Scaling up of tubular proton ceramic electrolysers

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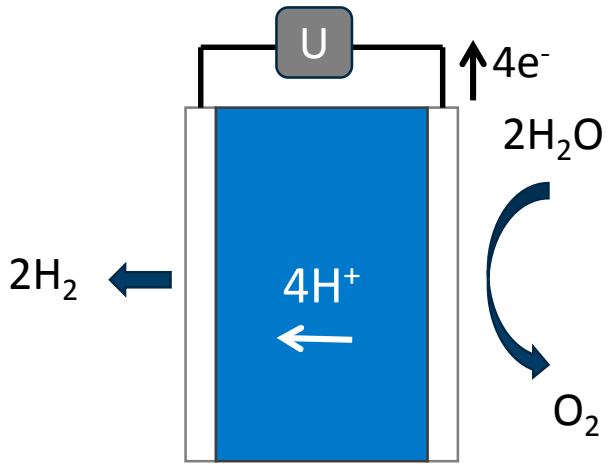
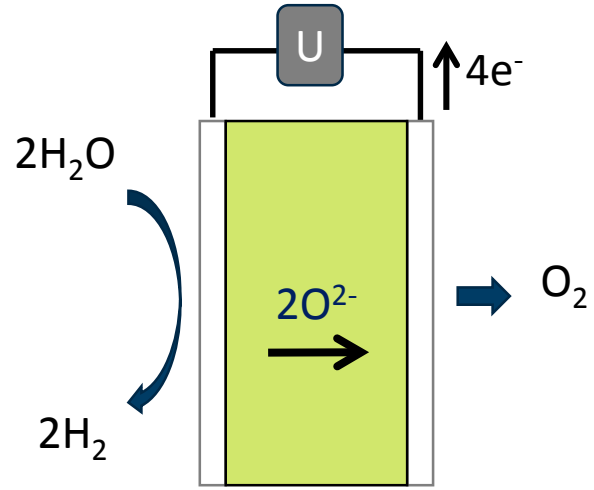
High pressure PCE

- Dry Hydrogen
- pH_2 is balanced with pH_2O+pO_2

Proton Ceramic Electrolyser PCE



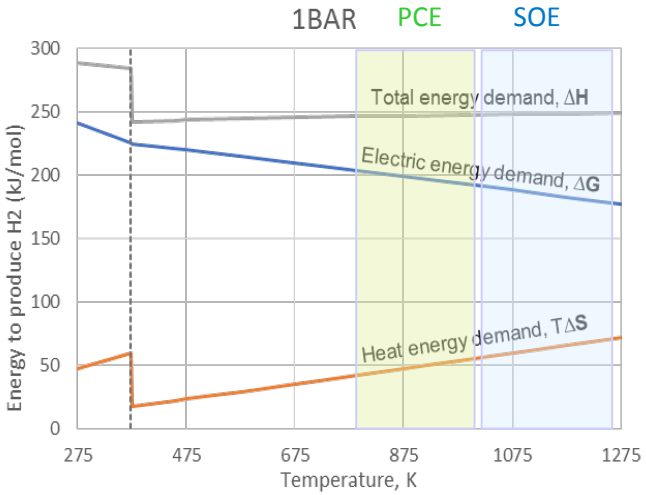
Solid oxide electrolyser SOE

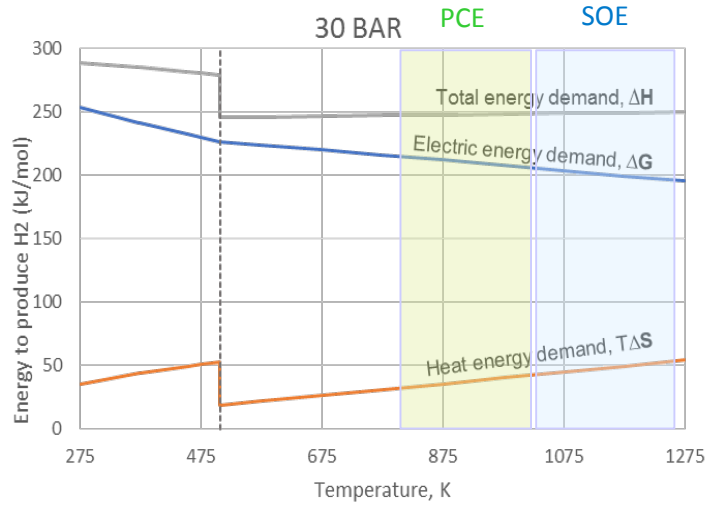


Advantages

- Intermediate operating temperature : 400 - 600 °C
- Electrochemical compression: pressurized H_2
- More efficient coupling with renewable sources

(heat, steam, electricity)





Tubular design

- 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
- !! Challenging current collection!!

Outlook

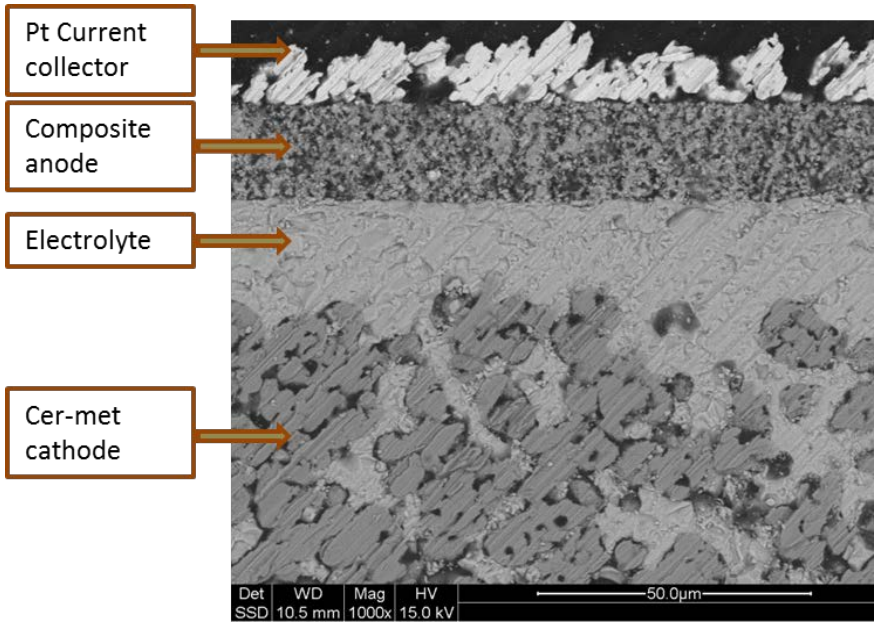
- Materials
- Mass scale production routes
- Sealing technologies
- Results on high pressure electrolysis
- Scaling up activity

Materials

- Electrolyte: $BaZr_{1-x-y}Ce_xY_yO_{3-\delta}$
  (10-20% Y ; 10-20% Ce)
- Cathode: Ni + $BaZr_{1-x-y}Ce_xY_yO_{3-\delta}$
- Anode: Oxide + $BaZr_{1-x-y}Ce_xY_yO_{3-\delta}$

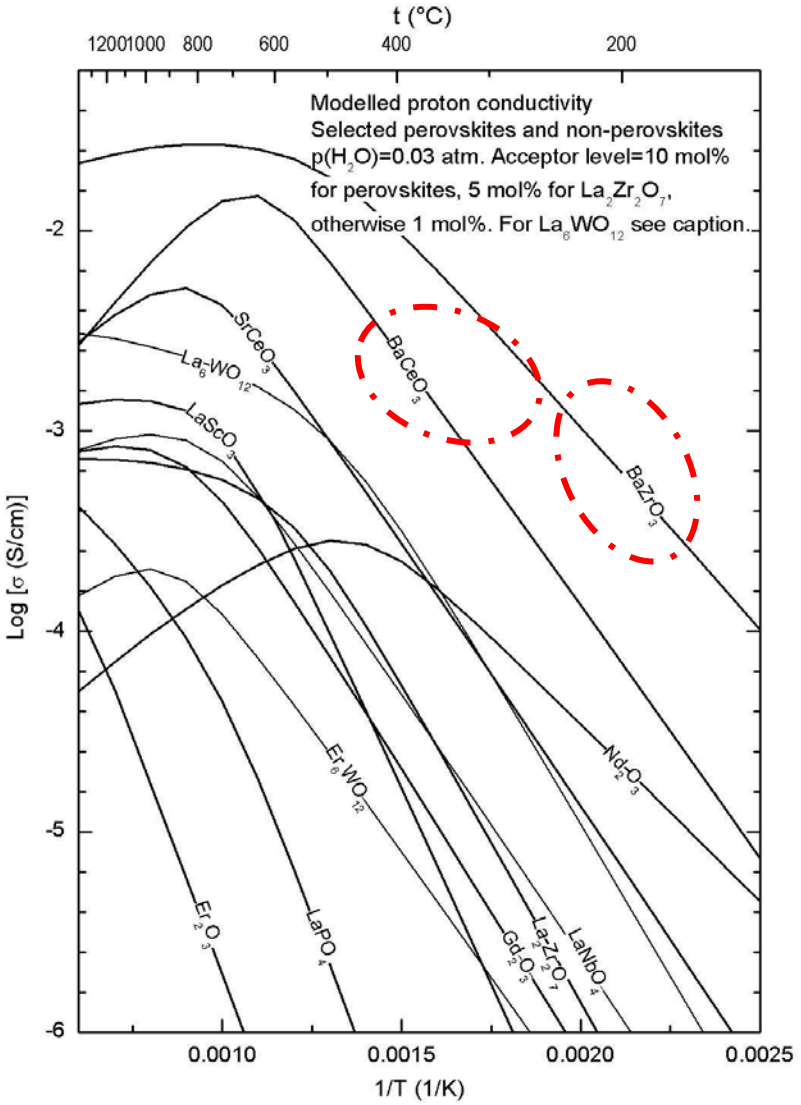
LSM

Double perovskite
(Ba,Co, Gd, La)



Electrolyte

- $BaZr_{1-x-y}Ce_xY_yO_{3-\delta}$ 10-20% Y ; 10-20% Ce
  - 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



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.

Solid state reactive sintering (SSRS)

Wet milling of precursor powders:
NiO (sintering additive) + $BaCO_3$,
Y_2O_3, ZrO_2, CeO_2

↓

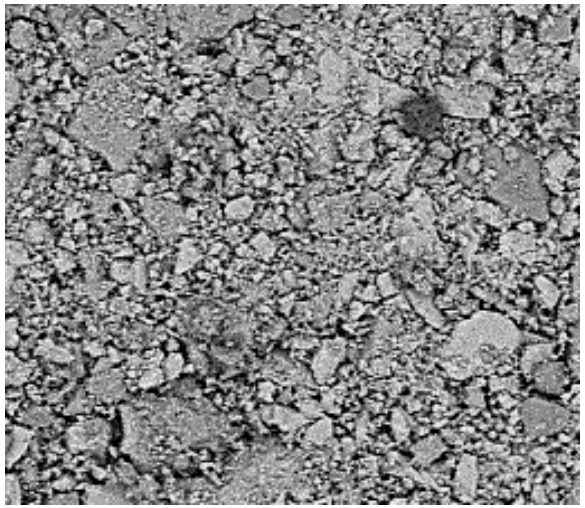
Drying of powders in oven

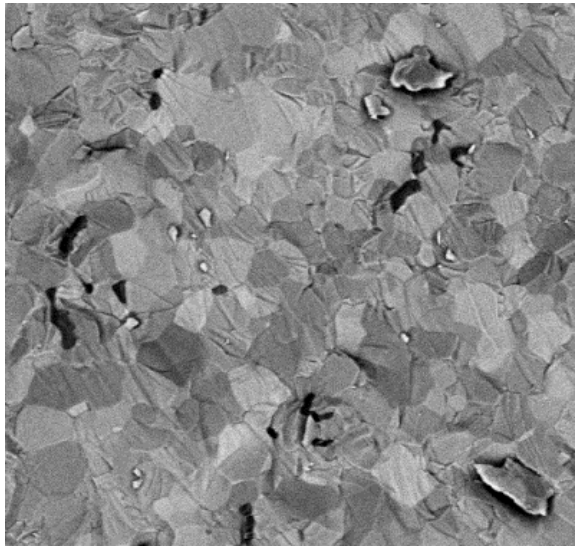
↓

Pressing and sintering

↓ *Liquid phase assisted sintering*

BZCY based dense pellets
with 1 wt. % NiO @ 1500°C



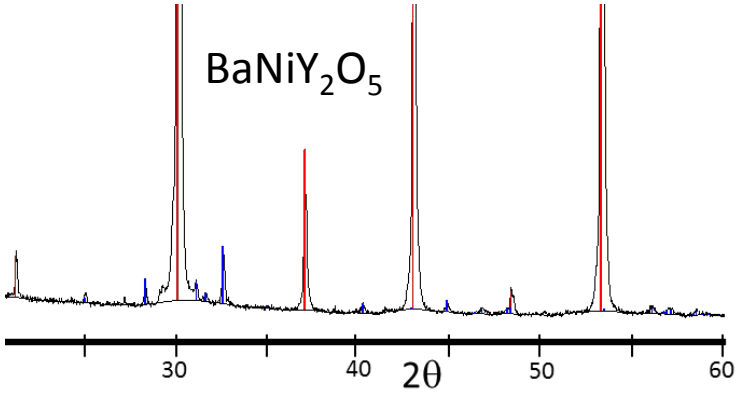


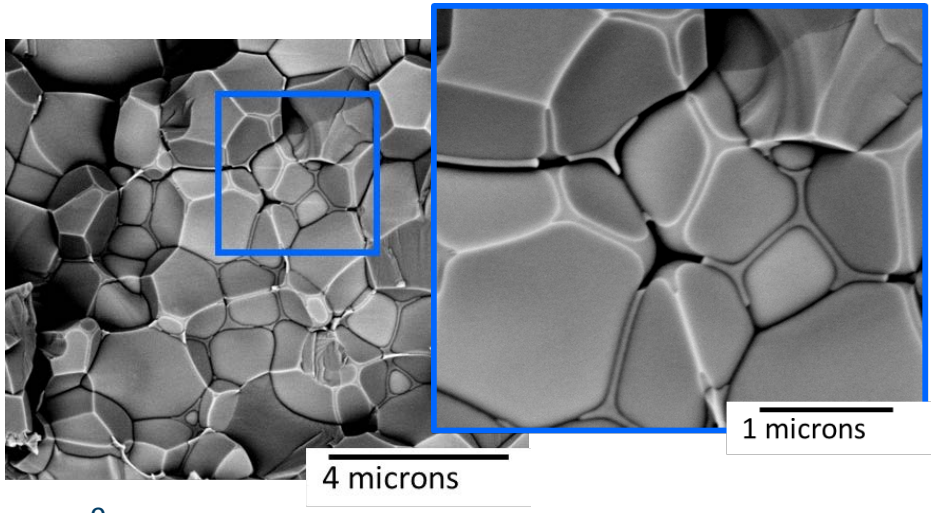
HT-XRD
E FEG-SEM
Dilatometry
DSC
TGA/DTA

G. Coors 2011, www.intechopen.com , J. Tong, Ryan O'Hayre et a., J. Mater. Chem., 2010, 20

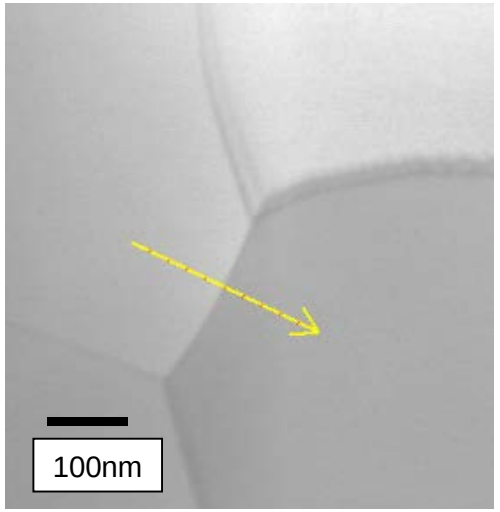
Where is Ni?

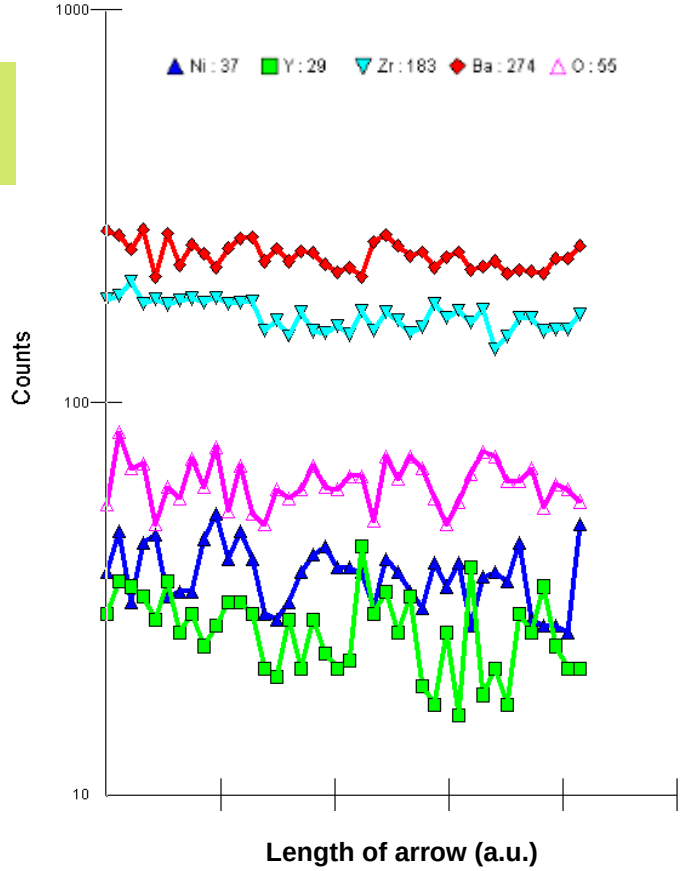
Ni in $BaNiY_2O_5$



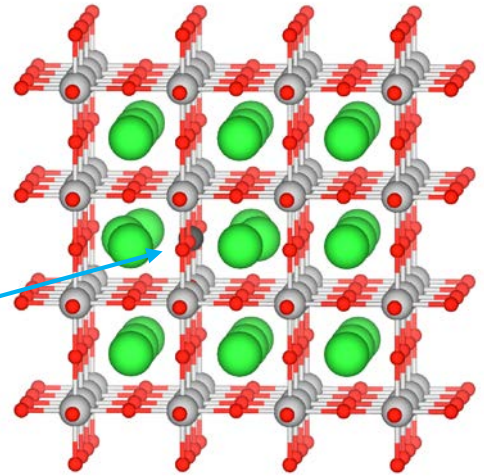


Ni is distributed in grains and grain boundaries





$Ni_i^{\bullet\bullet}$

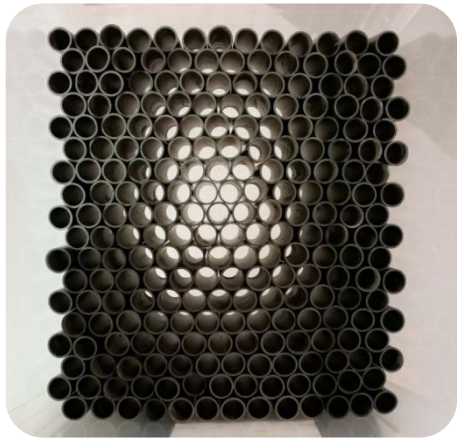


Stable interstitial Ni position (0.5, 0, 0)

Periodic DFT calculations
4x4x4 (320 atom) supercell
2x2x2 k-point grid

Solubility of transition metal interstitials in proton conducting $BaZrO_3$ and similar perovskite oxides, Jonathan M. Polfus, Marie-Laure Fontaine, Annett Thøgersen, Marit Riktor, Truls Norby and Rune Bredesen Journal of Materials Chemistry A

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

↓

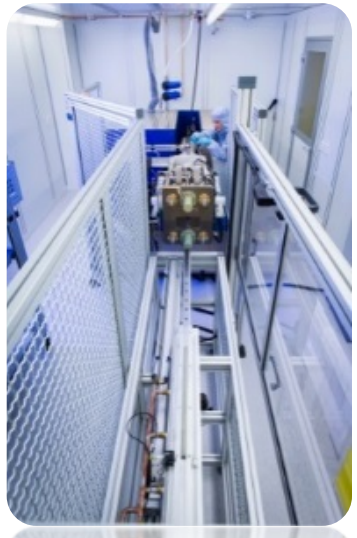
Drying, cutting to 40 cm

↓

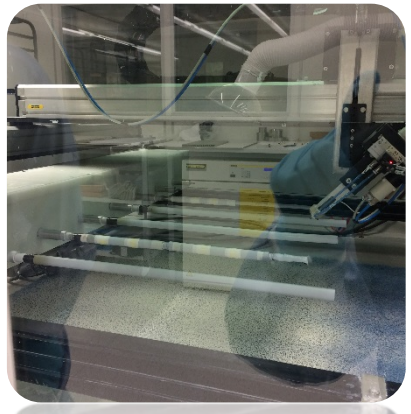
Spray-coating with suspension of SSRS mixture

↓

Sintering



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)

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

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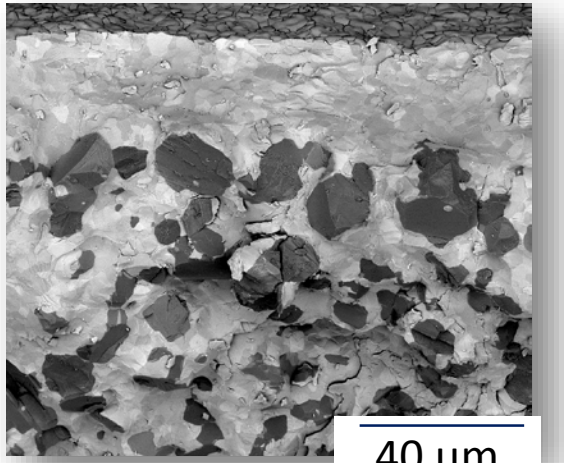
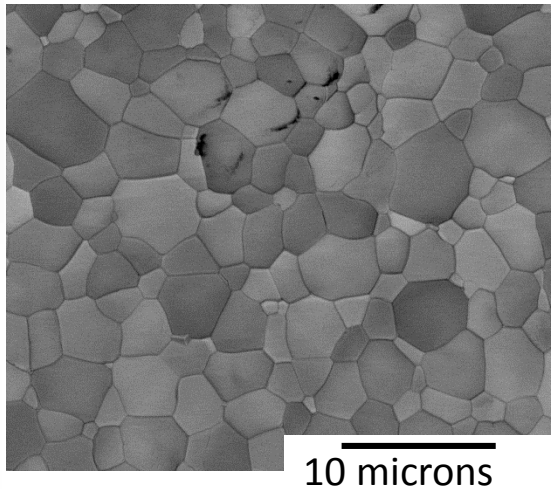
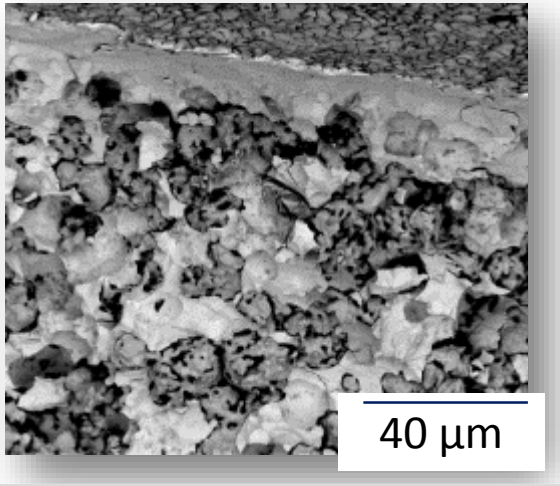
Half-cells before and after reduction



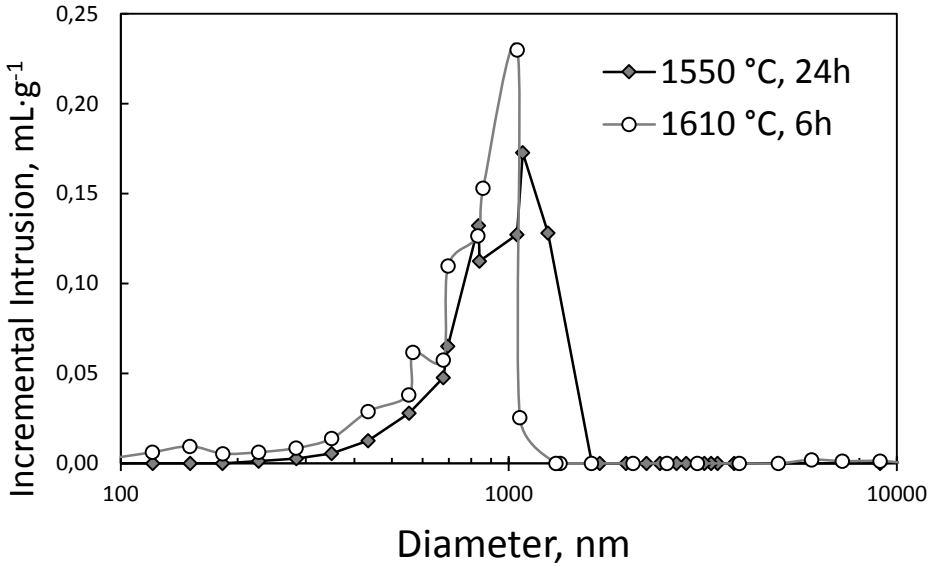
Sintered cell





Sintered reduced cell

Hg-porosimetry

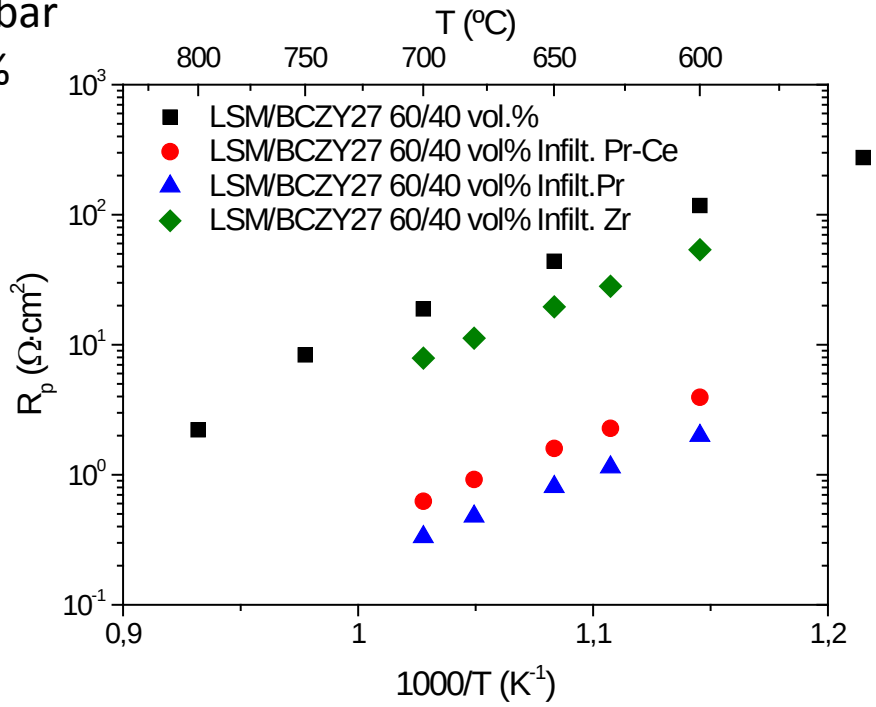


Between 27-32 vol% porosity (with 60 vol% Ni)

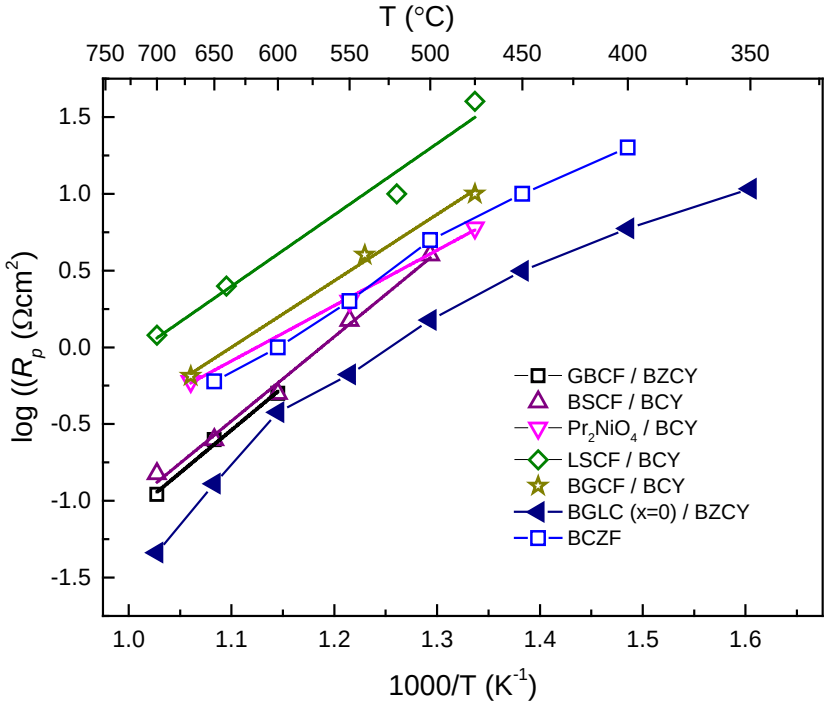
Steam electrode materials

$La_{0.8}Sr_{0.2}MnO_3/BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$
(symmetrical disk samples)

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



$Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$
(symmetrical disk samples)



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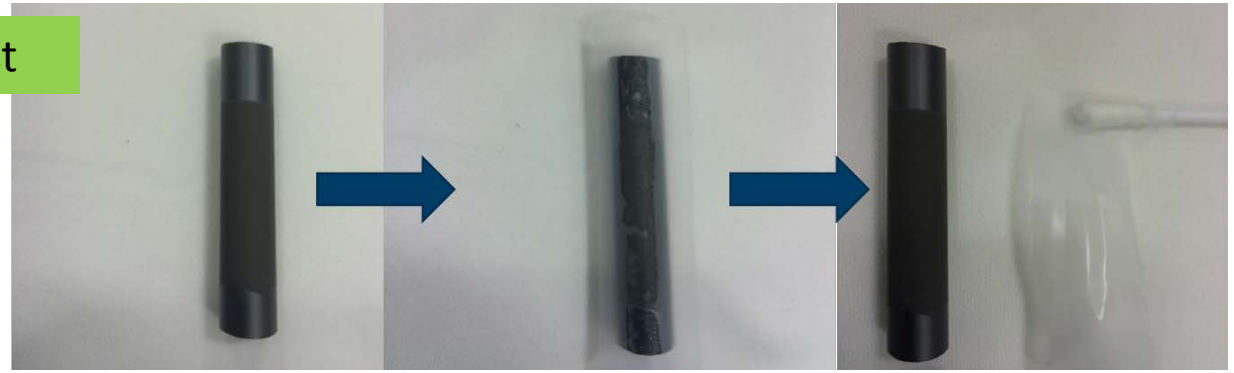
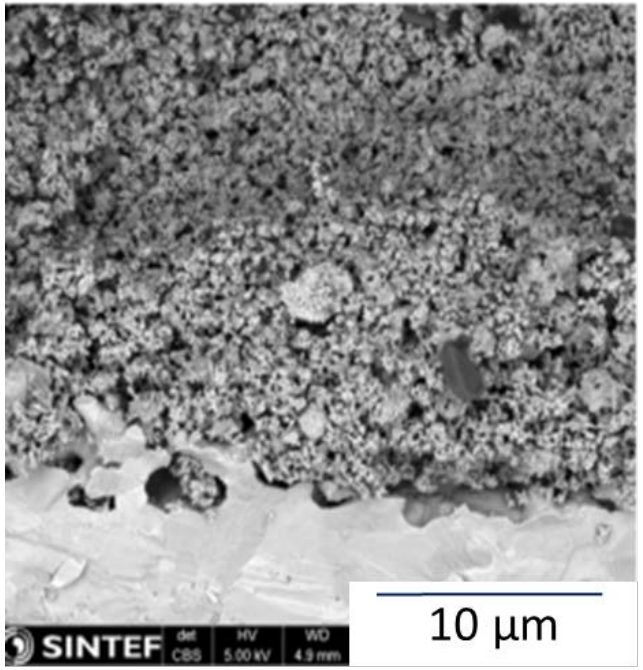
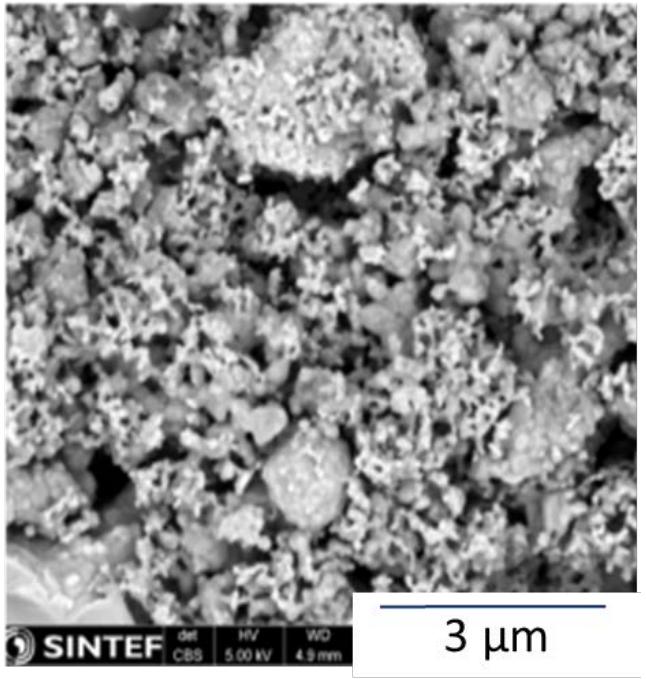
Manufacturing

- Dip-coating in oxide based suspensions (water or alcohol)
- Drying in air
- Annealing in air

Tape-test







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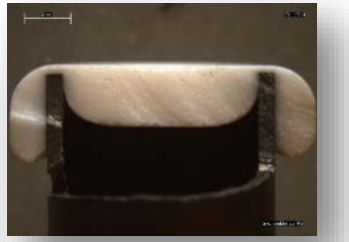
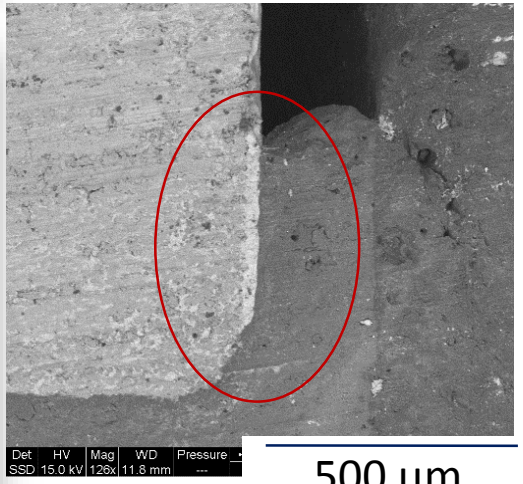
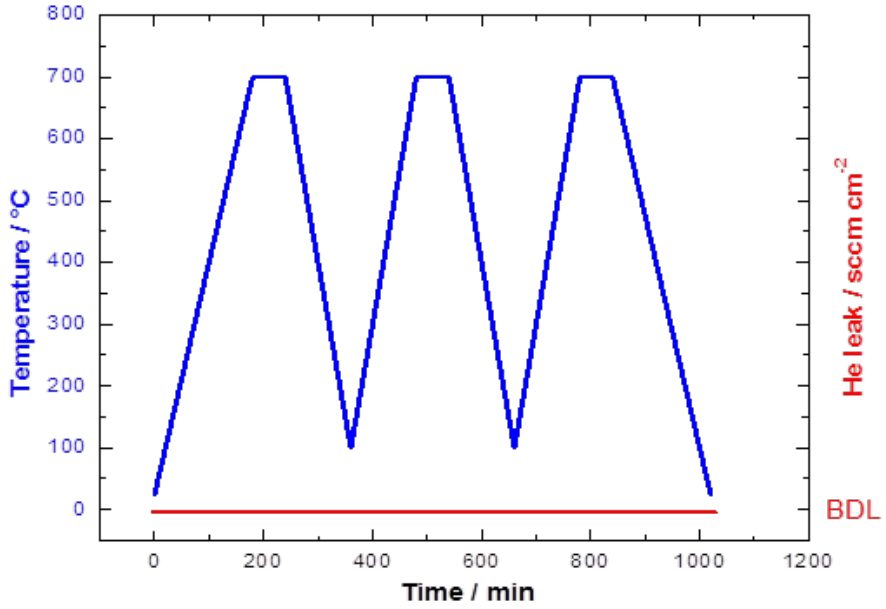
Sealing technology





500 µm



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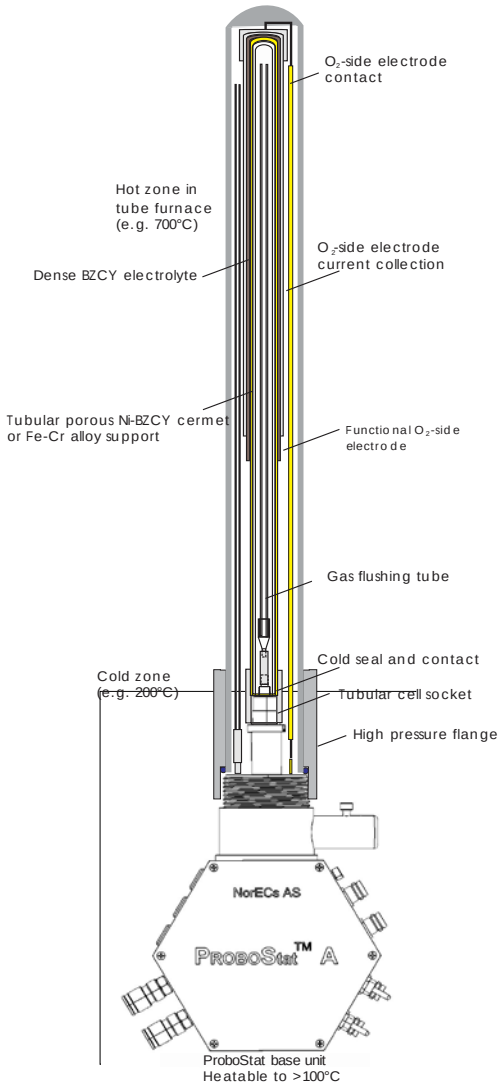
Complete cells

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



Cell Area:
5- 11 cm^2

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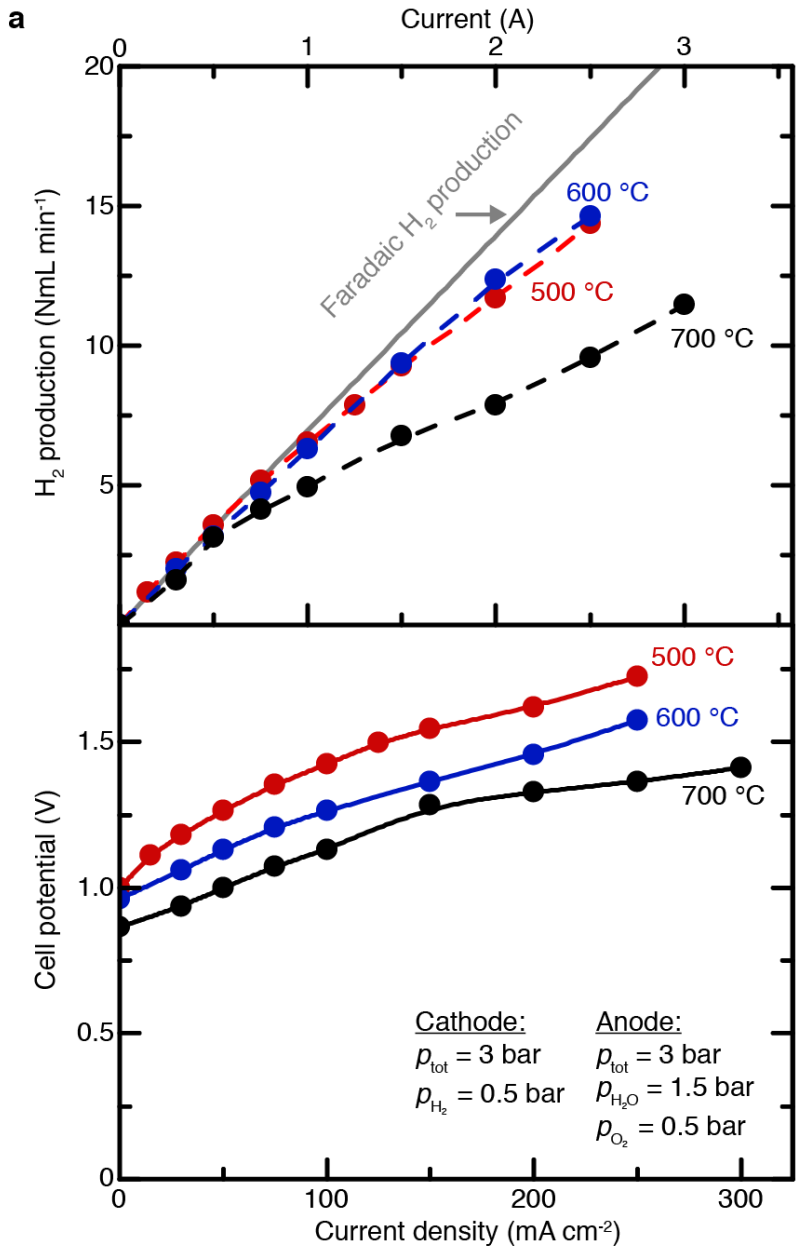
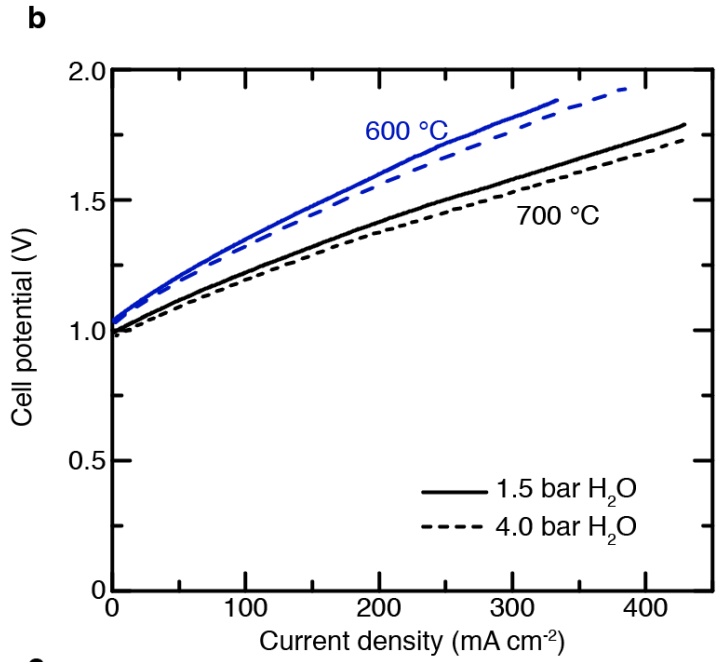
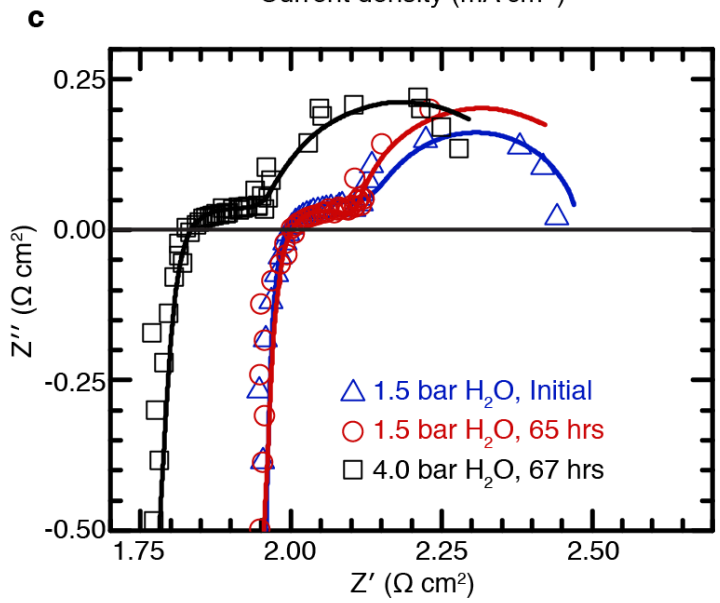
Performance

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

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

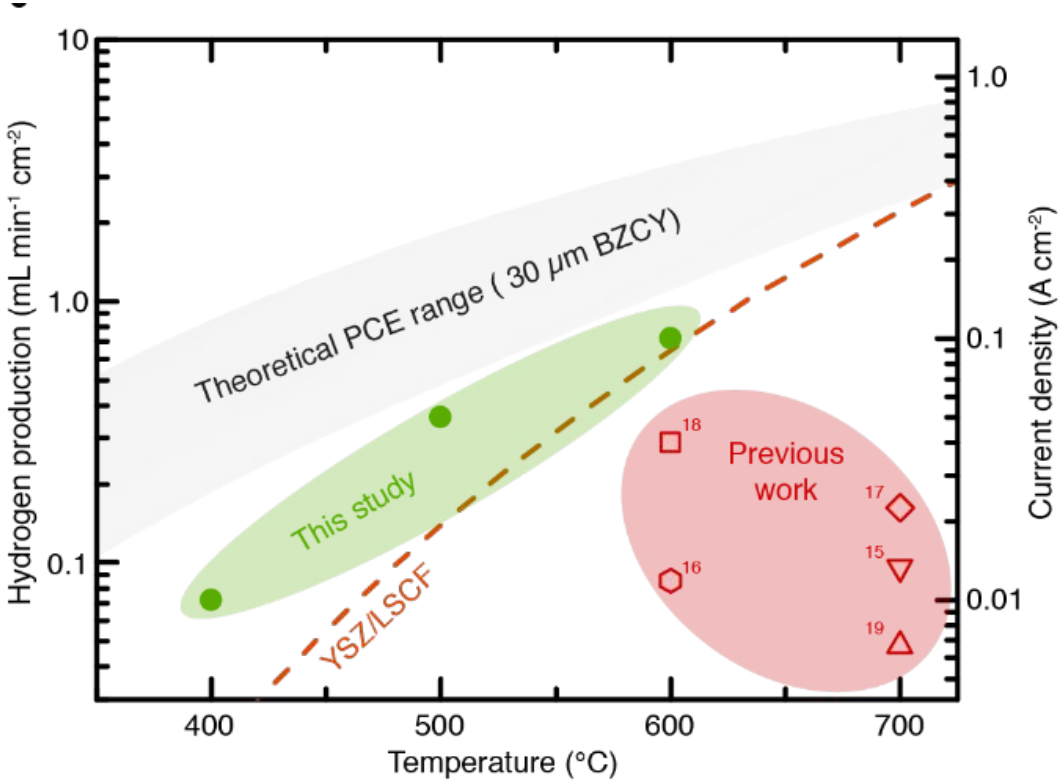






Summary

- Scalable production route
- Faradaic efficiency > 90%
- H_2 production rate > 10 ml/min at 500°C
- Ohmic losses observed during lab scale testing
  - Improvement of electrode + current collection design in progress



Next step

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

The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement n° 621244.

Research Council of Norway for the BIOPCFC project (number 219731/O70)

GAMER is a European research project co-financed by the European Union's Horizon 2020 research and innovation program and the Fuel Cells and Hydrogen Joint undertaking under grant 779486.