





SEGMENTED-IN-SERIES PROTON CONDUCTING TUBULAR ELECTROLYSERS

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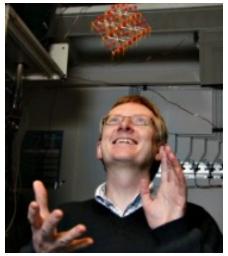
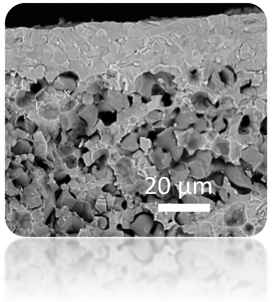
UiO Department of Chemistry
University of Oslo

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

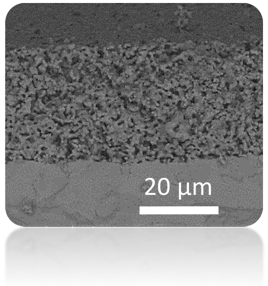


Electra

Fabrication of BZY-based segmented-in-series tubular electrolyser cells



Development of mixed proton-electron conducting anodes

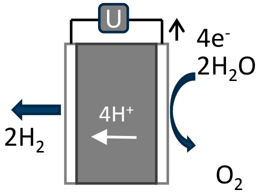


Presentations:

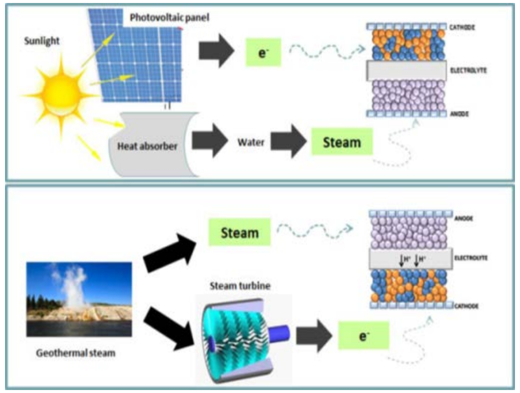
- *Nuria Bausá et al.: LSM/BZCY (19/09)*
- *Ragnar Strandbakke et al.: BGLC / BZCY (20/09)*

1 kW module development

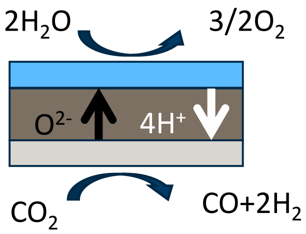
H_2 production from steam and electricity

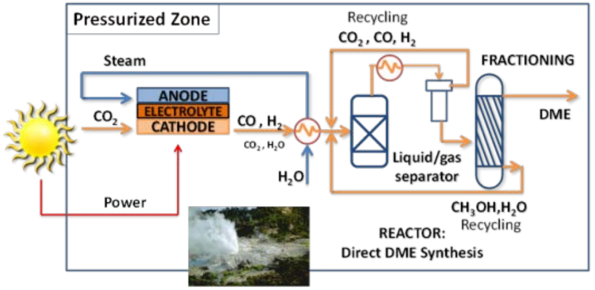


Presentation: Einar Vøllestad et al. (22/09)



DME/Ethanol production from steam, CO_2 and electricity



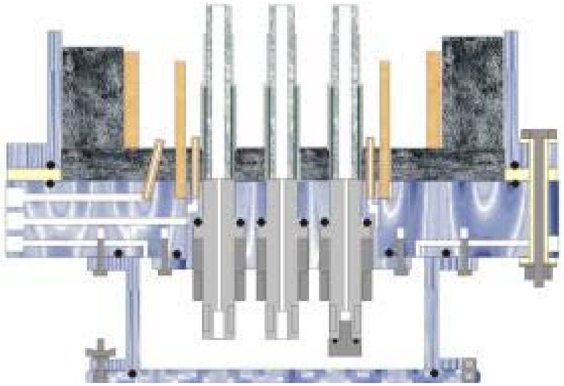


CSIC — Consejo Superior de Investigaciones Científicas | CoorsTek Membrane Sciences | UiO Department of Chemistry, University of Oslo | Marion Technologie | ABENGOA HIDROGENO | Carbon Recycling International | SINTEF

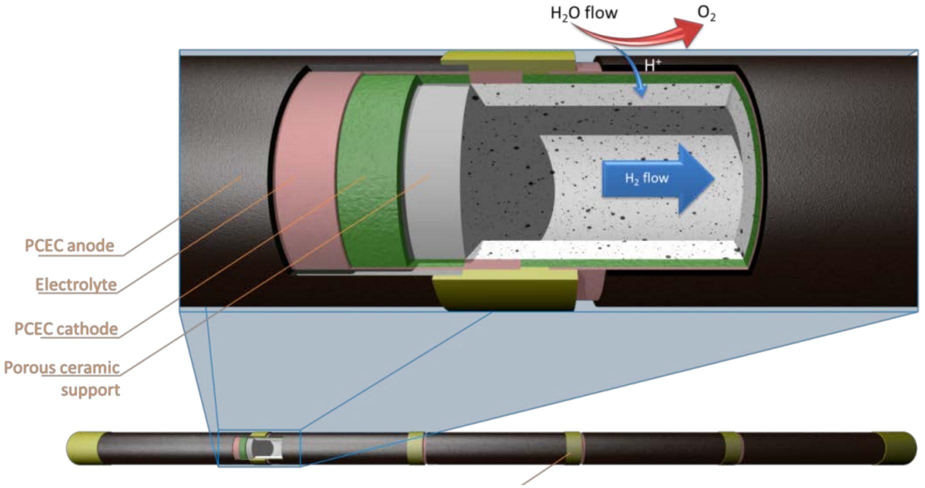
Scaling up tubular proton ceramic electrolysers

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

- Segmented-in-series cells
  - Higher tube voltage – lower tube current

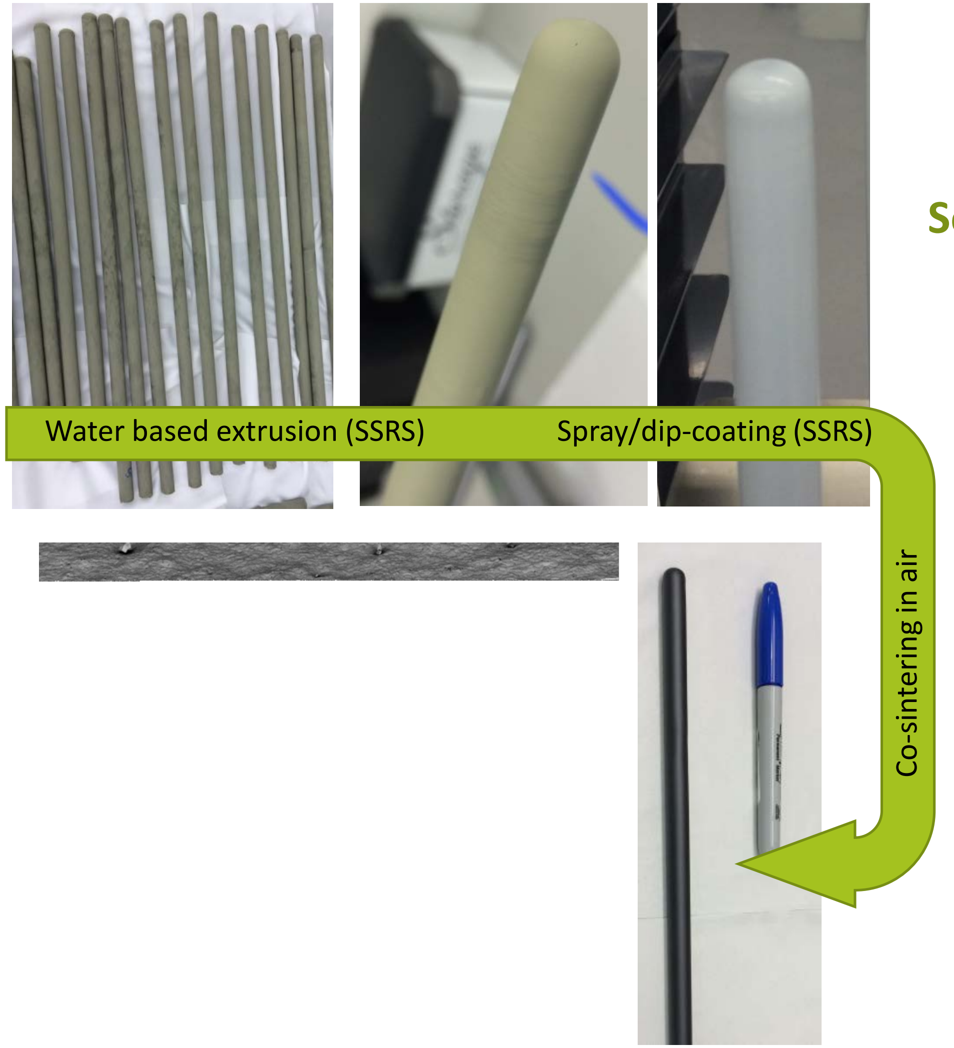


Courtesy: UiO



Courtesy: CSIC

Segmented-in-series cells by STACKING



Solid state reactive sintering:

- Limited number of processing steps
- Fast sintering
- Lower CO_2 emissions
- Lower cost

COORSTEK
MEMBRANE SCIENCES

BZCY-NiO//BZCY

$BaZr_{0.70}Ce_{0.20}Y_{0.10}O_3$ $BaZr_{0.90}Y_{0.10}O_3$

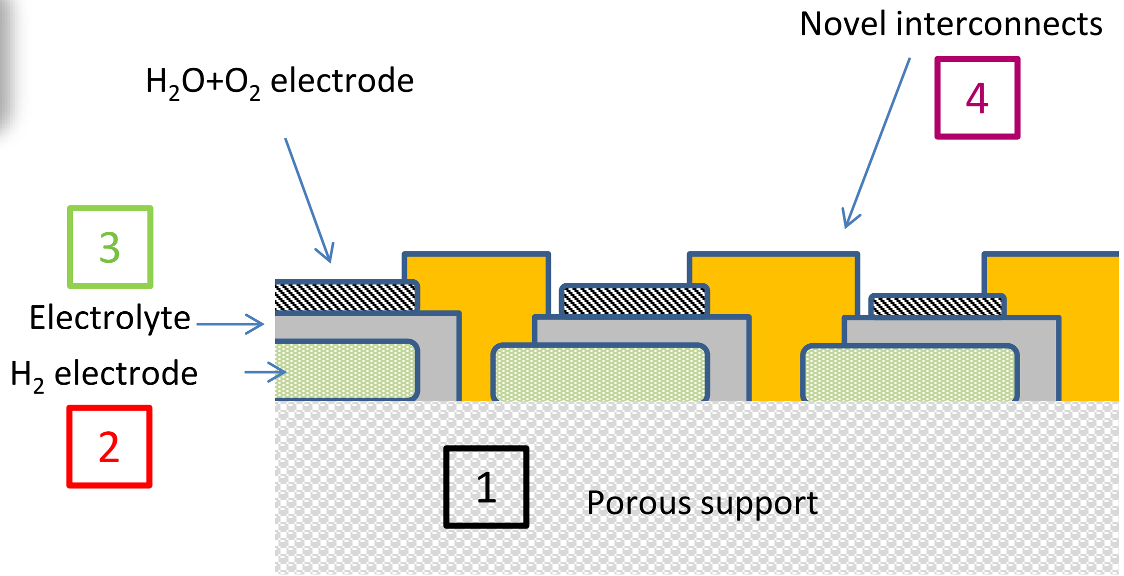
Segmented-in-series cells by PRINTING-MASKING

Easier fabrication route
Mass scale production

- **Step 1:**
  Materials screening
  (sintering shrinkage; TEC; reactivity study, etc.)

- **Step 2:**
  Selection of most promising materials and processing routes

- **Step 3:**
  Manufacturing of half-cells



1 — BZCY72

2 — BZY10 or BZCY72 + NiO

3 — BZCY72 or BZY10

4 — Oxides (SINTEF, UiO)
Glass composites (CSIC)

$BaZr_{0.90}Y_{0.10}O_3$

$BaZr_{0.70}Ce_{0.20}Y_{0.10}O_3$

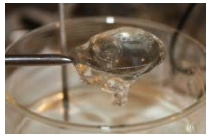
SINTEF

Manufacturing process based on SSRS

Powder conditioning

- Milling of $BaSO_4$, CeO_2, Y_2O_3, ZrO_2 powders
- Drying
- Sieving
- Batching

Pastes preparation



Slurries preparation

- Water based slurry for SSRS mixtures

Clean room class 7

Production of tubes by extrusion and collars

- Drying
- Cutting

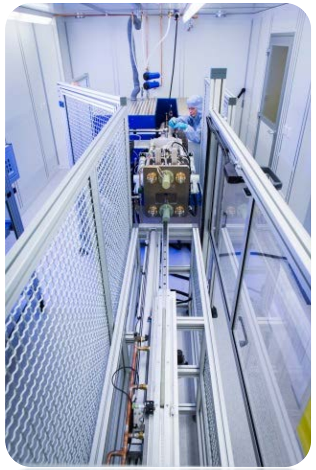
Dip-coating of fuel electrode and electrolyte

- Drying step @controlled T

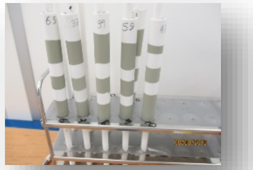
Co-sintering of layers

Dip-coating of interconnect

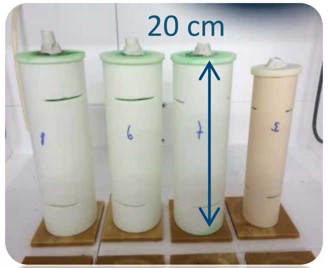
Firing



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



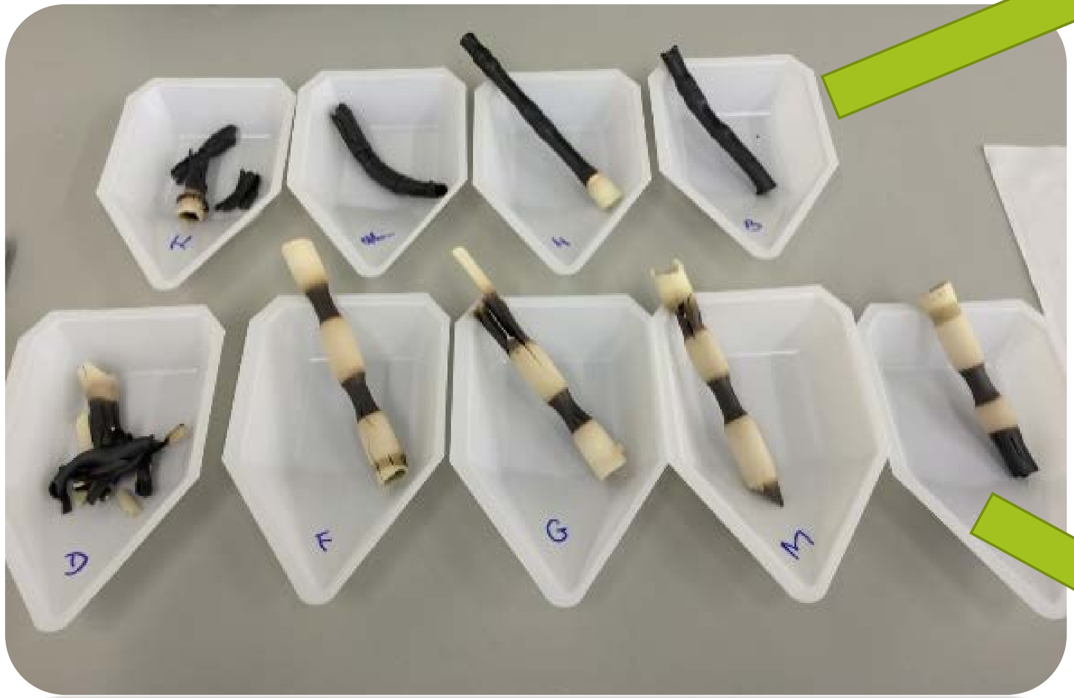
Semi-automatic dip-coater for 1 m long sample (batch of 8 samples)



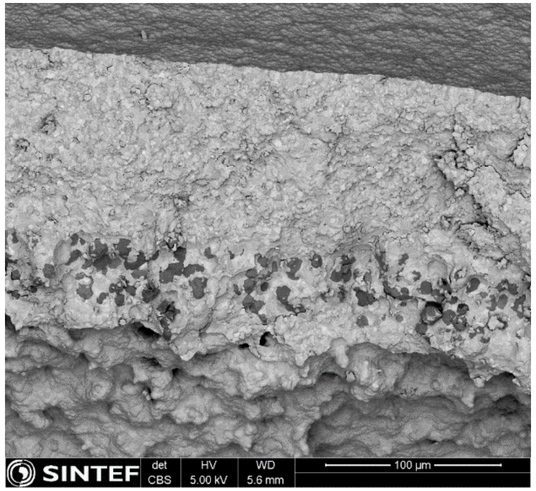
Hang-firing

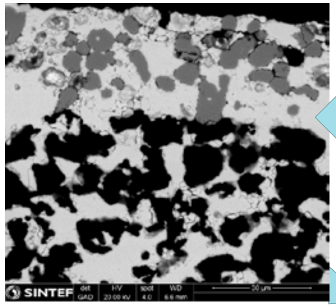
Electra

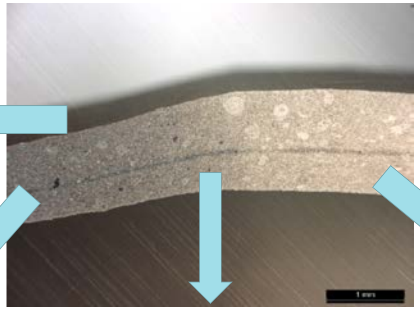
Challenges

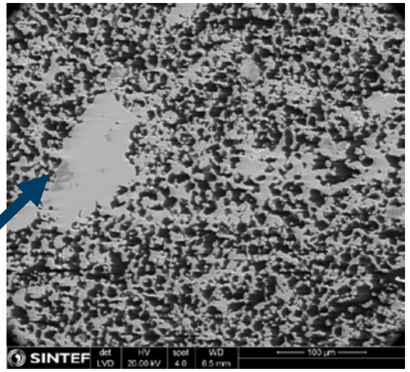


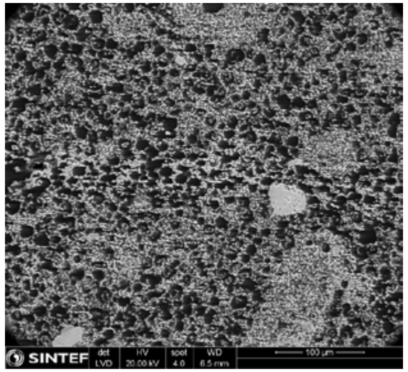
Co-sintered support + electrode + electrolyte

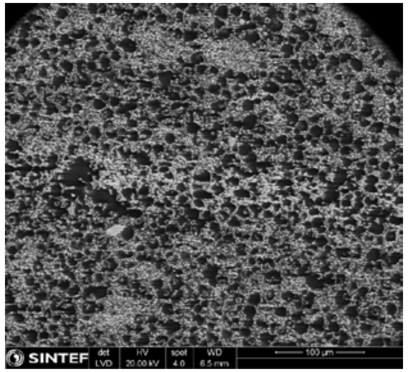










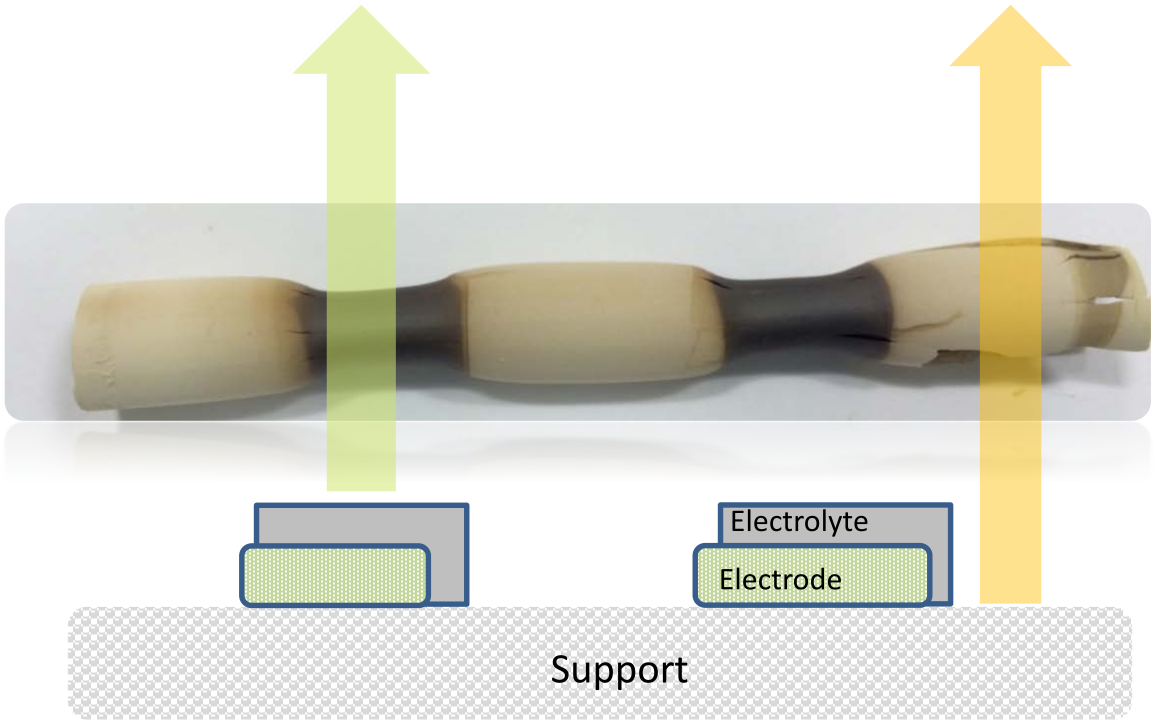


EDS: Ni

Routes for tailoring shrinkages

Pore formers and sintering aid

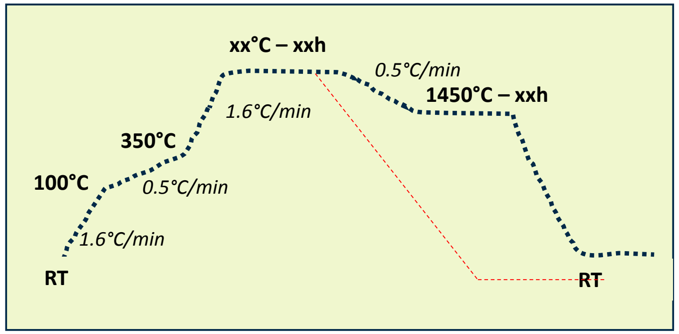
- Addition of pore formers (A) in the electrode + reduction of temperature
- Addition of sintering aid + pore formers (B) in the support

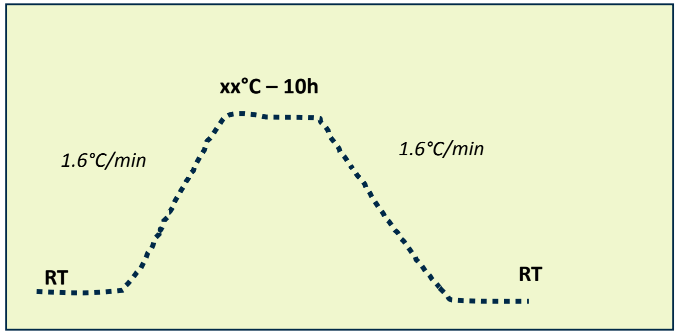


Various thermal profiles

Temperature:
- 1500 °C
- 1525 °C
- 1530 °C
- 1540 °C
- 1550 °C
- 1600 °C

Dwell:
- 2h
- 5h
- 10h





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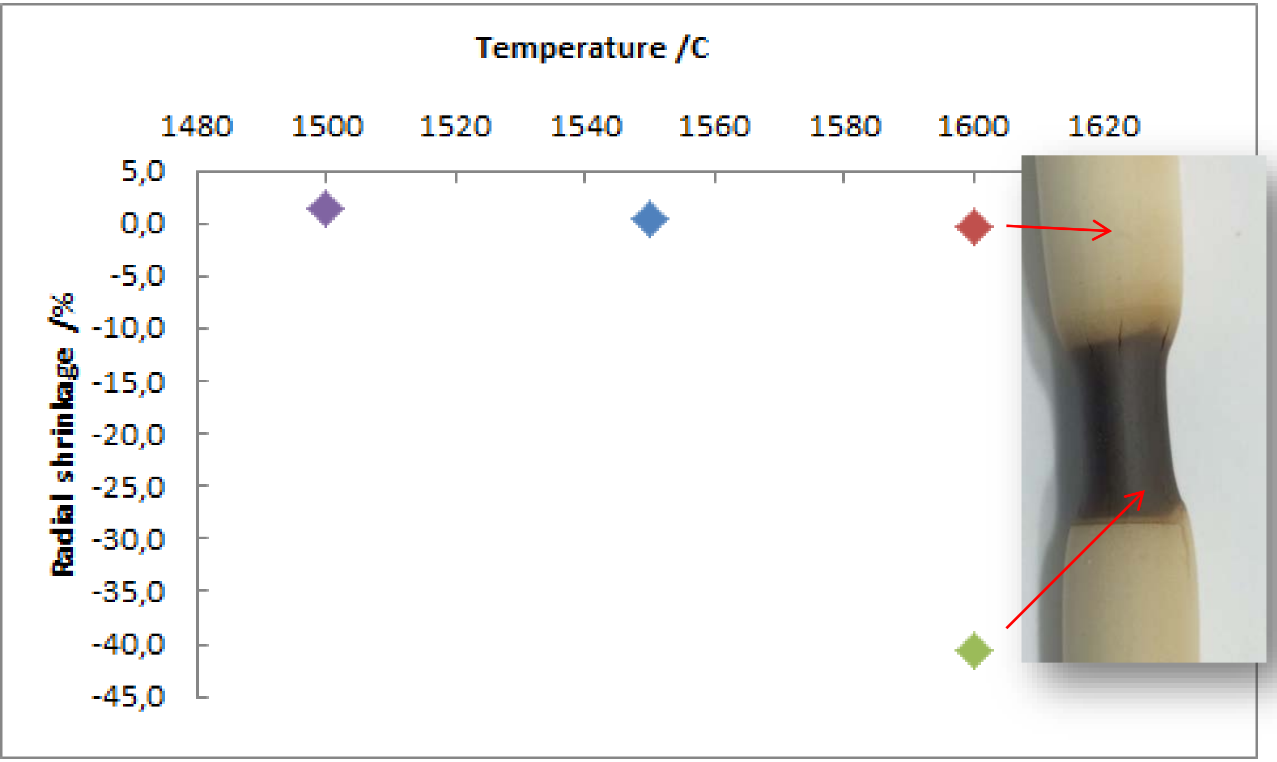
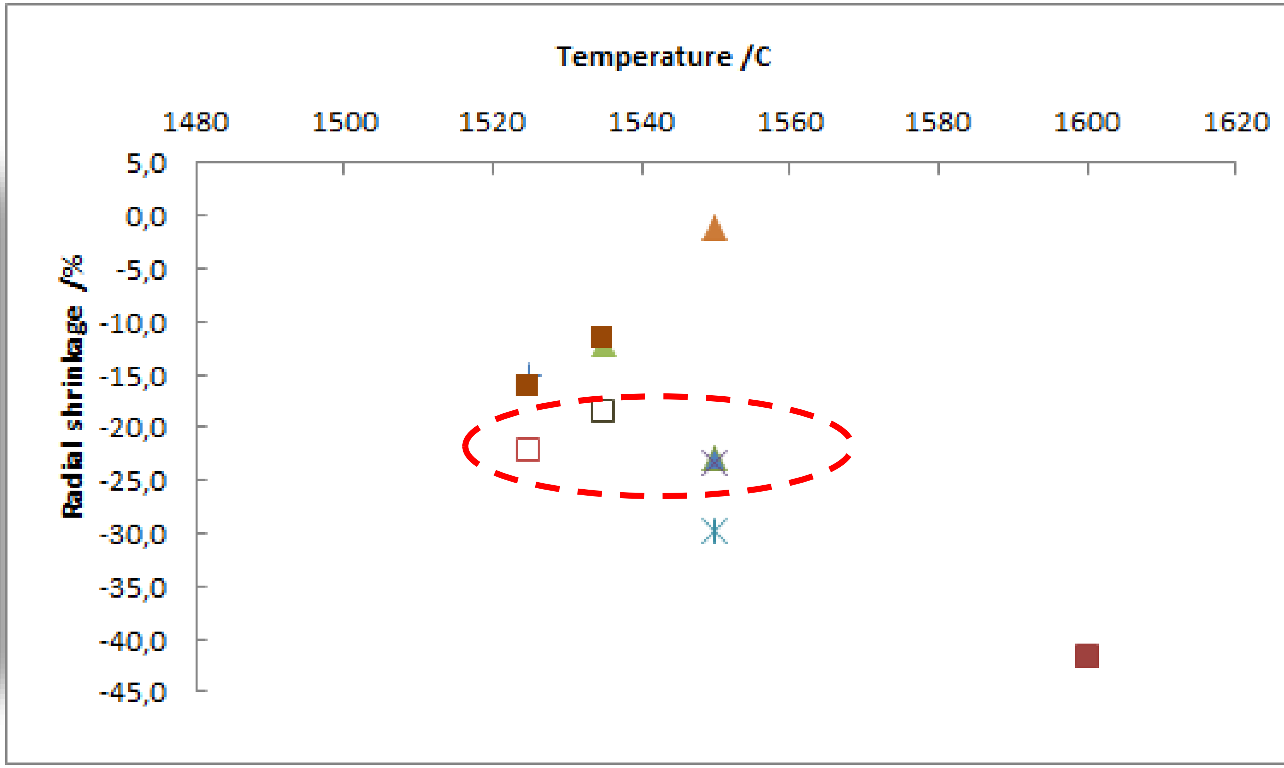
Sintering shrinkage

"REFERENCE CASE"

SUPPORT WITH ADDITION OF SINTERING AID + ELECTRODE with PF + ELECTROLYTE



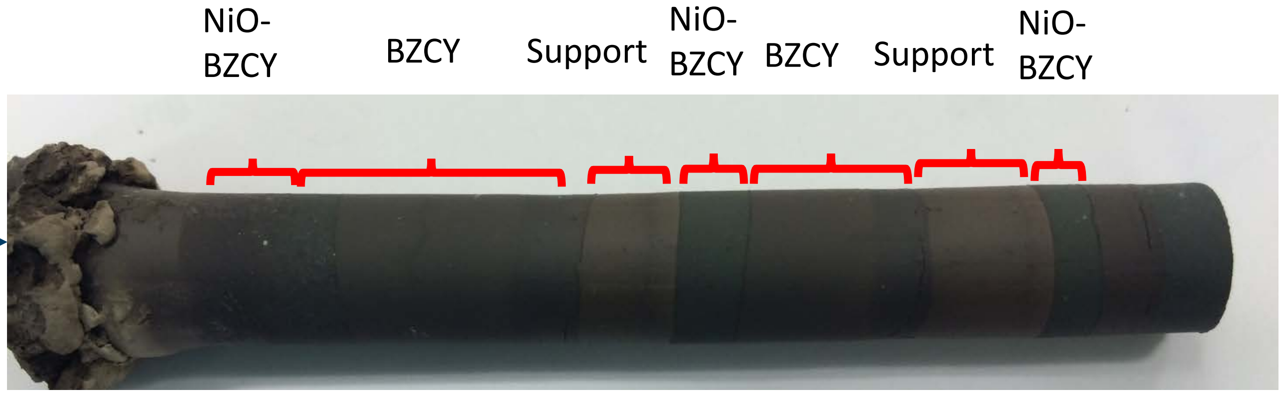


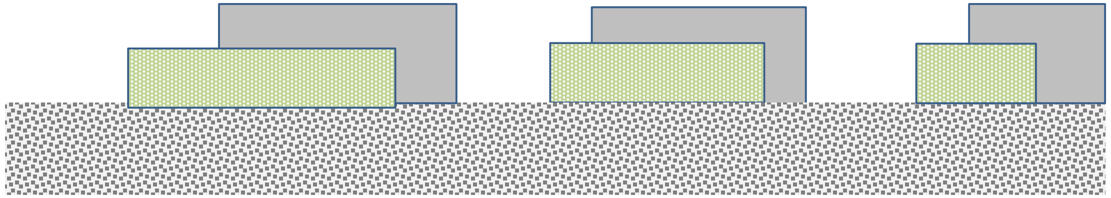
DIFFERENTIAL SHRINKAGE ALONG THE TUBE

UNIFORM SHRINKAGE ALONG THE TUBE

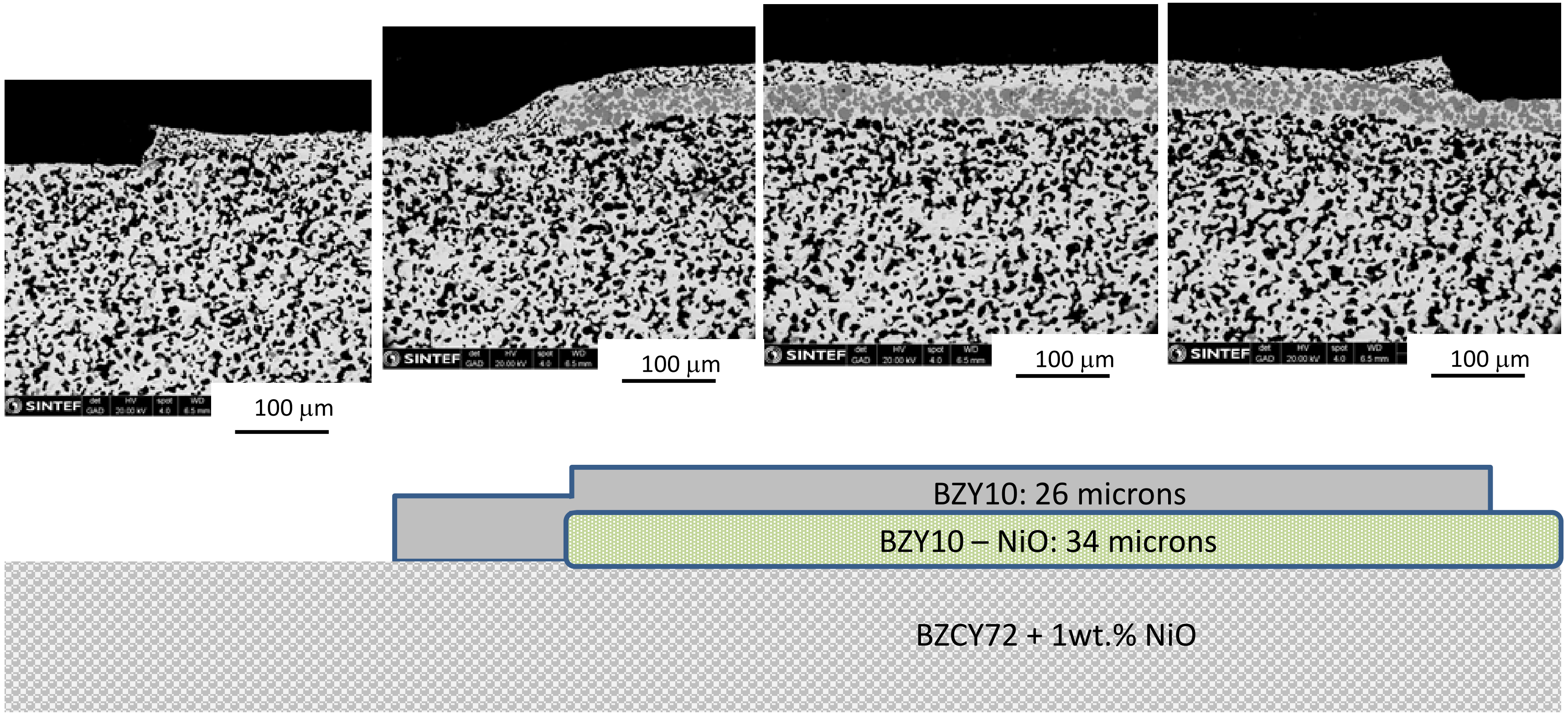
Sintering @ 1550 °C - 5h

Collar for hang-firing



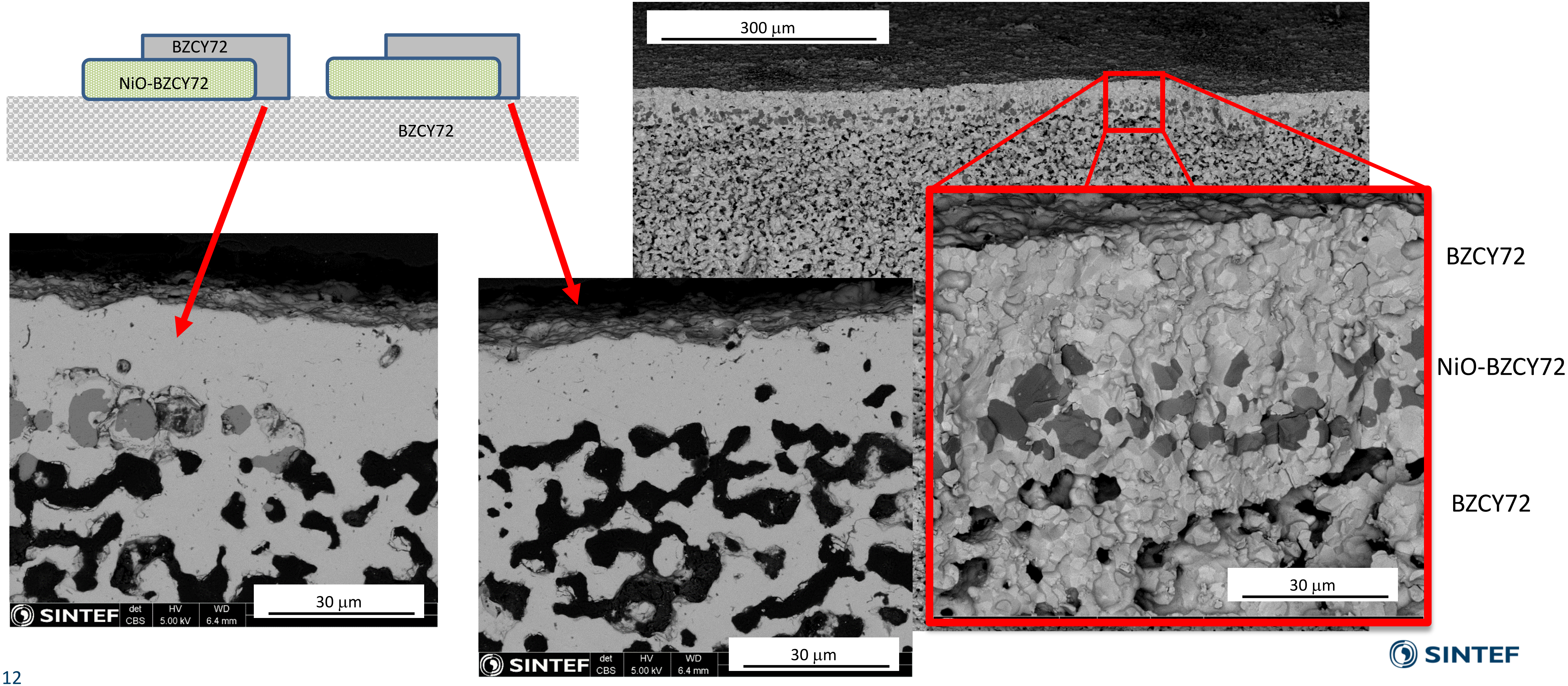


Sintering 1550 °C - 5h



Polished sample in resin: one segment

Sintering 1550 °C - 10h



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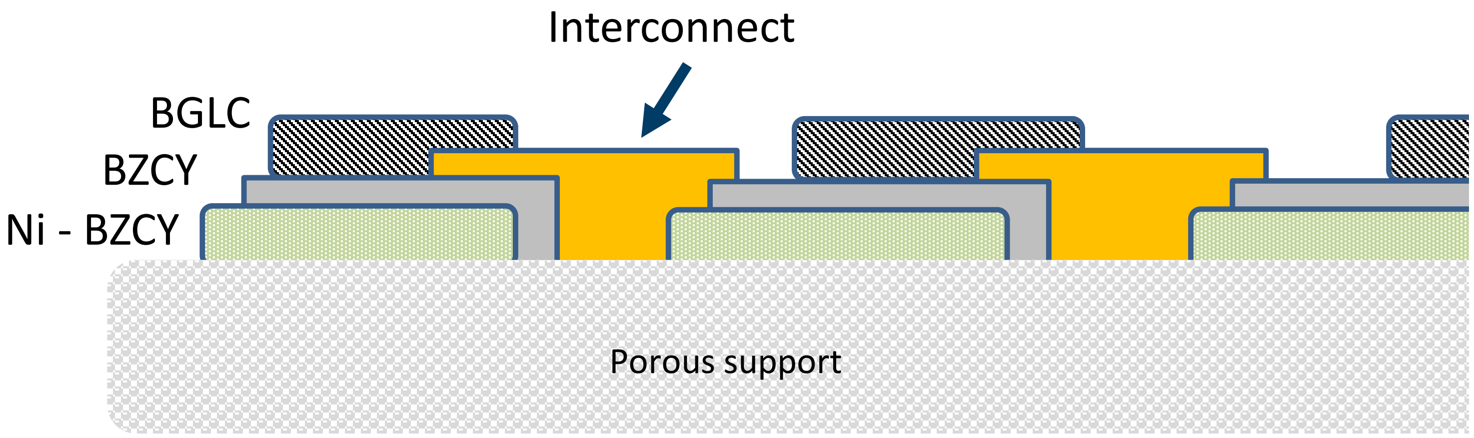
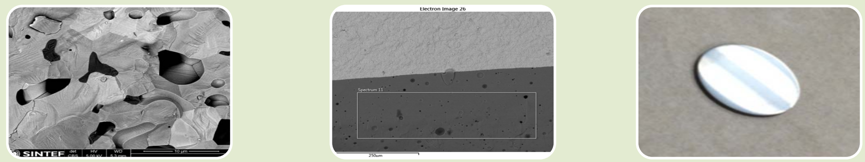
Interconnects

Requirements:
- *Stability/conductivity required in air and reducing conditions*
- *Gas tightness*
- *TEC similar to other components*



Contact area between BGLC//interconnect//Ni : ~1.5 cm^2
Thickness of interconnected area ~20 μm
Total resistance: 10^{-3} Ω with interconnect conductivity of 1 Scm^{-1}.

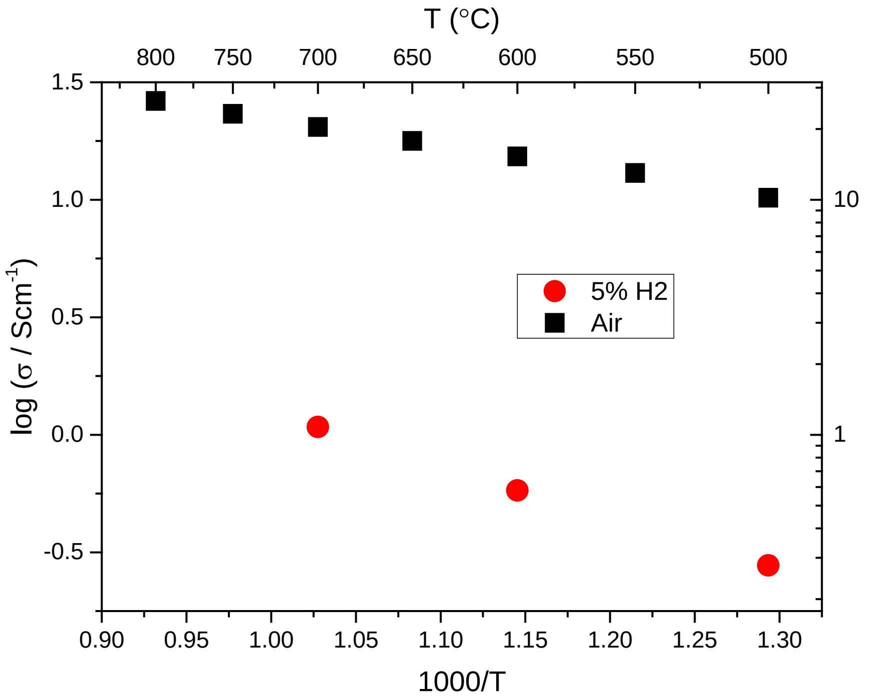


LSCM (SINTEF, UiO)	Glass - Metal composites (CSIC)	BGLC – $TiNb_2O_7$ (SINTEF, UiO)

$La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_{3-\delta}$

Dense pellets prepared by co-sintering LSM and LSC (1:1 mol. ratio) at 1500 °C; XRD analysis + Rietveld refinements + SEM: single phase

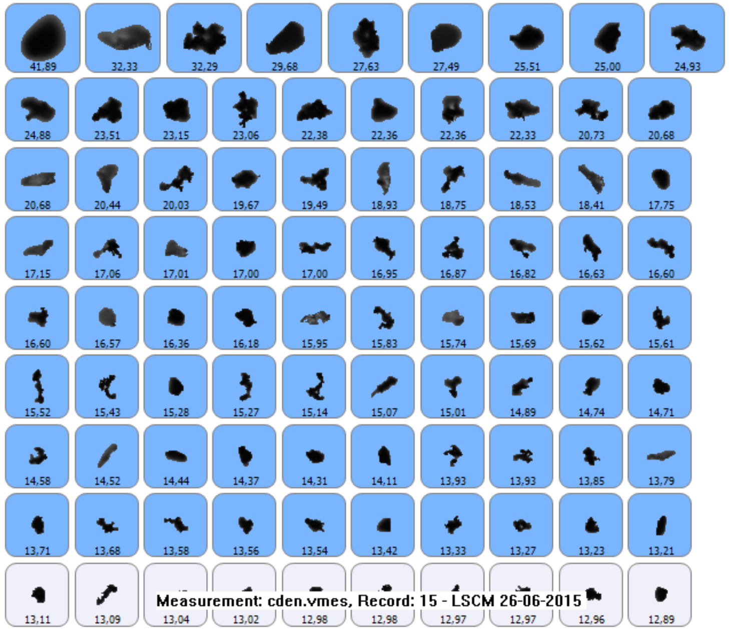
Conductivity in air and 5 % H_2 in Ar

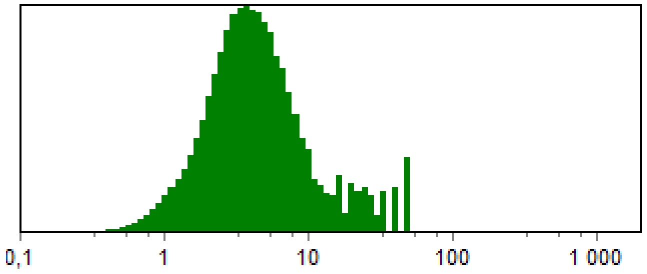


Spray-coating of interconnect

- Crushed pellets
- Planetary milling
- Sieving

D(10)= 1,6 um
D(50)= 4,1 um
D(90)= 15,6 um



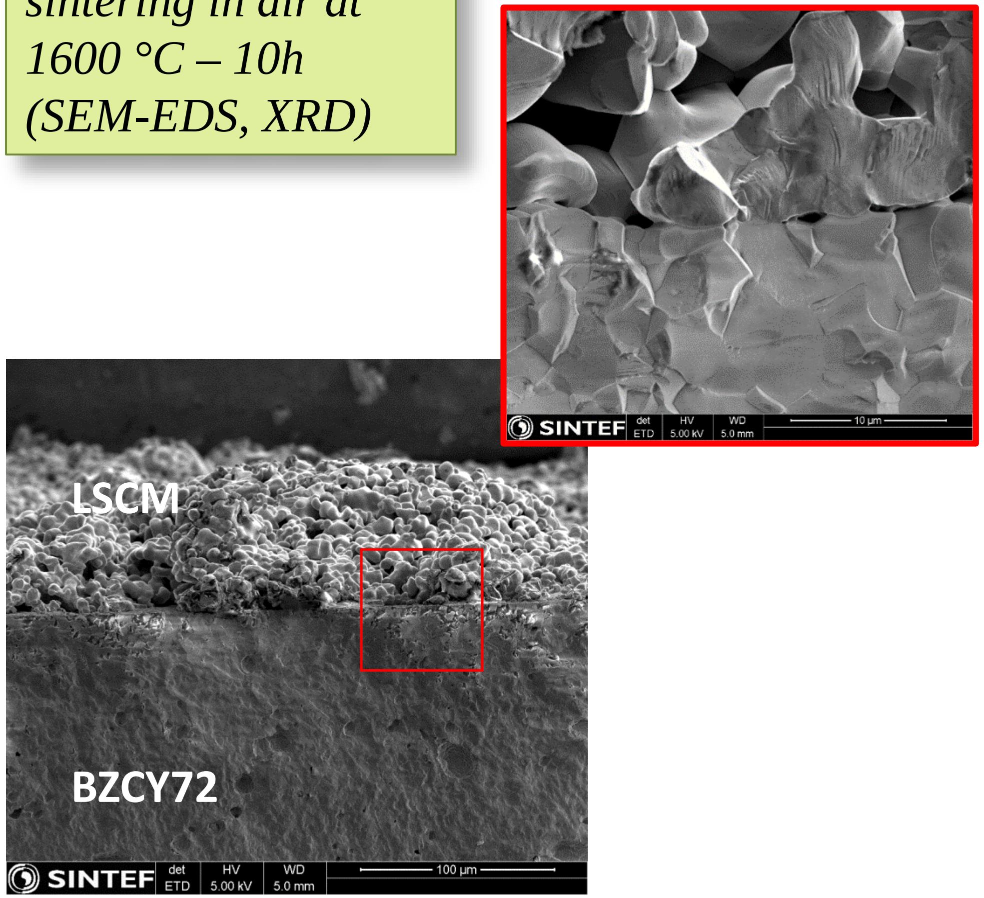


Malvern G3

SINTEF

$La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_{3-\delta}$

Compatibility after sintering in air at 1600 °C – 10h (SEM-EDS, XRD)



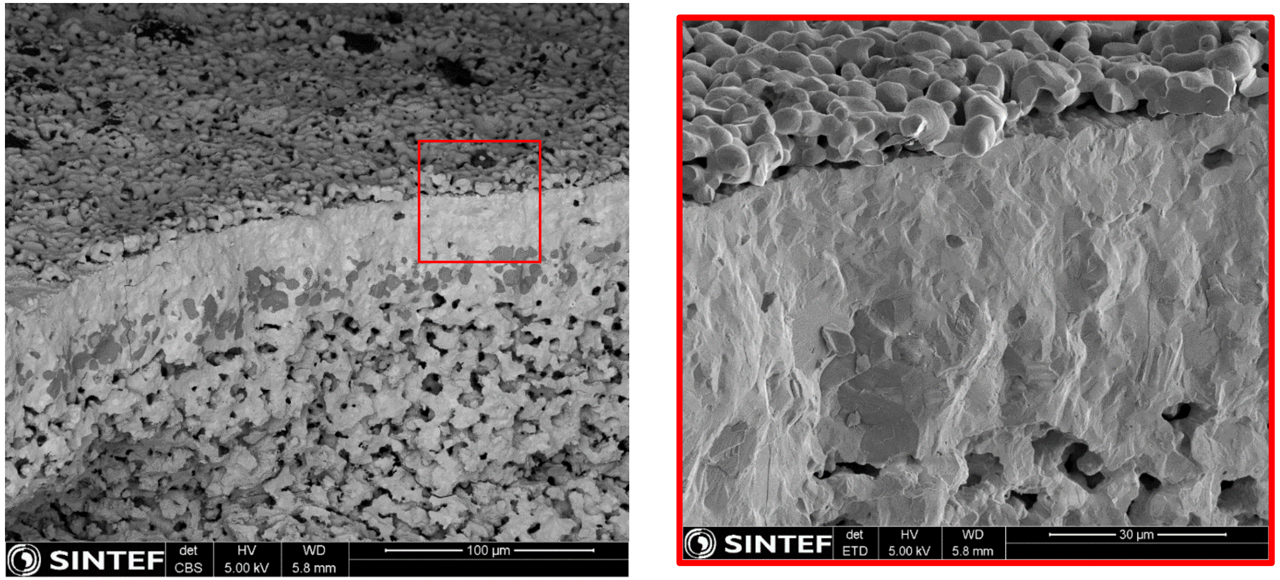
Spray-coating of LSCM and sintering at 1500 °C on SIS cells

LSCM

BZCY72

NiO-BZCY72

BZCY72



Conclusions

- Segmented-in-series tubular cells
- Protocols for manufacturing of cells currently being tuned to tailor thickness and porosity/density of the functional layers
  - Investigation of interconnect materials in progress:
    - Several materials under investigation
    - Various protocols for coating and sintering under investigation

Acknowledgements

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.