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Proton conducting electrolytes integrated in tubular segmented-in-series cells for pressurized hydrogen production

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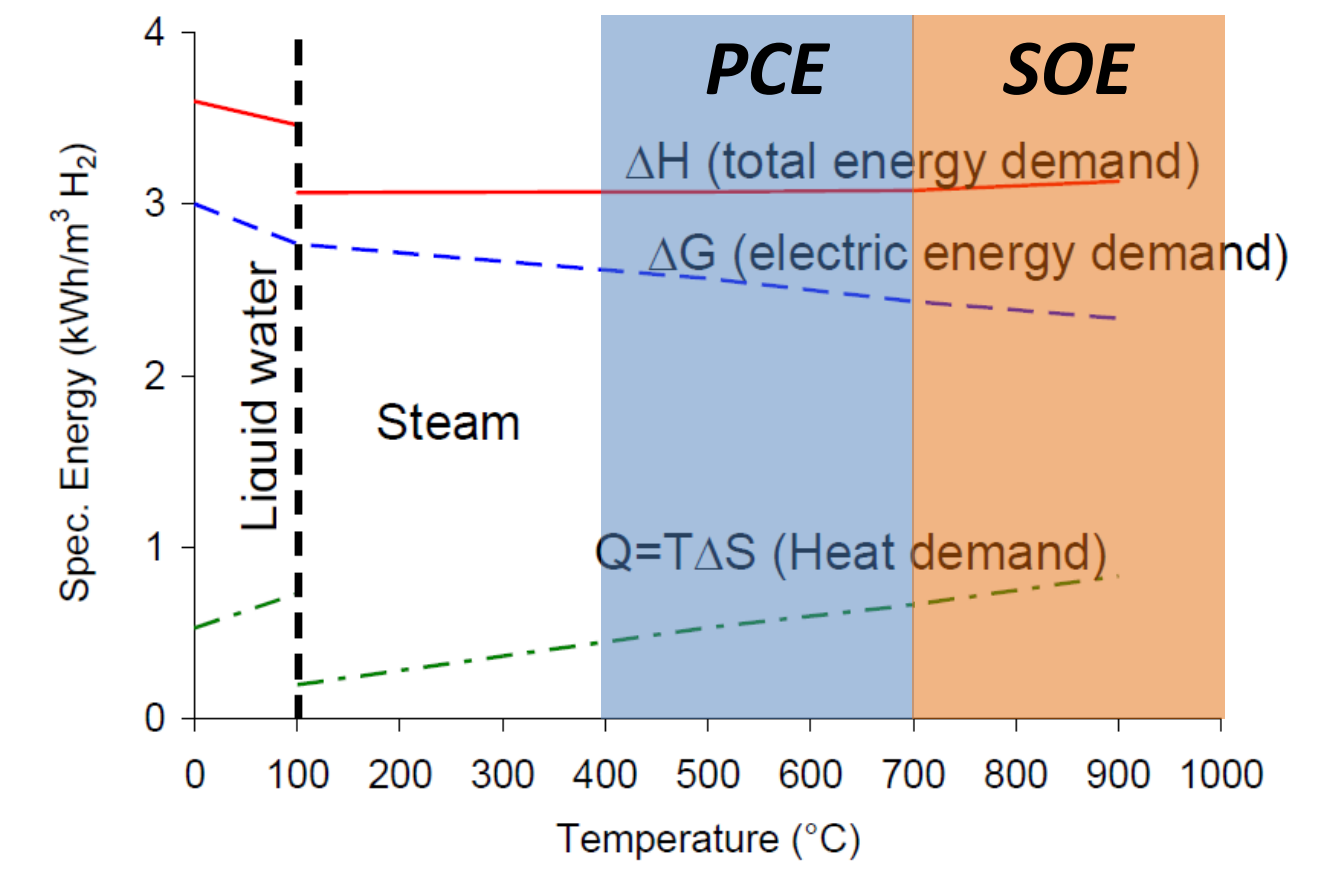
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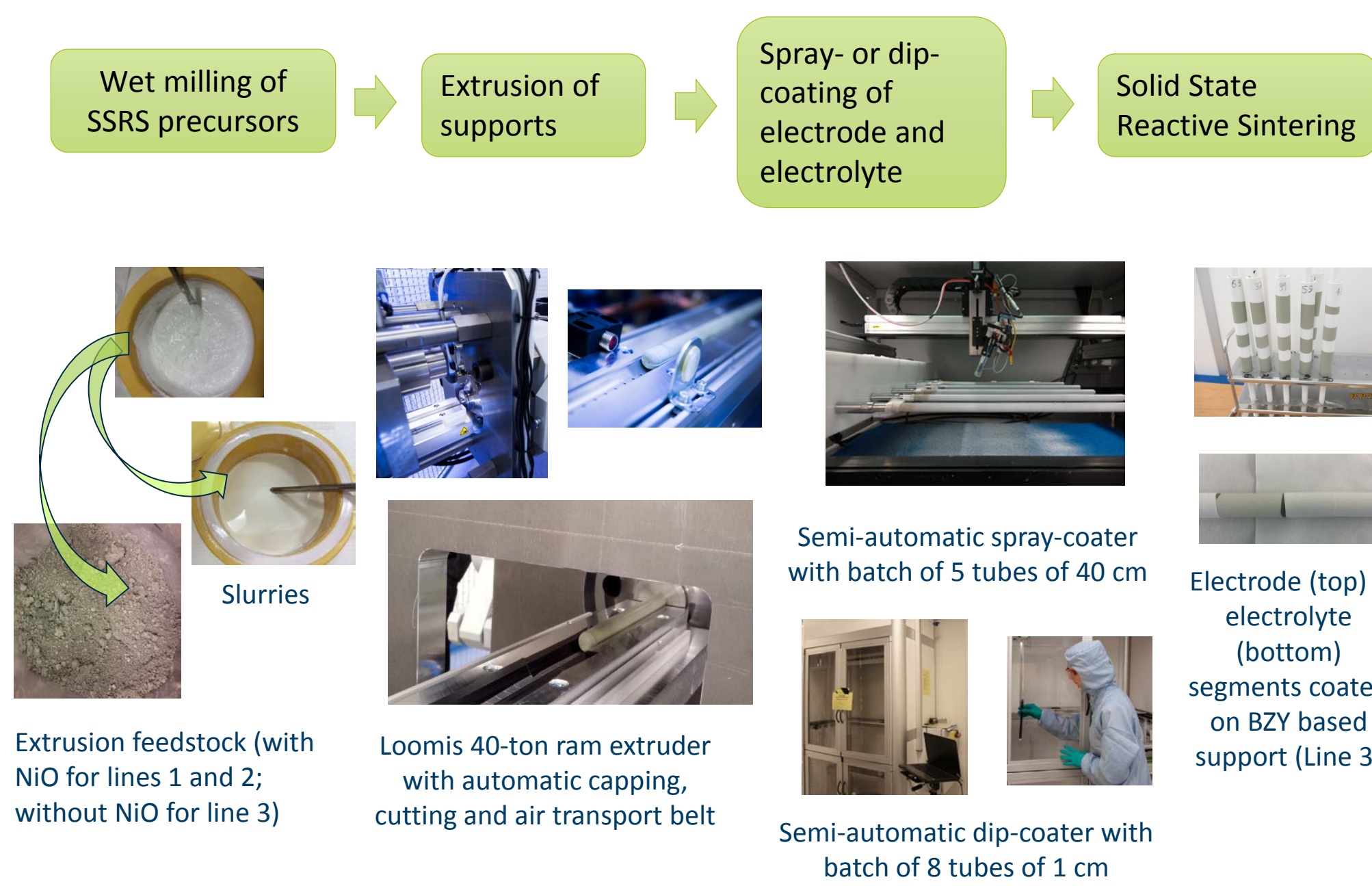
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High temperature electrolysis of steam offers high efficiency of conversion of renewable and peak electricity to H₂ and may increase efficiency further by utilising available sources of heat and steam. Solid oxide electrolyser cells (SOE) utilize oxide ion conducting electrolytes, operate around 800 °C and produce hydrogen on the steam feed side. Separation and drying of H₂ costs energy and adds plant complexity and footprint. High temperature proton conducting electrolyte instead pumps protons (H⁺) and forms dry H₂, leaving O₂ on the steam side. PCEs thus require less separation process stages and can produce pressurised dry H₂ directly. Protons exhibit lower activation energies than oxide ions, and ceramic proton conductors may thus be able to operate at lower temperatures – 600-800°C – closer to the ideal range for integration with solar and geothermal plants. In ELECTRA scalable fabrication of PCE is pursued along three lines with increasing risks and rewards. All cells consist of a porous Ni-BZCY based cathode for the H₂, a thin dense BZCY-based electrolyte, a porous anode for the H₂O+O₂ side, and a current collector system. Various anode materials were screened for their compatibility with BCZY based electrolyte and stability, including La₂NiO_{4+δ}, LSM, BSCF, Ba_{1-x}Gd_{0.8}La_{0.2+x}Co₂O_{6-δ} (x = 0-0.5) (BGLC) and LSCF.



Manufacturing all lines in clean room class 7



Line 3: Segmented-in-series cells by printing

Line 3: based on one end-closed porous BZY extruded tube, on which segments of cathode, electrolyte, and interconnect are sequentially applied and co-sintered.

Investigated materials

Porous supports

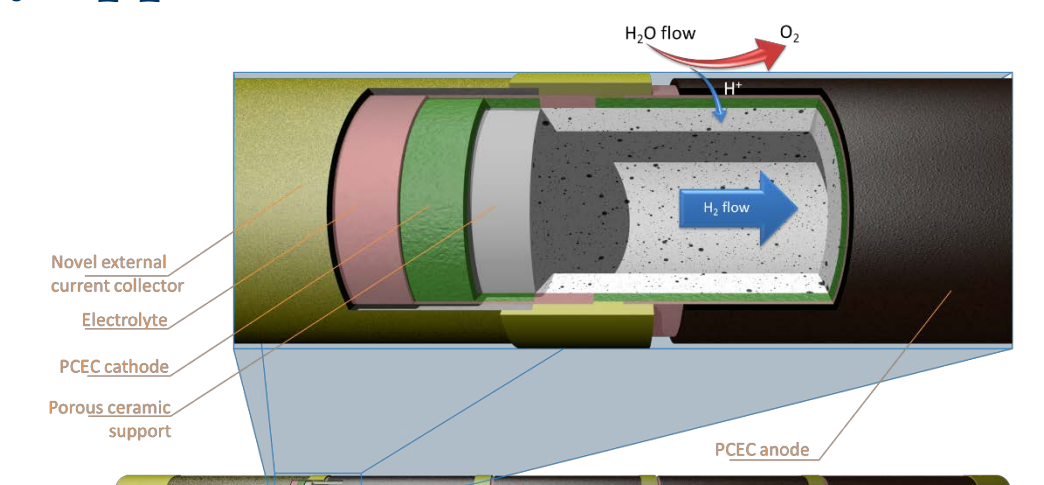
- BZY10 (SSRS; 20% Ce, 10% Y) + sintering aid + pore formers

PCEC cathode

- BZY10 (SSRS or oxide; 10% Y) + NiO
- BZY72 (SSRS or oxide) + NiO

Electrolyte

- BZY72 (SSRS or oxide)
- BZY10 (SSRS or oxide)

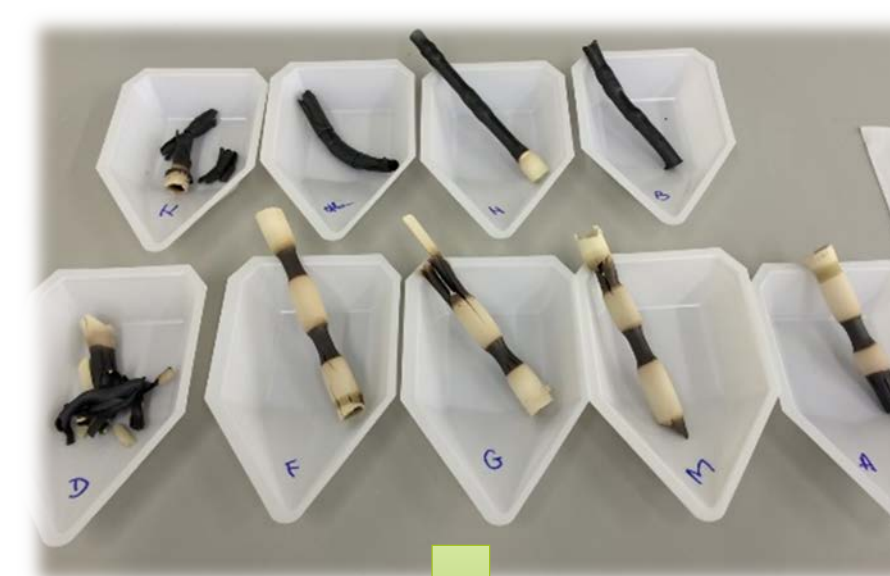


Novel interconnect materials and PCE anodes are under investigation, and will be applied in a second fabrication step.

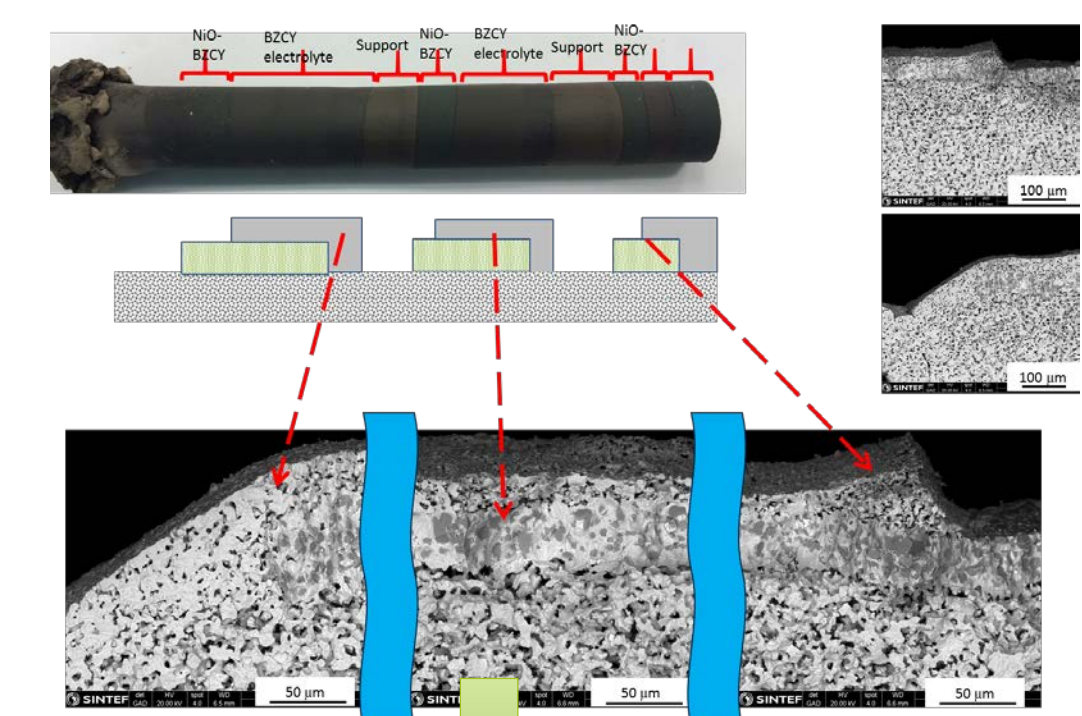
Examples of critical challenges during manufacturing

Differential sintering shrinkage between "coated" and "un-coated segments"

Tailoring microstructure of the three layers

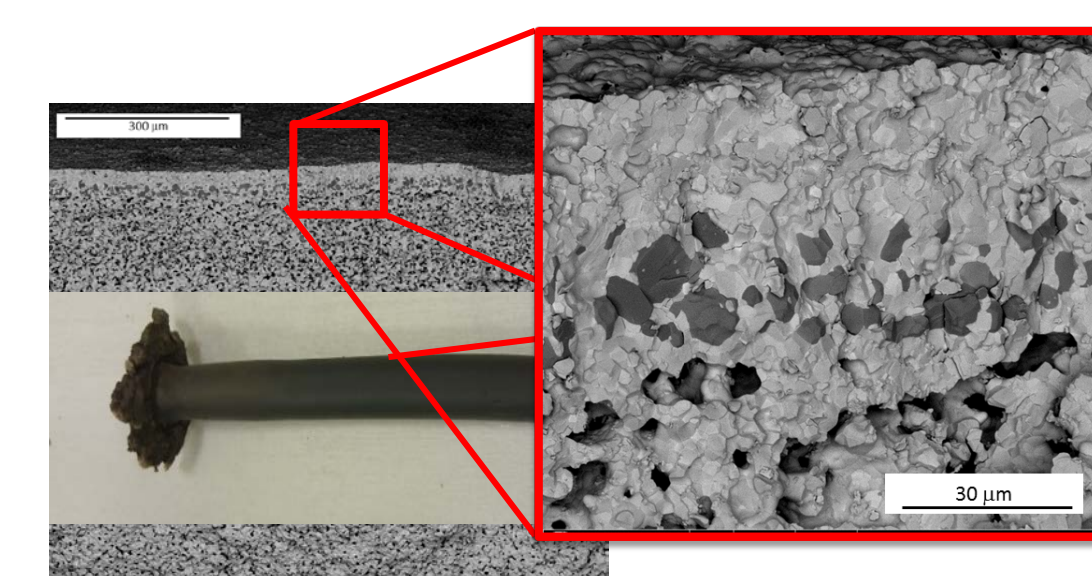


Use of both pore former and sintering aid to adjust sintering shrinkage



Annealing parameters were adjusted

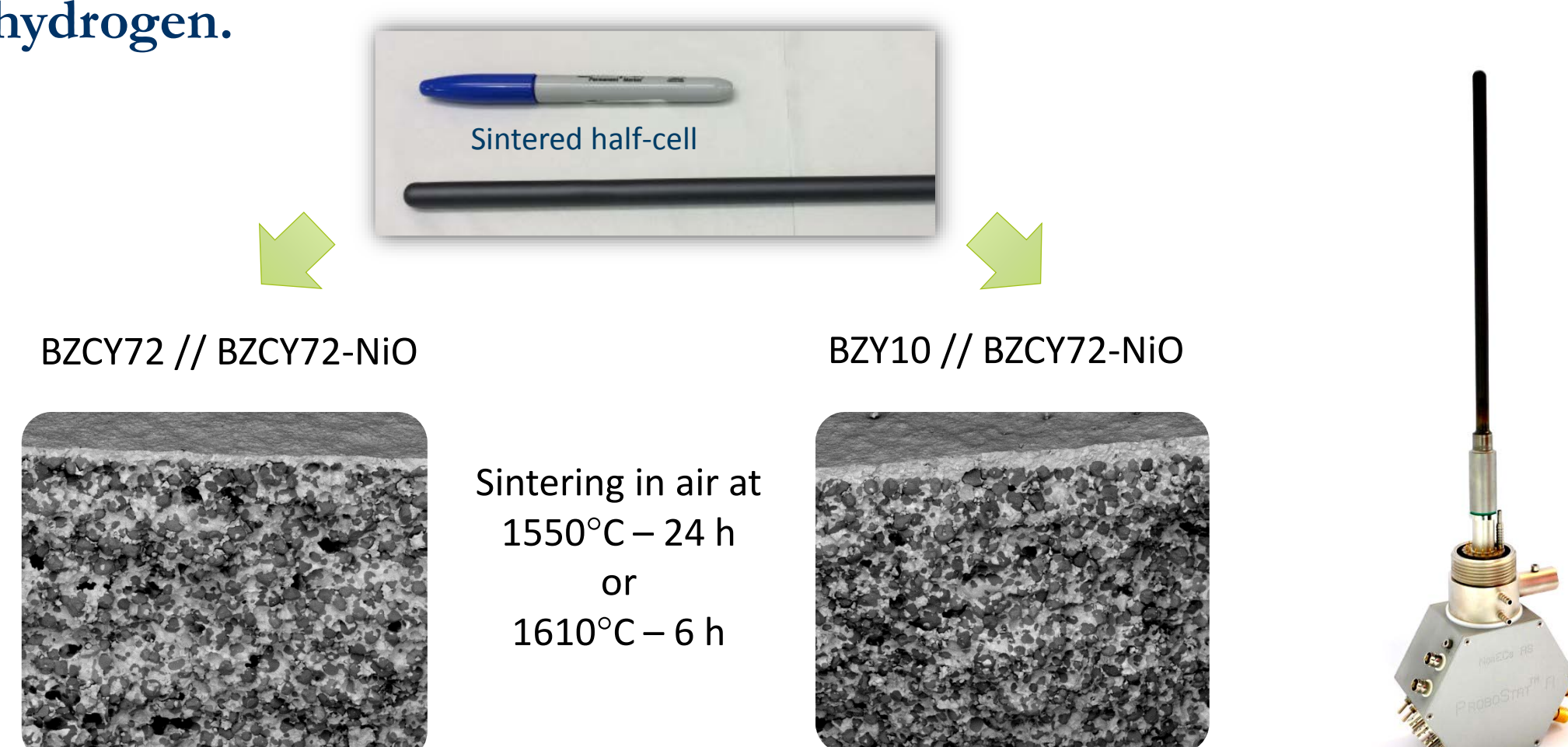
Segmented-in-series half-cells produced after adjustment of parameters



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

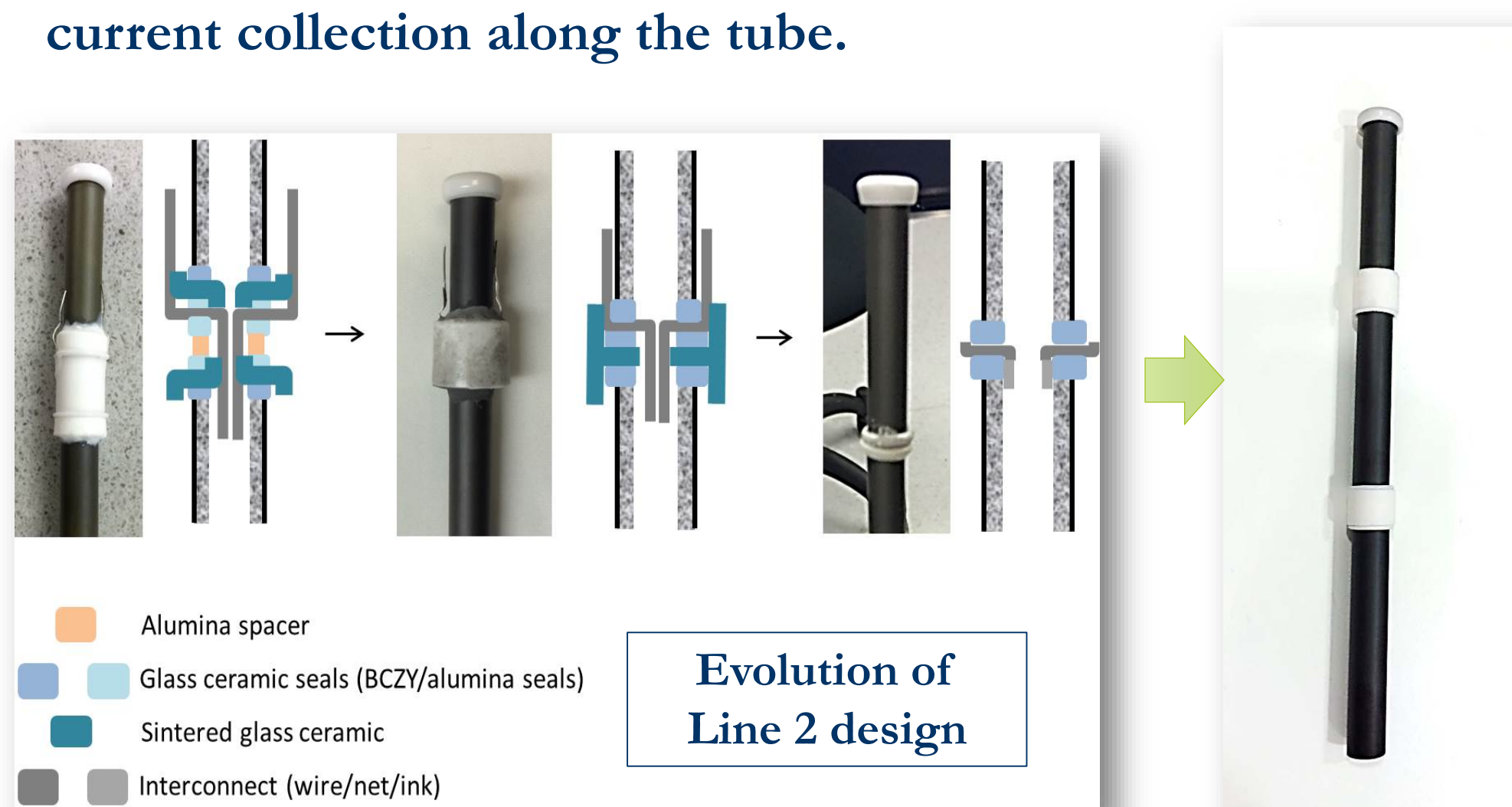
Line 1: Tubular cells

Line 1: based on solid state reactive co-sintering of BZY based electrolyte coated on a slip-cast or extruded NiO based composite tube, with subsequent reduction of NiO to Ni in hydrogen.



Line 2: Segmented-in-series cells by stacking

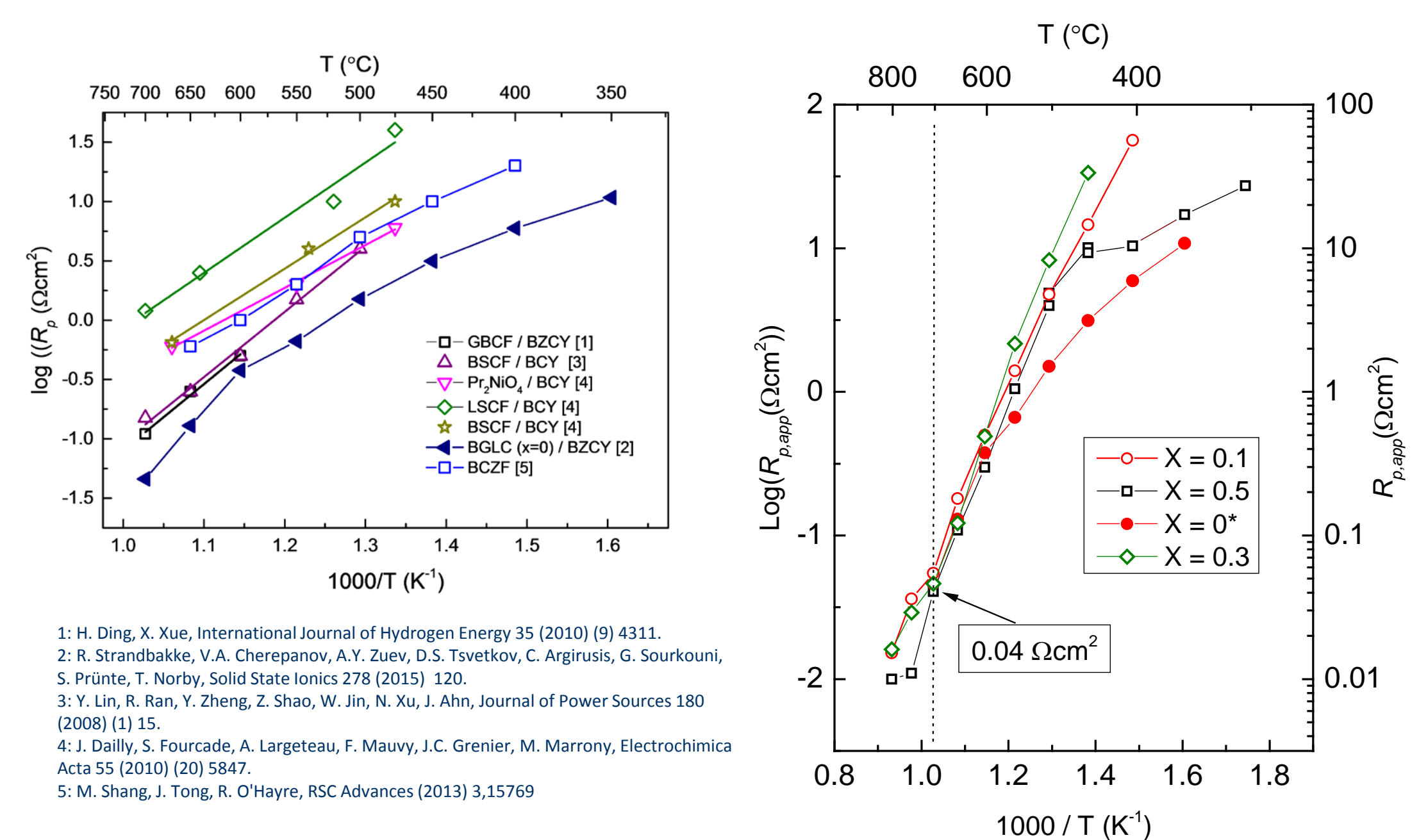
Line 2: based on BZCY tubes, which are cut and stacked in series to build voltage and reduce overall current to improve current collection along the tube.



- Alumina spacer
- Glass ceramic seals (BCZY/alumina seals)
- Sintered glass ceramic
- Interconnect (wire/net/ink)

Evolution of Line 2 design

Ba_{1-x}Gd_{0.8}La_{0.2+x}Co₂O_{6-δ} displays best PCE O₂-H₂O-electrode performance (symmetrical disk samples)



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