SINTEF

UiO : Department of Chemistry
University of Oslo

Electra

FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

Proton Conducting Electrolysers with Tubular Segmented-in-series Cells for Hydrogen Production

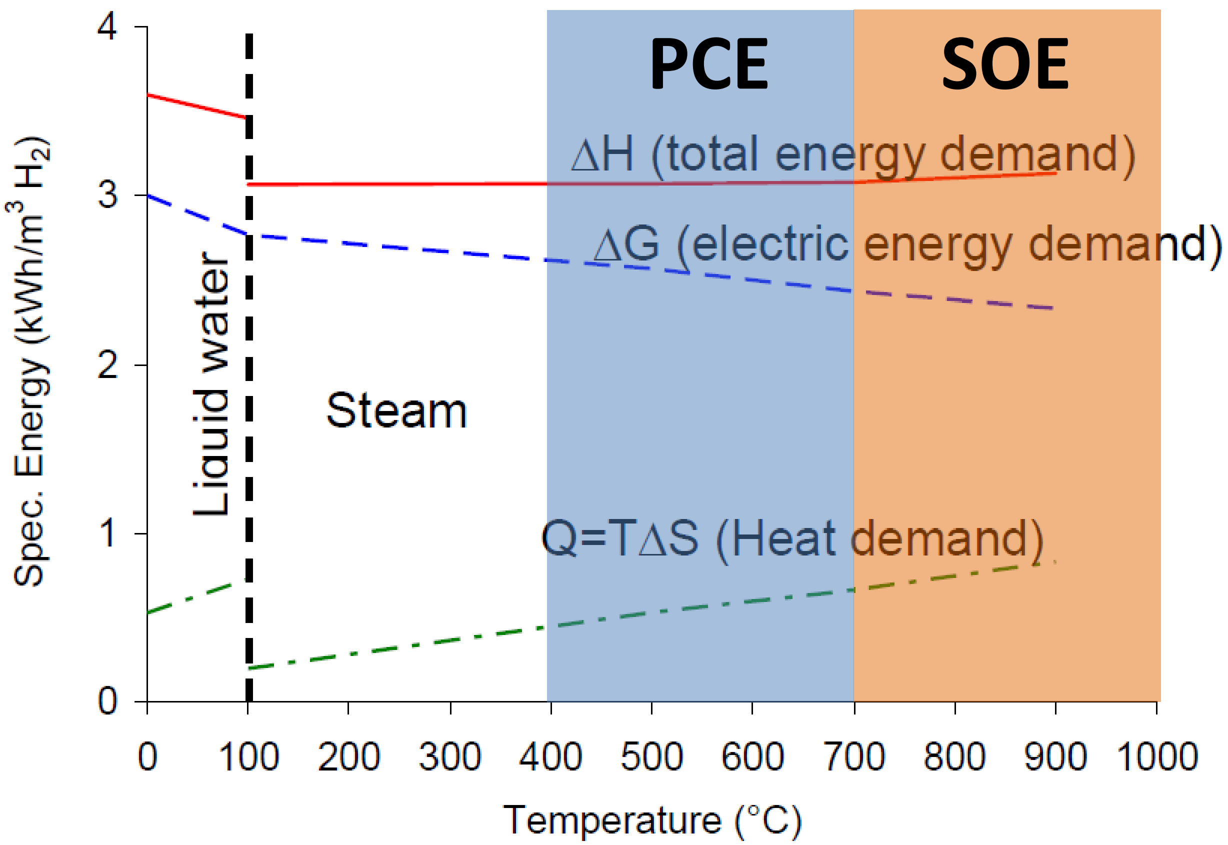
Marie-Laure Fontaine[1], Einar Vøllestad[2], Jonathan M. Polfus[1], Wen Xing[1], Zuoan Li[1], Ragnar Strandbakke[2], Christelle Denonville[1], Truls Norby[2], Rune Bredesen[1]

[1] *SINTEF Materials and Chemistry, Norway*

[2] *University of Oslo, Norway*

Ceramic Electrolysers: utilizing waste heat

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



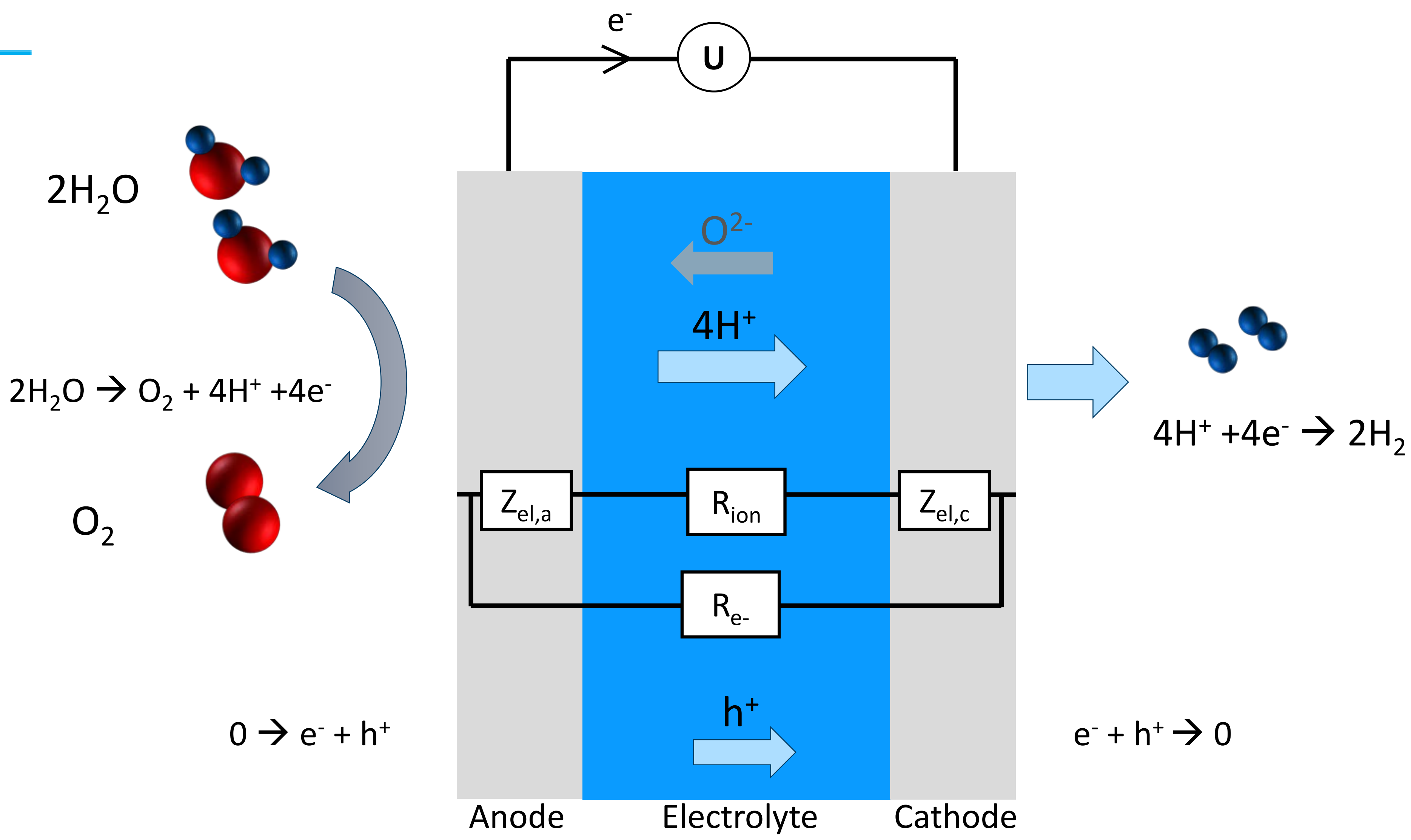
Solid Oxide Electrolyzers (SOE)

- Well proven technology
- Long term stability challenges
  - Delamination of O_2-electrode
- Higher temperature

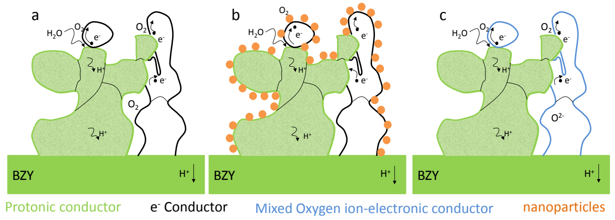
Proton Ceramic Electrolysers (PCE)

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

Operating Principles of Proton Ceramic Electrolysers (PCEs)



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



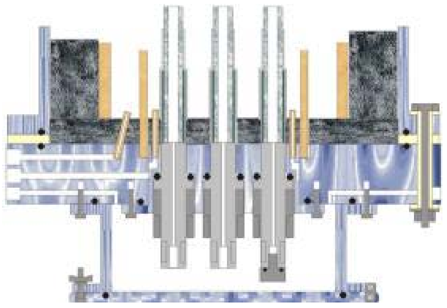
Development of tubular cathode supported electrolyte cell

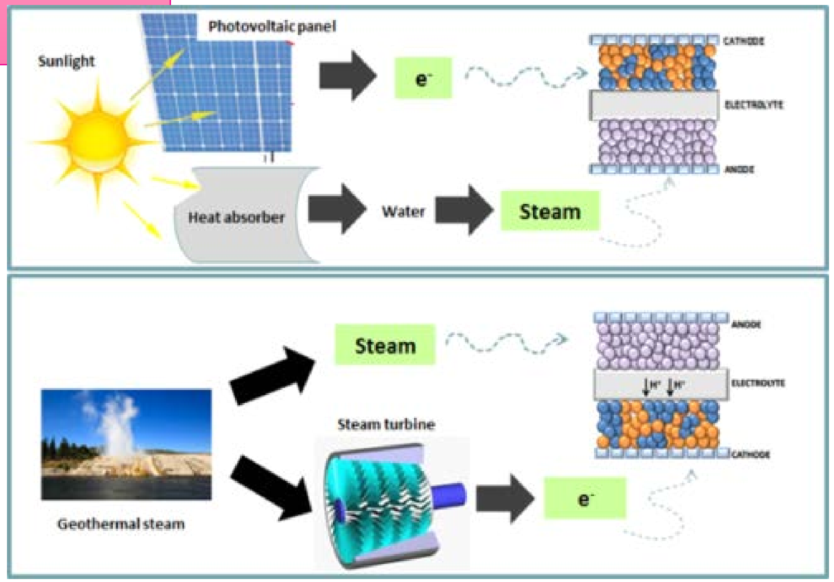
Development and optimization of anodes and current collection

Single tube module development and testing

Multi-tube module testing
Aim: 1kW demo

Process integration and evaluation

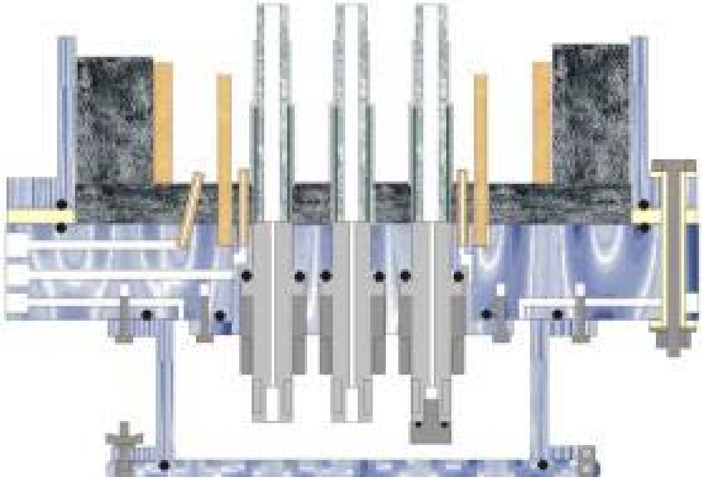




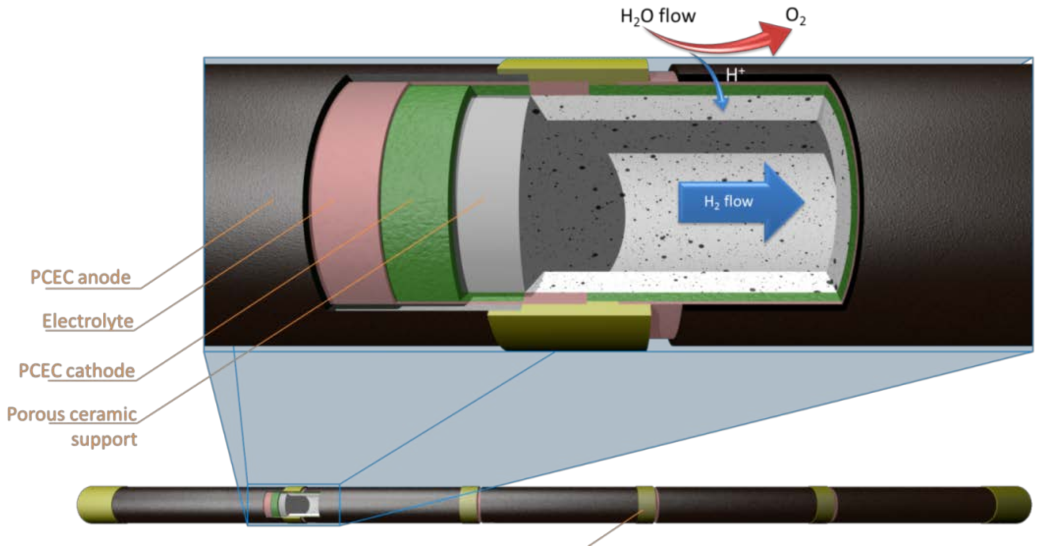
CSIC Consejo Superior de Investigaciones Científicas · CoorsTek Membrane Sciences · UiO Department of Chemistry, University of Oslo · Marion Technologie · Abengoa Hidrogeno · Carbon Recycling International · SINTEF

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

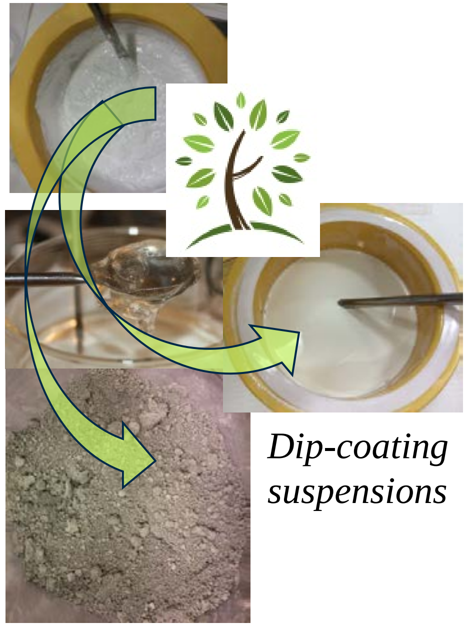


- Segmented-in-series cells
  - Retain high voltage



Scaling up tubular proton ceramic electrolysers

Wet milling of precursors



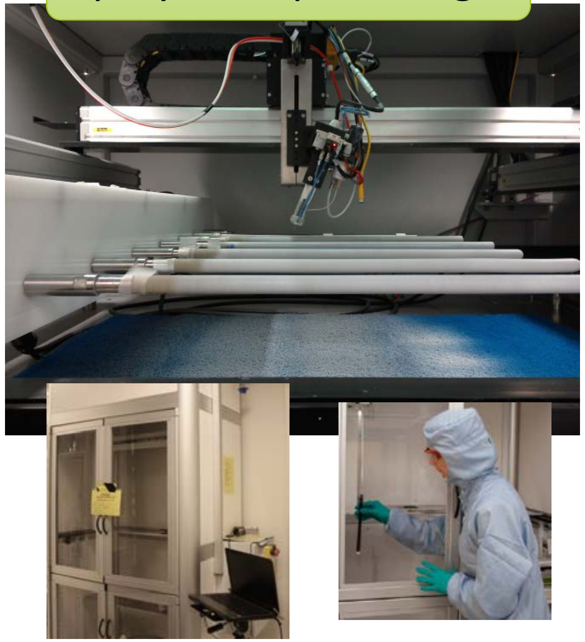
Dip-coating suspensions

BZCY-NiO paste

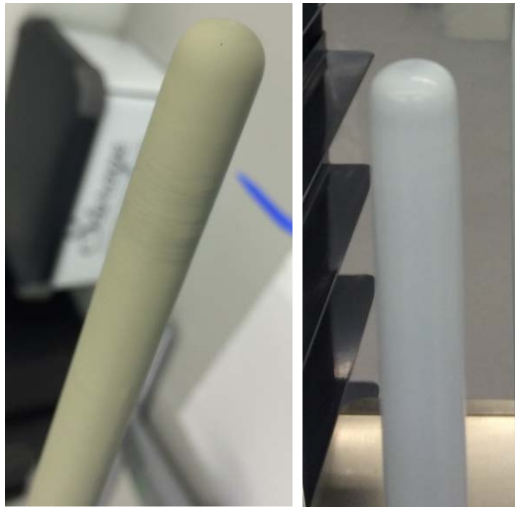
Extrusion of BZCY-NiO support

CoorsTek
MEMBRANE SCIENCES

Spray- or dip-coating

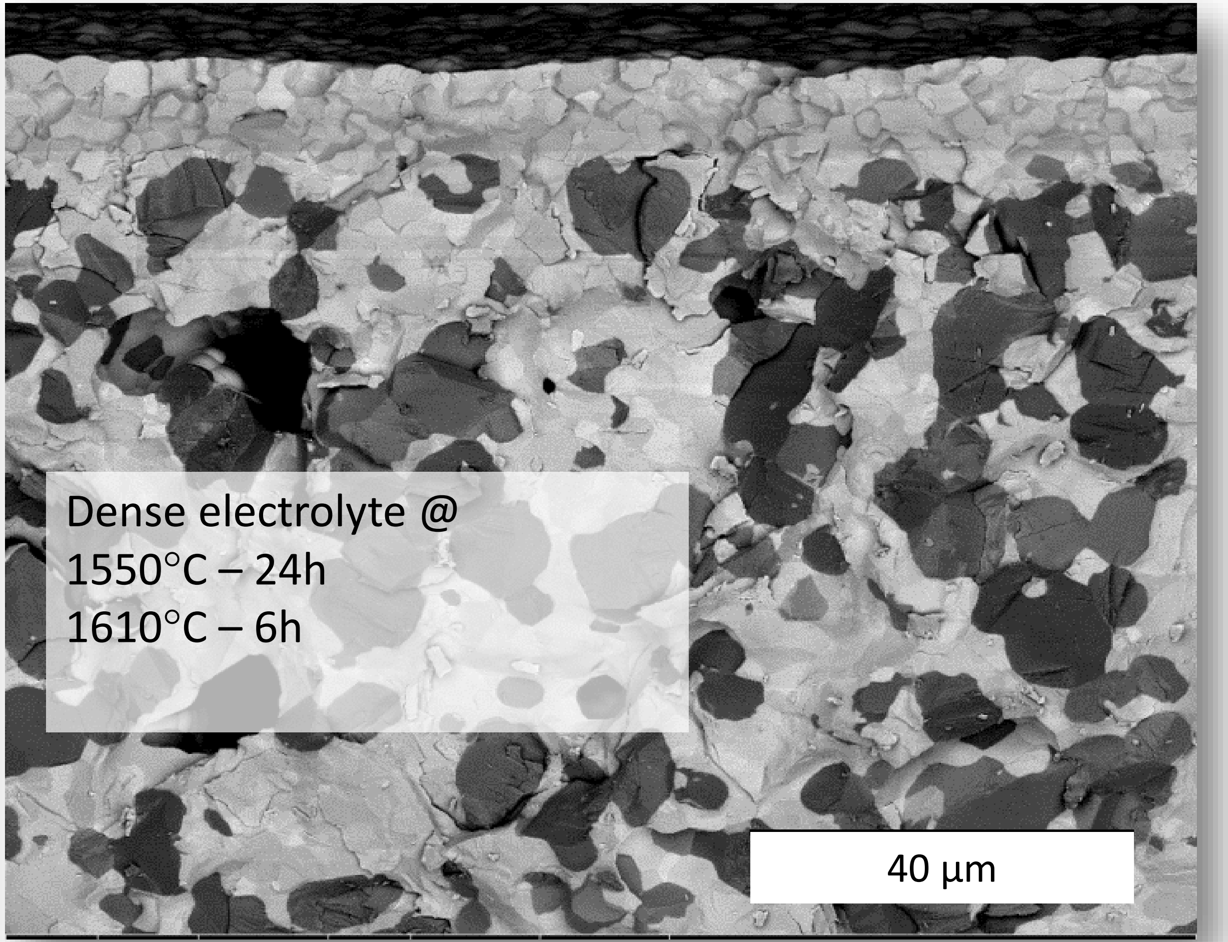


Solid State Reactive Sintering



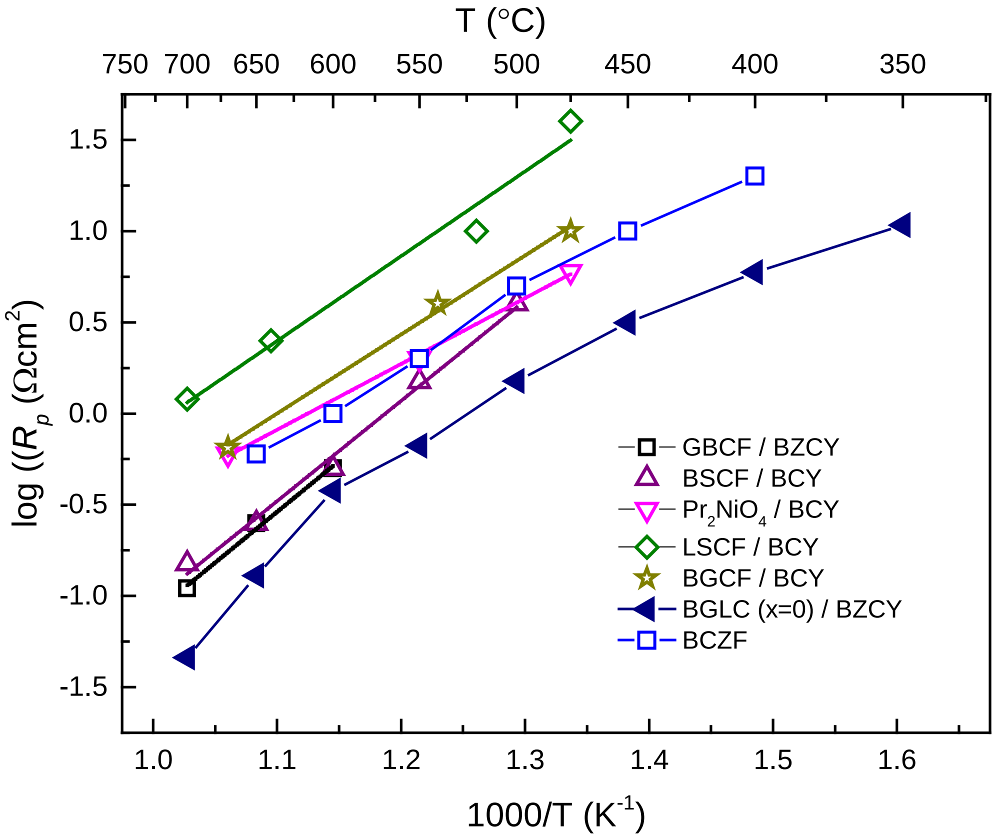
$BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$ (BZCY72)

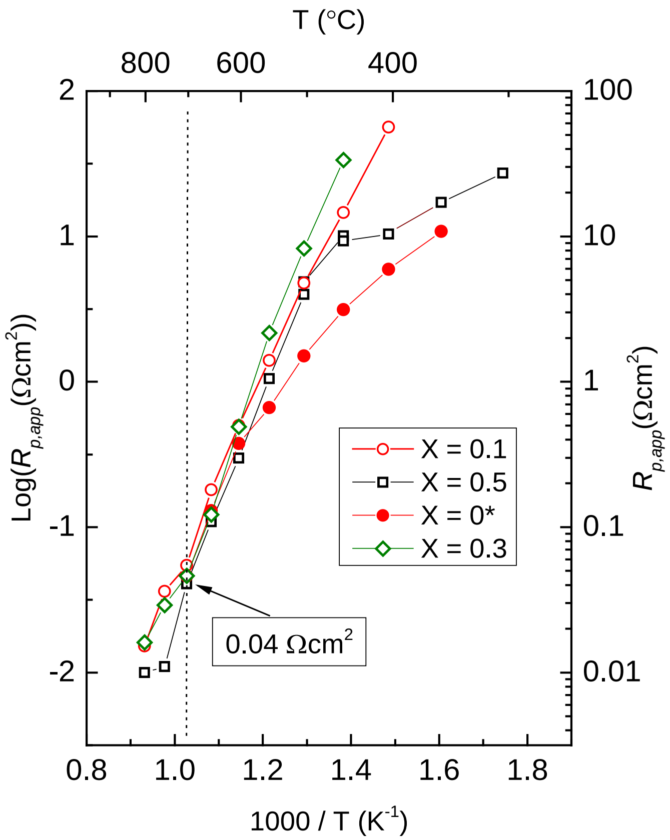
Scaling up tubular proton ceramic electrolysers



SINTEF

Development of new steam electrode materials



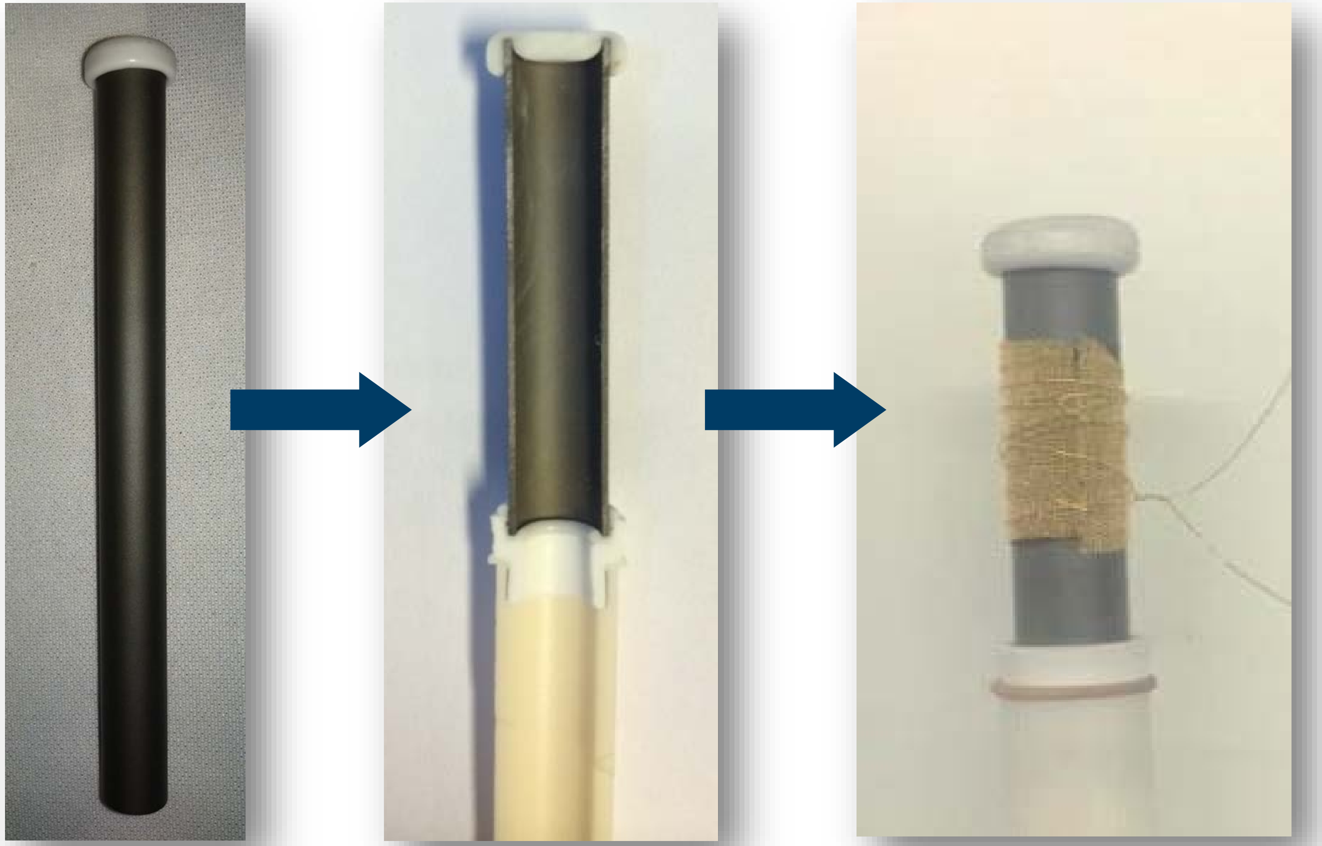


$Ba_{1-x}Gd_{0.8}La_{0.2+x}Co_2O_{6-\delta}$ displays best PCE steam electrode performance (symmetrical disk samples)

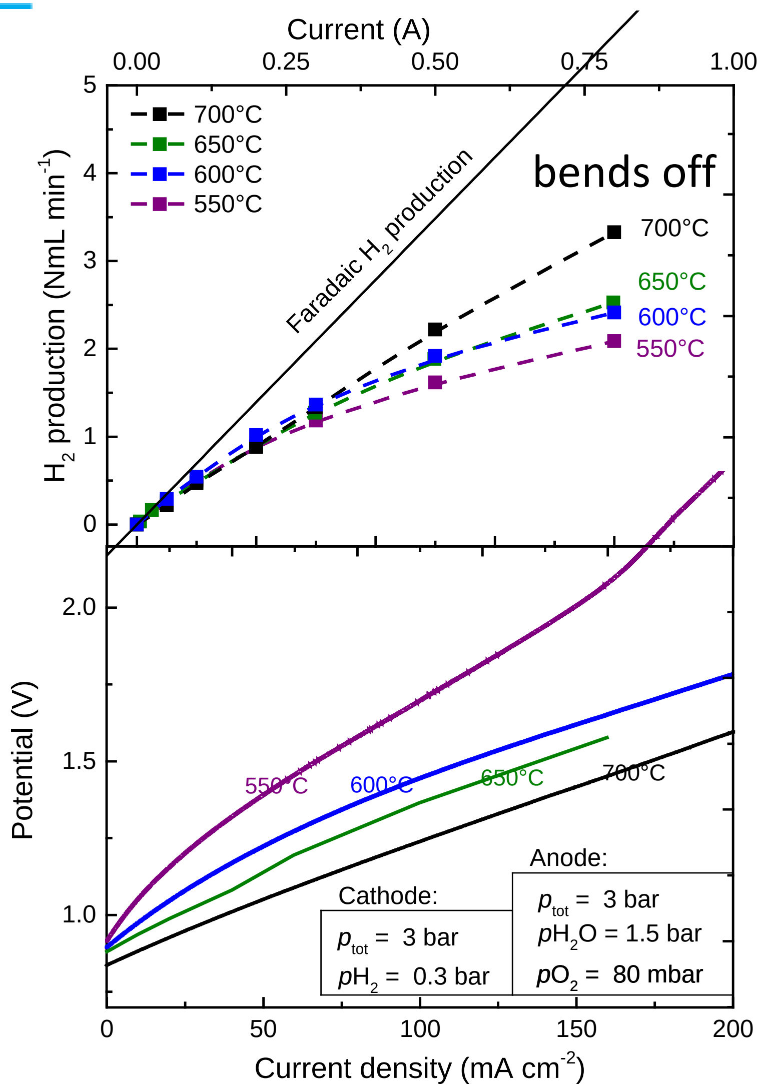
SINTEF

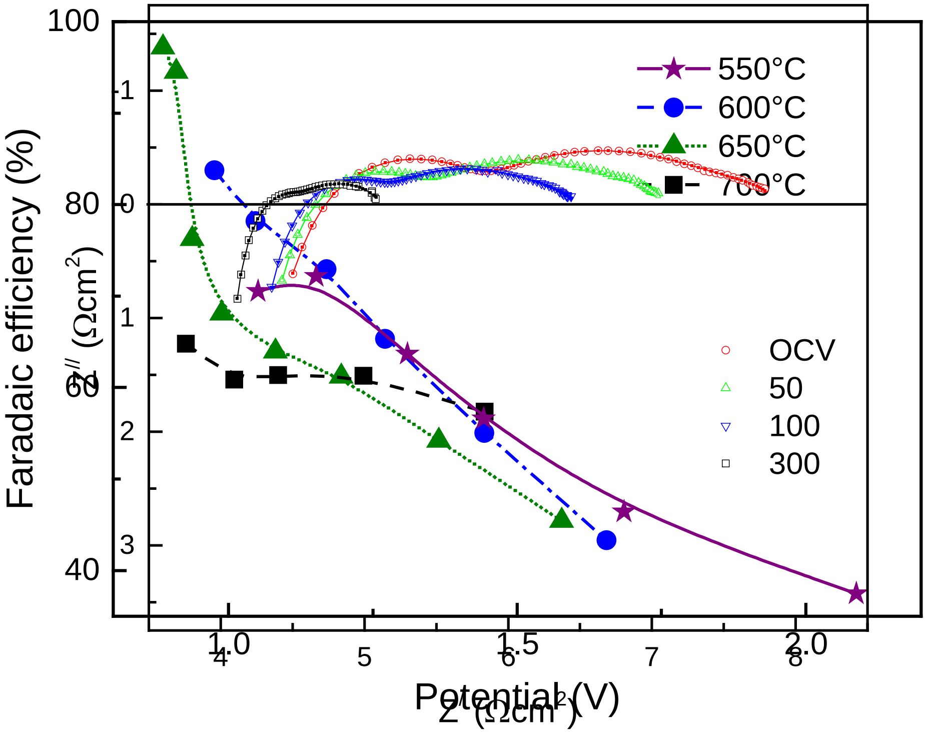
Steam electrode processing

1. Cap and seal using glass-ceramic from CoorsTek
2. Deposit $Ba_{0.7}Gd_{0.8}La_{0.5}Co_2O_{6-\delta}$ as steam electrode by paint brush
3. Firing in dual atmosphere:
   - 1000 °C
   - 2% O_2 outside, 5% H_2 inside
   - E_{cell} = 1.4 V during firing
4. Gold paste applied as current collector



Electrolysis with BGLC electrode





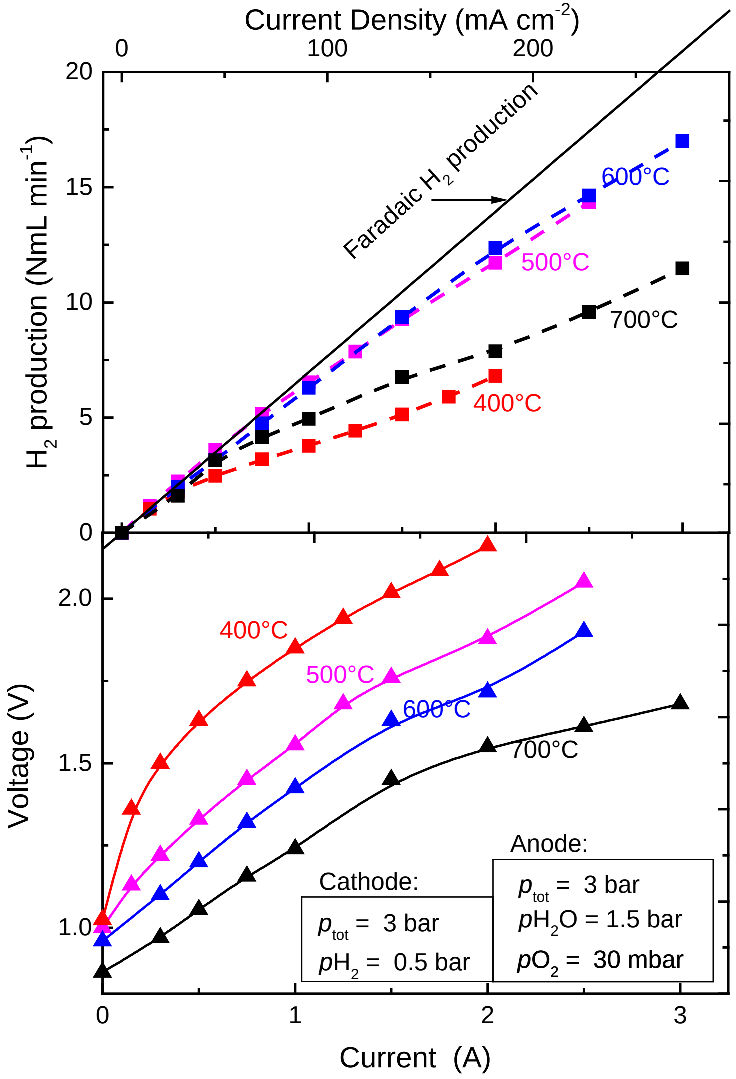
Post-characterization: poor electrode adhesion

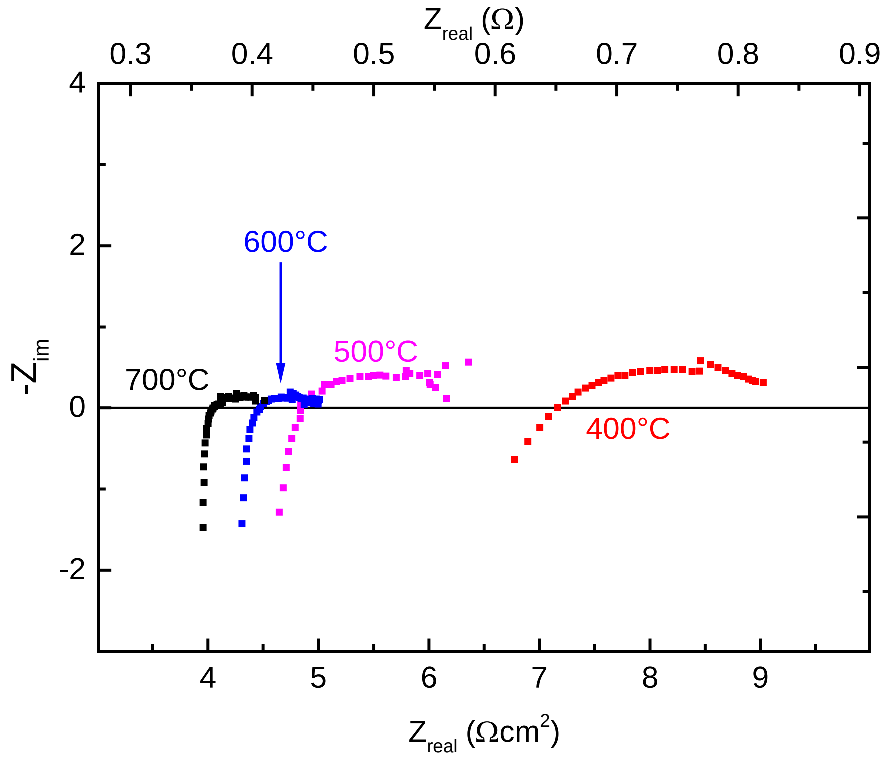
SINTEF

Steam electrode processing

1. $BZCY72\text{-}Ba_{0.5}Gd_{0.8}La_{0.7}Co_2O_{6-\delta}$ applied as steam electrode
   - Fired in air at 1200°C for 5h
   - Infiltrated with nanocrystalline $Ba_{0.5}Gd_{0.8}La_{0.7}Co_2O_{6-\delta}$
   - Thin Pt layer current collection
2. Capped and sealed at 1000°C
   - Semi-dual atmosphere to keep BGLC layer intact
3. NiO reduction at 800°C in 10% H_2 for 24h
   - Kept in electrolytic bias during reduction to avoid re-oxidation

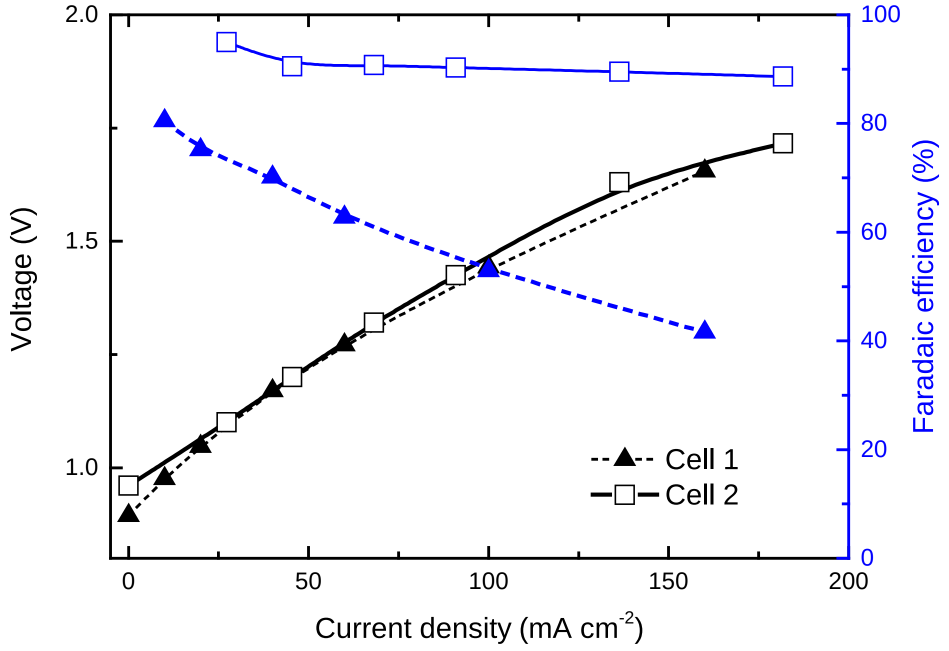
Electrolysis with BZCY-BGLC composite electrode

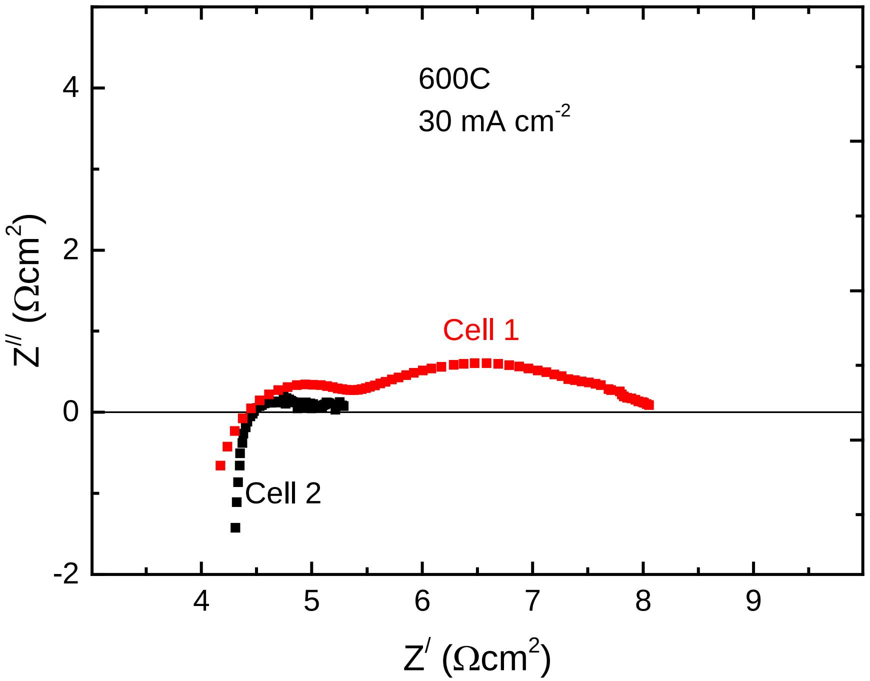




SINTEF

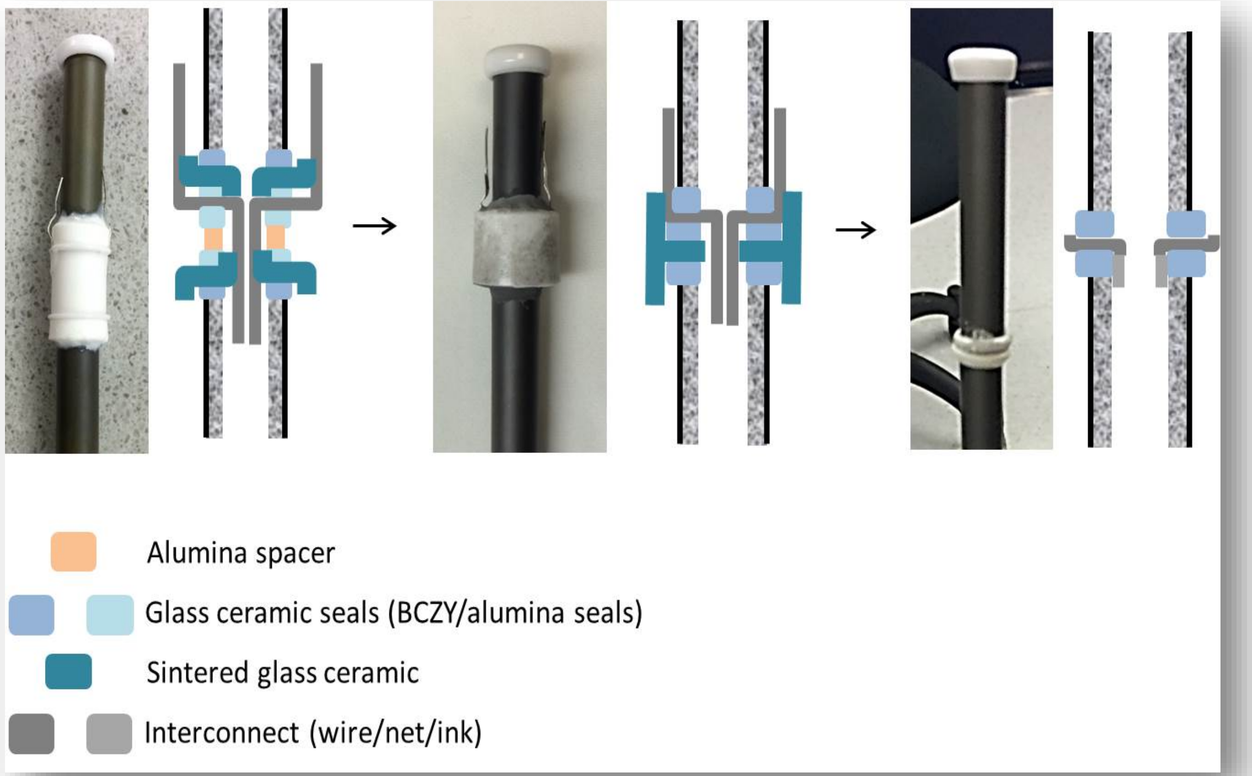
Improved faradaic efficiency primarily due to enhanced electrode kinetics

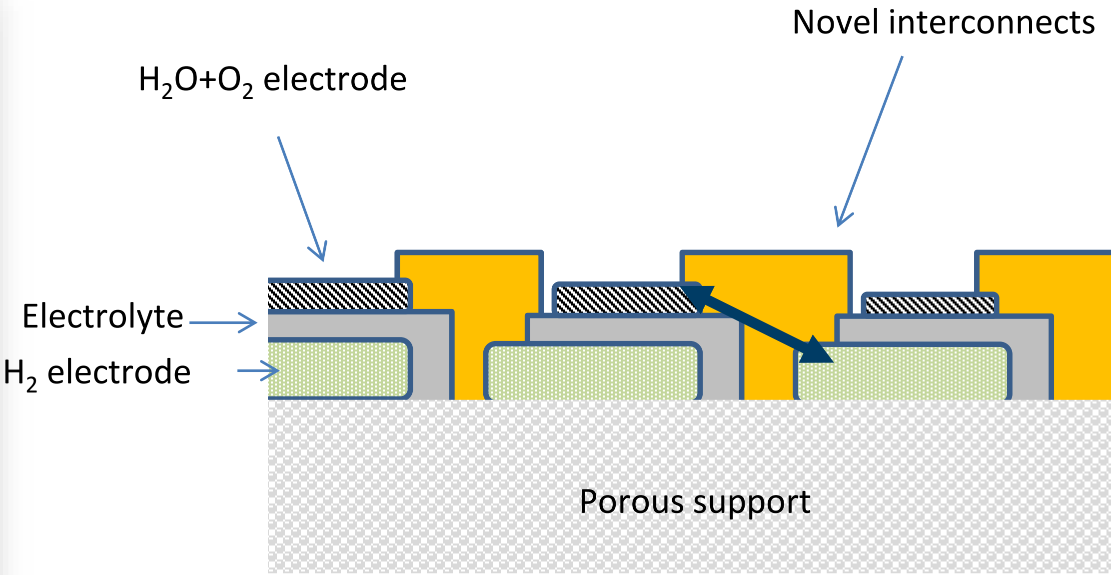




SINTEF

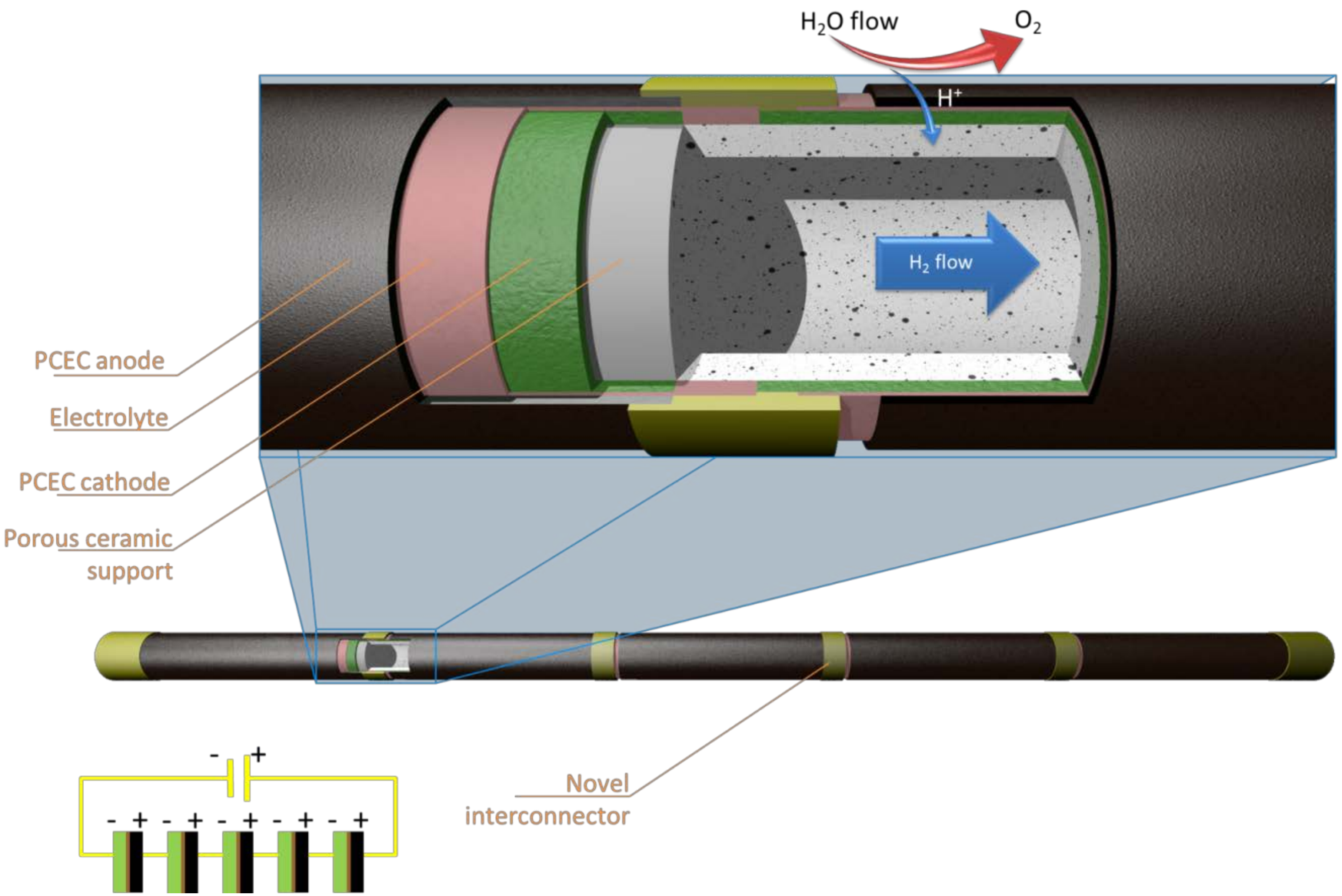
Segment-in-series: print masking





SINTEF

Segment-in-series: print masking

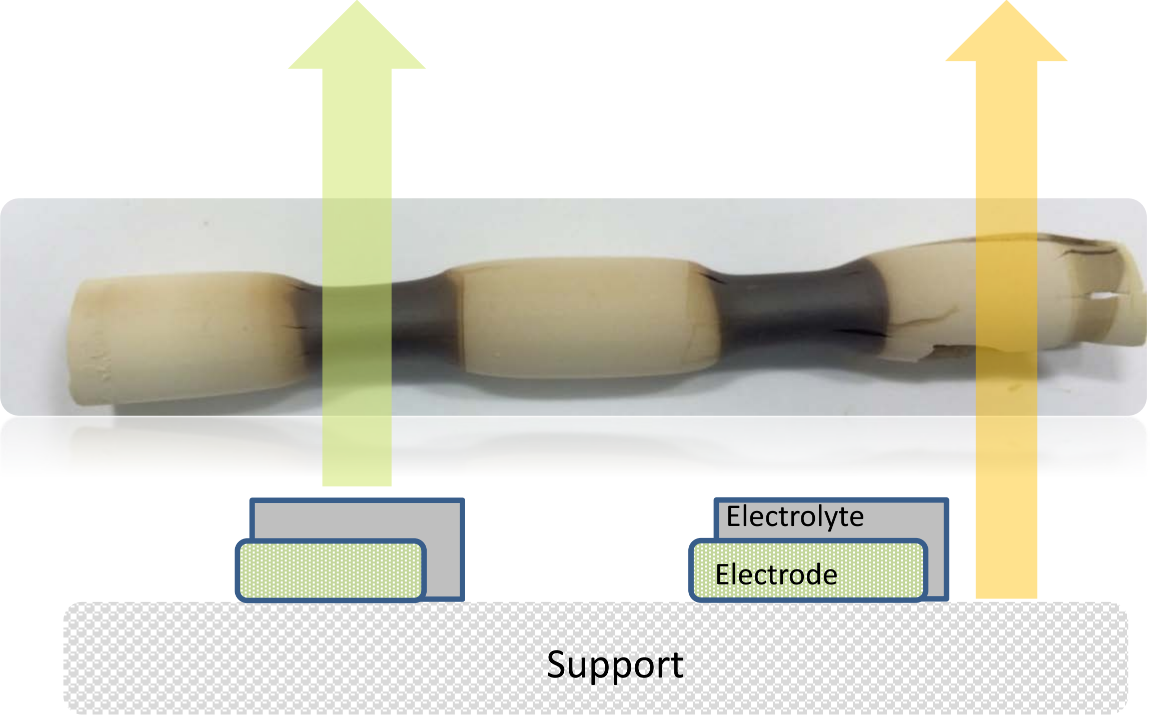


Segment-in-series: print masking

Pore formers and sintering aid

- Addition of pore formers (A) in the electrode + reduction of temperature

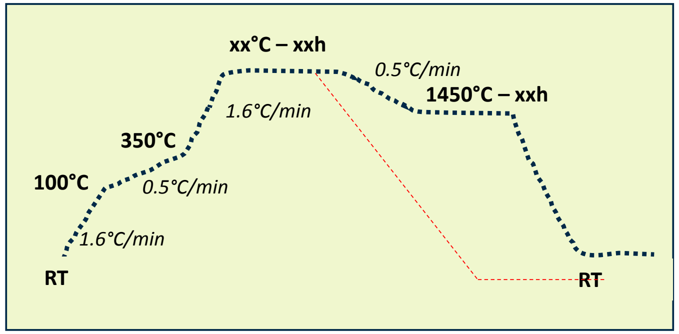
- Addition of sintering aid + pore formers (B) in the support

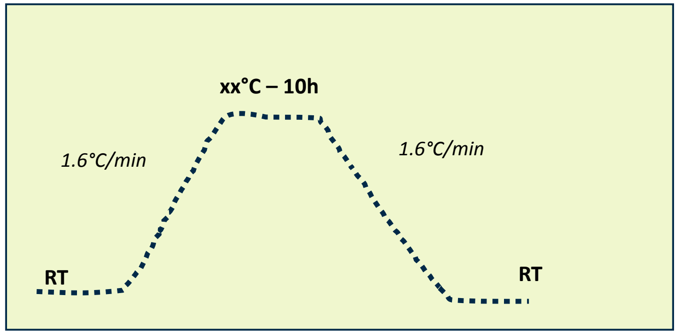


Various thermal profiles

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

Dwell:
- 2h
- 5h
- 10h

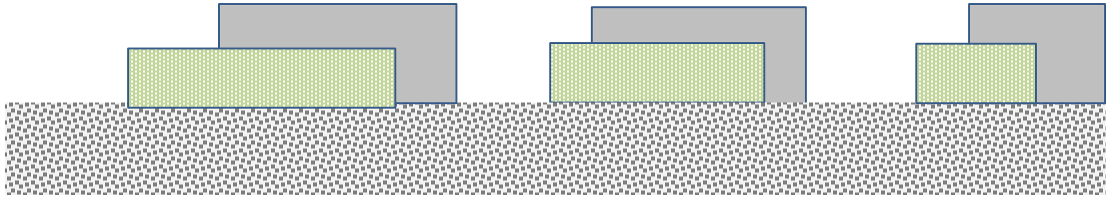




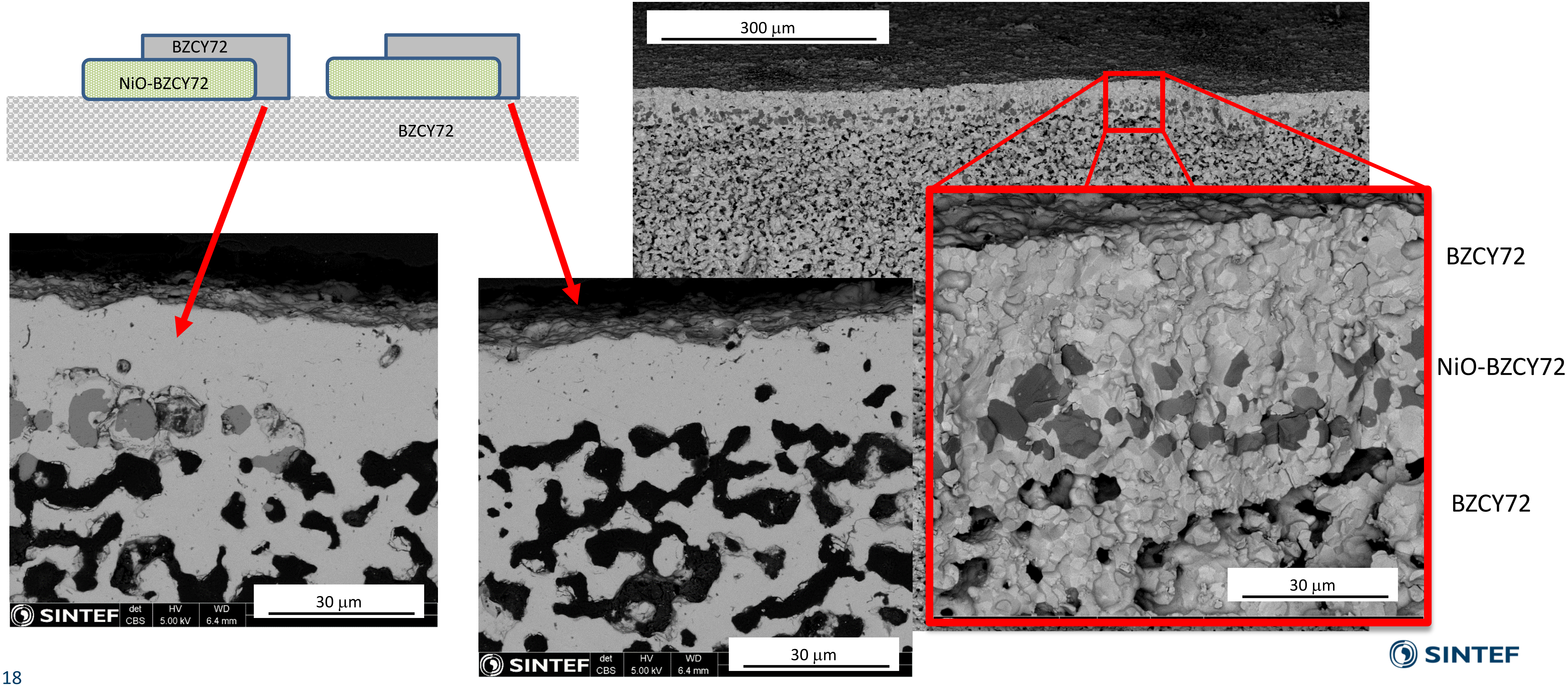
SINTEF

Segment-in-series: print masking

Collar for hang-firing

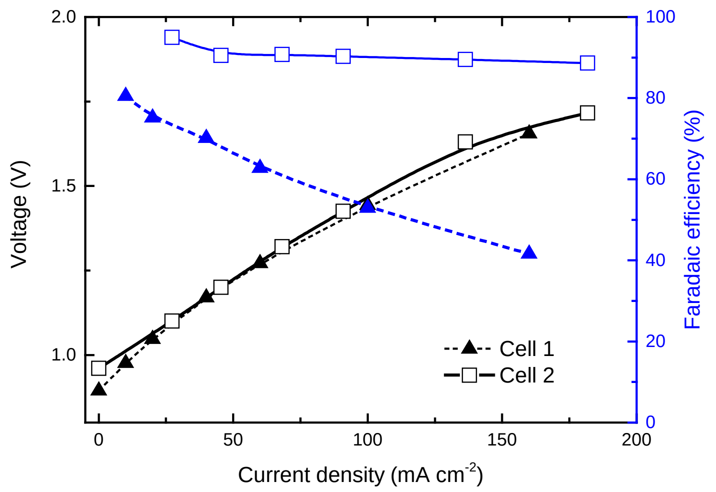


Segment-in-series: print masking



SINTEF

Conclusions



- Tubular PCEs fabricated
  - BZCY-NiO tubular cathode support
  - Spray coated BZCY72 electrolyte
  - BGLC-BZCY72 steam electrode
- Enhanced faradaic efficiencies observed with improved anode performance
  - Current densities of **220 mA cm^{-2} at 600°C** obtained with > **80% faradaic efficiency**
  - PCEs may suffer from electronic leakage due to p-type conductivity in oxidizing 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.

Marie-Laure Fontaine[1], Einar Vøllestad[2], Jonathan M. Polfus[1], Wen Xing[1], Zuoan Li[1], Ragnar Strandbakke[2], Christelle Denonville[1], Truls Norby[2], Rune Bredesen[1]

[1] *SINTEF Materials and Chemistry, Norway*
[2] *University of Oslo, Norway*