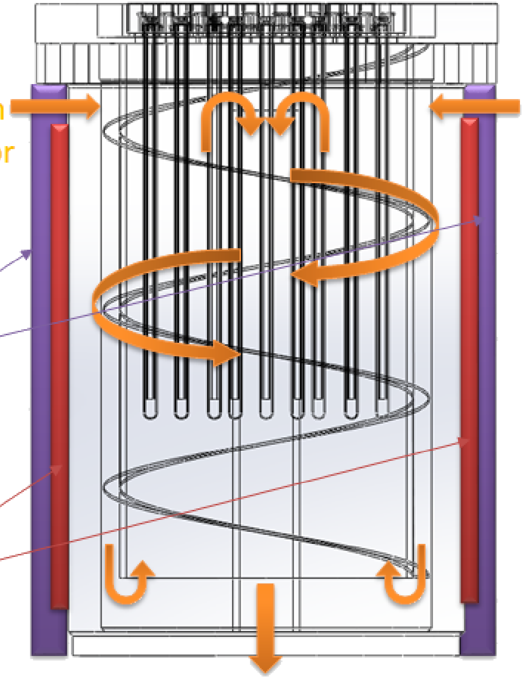
- Temperature: 700 °C
- Pressure:
  - Total: 20 bar
  - Steam: 5 bar
- Steam temperature: 250-300°C

Geometry design:

- Isothermal conditions (700°C along tubes)
- Good fluid dynamics (oxygen/steam concentration)
- Mechanical strength
- Thermal resistance
- Costs optimization (materials, manufacturing, time)

Sealing purpose:

- Possibility of close and turn individual tube off during operation
- Low temperature gaskets



Next steps

Game changer in high temperature steam electrolysis with novel tubular cells integrated in a 10 kW module for pressurized hydrogen production

- SINTEF AS (coordinator) (Norway)
- CoorsTek Membrane Sciences AS (Norway)
- Agencia Estatal Consejo Superior de Investigaciones Cientificas (Spain)
- CRI EHF (Iceland)
- University of Oslo (Norway)
- MC2 Ingenieria y Sistemas SL (Spain)
- Shell Global Solutions International BV (The Netherlands)

GAMER activities

- Optimisation of cell design and key enabling technologies (seals, interconnects, manifolds)
- Industrial pilot production of tubular cells
- Design and engineering of a pressurized 10 kW electrolyser
- Installation, commissioning and testing of the electrolyser
- Process design, LCA and techno-economic evaluation of the electrolyser integrated in CO_2 to liquid fuels/chemicals plant
- Dissemination and exploitation

Acknowledgments

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