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TOR VERGATA UNIVERSITÀ DEGLI STUDI DI ROMA

Anode-Electrolyte Integration Techniques For Proton-Conducting Fuel Cell Manufacturing

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Background

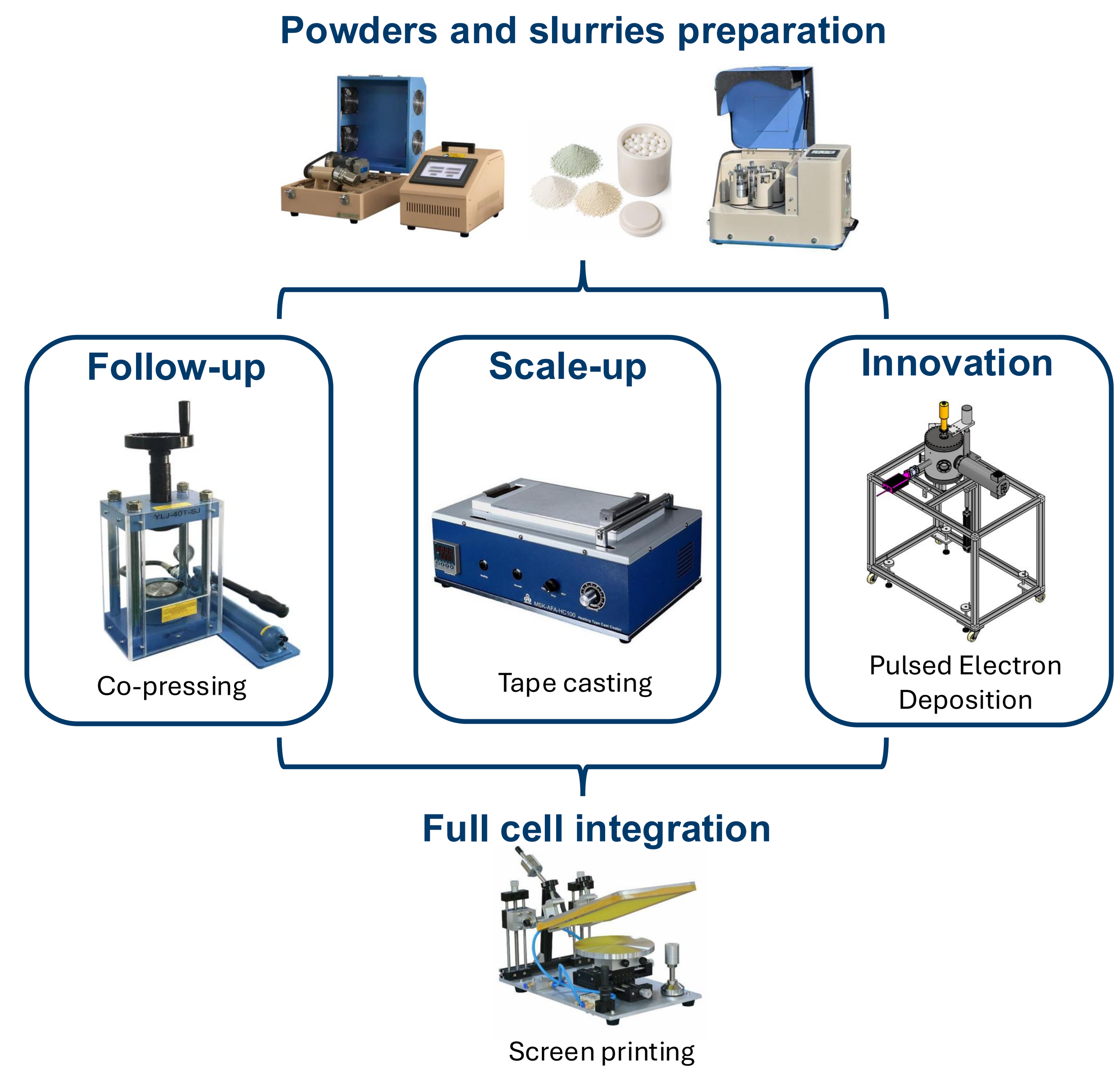
Several challenges are still encountered in the manufacturing of Proton-Conducting Fuel Cells (PCFCs), a valuable technology for clean energy production in the H_2 value-chain, since they can operate at lower temperatures compared to SOFC (i.e. 400-700°C).

PCFCs deployment is hampered by successful integration of thin, dense, crystalline and defect free electrolyte with fuel and air electrodes, required to reduce ohmic resistance and increase the cell power density while ensuring separation between oxidizing and fuel gases.

Traditional (i.e. die-pressing, tape-casting) and innovative technologies (i.e. physical vapor deposition) have been investigated for the integration of PCFC components, without identifying a preferred solution [1].

Following an initial study on die-pressed electrolytes, co-pressing and tape casting methods were investigated as traditional techniques for the anode-electrolyte integration focusing on their advantages and drawbacks. Pulsed Electron Deposition (PED) technique was studied as innovative approach since it allows homogeneous thin films deposition with controlled thickness while maintaining the stoichiometry of the material target [2].

Commercial ceramic powder $BaCe_{0.7}Zr_{0.2}Y_{0.1}O_{3-\delta}$ by Cerpotech S.A. (BCZY721) was used for the proton conducting electrolyte, while NiO:BCZY (60/40 wt%) cermet was prepared from NiO(II) and BCZY721 powders and used for the fuel electrode.

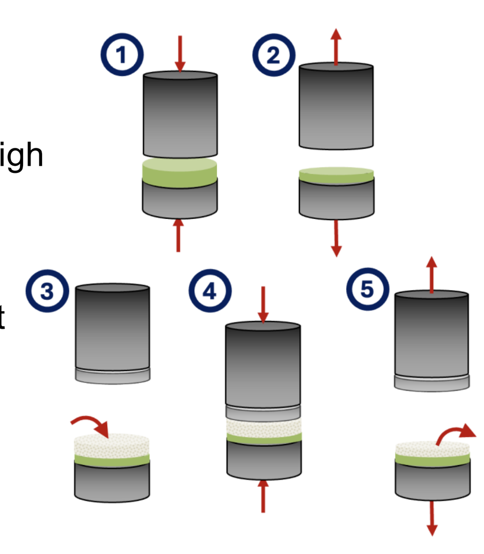


Co pressing

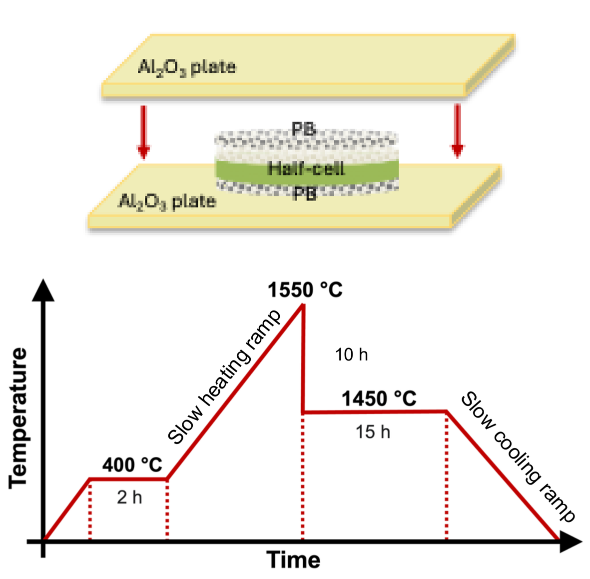
Procedure

Anode:
NiO:BCZY721 mixed with High Energy Ball Mill and sieved

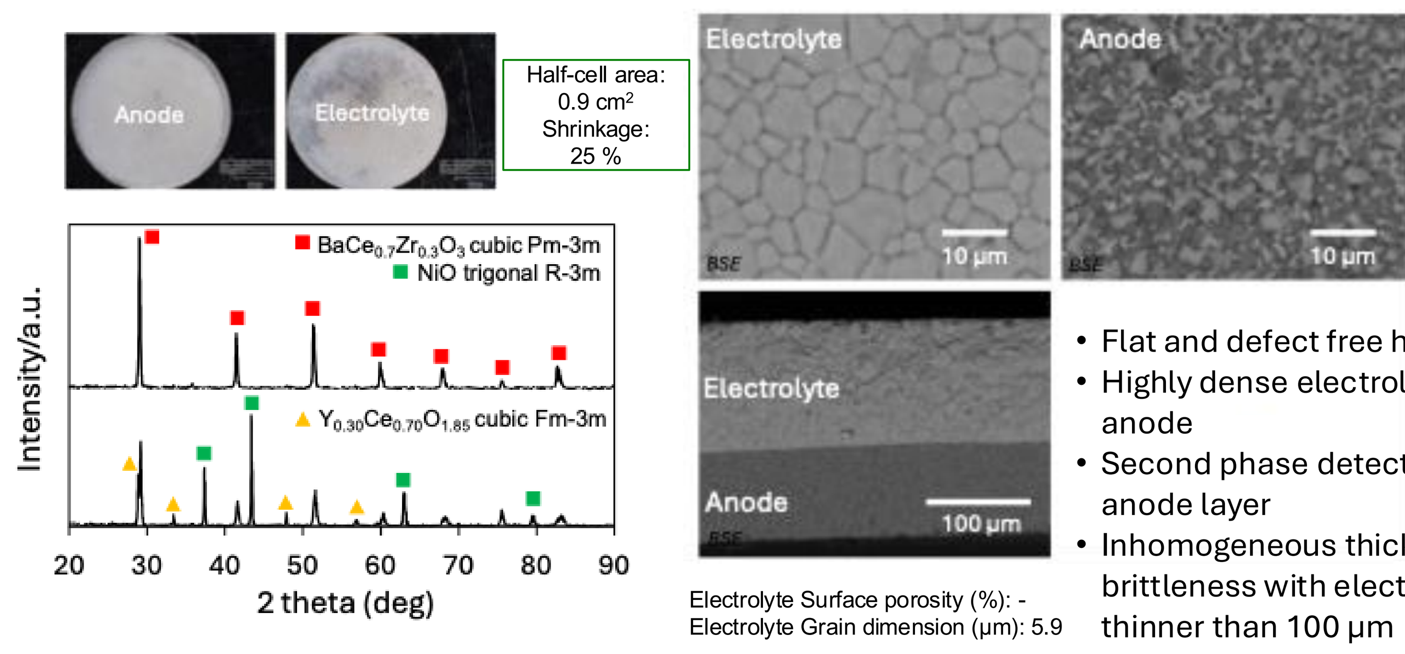
Electrolyte:
BCZY721 ground with 5%wt PVP and sieved



Sintering set-up [3]

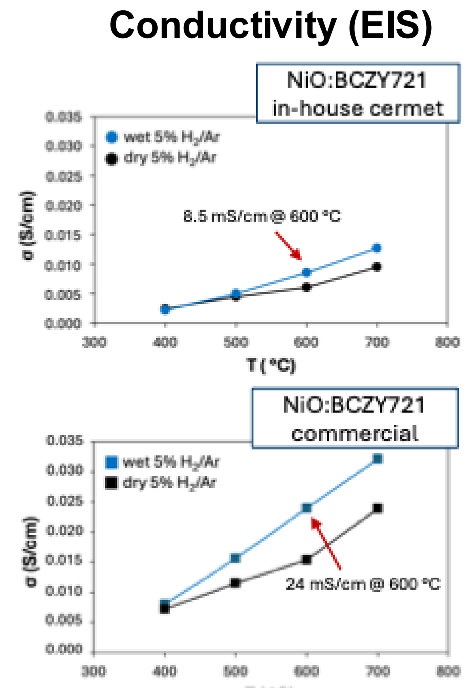


Characterization



- Flat and defect free half-cells
- Highly dense electrolyte and anode
- Second phase detected at the anode layer
- Inhomogeneous thickness and brittleness with electrolytes thinner than 100 µm

Conductivity (EIS)

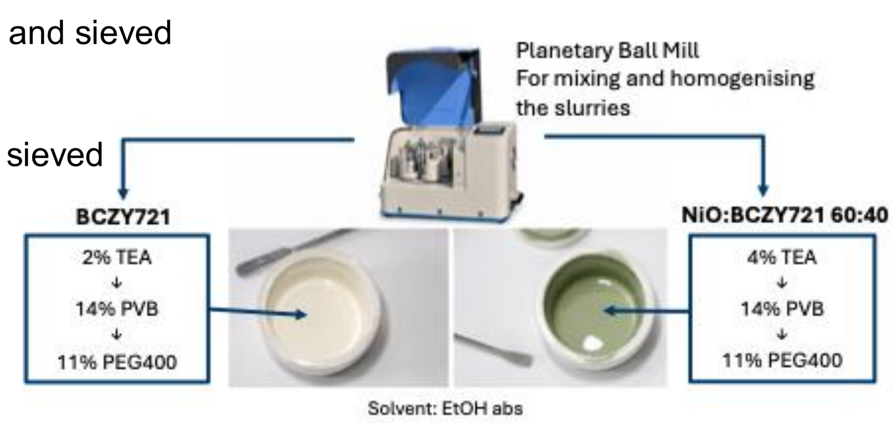


Tape casting

Procedure

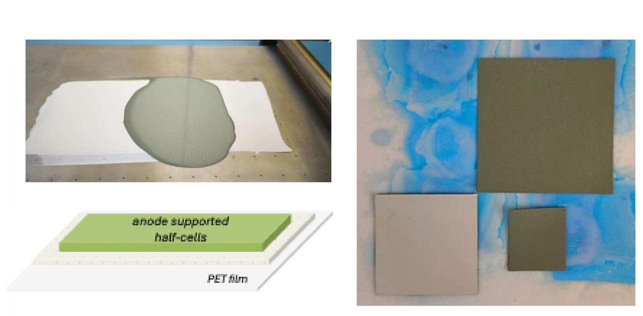
Anode:
NiO:BCZY721 ball milled and sieved

Electrolyte:
BCZY721 ball milled and sieved



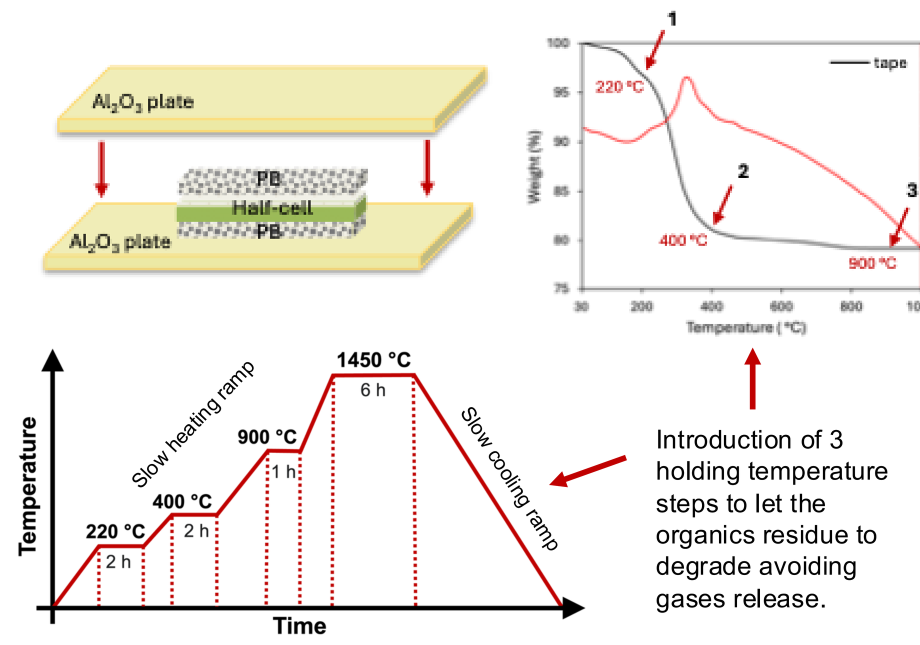
- TEA was chosen as dispersant (upon sedimentation test).
- Commercial PVB and PEG400 are then added as binder and plasticizer.
- Introduction of a porogen (rice starch 6 wt%) to fabricate a supporting layer

Tape casting parameters



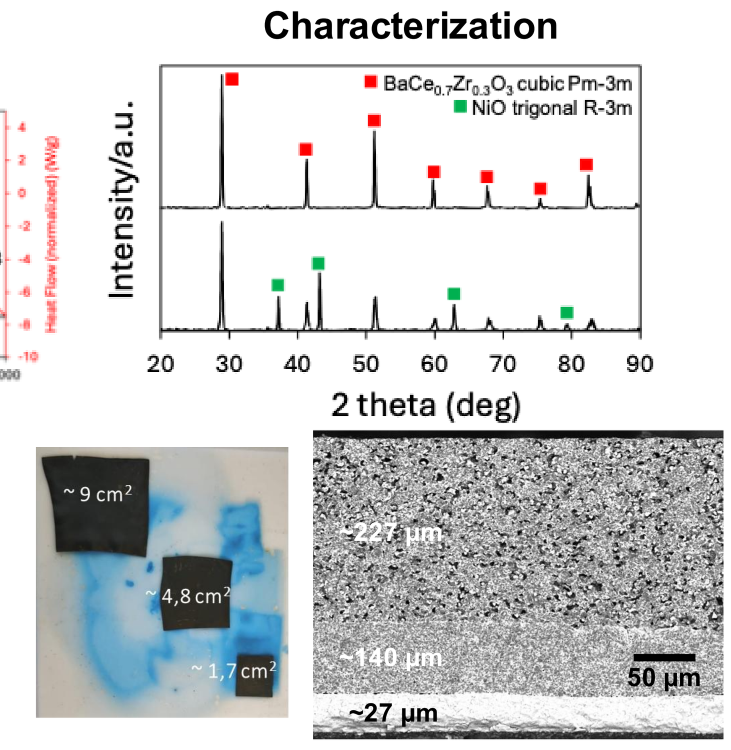
Blade gap for the electrolyte:
100 µm
Blade gap for the anode functional layer:
500 µm
Blade gap for the anode porous layer:
1000 µm
Deposition speed:
8 mm/s

Sintering set-up



Introduction of 3 holding temperature steps to let the organics residue to degrade avoiding gases release.

Characterization

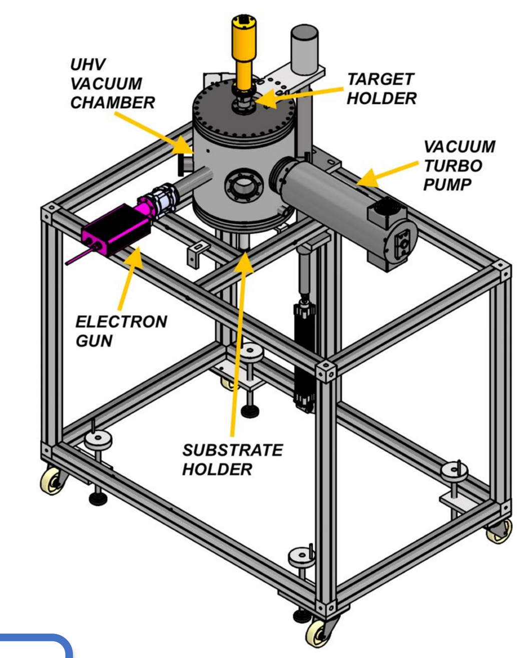


PED

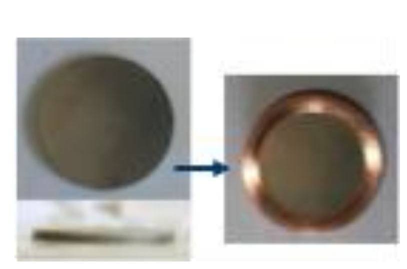
PED equipment assembled and tested includes:

- vacuum chamber (base pressure $4x10^{-6}$ mbar)
- rotating substrate and rotating target holder (target substrate d = 50 mm).

The ablated perovskite ceramic target by pulsed electron beam is emitted in the form of highly ionized plasma plume and deposited onto the substrate.

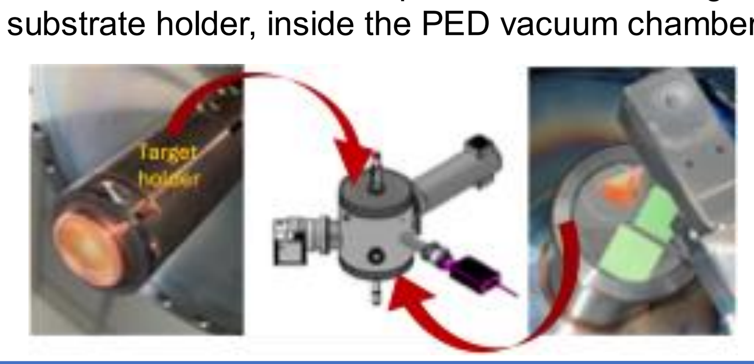


In-house target preparation with BCZY721

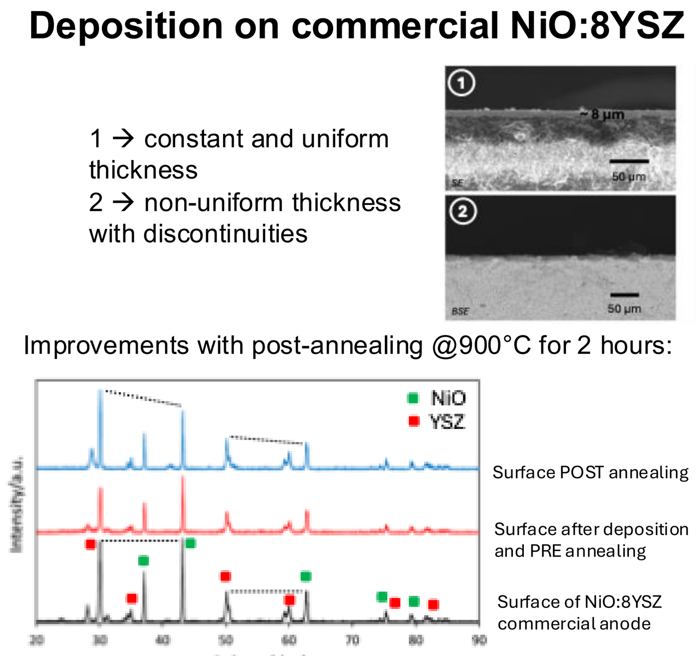


Highly dense and crystalline target produced by following the two-step heating procedure [3].

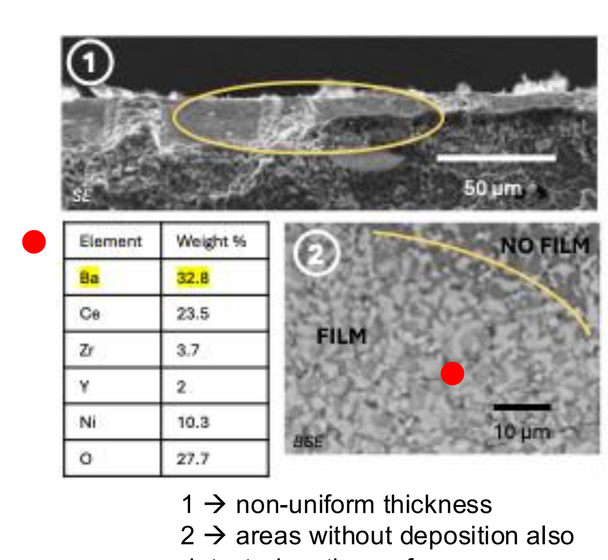
Anode substrates were placed on the rotating substrate holder, inside the PED vacuum chamber



Deposition on commercial NiO:8YSZ



Deposition on NiO:BCZY721



Element	Weight %
Ba	32.8
Ce	23.5
Zr	3.7
Y	2
Ni	10.3
O	27.7

1 → non-uniform thickness
2 → areas without deposition also detected on the surface

EDX analysis on gray spots, revealed BCZY721 elements on anode surface

Conclusion and Outlooks

Advantages and drawbacks encountered comparing the three different fabrication techniques:

Co-pressing
✓ fast and rather simple techniques that do not require high use of organic additives nor hazardous solvent. Good electrolyte densification can be reached and low shrinkage.
X Low scalability and no possibility to fabricate anode-supported cells as we cannot go below 100-150 µm

Tape-casting
✓ Scalable and already industrialized technique. Anode-supported with thin electrolyte can be fabricated with reproducibility.
X Large quantities of slurry and additives needed. Often hazardous solvents need to be used to get right viscosity. Shrinking and cracking of the cells during sintering is hard to control. Large use of sacrificial powder is needed.

PED
✓ Thin film deposition with theoretical thickness control and stoichiometry of the target transfer.
X Hard to obtain uniform deposited layer and to transfer the target stoichiometry to the substrate.

References

[1] S. Chen et al., Advancement in materials materials and strategies for reliable and high-efficiency proton-conducting electrolytes in solid oxide cells, Chemical Engineering Journal 519, 16466 (2025).
[2] M. Nistor et al., Pulsed electron beam deposition of oxide thin films, J. Phys. D: Appl. Phys 41 165205 (2008).
[3] L. Freschi et al., Higly dense barium cerate-zirconate electrolytes through a practical two-step sintering route for proton-conducting fuel cells, Ceramic International 52, 15949-15958 (2026)

Acknowledgement

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