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CERAMIC MULTILAYER FOR ENERGY APPLICATIONS

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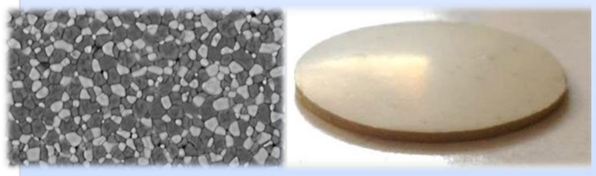
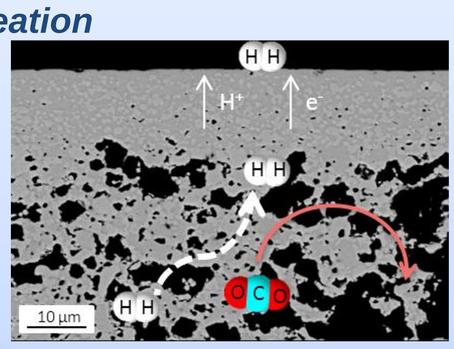
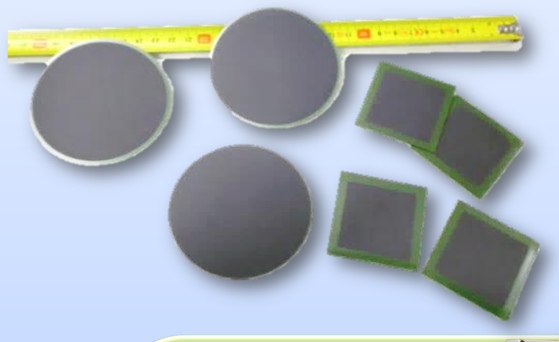
Layered ceramic composites, due to the possibility of combining layers of different composition and/or microstructures, have been widely exploited for energy applications. Even if these structures are generally produced through well established and industrialized technologies, their fabrication generally requires specific expedients to avoid detrimental defects such as cracks, delamination, warping, unsuitable microstructure/densification, etc. In this work, the key-issues related to the ceramic multilayers production were investigated, analyzing, as case-study, Solid Oxide Fuel Cells & Electrolyzers (SOFC/SOEC) and dual phase ceramic membranes for hydrogen permeation.

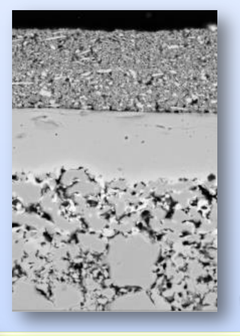
Proton conductive ceramic membranes for hydrogen permeation

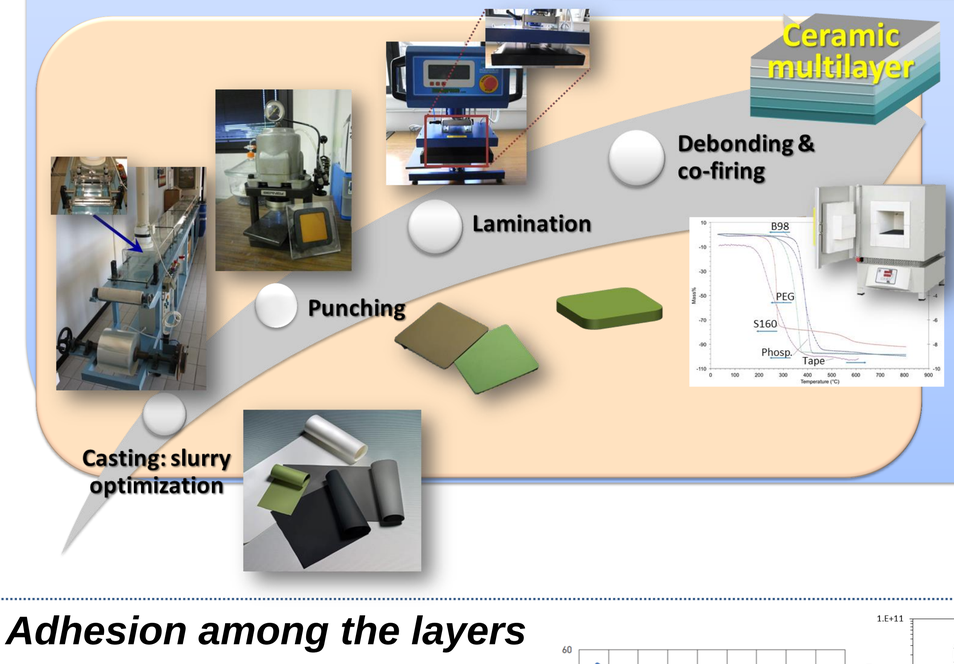




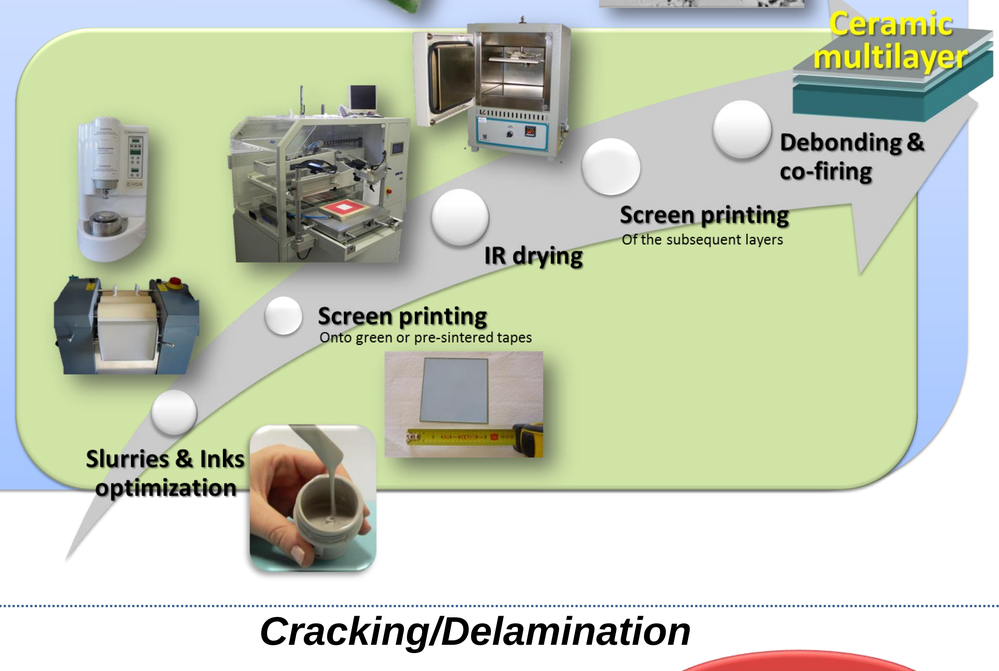
Solid Oxide Fuel Cells & Electrolyzer (SOFC/SOEC)







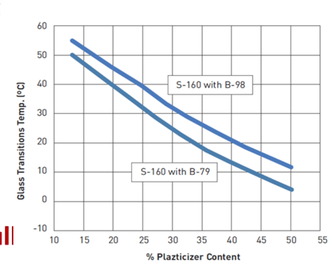
Well established and industrialized technology. However the compositions of the tape cast slurries & inks must be perfectly tailored to couple the two different techniques.

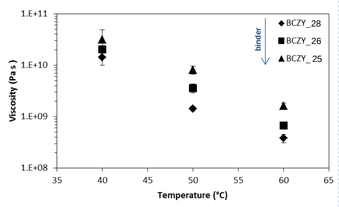


Adhesion among the layers

The tape casting process must consider the careful optimization of the lamination parameters (Temperature, Pressure, Time)

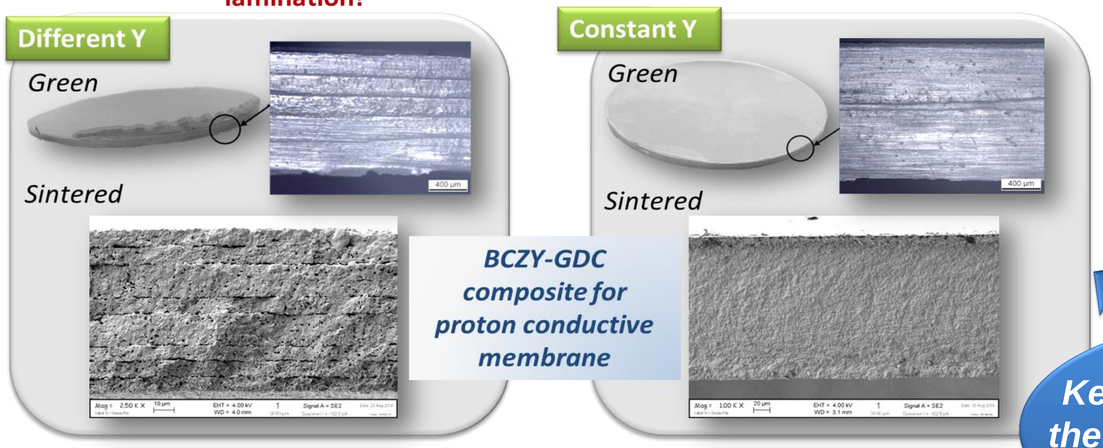
The binder/plasticizer vol ratio (Y) is a foundamental parameter to have a succesfull lamination!





↑ vol binder →↓ viscosity – lamination improved

Dynamic Mechanical Analysis (DMA)

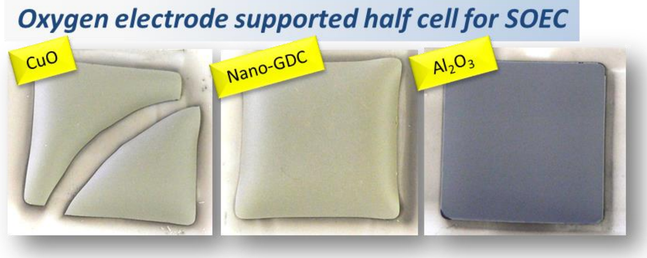


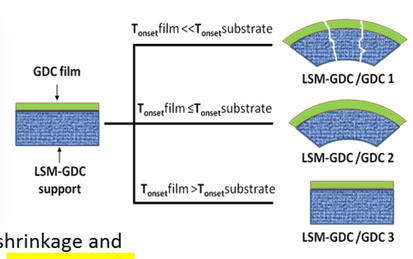
Cracking/Delamination

The study of the thermomechanical behaviour of each layer is crucial to prevent cracking, delamination, distorsion.

TEC, Shrinkage level, shrinkage rate

Oxygen electrode supported half cell for SOEC





The integrity and the planarity depends on the onset sintering T, linear shrinkage and maximum sintering rate T of the film and support layer → modulated by sintering aids

$$\dot{k} = \frac{6(m+1)^2 mn}{m^4 n^2 + 2mn(2m^2 + 3m + 2) + 1}\Delta\dot{\varepsilon}$$

$m = t_1/t_2$

$n = \eta_1(1-\nu_2)/\ [\eta_2(1-\nu_1)]$

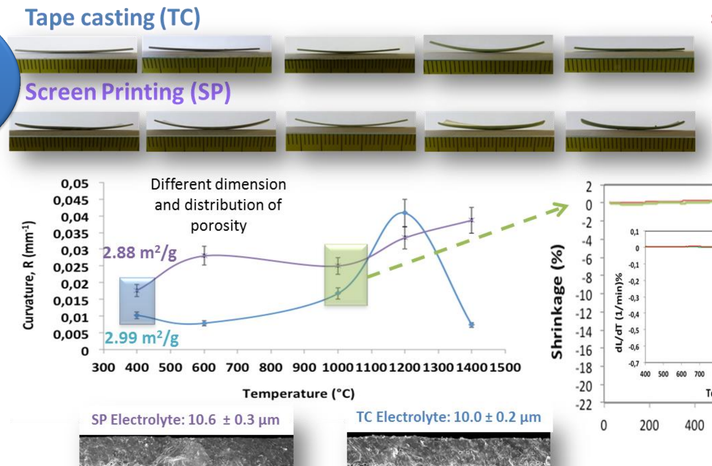
k = normalized curvature;
m = layer thickness ratio;
n = viscosity ratio;
η = uniaxial viscosity;
ν = viscous Poisson ratio;
t = layer thickness
Δε = difference in the strain rates

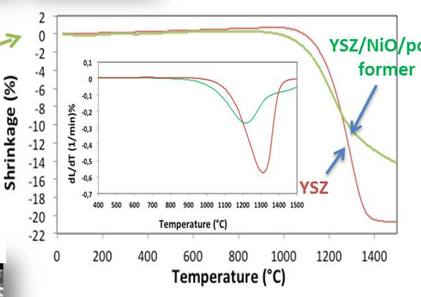
Warping & Cambering

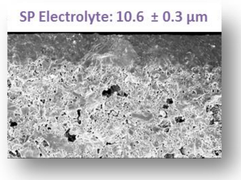
Anode-Supported Half-cells for SOFCs

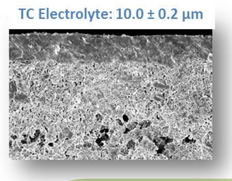
Tape casting (TC)

Screen Printing (SP)









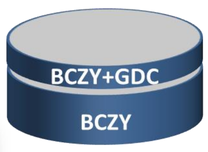
The cambering behaviour is strictly related to the technique used that influences the starting green density, the powder and pores distribution in the layer, and the interaction with the support

A common method to limit warpage effects in multilayers is the application of a suitable load during sintering (Constrained Sintering)

Key-issues related to the ceramic multilayers production

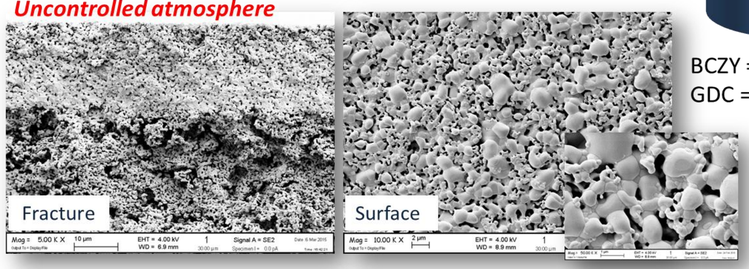
Sintering atmosphere control

BCZY-GDC composite for proton conductive membrane

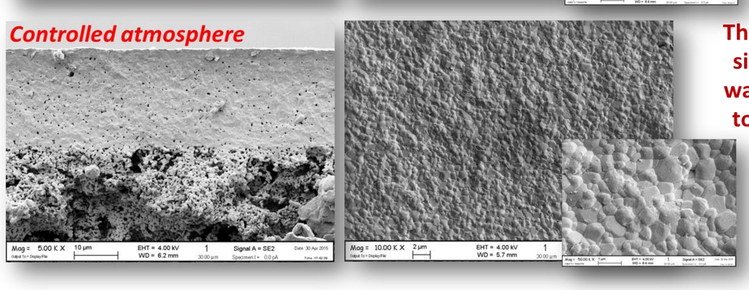


BCZY = $BaCe_{0.65}Zr_{0.2}Y_{0.15}O_3$
GDC = $Ce_{0.8}Gd_{0.2}O_{1.9}$

Uncontrolled atmosphere



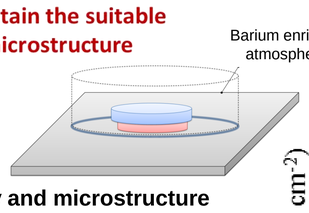
Controlled atmosphere



The strict control of the sintering atmosphere was found to be crucial to obtain the suitable microstructure

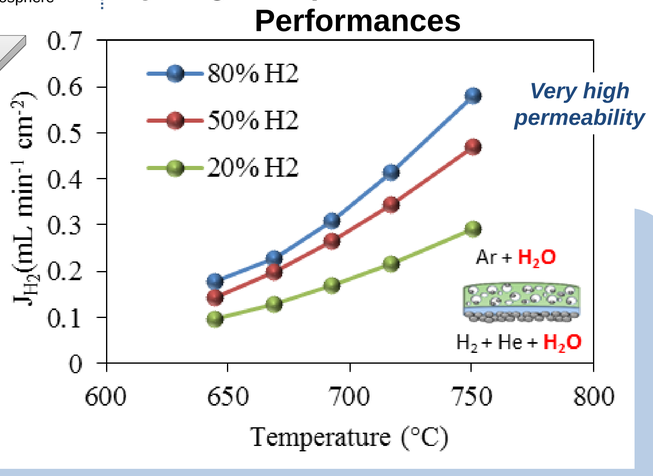
Ba losses

$$BaCe_{0,65}Zr_{0,20}Y_{0,15}O_{3-\delta} \leftrightarrow x\ BaO\uparrow + Ba_{1-x}Ce_{0,65}Zr_{0,20}Y_{0,15}O_{1-\delta-x}$$



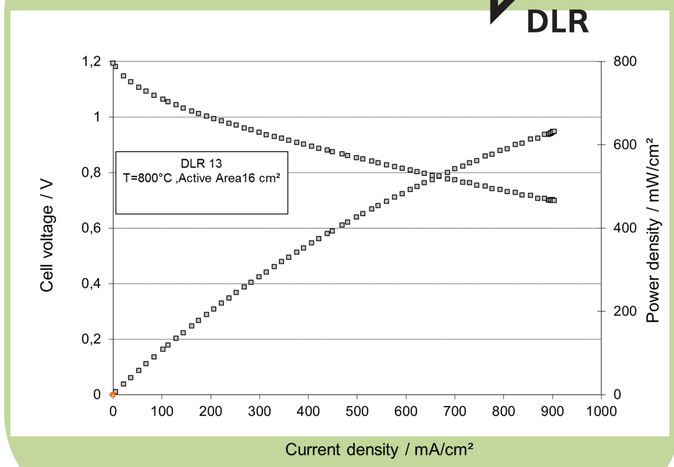
An excess of Ba was necessary to obtain the exact stoichiometry and microstructure

Hydrogen Separation Membrane Performances



Performance in agreement with the literature data

DLR



Solid Oxide Fuel Cells Performances

These devices were successfully produced by tape casting/screen printing by carefully controlling each step of the productive process.

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