UiO : Department of Chemistry
University of Oslo

SINTEF

SMN
SENTER FOR MATERIALVITENSKAP OG NANOTEKNOLOGI

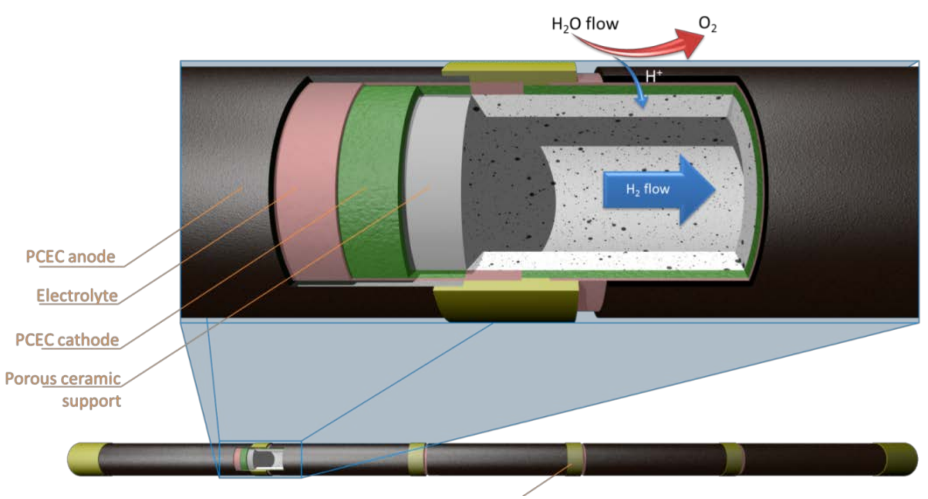
# Development of Tubular Proton Conducting Electrolysers

Einar Vøllestad[2], M.L. Fontaine[1], C. Denonville[1], R. Strandbakke[2], J.M. Serra[3], D.R. Beeaff[4], C. Vigen[4] and T. Norby[2]

*[1] SINTEF Materials and Chemistry, [2] University of Oslo, [3] CSIC, [4] CoorsTek Membrane Sciences AS*

Electra

FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING



UiO : Department of Chemistry
University of Oslo

SMN
SENTER FOR MATERIALVITENSKAP OG NANOTEKNOLOGI

# Development of Tubular Proton Conducting Electrolysers

Einar Vøllestad[2], M.L. Fontaine[1], C. Denonville[1], R. Strandbakke[2], J.M. Serra[3], D.R. Beeaff[4], C. Vigen[4] and T. Norby[2]

*[1] SINTEF Materials and Chemistry, [2] University of Oslo, [3] CSIC, [4] CoorsTek Membrane Sciences AS*

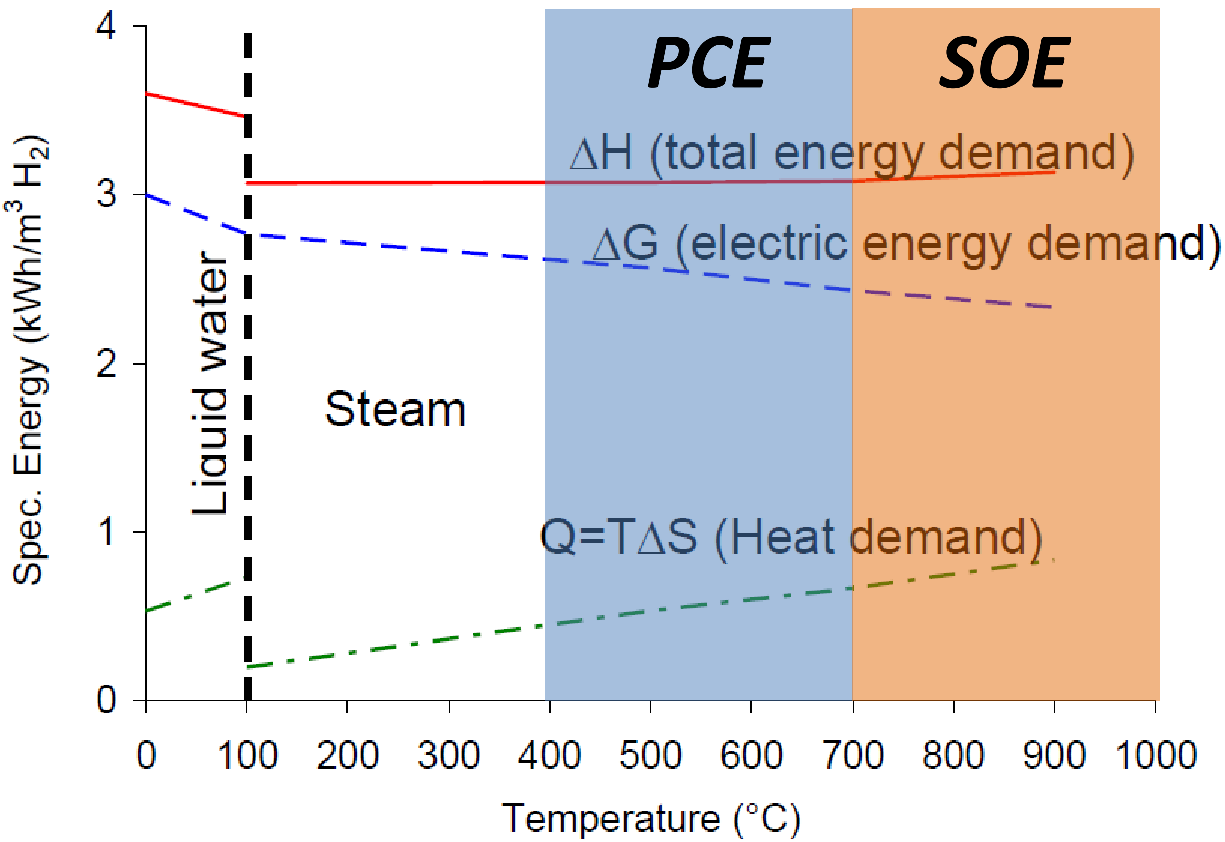
Electra

FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

- Why high temperature proton ceramic electrolysers?
- Processing and performance of early-stage single cells
- Up-scaling strategies for tubular proton ceramic electrolysers

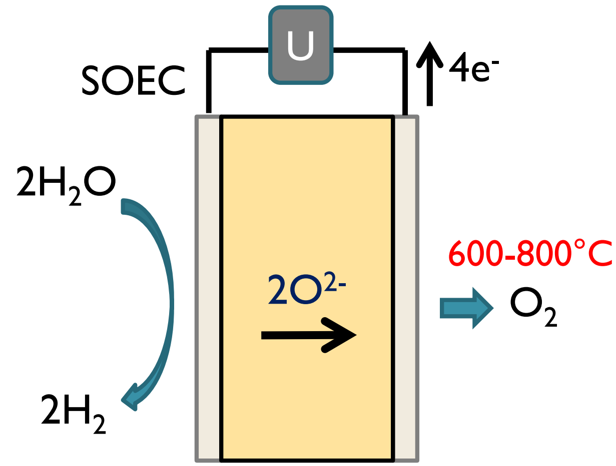
# High temperature electrolysis enables utilization of waste heat resources

$$2H_2O \overset{\Delta H}{\Rightarrow} 2H_2 + O_2$$

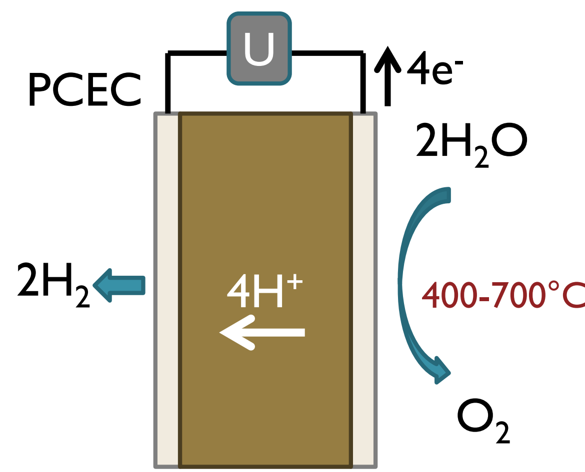


# Key differences between SOE and PCE
## - advantages and challenges

- Solid Oxide Electrolysers
  - Well proven technology
    - Scalable production
    - High current densities at thermo-neutral voltage
  - Long term stability challenges
    - Delamination of $O_2$-electrode
    - Oxidation and degradation of Ni-electrode with high steam contents
  - High temperatures

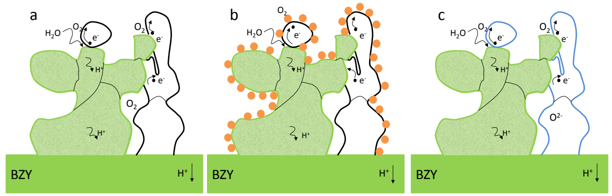



- Proton Ceramic Electrolysers
  - Less mature technology
    - Fabrication and processing challenges
  - Produces dry $H_2$ directly
  - Potentially intermediate temperatures
    - Slow $O_2$-electrode kinetics



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

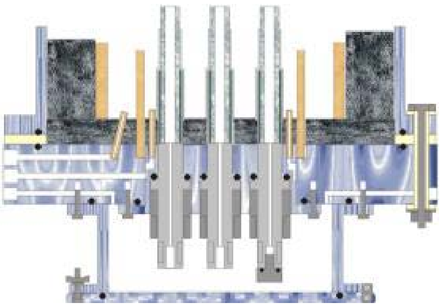
FCH Fuel Cells and Hydrogen Joint Undertaking



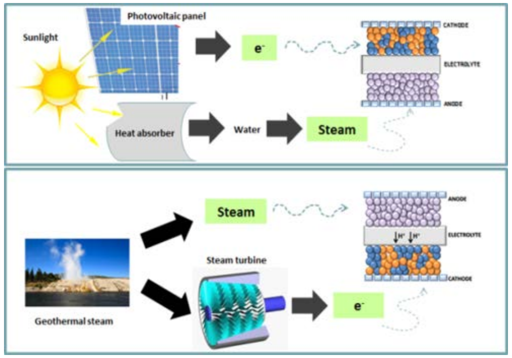

Development of tubular cathode supported electrolyte cell

Development and optimization of anodes and current collection

Single tube module development and testing



Multi-tube module testing
Aim: 1kW demo



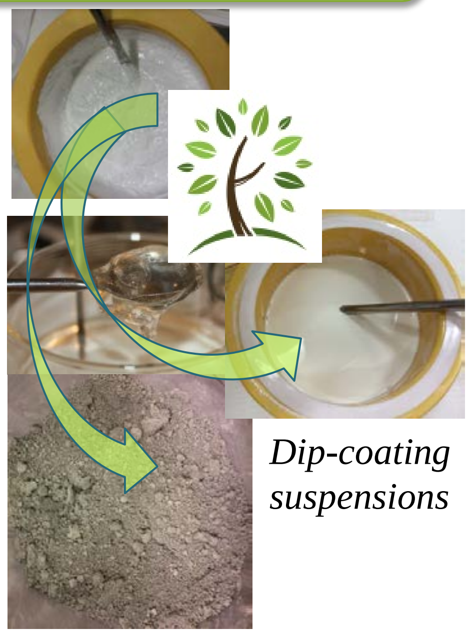

Process integration and evaluation

UiO : Department of Chemistry, University of Oslo · SINTEF · Marion Technologie · ABENGOA HIDROGENO · CoorsTek Membrane Sciences · Carbon Recycling International · CSIC · Electra

# Tubular half-cell production

CoorsTek MEMBRANE SCIENCES

Wet milling of precursors

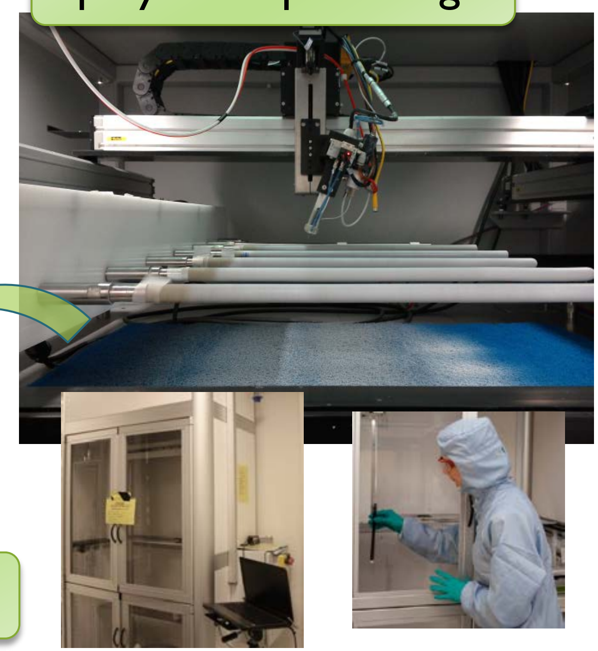


*Dip-coating suspensions*

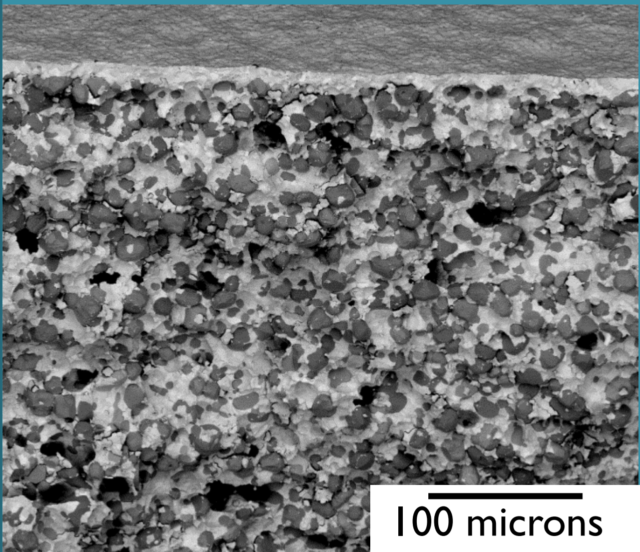
*NiO based paste*

Extrusion of BZCY-NiO support

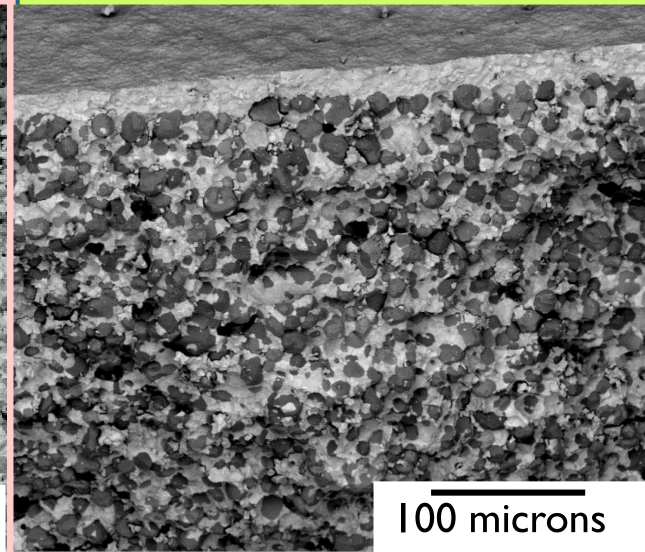
Spray- or dip-coating



Solid State Reactive Sintering



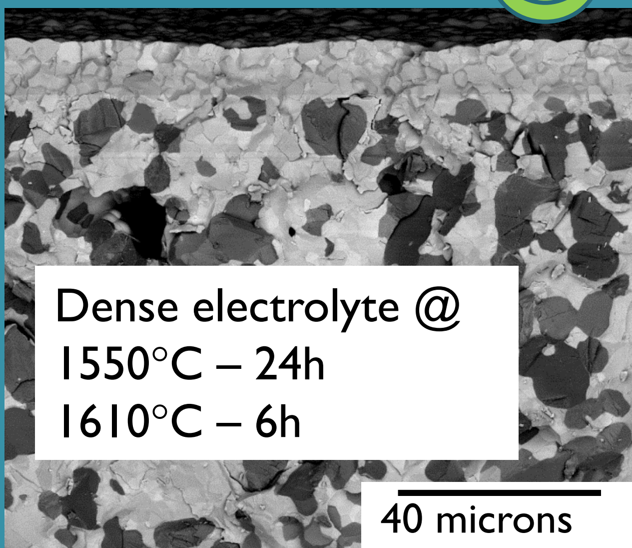





BZCY72 // BZCY72-Ni

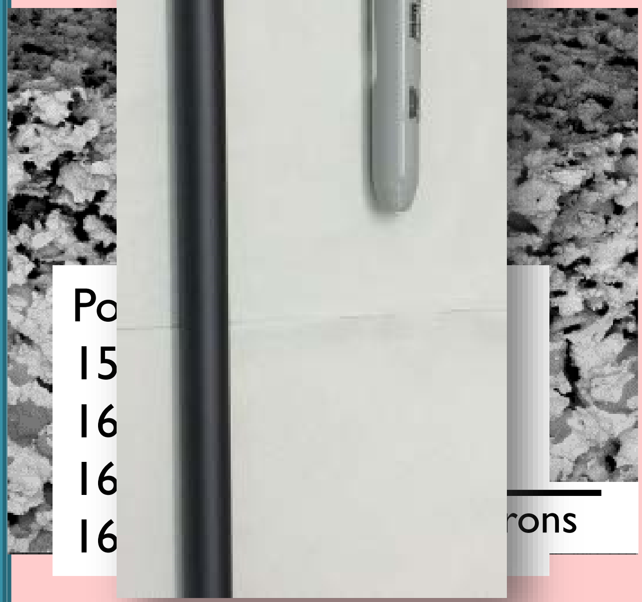
BZY

BZY10 // BZCY72-NiO




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

Po
15
16
16
16

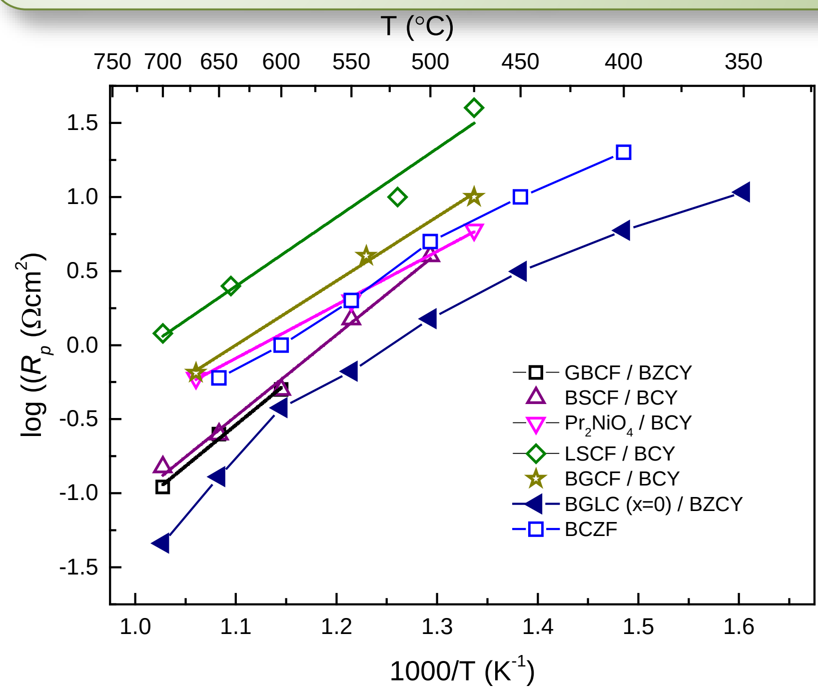


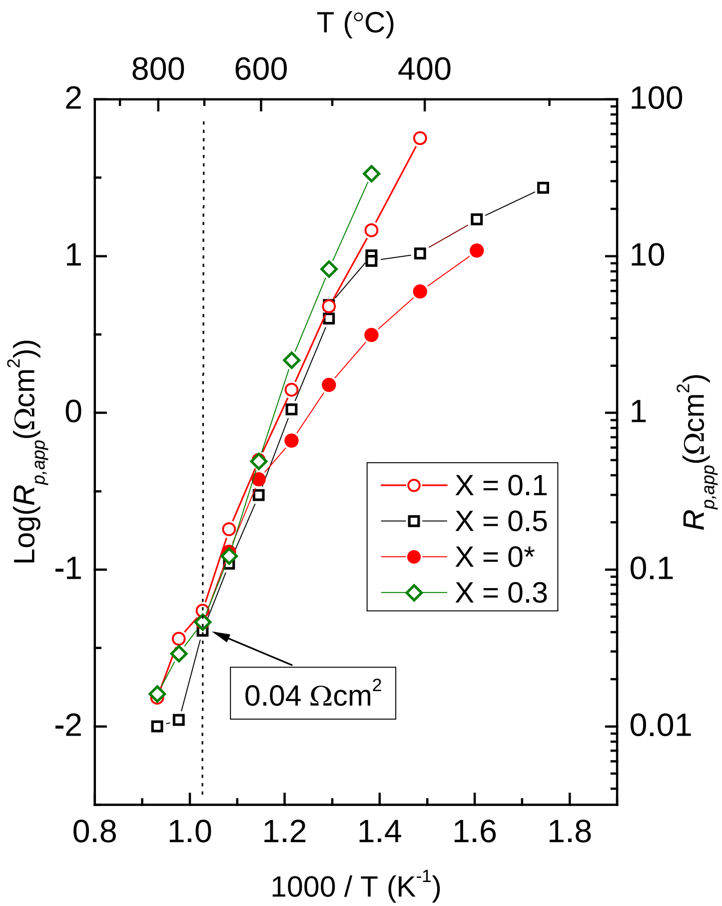


Dense electrolyte @
1550°C – 24 h
1610°C – 6 h

# Development of new anode materials

$Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$ displays best PCE $O_2$-$H_2O$-electrode performance (symmetrical disk samples)



# Anode processing on tubular cells

Single segment, reduced at 1000°C for 24h in 5% $H_2$

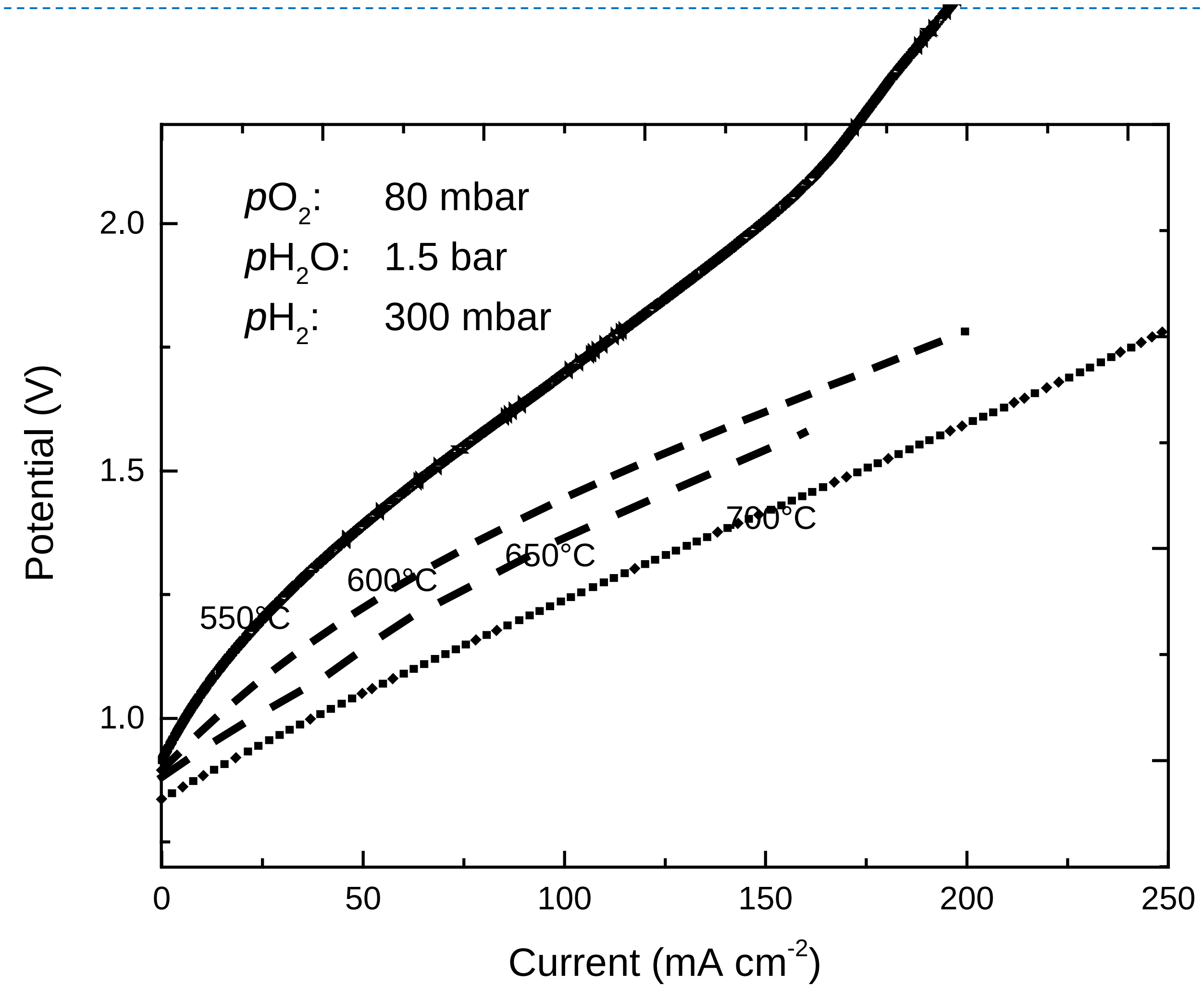
Capped and sealed using custom-made glass ceramic (CoorsTek Membrane Sciencies)

Steam electrode (BGLC785) drip-coated and brush-painted

Fired in dual atmosphere with applied bias:
- 2% $O_2$ outside, 5% $H_2$ inside
- $E_{cell}$ = 1.4 V during firing (above 500°C)

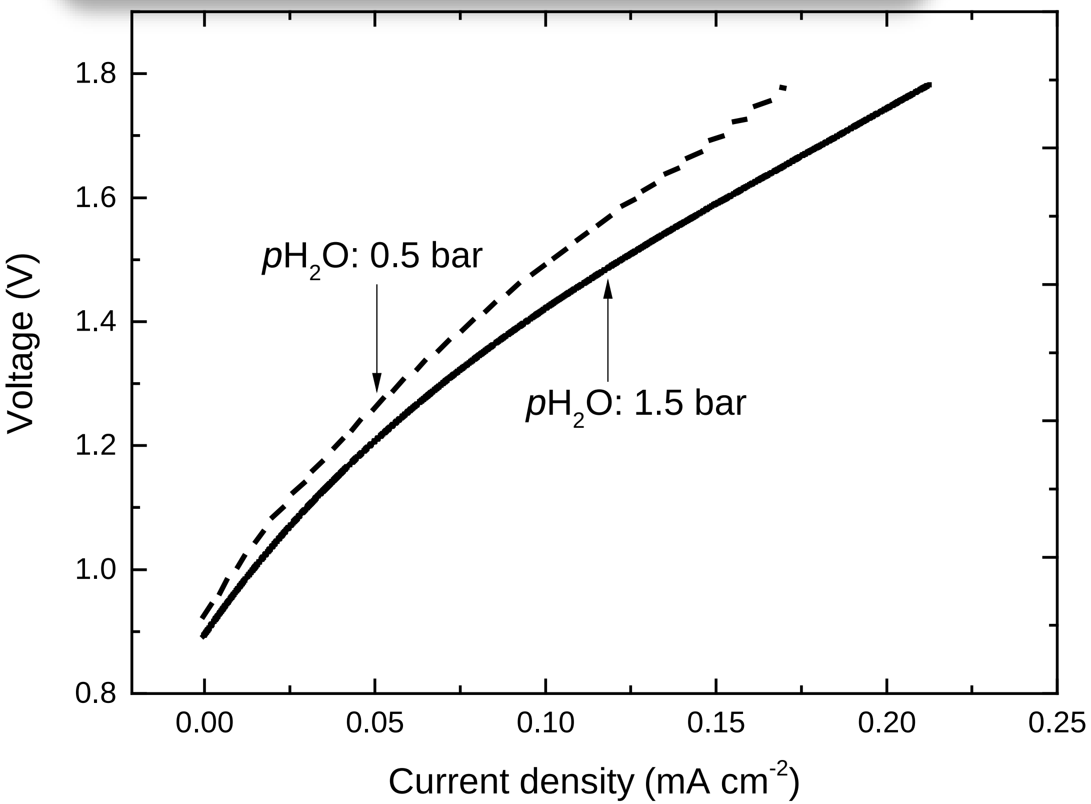
Electrolysis tests using gold as the current collector

# Electrolysis tests of single cell

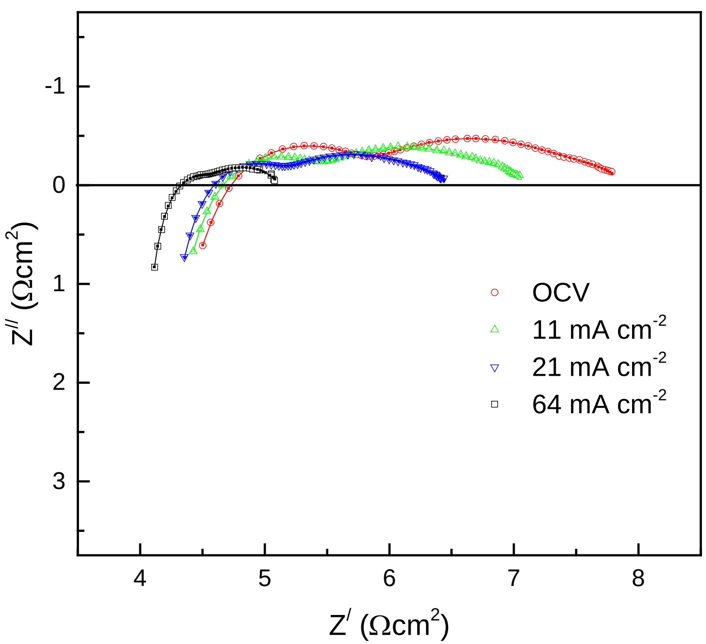


# Improved performance with increasing steam content and current load

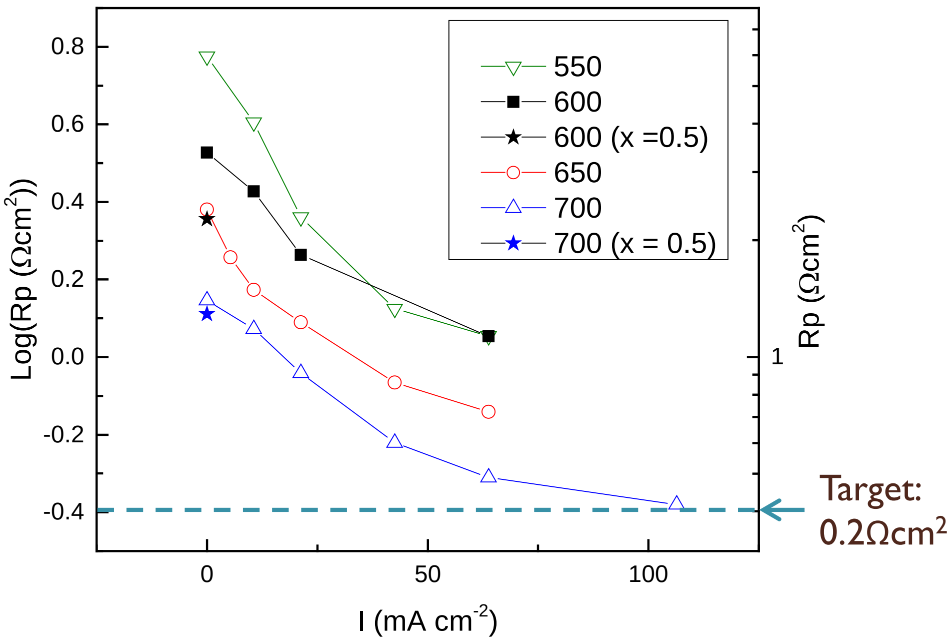
Both electrolyte and electrode performance improved with increased steam content

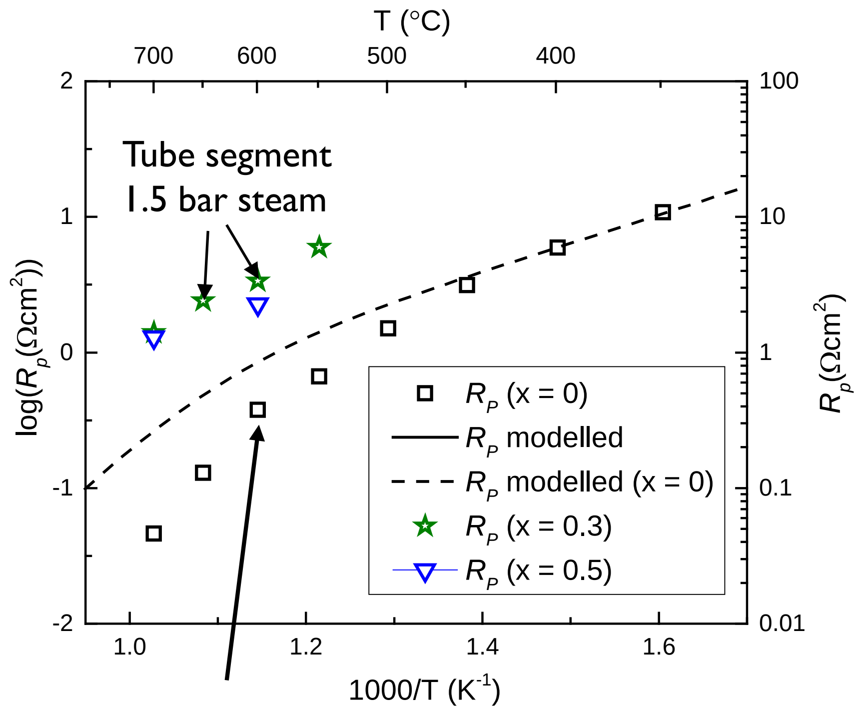



High ohmic resistance indicates current collection limitations



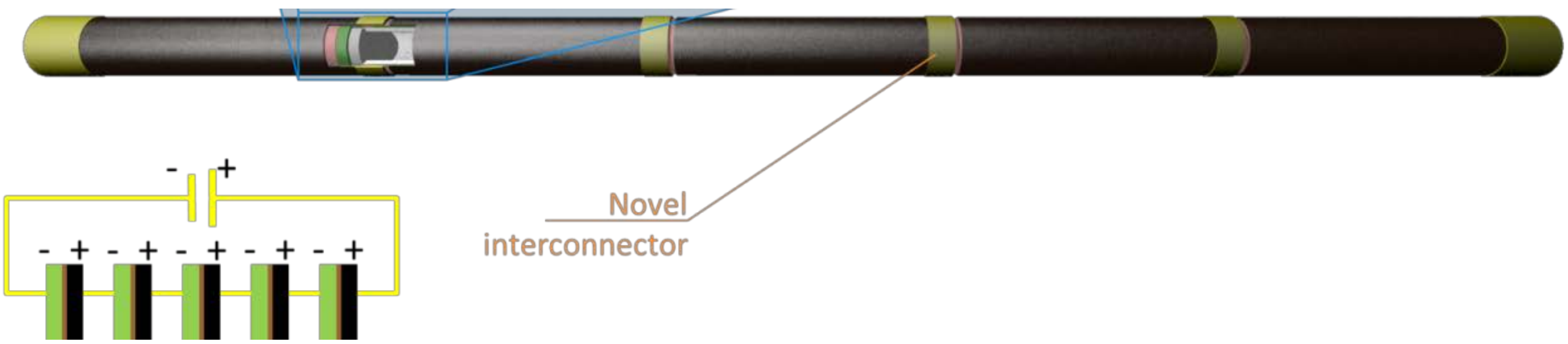
# Electrode resistance an order of magnitude higher than expected values from button cell testing



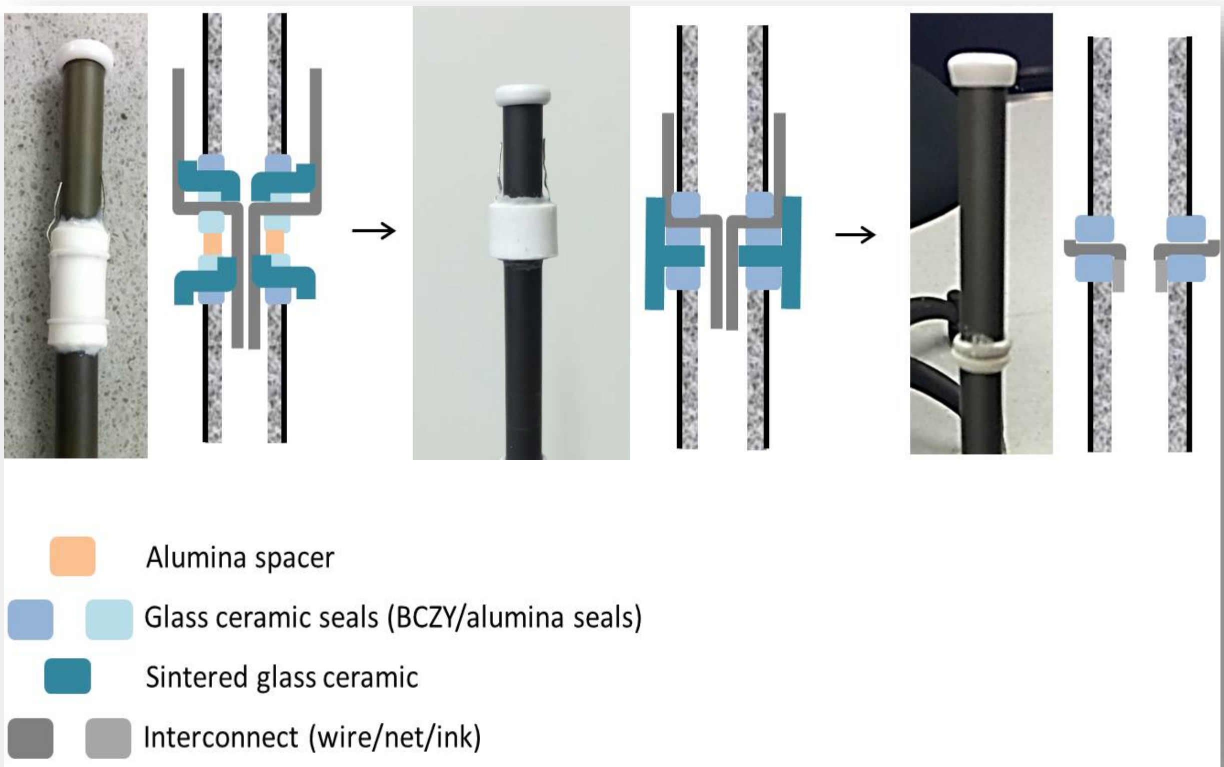




Button cell wet air

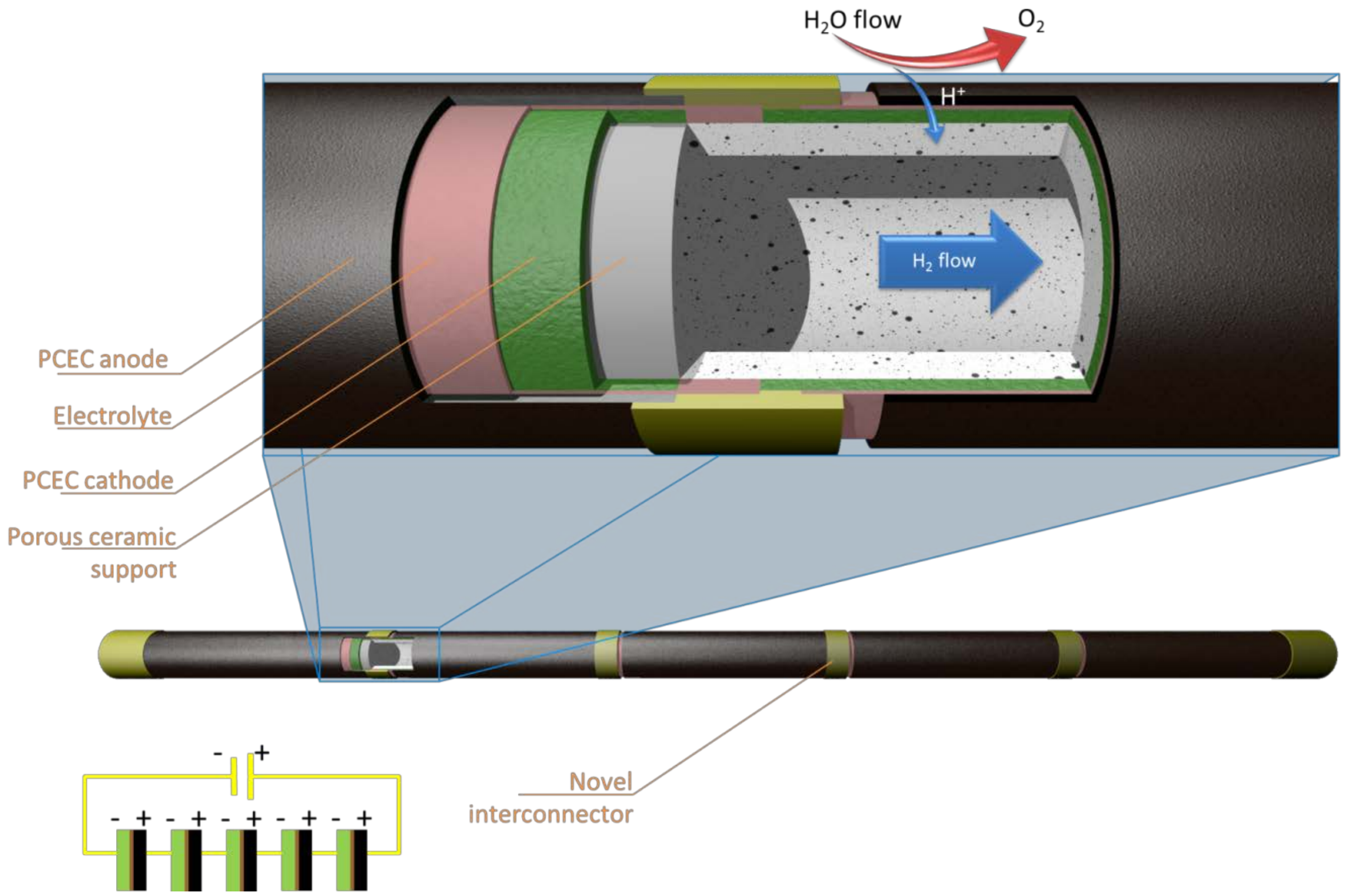
# Scaling up – segmented tubes to drive up the voltage



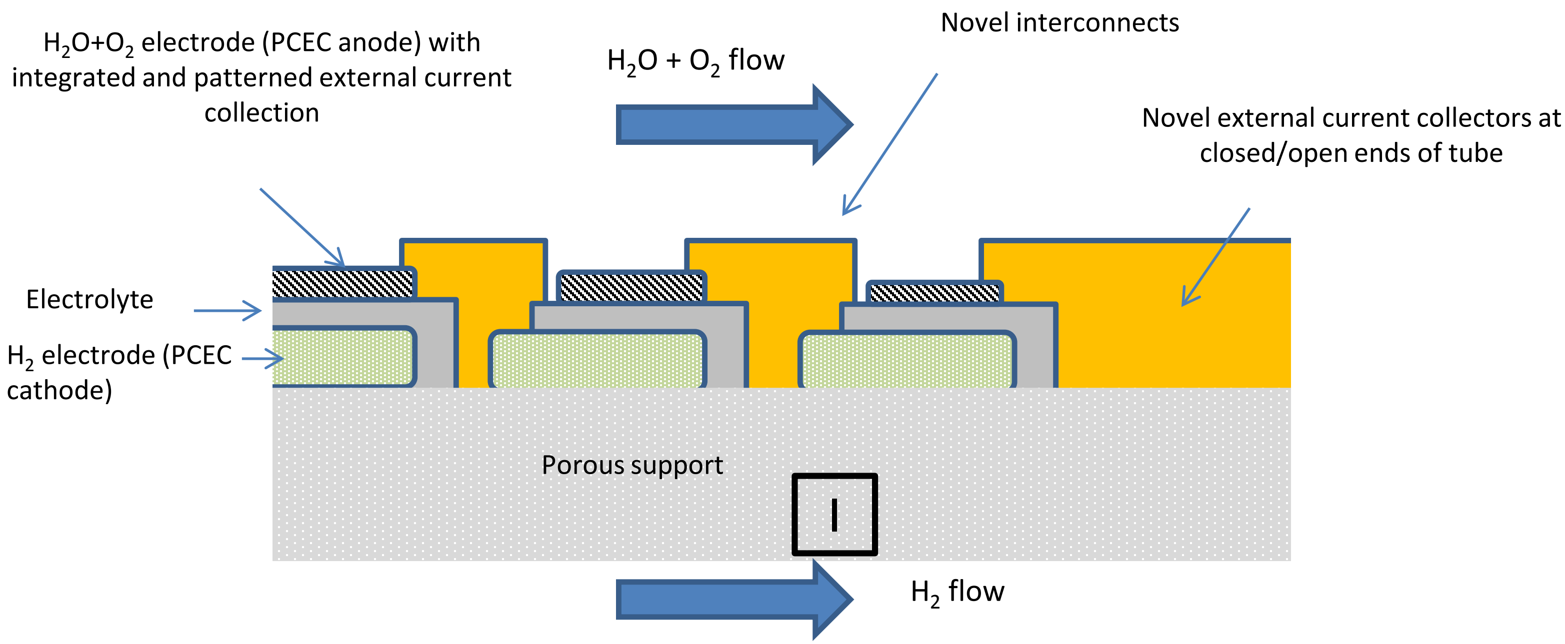
# Scaling up – stacking individual segments




# Scaling up – "Printing in series"



# Segmented-in-series tubular cells




1 — BZCY (SSRS) + sintering aid + pore formers

2 — BZY10 (SSRS or oxide) or BZCY72 (SSRS or oxide) + NiO

3 — BZCY72 or BZY10 (SSRS or oxide)

# Manufacturing process

Powder conditioning

- Milling of SSRS precursors and oxide powders
- Drying
- Sieving
- Batching

Pastes preparation

Clean room activities

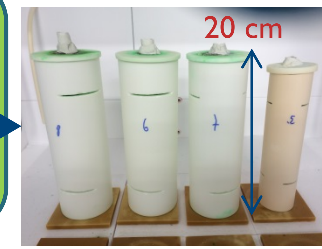
Production of tubes by extrusion and collars

- Drying
- Cutting
- Masking and coating

Dip-coating of tubes

- Drying in air (organic based coating) or at 60°C for water based suspensions

Annealing of tubes (hang-firing)

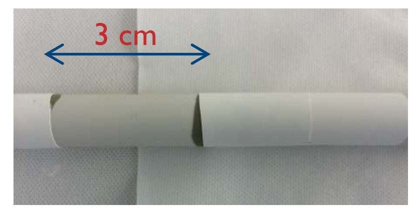


*Hang-firing of cells*

Slurries preparation

- Water based slurry for SSRS mixtures
- Organic based slurries for oxide mixtures

*Green supports with electrodes*



*Green support coated with cathode (green) and electrolyte (white) layers*

# Parameters investigated

**Supports**

Shrinkage; porosity
- Annealing
- PF content
- Sintering aid

**Support + fuel electrode**

Shrinkage, porosity
- Coated part
- Uncoated part

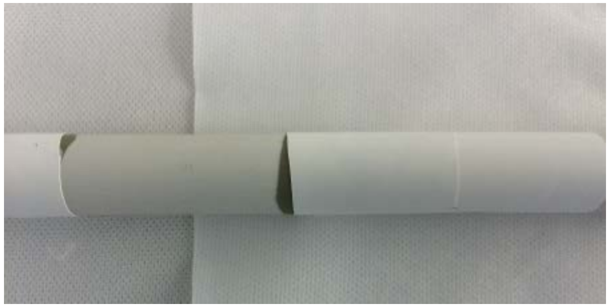
Thickness of electrode
- Viscosity
- Powder loading

**Support + fuel electrode + electrolyte**

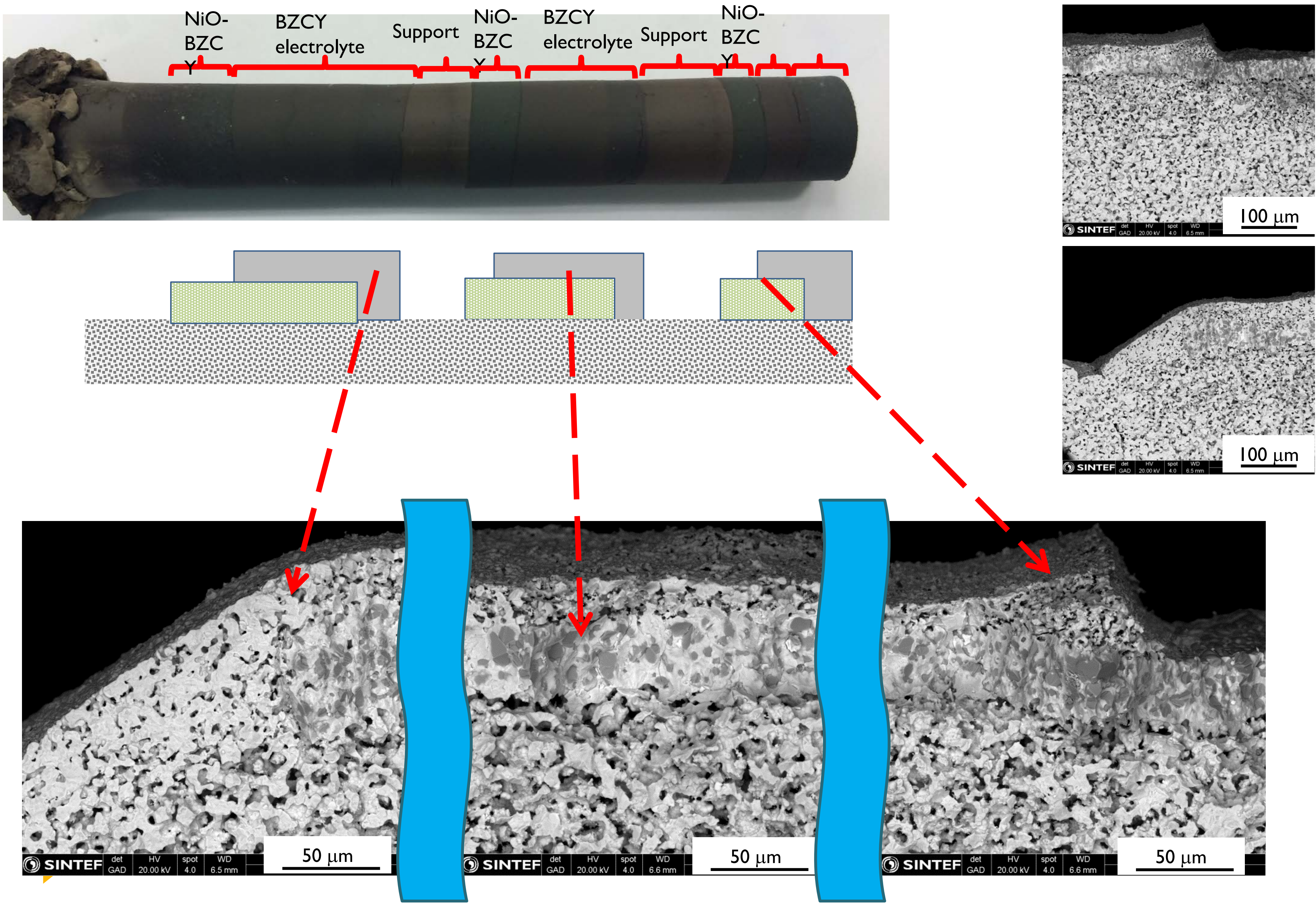
Shrinkage, porosity
- Coated part
- Uncoated part

Thickness of electrode
- Viscosity
- Powder loading

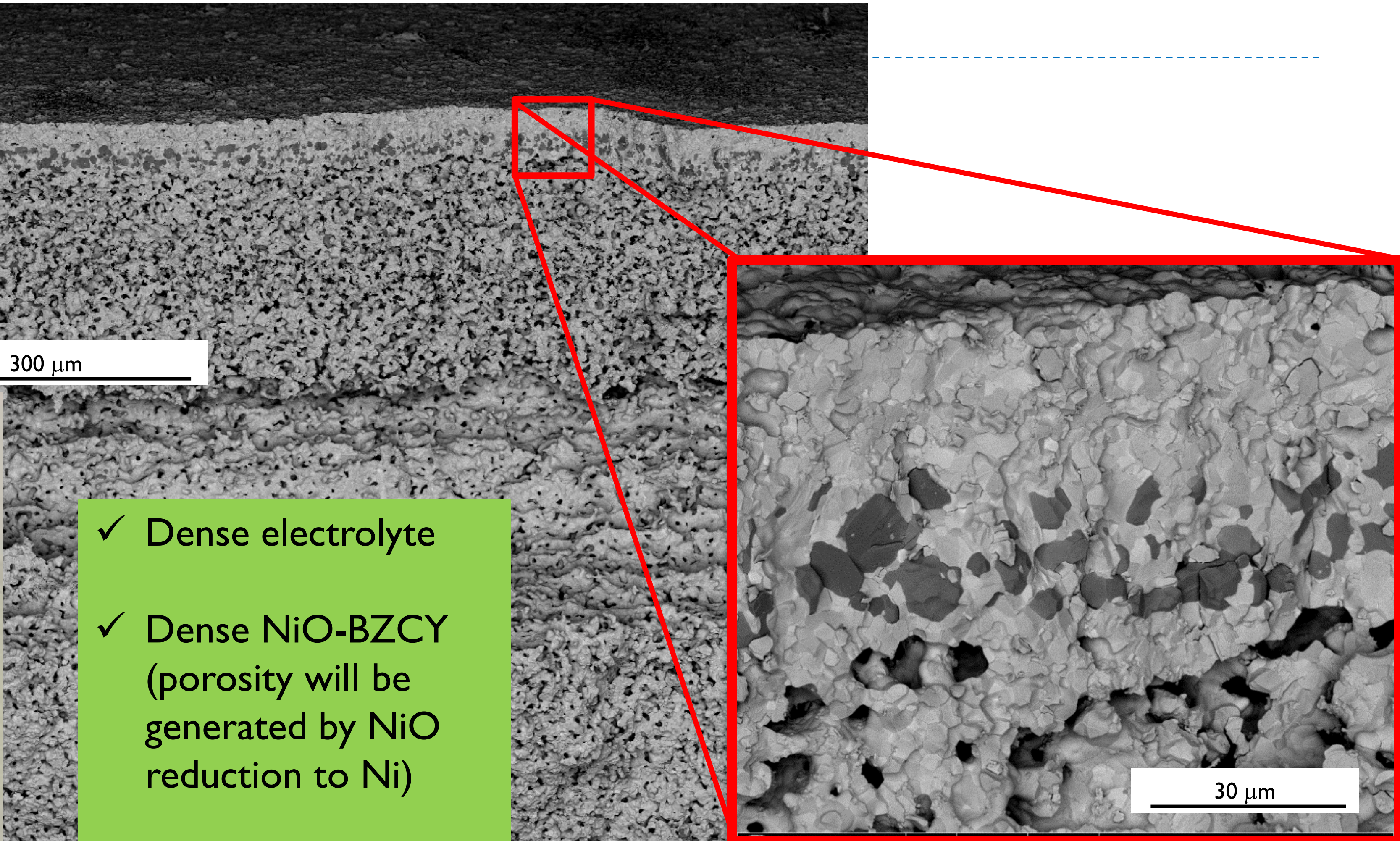
Thickness and densification of electrolyte
- Oxide vs SSRS
- Powder loading



# Broken section: several segments; non-optimized sintering



# Optimized processing parameters for multi-layer sintering




- ✓ Dense electrolyte
- ✓ Dense NiO-BZCY (porosity will be generated by NiO reduction to Ni)
- ✓ Porous BZCY support

# Conclusions

- High temperature proton ceramic electrolysers can produce dry, pressurized hydrogen
- Processing and manufacturing of tubular half cells is now well established
- State-of-the-art electrolyser anodes are developed on button cell scale
  - Deposition and firing protocols for tubular cells currently being developed
- Segmented-in-series tubular cells are needed to reduce total current of tubes in real operational conditions

# 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.

Thank you for your attention!