$BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$-$Ce_{0.85}Gd_{0.15}O_{2-\delta}$ composite MIEC membrane for H_2 purification

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ICMATE Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia

Outline

- **Dense MIEC ceramic membranes for H_2 separation**

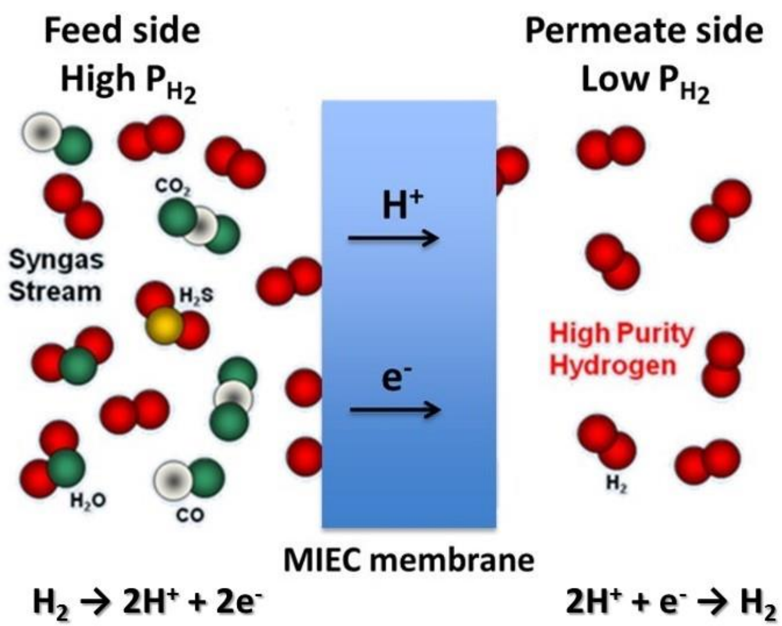
- **$BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$-$Ce_{0.85}M_{0.15}O_{2-\delta}$ (M = Gd, Y, Sm) MIEC membranes :**

  - Preparation and characterization
  - Chemical stability under CO_2 and syn-gas atmosphere
  - Chemical stability under H_2S atmosphere
  - *In-situ* synchrotron XRD analyses under H_2 atmosphere

- **Conclusions and perspectives**

Why MIEC membranes?

Dense ceramic membranes based on mixed ionic and electronic conductors (MIEC) have been considered extremely interesting materials **for H_2 separation thanks to their capability to work at high temperatures (T > 600°C).**



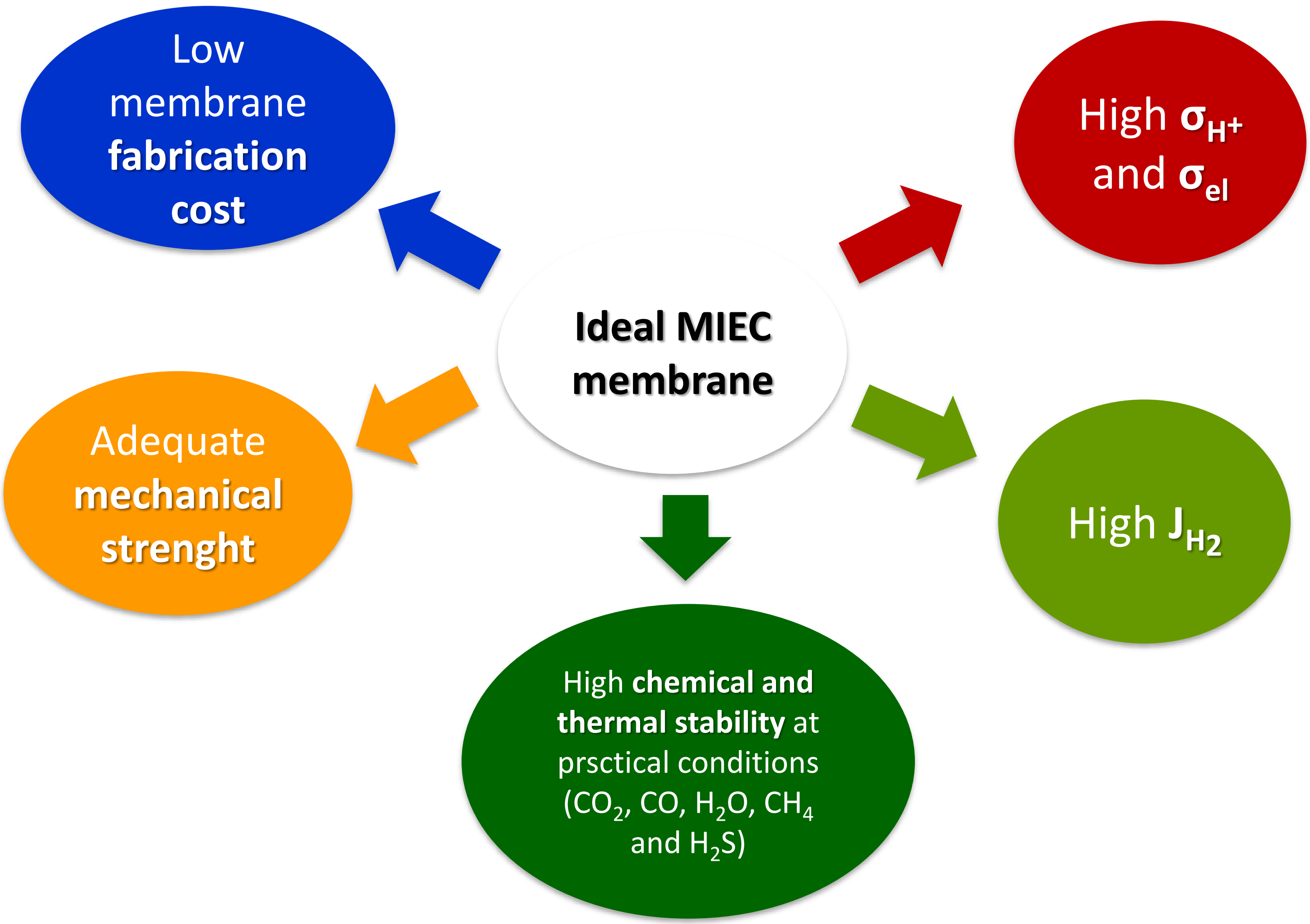
The J_{H_2} is described by the **Wagner equation:**

$$J_{H_2} \propto \frac{RT}{2F^2 L} \frac{\sigma_{H^+}\sigma_{el}}{\sigma_{H^+} + \sigma_{el}} \ln\left(\frac{p_{H_2}^{in}}{p_{H_2}^{out}}\right)$$

Advantages

- **No need of external power**
- **100% selective**
- **Possible integration in the reforming plants**

Requirements for MIEC membranes



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Our strategy

H^+-conductor + e^--conductor = Dual-phase membrane

$BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$ (BCZ20Y15)

H^+-conductor

S. Barison Et al. *Journal of Materials Chemistry* 18 **(2008)** 5120.

- **High proton conductivity** in 500-700°C range: $\sigma \geq 1x10^{-2}$ S cm^{-1} at 600°C.
- Good chemical and thermal **stability in CO_2 and H_2O**

$Ce_{0.85}M_{0.15}O_{2-\delta}$ (MDC15, M = Y, Gd, Sm)

e^--conductor

M. Mogensen, Et al. *Solid State Ionics* 129 **(2000)** 63.

- **n-type electronic conductivity** at reducing conditions (T>600°C)
- Good chemical and thermal **stability in CO_2 and H_2O**

BCZ20Y15-MDC15 50:50 and 60:40 volume ratio

E. Rebollo, C. Mortalò, S. Escolastico, S. Boldrini, S. Barison, J. M. Serra, M. Fabrizio, *Energy Environ. Sci.* 2015, **8**, 3675.

Synthetic procedure

$BaCe_{0.65}Zr_{0.2}Y_{0.15}O_{3-\delta}$
Commercial powders

Aid sintering ZnO

$Ce_{0.85}M_{0.15}O_{2-\delta}$ (M = Gd, Y, Sm)
Prepared by SSR

↓

Ball milling

↓

150 μm and 45 μm sieving

↓

Uni-axially pressing

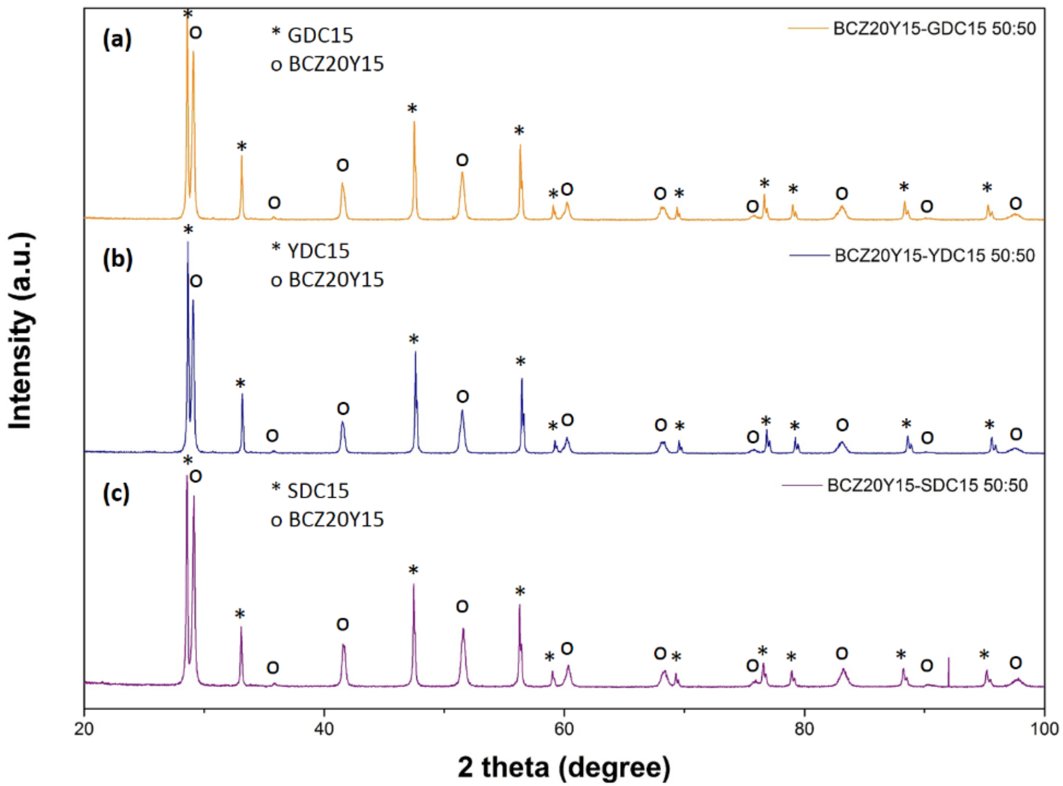
↓

Sintering 5 h 1450°C

↓

$BaCe_{0.65}Zr_{0.2}Y_{0.15}O_{3-\delta}$- $Ce_{0.85}M_{0.15}O_{2-\delta}$
Symmetric MIEC BCZ20Y15-MDC membranes

XRD analyses



Only **BCZ20Y15** and **MDC15** phases detected.

- **Rietveld refinement**:
- ✓ **MDC15 →** cubic ***Fm-3m*** space group
- ✓ **BCZ20Y15 →** orthorhombic ***Pnma*** space group

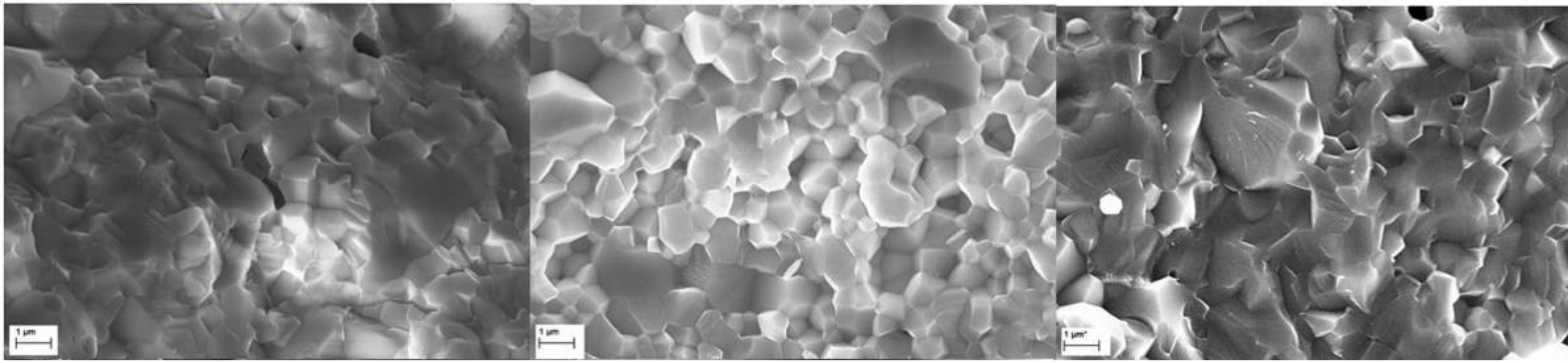
No interaction, no evidence of Zn substitution in the crystal structures or undesired phases

SEM analyses

BCZ20Y15

+

GDC15 | YDC15 | SDC15

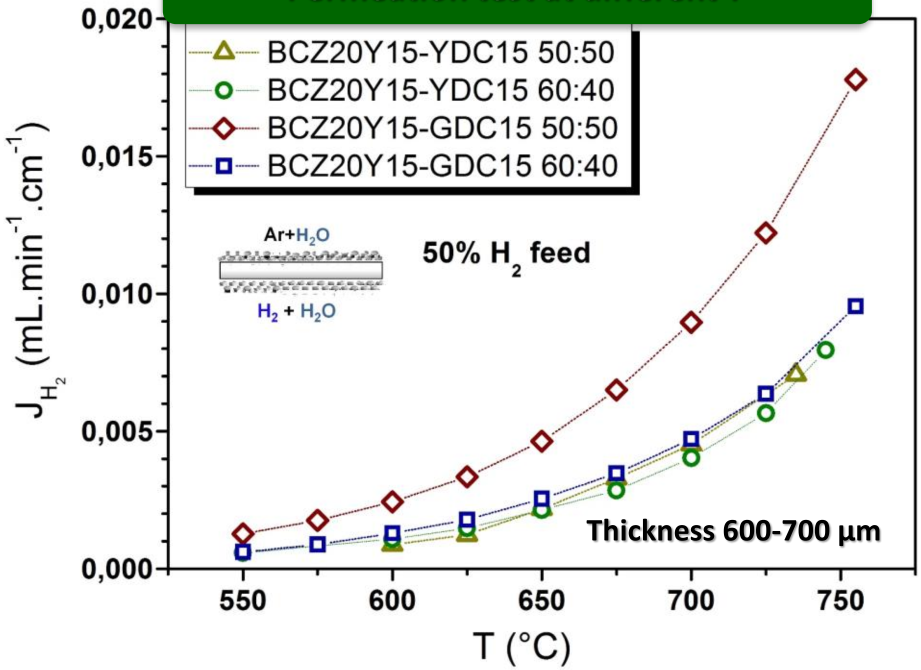


- Homogenous grain distribution
- No open porosity
- Crack-free

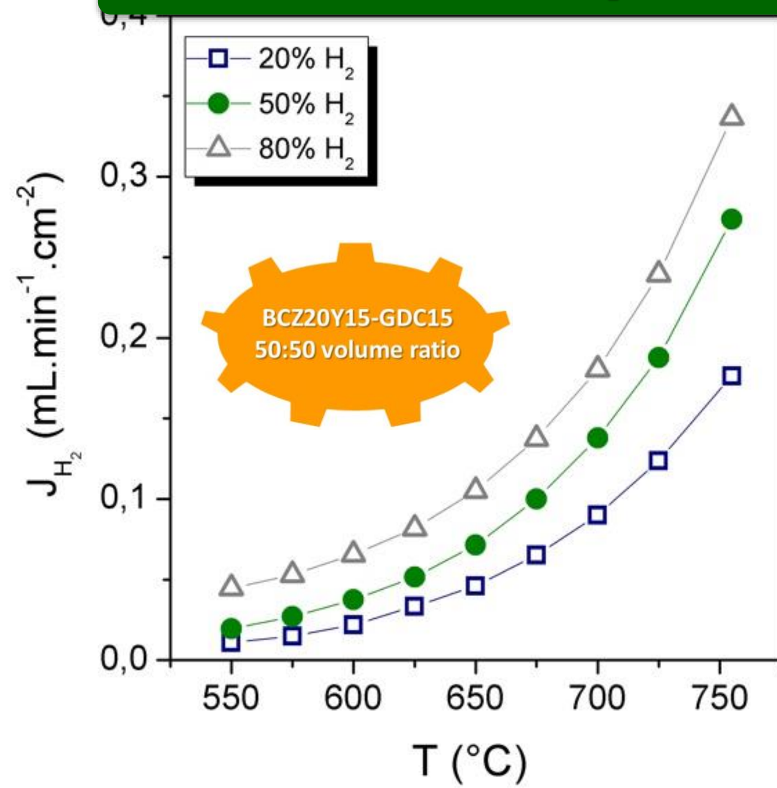
High-density (ρ_{rel} > 95%) symmetric membranes

H_2 permeability

Permeation test at different T



Permeation test at different % H_2 feed and T



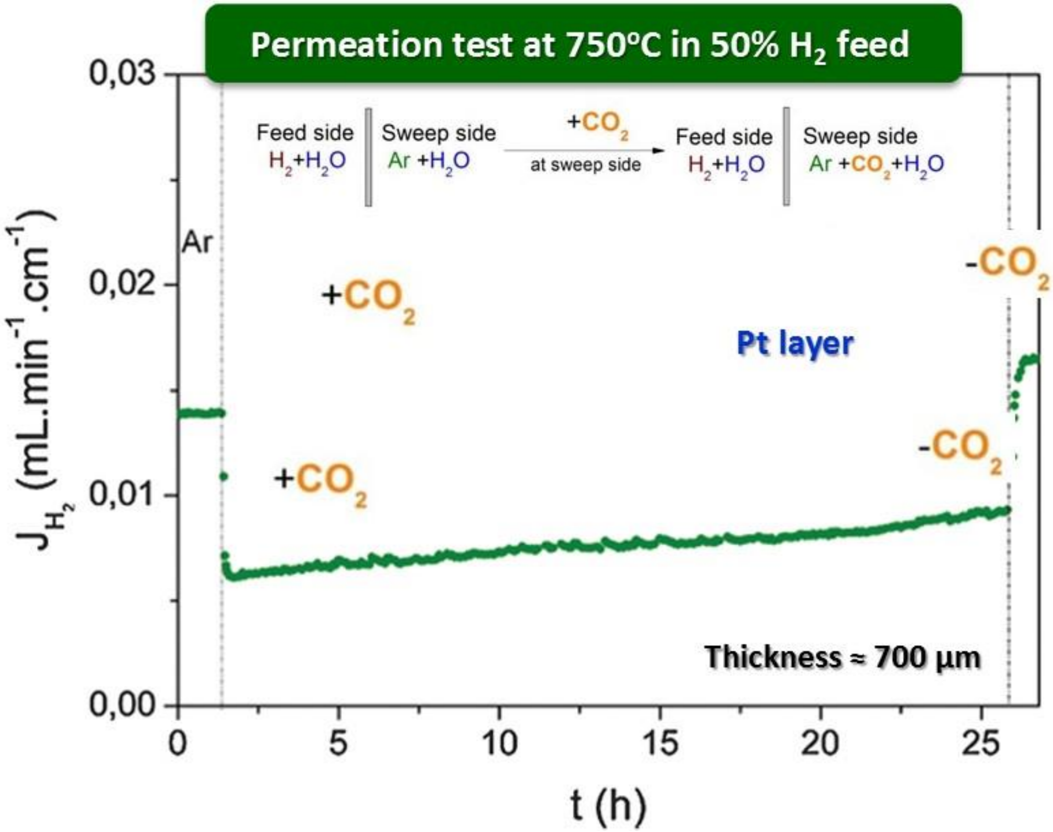
BCZ20Y15-GDC15
50:50 volume ratio

J_{H_2} = 0.27 mL·min^{-1}·cm^{-2} at 755°C

(H_2 permeation measurements were performed by the group of prof. Serra from ITQ of Valencia)

E. Rebollo, C. Mortalò, S. Escolastico, S. Boldrini, S. Barison, J. M. Serra, M. Fabrizio, *Energy Environ. Sci.* 2015, **8**, 3675.

Permeability under CO_2



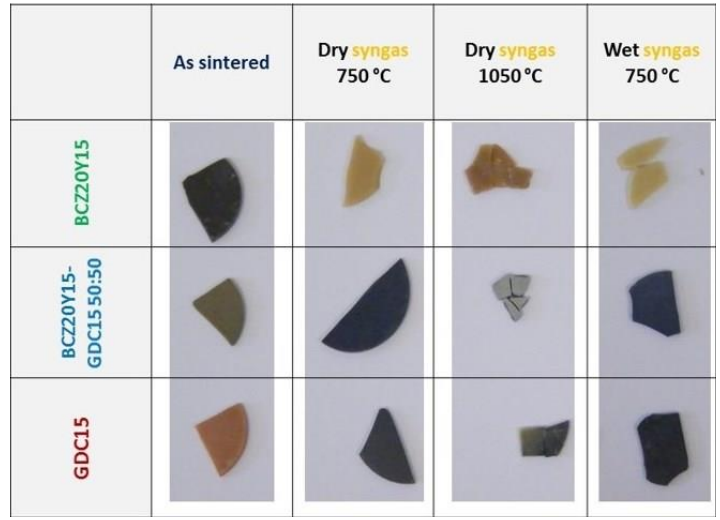
Very good chemical stability under CO_2-rich atmosphere → **J_{H_2} was totally recovered when the sweep gas was switched to Ar** (CO_2/H_2 competitive adsorption on the membrane surface)

(measurements performed by the group of prof. Serra from ITQ of Valencia)

E. Rebollo, C. Mortalò, S. Escolastico, S. Boldrini, S. Barison, J. M. Serra, M. Fabrizio, *Energy Environ. Sci.* 2015, **8**, 3675.

Chemical stability under syn-gas

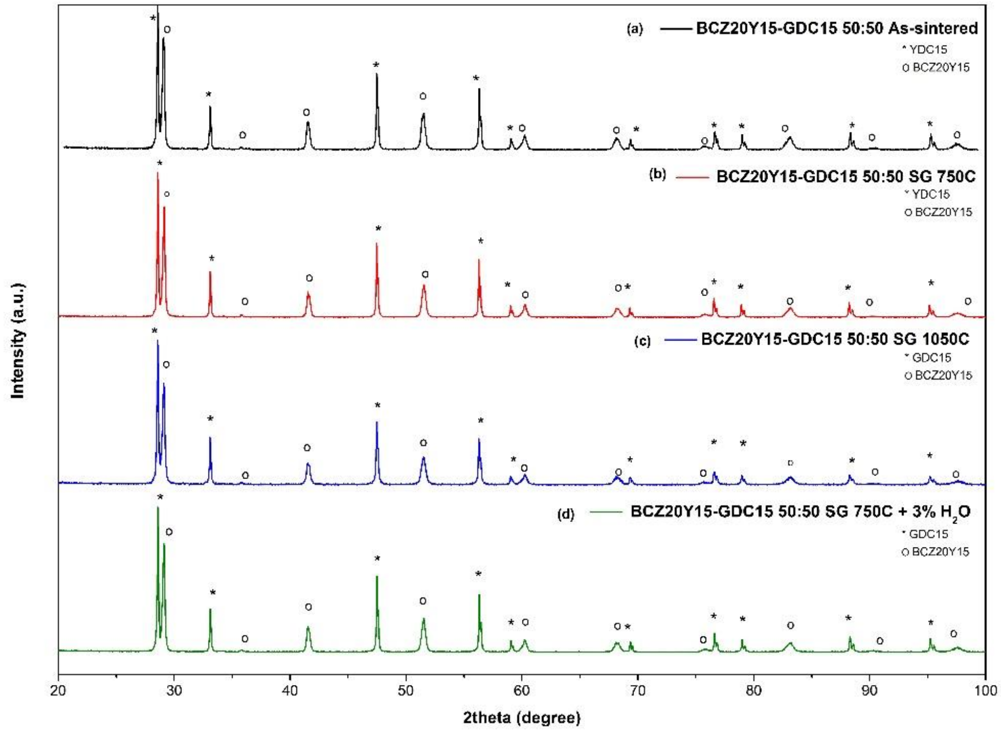
- **Thermal treatments under syn-gas atmosphere**



Treatment	T (°C)	Dwell time	Atmosfera (% moli)
Dry syn-gas	750	30 h	15% CO_2, 15% CO, 10% H_2, 3% CH_4, 57% N_2
	1050	30 h	15% CO_2, 15% CO, 10% H_2, 3% CH_4, 57% N_2
Wet syn-gas	750	30 h	14.5% CO_2, 14.5% CO, 9.7% H_2, 2.9% CH_4, 3% H_2O, 55.4% N_2

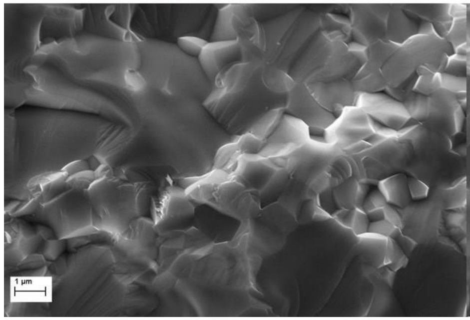
- ***Ex-situ* analyses after the thermal treatment under syn-gas atmospheres (X-ray diffraction, SEM-EDS, nano-indentation)**

Chemical stability under syn-gas

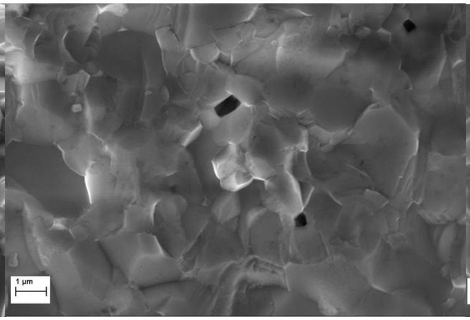


No carbonate-based phases, no evidence of interaction or degradation

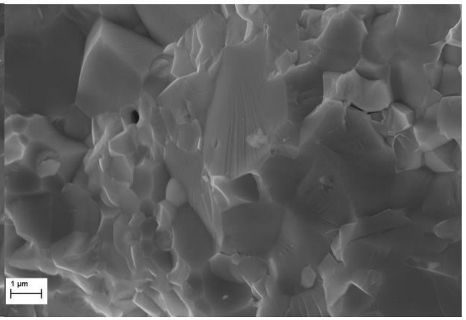
@ 750°C WET



@ 750°C DRY



@ 1050°C DRY

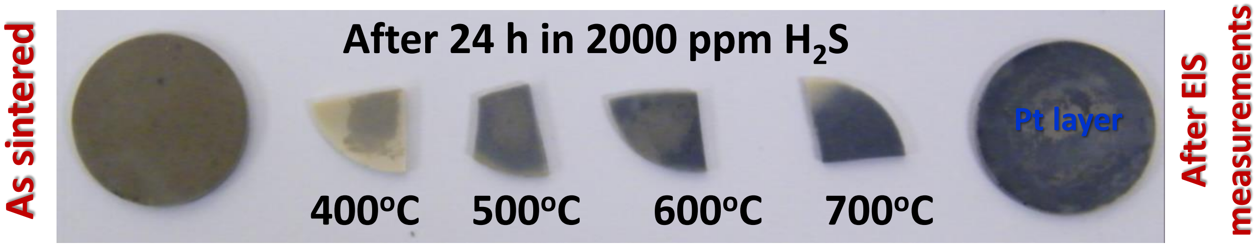


C. Mortalò, E. Rebollo, S.M. Deambrosis, V. Zin, F. Montagner, M. Fabrizio, *in preparation*.

Chemical stability under H_2S

- ***In-situ* EIS measurements under H_2S/H_2 atmosphere**
  (performed by Dr. Escolástico at Karlsruhe Institute of Technology)

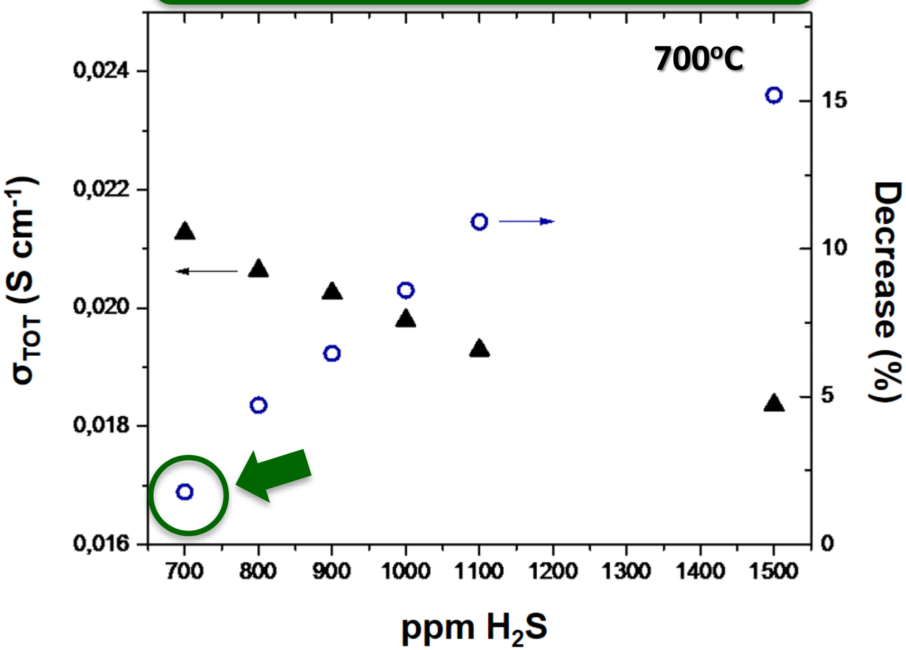
- Measurements at **400°C, 500°C, 600°C and 700°C** (Dwell time of 24 hours) **under wet 10% H_2/N_2 (2.5% H_2O), ≈ 2000 ppm H_2S**
- Measurements at **700°C** (Dwell time of 24 hours) **under wet 10% H_2/N_2 (2.5% H_2O) and different H_2S concentrations (700-1500 ppm H_2S)**



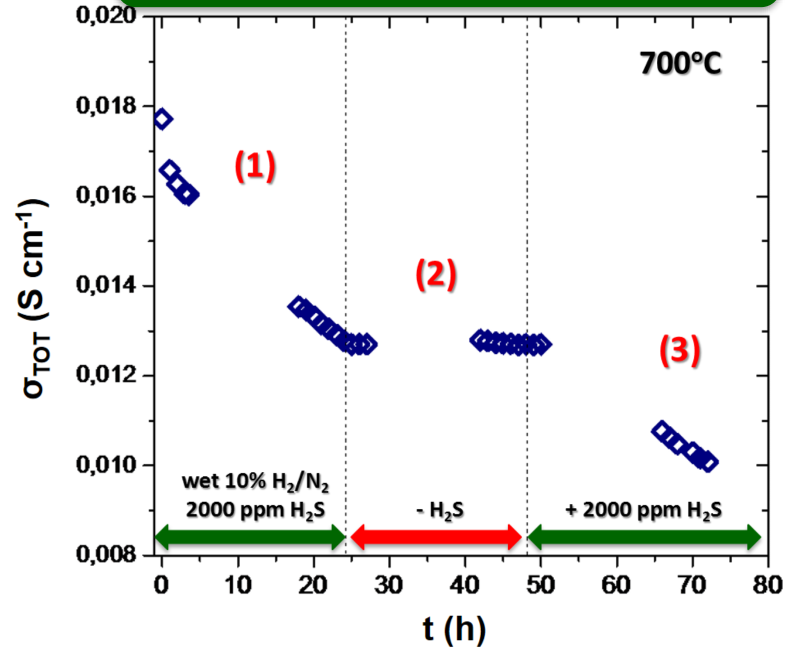
- ***Ex-situ* analyses after the thermal treatment under H_2S/H_2 atmosphere (X-ray diffraction, SEM-EDS, X-ray photoelectron spectroscopy)**

In-situ EIS measurements

Total conductivity under wet 10%H_2/N_2 and different H_2S concentration



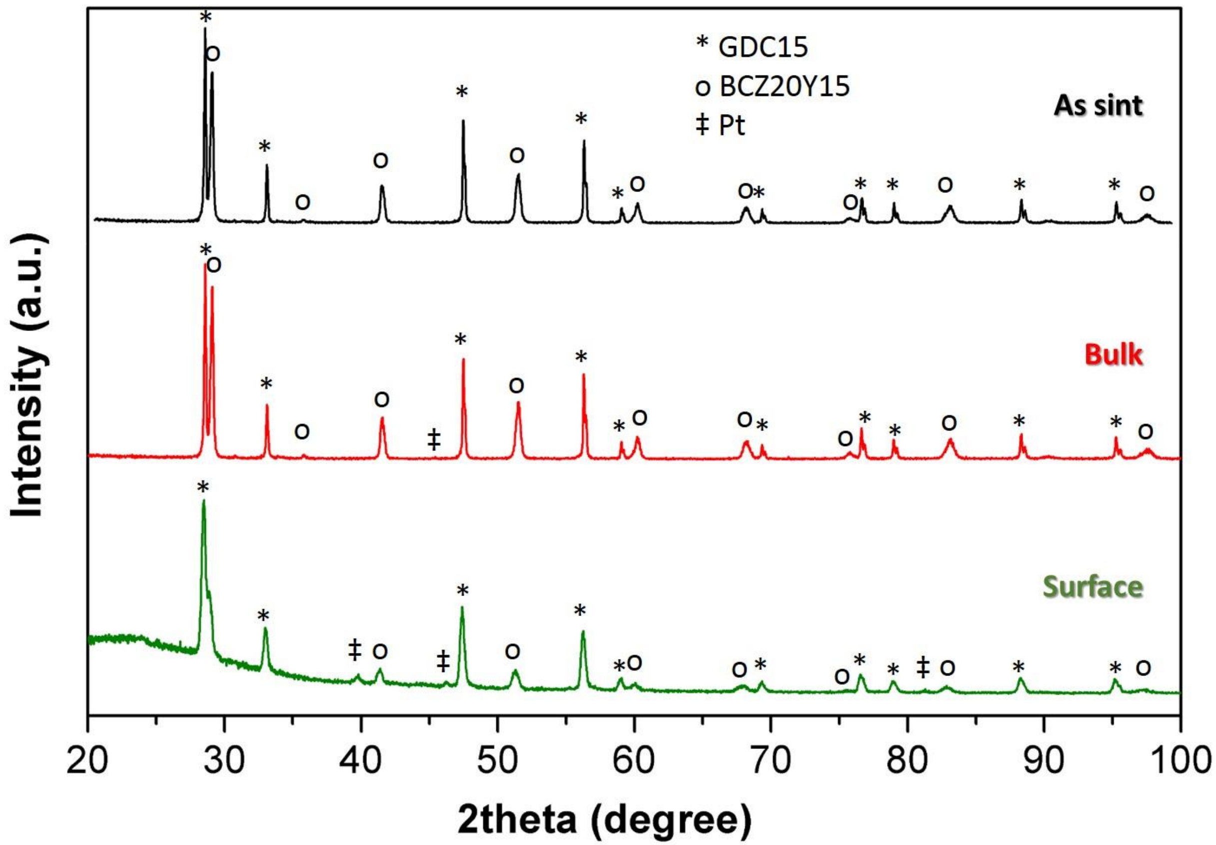
Total conductivity under wet 10%H_2/N_2 and different conditions



- The **decrease of σ_{TOT} increase with increasing the H_2S content** → with 1500 ppm the loss was > 15%, while with **700 ppm of H_2S** it was **only ≈ 2%**
- The **degradation** is **not a reversible process** and it is probably due to a **chemical interactions between the BCZ20Y15-GDC15 membrane and H_2S**

C. Mortalò, E. Rebollo, S. Escolastico, S. Deambrosis, K. Haas Santo, M. Rancan, R. Dittmeyer, L. Armealo, M. Fabrizio, *J. Membr. Sci. 564* (**2018**) 123

XRD analyses after 24h under 2000 ppm H_2S

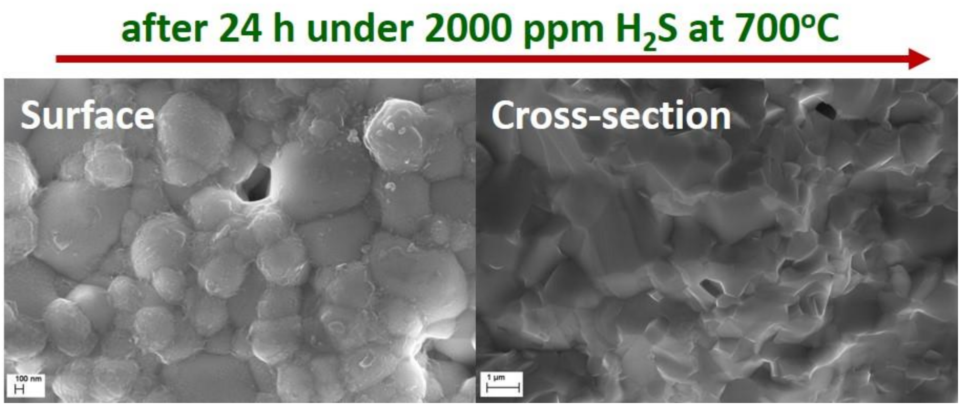


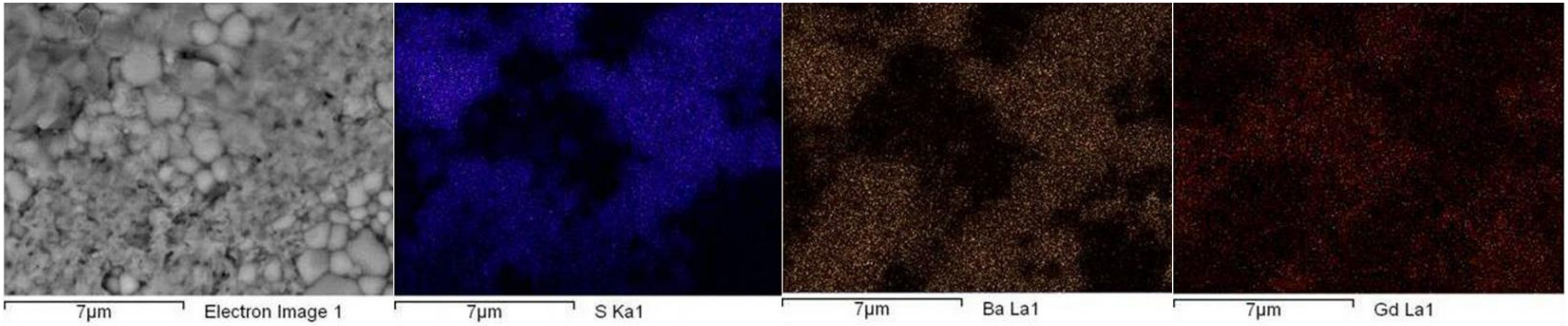
Only **BCZ20Y15** and **GDC15** phases detected

No sulfur-based phases, no evidence of interaction or degradation of the membrane

C. Mortalò, E. Rebollo, S. Escolastico, S. Deambrosis, K. Haas Santo, M. Rancan, R. Dittmeyer, L. Armealo, M. Fabrizio, *J. Membr. Sci. 564* (**2018**) 123

SEM analyses



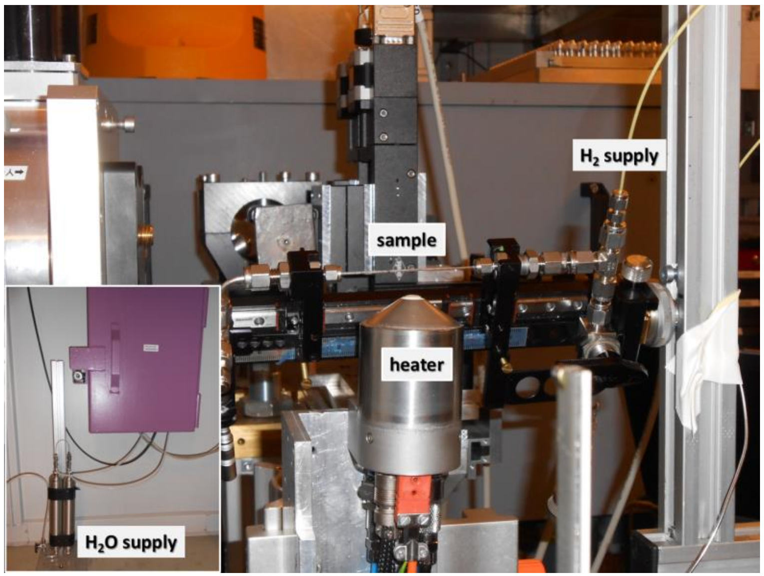


- **No apparent degradation in the bulk** → **fully dense structure** and **no modification in the grain dimension** compared to the as-sintered membrane
- **Evident degradation of the surface** → **S-containing phases associated to the Ba-containing phase** (confirmed also by XPS analyses)

Chemical stability under H_2

- ***In-situ* HT-XRD analyses under H_2 atmosphere**

DESY synchrotron (Hamburg, Germany) at Beamline P.02.1 at PETRA III



Method	
Static mode ***equilibrium conditions for 30 minutes*** RT, 300°C, 450°C, 600°C and 750°C	Dry 100% H_2 Wet H_2 (saturated on H_2O)
Dynamic mode ***non equilibrium conditions*** from RT to 800°C (each 20°C)	

Collaboration with the group of Dr. M. Dornheim and Dr. C. Pistidda from Helmholtz-Zentrum Geesthacht (Institute of Materials Research, Germany)

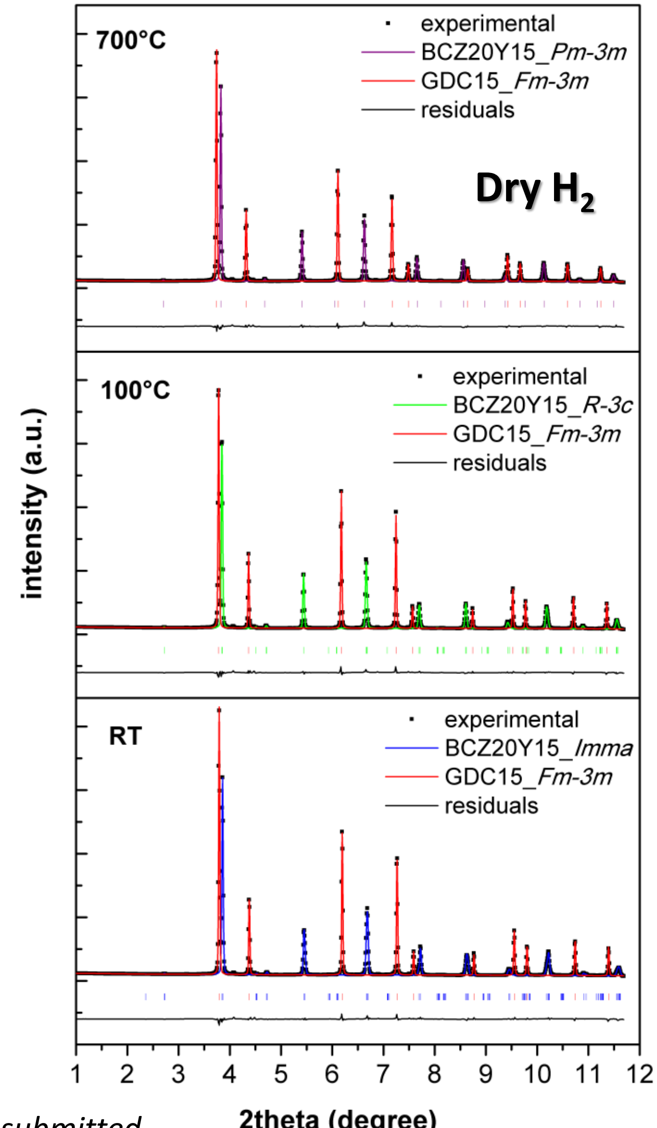
- **TPR** and **TGA analyses** under **H_2-containing atmosphere**

BCZ20Y15-GDC15 under dry and wet H_2

- No secondary phases → **good chemical stability** confirmed by *in-situ* XRD analyses.
- Evolutions of **BCZ20Y15** and **GDC15 structures** ***vs*** **T** are **the same under dry and wet H_2**.

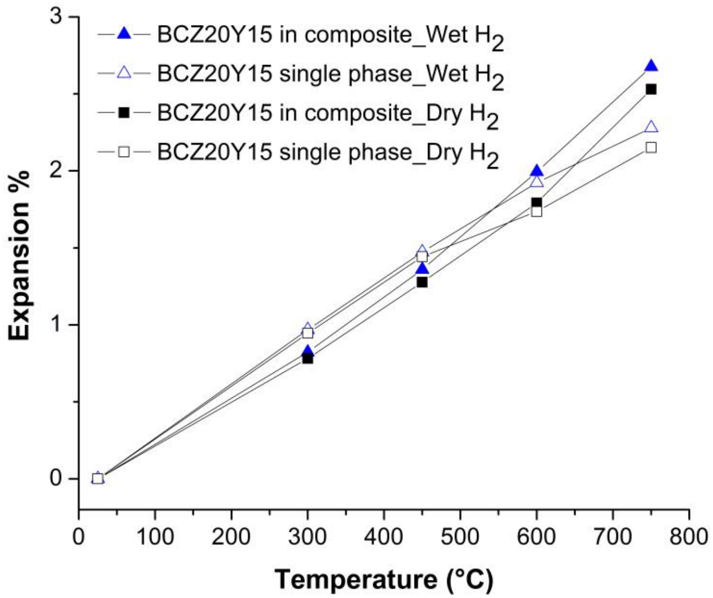
- GDC15: ***Fm-3m*** **cubic** structure identified at **all temperatures.**
- BCZ20Y15: **orthorhombic** ***Imma*** at **RT, orthorhombic** ***Imma*** → **rhomboedral** ***R-3c*** **at 100°C**, **rhomboedral** ***R-3c*** → **cubic** ***Pm-3m*** at **700°C**.

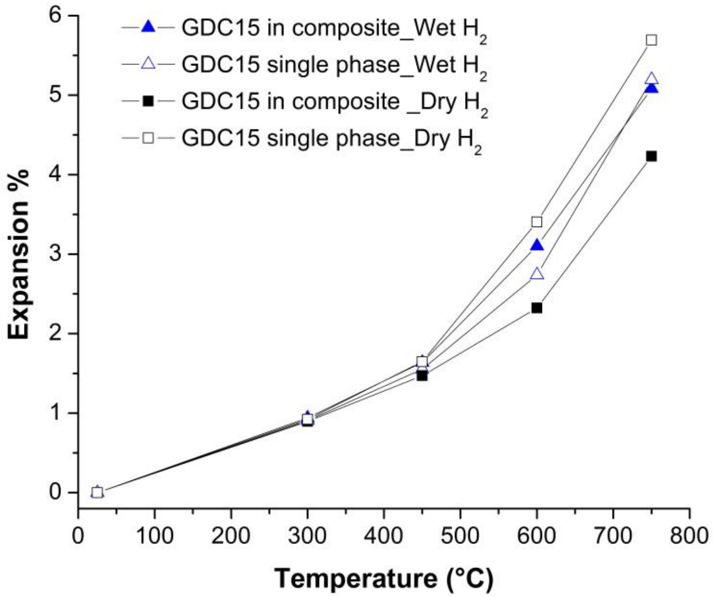
BCZ20Y15 phase transitions at lower temperature in the composite respect the individual phase → Synergistic effects of BCZ20Y15 and GDC15 phases in the composite



C. Mortalò, A. Santoru, C. Pistidda, E. Rebollo, M. Boaro, C. Leonelli, M. Fabrizio, *submitted.*

Cell expansion of BCZ20Y15 and GDC15





- At **T > 600°C BCZ20Y15 expansion** is **higher in the composite** respect the single phase materials **both under dry and wet H_2**.

- **Under dry H_2**, the **GDC15 expansion** is **higher** for the **single phase material** than in the composite.

BCZ20Y15 and GDC15 volume expansions tend to approach each other in the composite → *synergistic effect (confirmed also by TPR and TGA)*

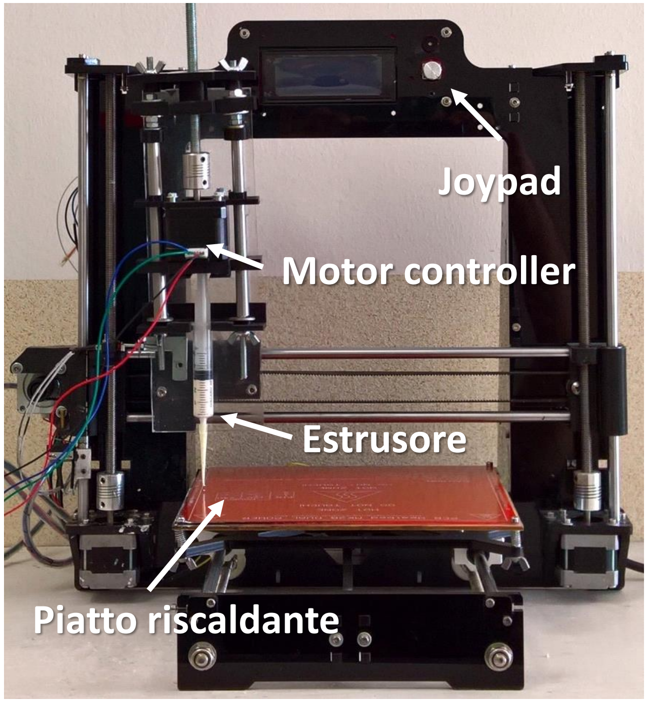
Conclusions

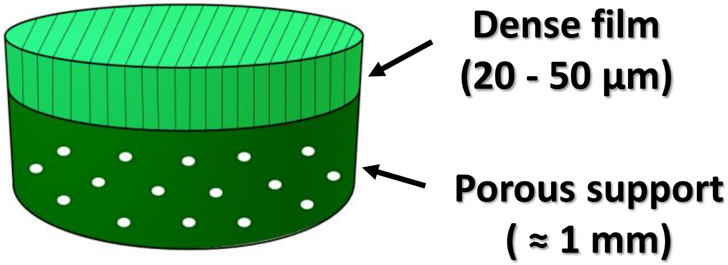
- **High H_2 flux → 0.27 mL·min^{-1}·cm^{-2} at 755°C**.
- **High chemical stability under CO_2-containing atmosphere → reversible drop of flux recovered after the CO_2 removal.**
- **High chemical stability under syn-gas atmosphere → no secondary phases detected after thermal treatment at 750°C and 1050°C (both dry and wet conditions).**
- **Adequate chemical stability under H_2S-containing atmosphere → only 2% of degradation observed under 700ppm H_2S at 700°C** (degradation seems limited to the top of the membrane).
- **Good chemical stability under H_2 atmosphere → no chemical interaction between BCZ20Y15 and GDC15 observed by in-situ XRD analyses (both dry and wet conditions).**
- **Synergistic effects of BCZ20Y15 and GDC15 phases observed in the composite →** (a) **BCZ20Y15 phase transitions revealed at lower temperature in the composite respect the individual phase**; (b) **BCZ20Y15 and GDC15 volume expansions tend to approach each other in the composite**.

BCZ20Y15-GDC15 MIEC composite shows very good performances **to be considered a promising dense ceramic membrane for H_2 purification at T > 600°C.**

In the future…

- Study of the **mechanical properties under practical conditions** (in progress).
- Permeability tests under syn-gas atmosphere.
- Development of BCZ20Y15-GDC15 membranes with **asymmetric design by additive maifacturing (in progress)** →**µ-extrusion 3D-printing**

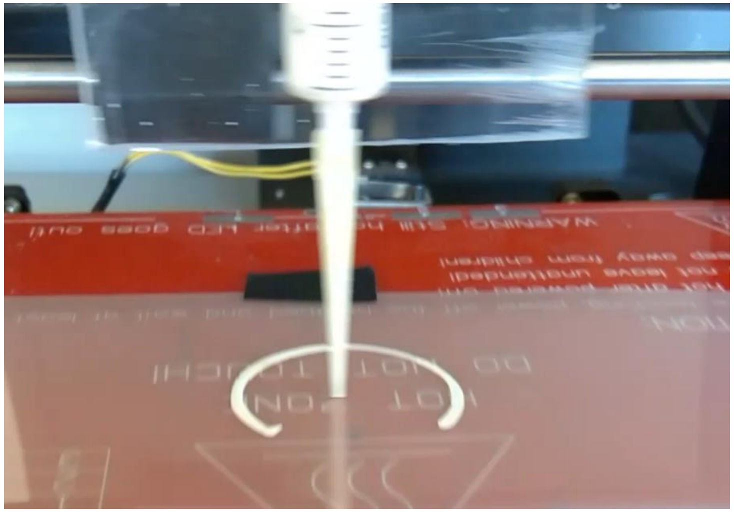


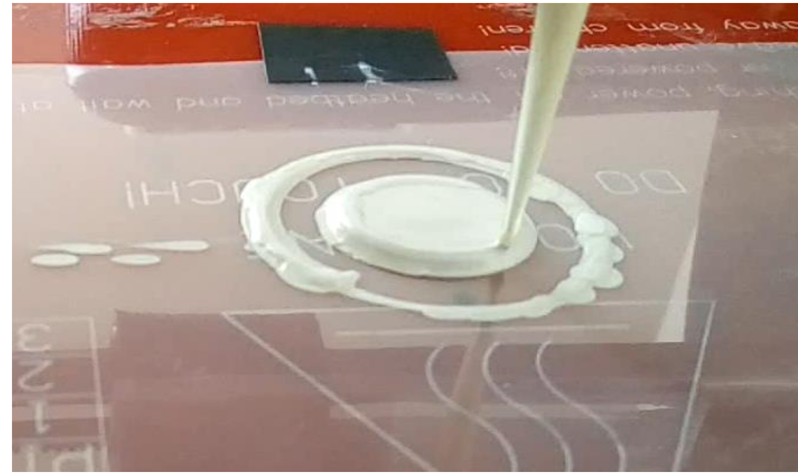


INKS prepared by ball milling:

1. Precursors powders (BCZ20Y15 and GDC15)
2. Porous agent (starch) if necessary
3. Solvent (IPA), dispersant (EG), legand, plasticizer

BCZ20Y15-GDC15 asymmetric membrane by 3D





After gradual evaporation of solvent

Collaborations and Aknowlodgments

- ICMATE-group: Dr. E. Rebollo, Dr. F. Montagner, Dr. S. M. Deambrosis, Dr. V. Zin, Dr. F. Agresti, Dr. S. Barison, S. Boldrini, Dr. E. Miorin, Dr. A. Famengo, Dr. R. Gerbasi, Dr. N. El Habra, M. Rancan, M. Fabrizio
- Group of Prof. Serra from ITQ of Valencia (Spain): S. Escolástico, C. Solis
- Karlsruhe Institute of Technology of Germany
- Group of Prof. Dr. M. Dornheim from Helmholtz-Zentrum Geesthacht (Institute of Materials Research, Germany): Dr. C. Pistidda, Dr. A. Santoru, Dr. C. Horstmann, Dr. G. Gizer
- UniMoRe: Prof. C. Leonelli, Dr. M. Cannio, Prof. L. Pasquali, Prof. M. Romagnoli, Ing. F. Andreola, Ing. M. Prestianni, Dr. P. Miselli
- University of Udine: Prof. M. Boaro, Dr. C. de Leitenburg and Dr. E. Aneggi
- …..

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Thank you for your attention!