$BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$-doped ceria ceramic composites for hydrogen separation

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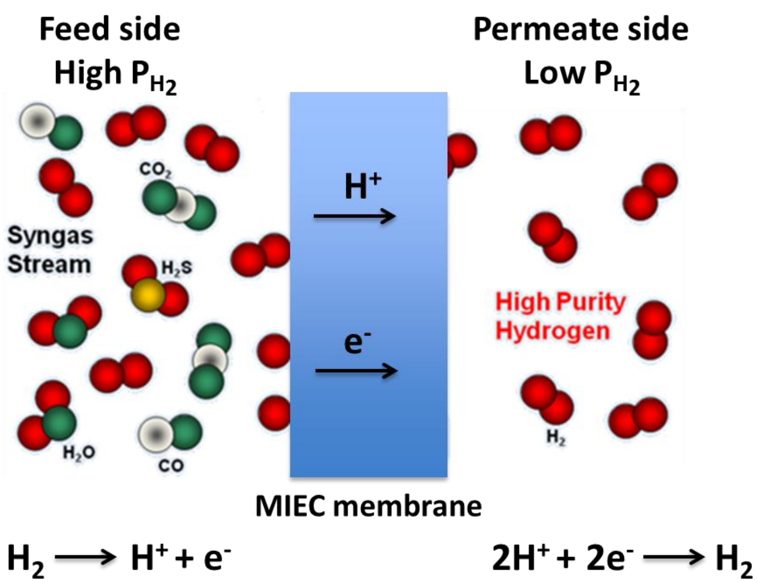
Overview

- Dense ceramic membranes: MIEC membranes.
- BCZY15-Doped Ceria ceramic-ceramic membranes
- Stability tests in syngas and Ar/H_2
- Stability tests and EIS measurements in H_2S
- Conclusions

Dense MIEC (Mixed ionic-electronic conductors) membranes

- **Dense Inorganic H_2 membranes →** promising methods for the production of high-purity H_2
- Membranes based on **Mixed ionic-electronic conductor (MIEC)** ceramics are appealing due to:



- ✓ **Selectivity:** incorporate H_2 into their lattices as charge protonic defects and electrons/holes

$$H_2O\ (g) + v_O^{\cdot\cdot} + O_O^x \leftrightarrow 2OH_O^{\cdot}$$

$$H_2(g) + 2O_O^x \leftrightarrow 2OH_O^{\cdot} + 2e^{\prime}$$

$$H_2(g) + 2O_O^x + 2h^{\cdot} \leftrightarrow 2OH_O^{\cdot}$$

- ✓ **Integrated** in industrial processes improving efficiency (membrane reactors): working temperatures T> 600° C

H$_2$ membranes requisites

- High H_2 permeation fluxes→ High Electronic and Ionic (protonic) conductivities
- Stability under operation conditions

Dense MIEC (Mixed ionic-electronic conductors) membranes

MIEC membranes

Single-phase membranes

- ✓ Perovskites ($SrCeO_3$, $BaCeO_3$, $BaZrO_3$)
- ✓ Fluorites (tungstates Ln_6WO_{12})
- ✓ Pyrochlores (doped $La_2Ce_2O_7$)

✗ H_2 permeation rate-limited by low electronic conductivity

Dual-phase membranes

from two compatible phases:

High H^+ conductor + High e^- conductor

Ceramic-Ceramic
Cer- Cer composites

- $La_{5.5}WO_{11.25-\delta}$-$La_{0.87}Sr_{0.13}CrO_{3-\delta}$
- $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ -$Sr_{0.95}Ti_{0.9}Nb_{0.1}O_{3-\delta}$
- $BaCe_{0.8}Eu_{0.2}O_{3-\delta}$-$Ce_{0.8}Y_{0.2}O_{2-\delta}$

Ceramic-Metallic
Cer-Met composites

- Ni-$BaCe_{0.9}Y_{0.1}O_{3-\delta}$
- Ni-$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$
- Ni-$La_{0.5}Ce_{0.5}O_{2-\delta}$
- Cu-$BaZr_{0.9}Y_{0.1}O_{3-\delta}$

<u>H_2 membranes based on MIEC challenges</u>

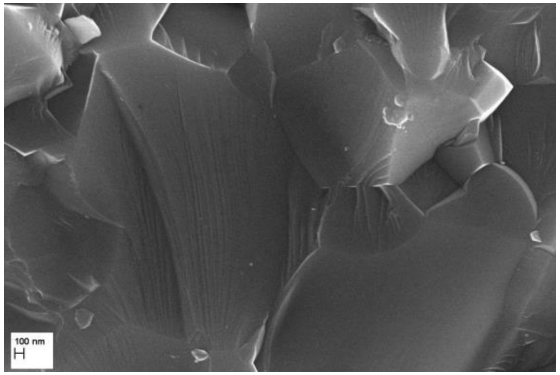
- ✗ Stability issues
- ✗ Permeability are still modest
- → Target H_2 flux **1-2 mL_n min^{-1} cm^{-2}** not reached

Our strategy…..

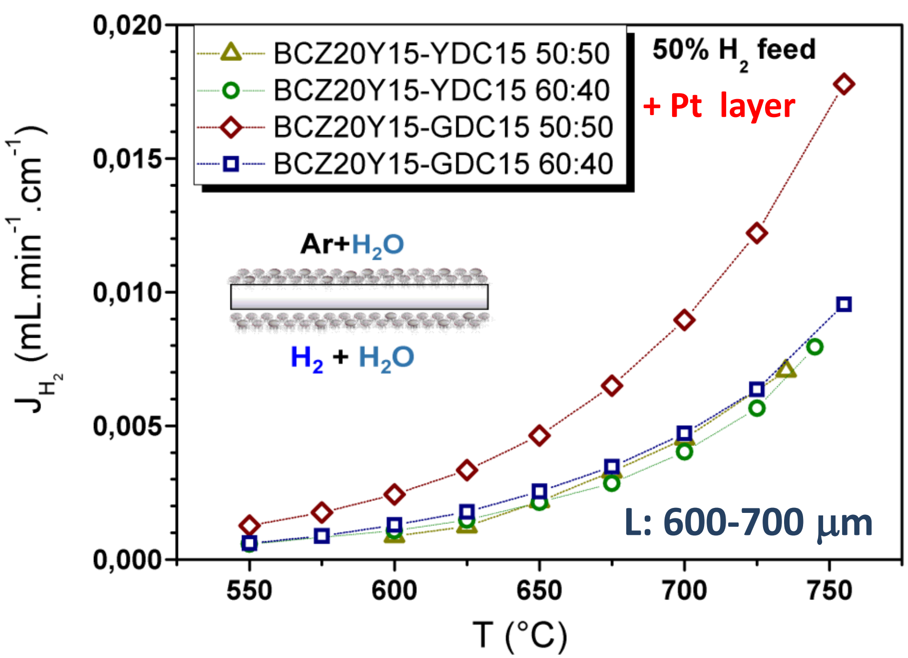
H^+-conductor	e^-conductor
$BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$ (BCZ20Y15)	$Ce_{0.85}M_{0.15}O_{2-\delta}$ (M:Y or Gd, YDC15 or GDC15)
✓ High H^+ conductivity $\sigma \geq 1x10^{-2}$ S cm^{-1} at 600°C.*	✓ e^- conductivity at reducing conditions T>600°C

* S. Barison, M. Battagliarin, T. Cavallin, L. Doubova, M. Fabrizio, C. Mortalò, S. Boldrini, L. Malavasi, R. Gerbasi *J. Mater. Chem.* (**2008**) *18* 5120.

BCZ20Y15-MDC15 composite membranes



- **BCZY15-MDC15 50:50** and **60:40** → symmetric dense (ρ>90%) membranes with homogenous grain distribution, no open porosity nor undesired phases (XRD, SEM).
- **H_2 permeation measurements** (performed by the group of prof. Serra from **ITQ of Valencia**)



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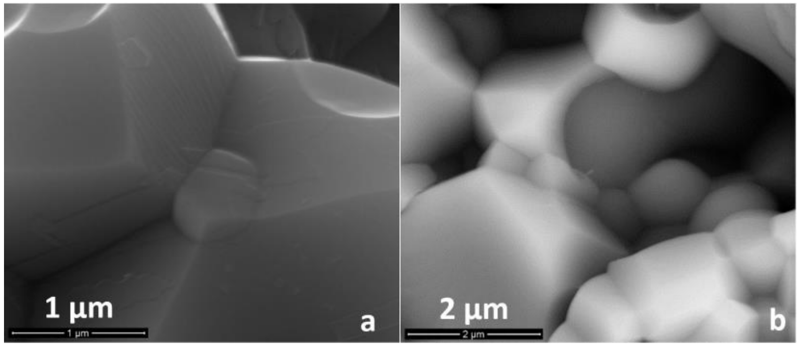
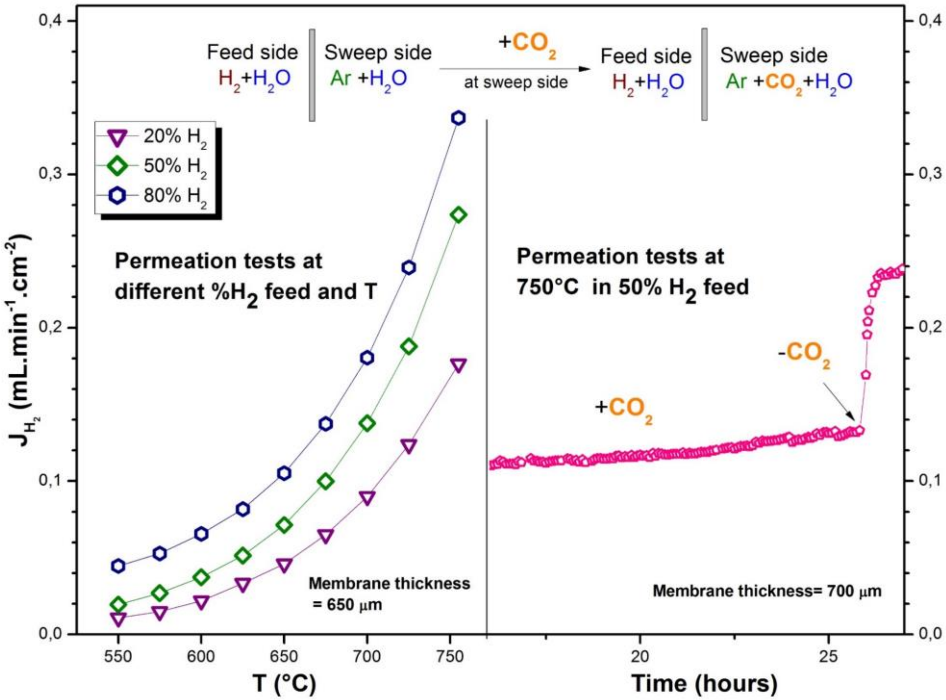
- **J_{H_2} > 0.12 mL·min^{-1}·cm^{-2}** at T≈**750ºC** → in line with the **best fluxes** reported in literature for **dense MIEC ceramic membranes.**
- **J_{H_2}** ↑ with **T** and ***p*H_2** **(Wagner Equation)**

✓ **BCZ20Y15-GDC15 50:50**: **J_{H_2} = 0.27 mL·min^{-1}·cm^{-2} at 755ºC** with both sides humidified → among the highest **J_{H_2}** reported so far for this type of membranes

✓ H_2 flux produced by : (1**) H^+ transport** through the membrane and (2) H_2 produced in the sweep side *via* **water splitting reaction** (oxygen ion transport from higher *p*O_2 to lower *p*O_2).

BCZ20Y15-MDC15 composite membranes





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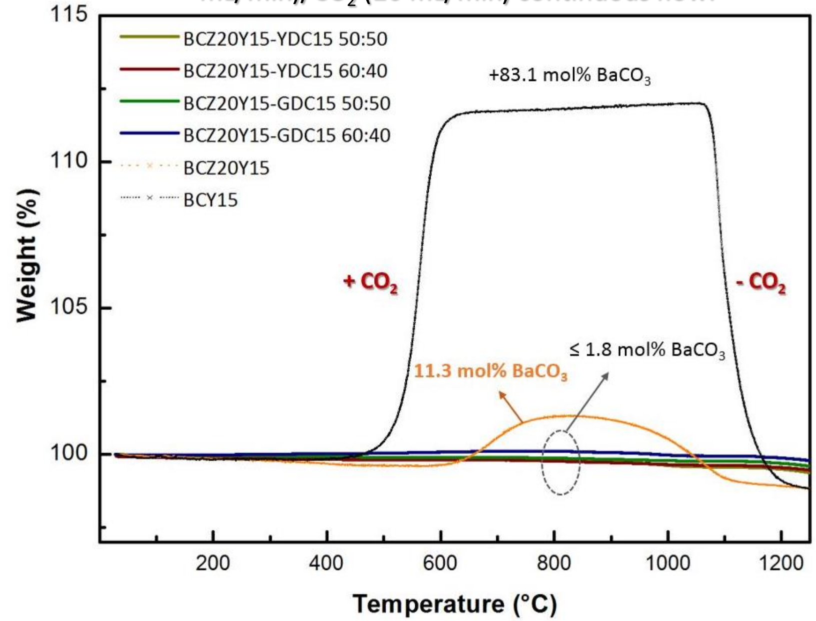
- **After permeation analysis** (SEM, XRD) → bulk do not show morphological changes and XRD patterns do not display additional peaks.
- Permeation and TGA tests under CO_2: **First evaluation** of the **composites stability** against **CO_2**

TGA curves for **membranes powders** in N_2 (100 mL/min)/CO_2 (20 mL/min) continuous flow.



Stability of BCZ20Y15-MDC15 composite membranes

- Besides the high flux, the chemical and mechanical **stability** of the membranes under **operation conditions** is the most important requirement for their practical applications.
- Direct contact between the phases at **high T** under **harsh environments** (presence of H_2, H_2O, CO, CO_2, and sulphides) may cause undesired phenomena such as structural changes, cation diffusion, mechanical modifications or chemical reactions that hamper the membranes transport performance.

$$BaCe_{1-x}Zr_xO_3 + CO_2 \longrightarrow BaCO_3 + Ce_{1-x}Zr_xO_2$$

$$BaCe_{1-x}Zr_xO_3 + H_2S \longrightarrow BaS + Ce_{1-x}Zr_xO_2 + H_2O$$

$$2CeO_2 + H_2 + H_2S \longrightarrow Ce_2O_2S + 2H_2O$$

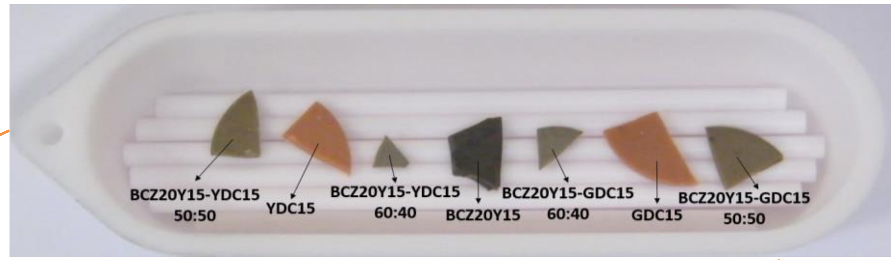
- **Composite membranes** and **precursors** exposed to **different atmospheres** and then analysed by **SEM** and **XRD:**
  - Syngas and H_2 treatments (all the compositions)
  - H_2S treatment (BCZ20Y15-GDC15 50:50)

Treatment		Dwell T (°C)	Dwell time	Atmosphere (% mol)
1	Dry syngas	750	30 h	15% CO_2, 15% CO, 10% H_2, 3% CH_4, 57% N_2
2	Wet syngas	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
3	High T dry syngas	1050	30 h	15% CO_2, 15% CO, 10% H_2, 3% CH_4, 57% N_2
4	Dry H_2	750	30 h	10% H_2 balanced Ar
5	Wet H_2	750	30 h	3% H_2O, 10% H_2 balanced Ar
6	H_2S*	700, 600, 500, 400	24 h	1973 ppm H_2S, 2.5% H_2O, 10% H_2 balanced N_2

** Work in progress: EIS analyses of composite and precursors are still under investigation in H_2S.*

Stability of BCZ20Y15-MDC15 composite membranes

Before syngas/H_2 treatments



Post 30h @750 C in syngas

Post 30h @750 C in wet H_2

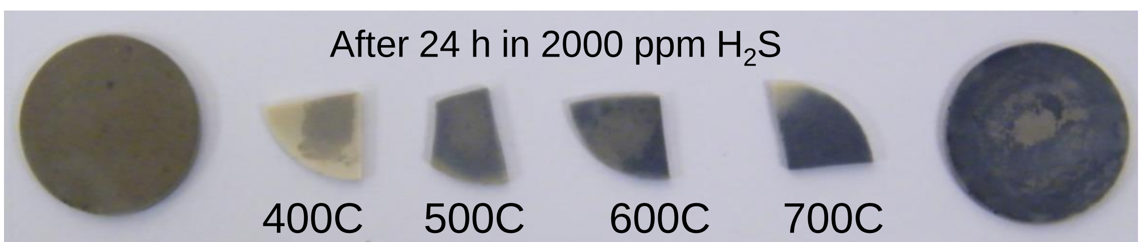
Post 30h @750 C in wet syngas

Post 30h @1050 C in syngas

Post 30h @750 C in H_2

H_2S treatments (in progress)

BCZ20Y15-GDC15 50:50



As sintered

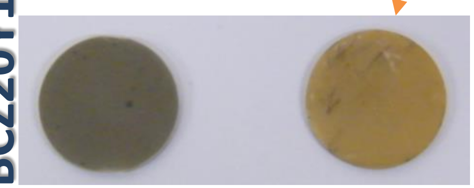
After EIS measurements

As sintered

After 24 h in 2000 ppm H_2S

GDC15

BCZ20Y155

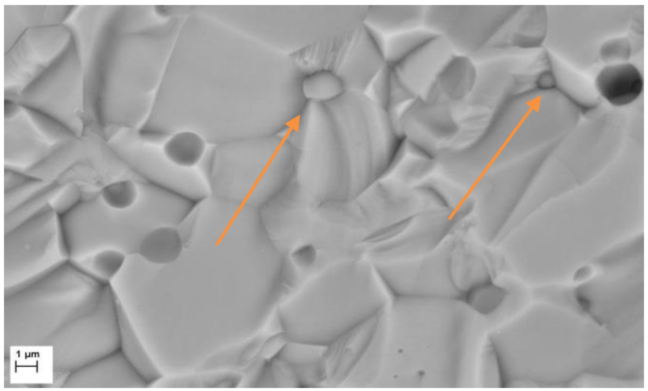


Syngas stability of BCZ20Y15-MDC15 composite membranes

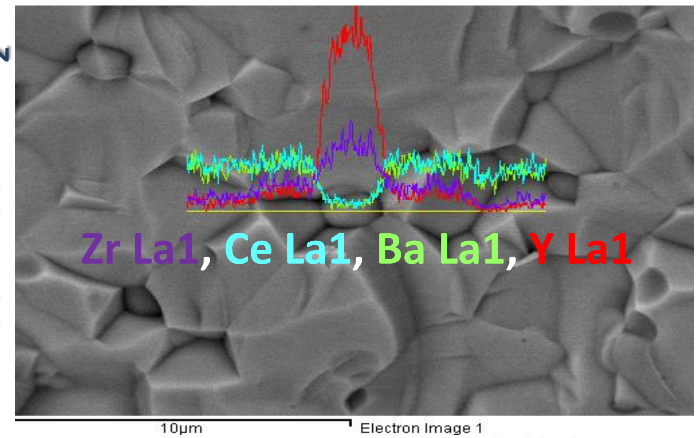
Single-phase BCZ20Y15

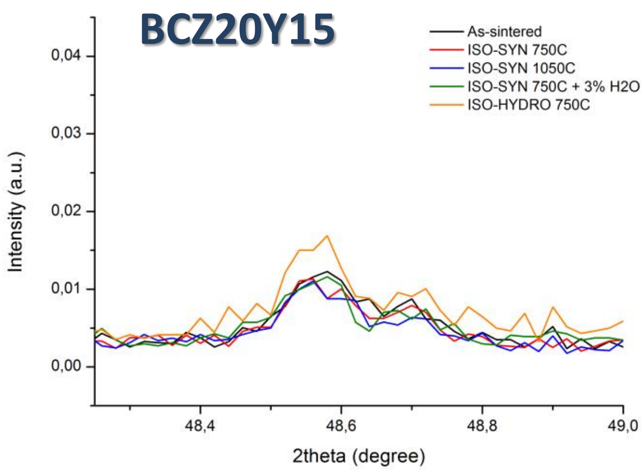
- All samples show **grains** identified as **Y_2O_3** by **SEM-EDS** analysis confirmed by Rietveld refinement on the XRD patterns.
- These grains were not detected on the composite membranes

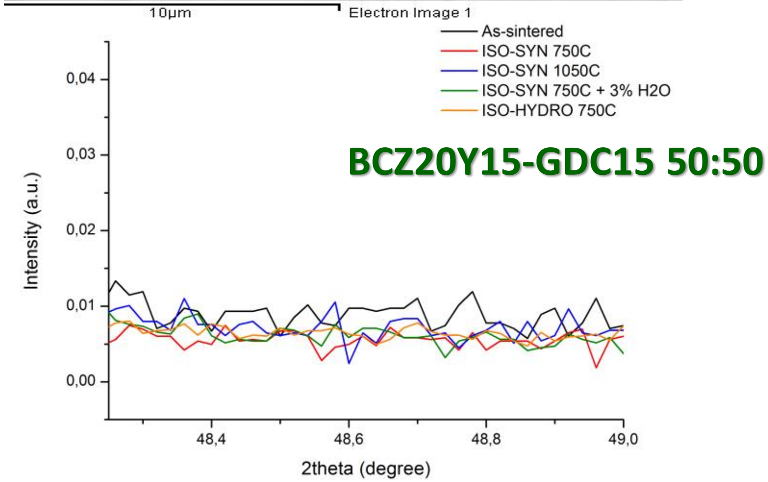
BCZ20Y15 POST 30h 750C in SG



BCZ20Y15 POST 30h 750C in H_2



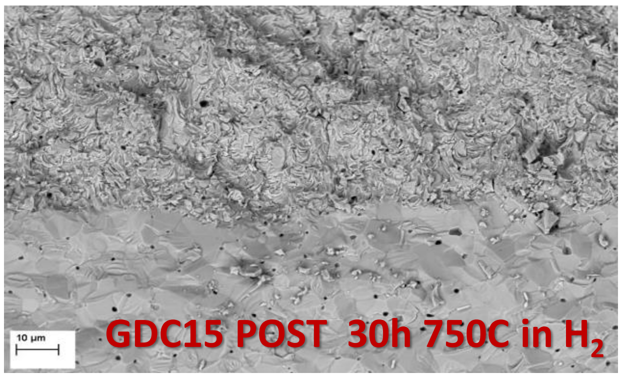


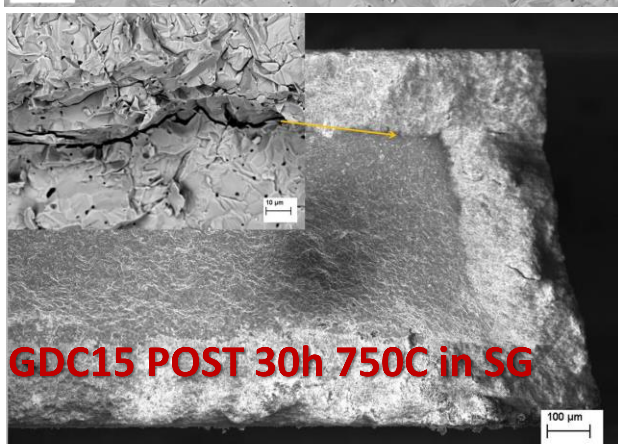


Syngas stability of BCZ20Y15-MDC15 composite membranes

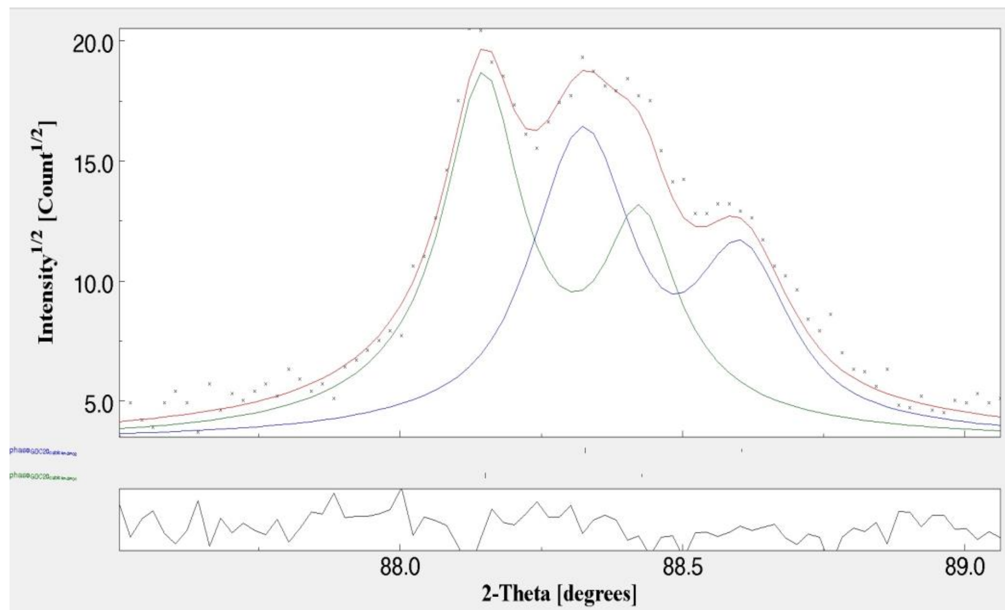
Single-phase GDC15 and YDC15

- SEM investigations of the samples show a layer near the surfaces with a **different morphology**. Rietveld refinement on XRD patterns confirm the presence of a more reduced ceria phase. The thickness of this layer varies under the different tested conditions. The $Ce^{4+} \rightarrow Ce^{3+}$ reduction produces **cracks** on the samples → **mechanical instability**





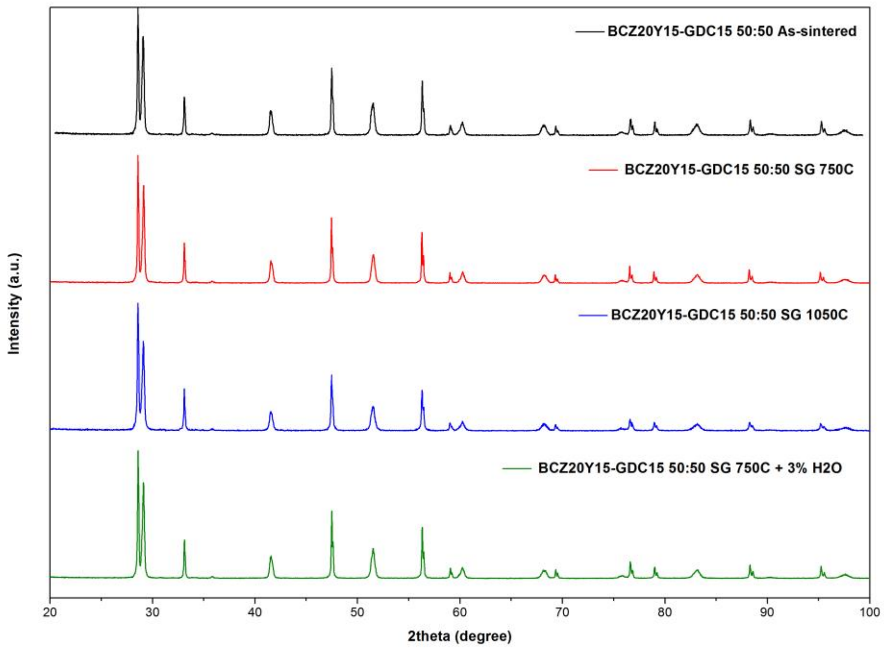
Detail of the **Rietveld refinement** on the XRD pattern of the GDC15 sample after **30h in SG at 1050C**

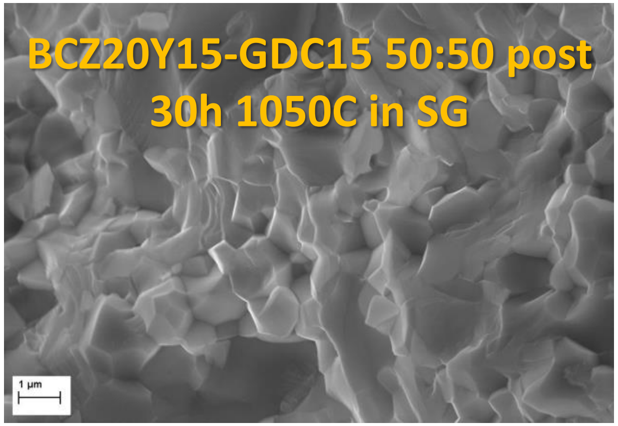


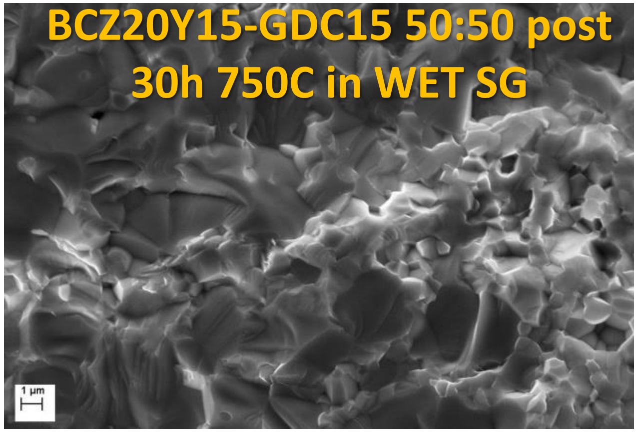
Syngas stability of BCZ20Y15-MDC15 composite membranes

BCZ20Y15-MDC15 50:50 and 60:40 composite membranes

- SEM-EDS investigations do not evidence **changes** in the **morphology** of the bulk and the surfaces of the samples. Undesired products were not detected by XRD.
- **Carbonates** were not identified after the exposure to syngas in the different conditions.
- Composite membranes were **crack-free**.
- **Y_2O_3** grains were not observed



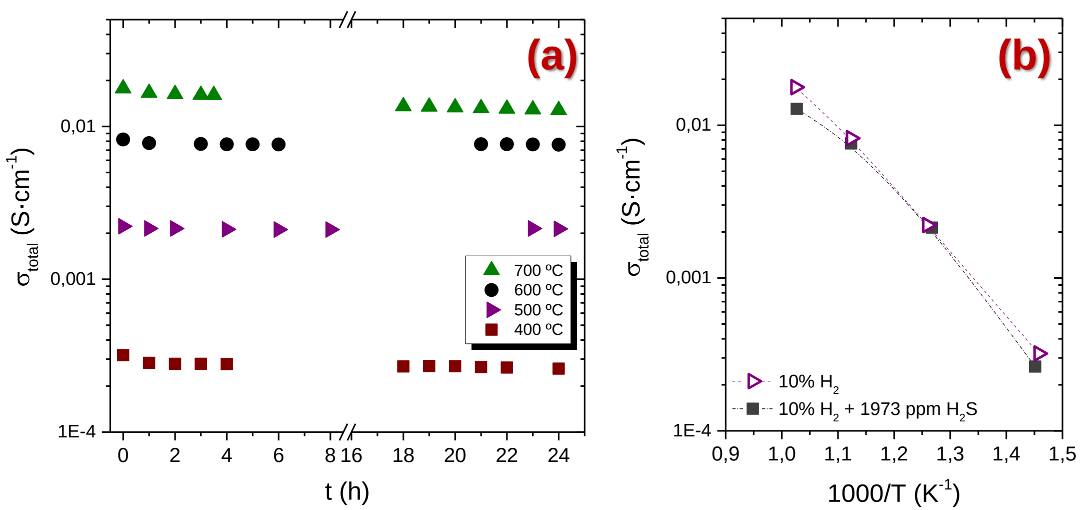




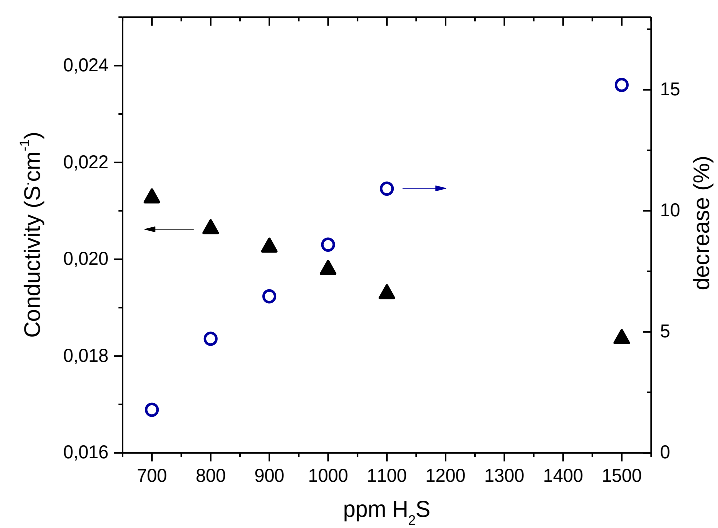
H_2S stability of BCZ20Y15-GDC15 composite membranes

Impedance spectroscopy (EIS) measurements (performed at KIT, still in progress)

- **At 400C and 500C:** total conductivity remains unchanged under H_2S
- **At 600C and 700C:** total conductivity decreases under H_2S. When the H_2S is removed from the feed, the conductivity remains stable but do not recover its initial value → not reversible process
- The decrease of the conductivity depends on the concentration of H_2S



Total conductivity for BCZ20Y15-GDC15 50:50 sample under wet 10%H_2 and 1973 ppm H_2S balanced with N_2 atmosphere as a function of time at different temperatures (a), comparison of the total conductivity as a function of the reciprocal temperature under wet 10% H_2 without and with H_2S (after 24 hours) (b).



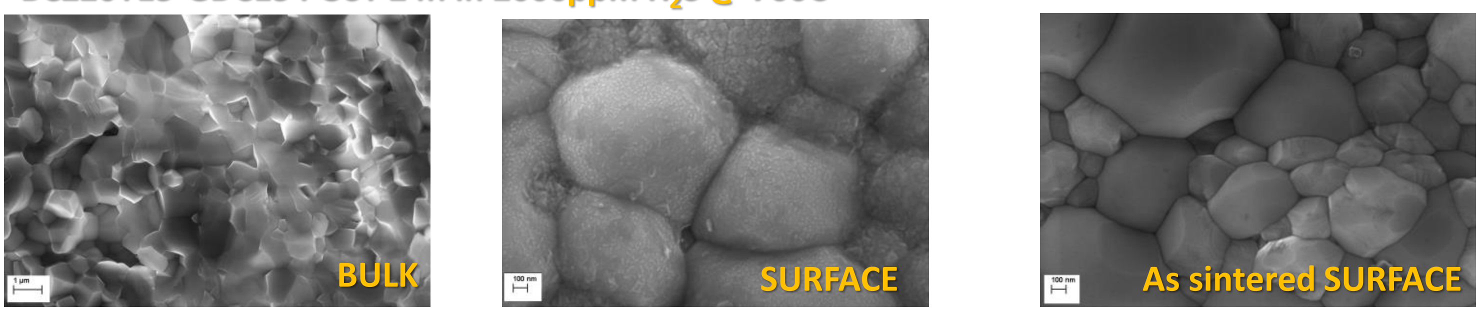
Total conductivity and % decrease under different H_2S concentrations at 700 °C (with wet 10%H_2 in N_2)

H_2S stability of BCZ20Y15-GDC15 composite membranes

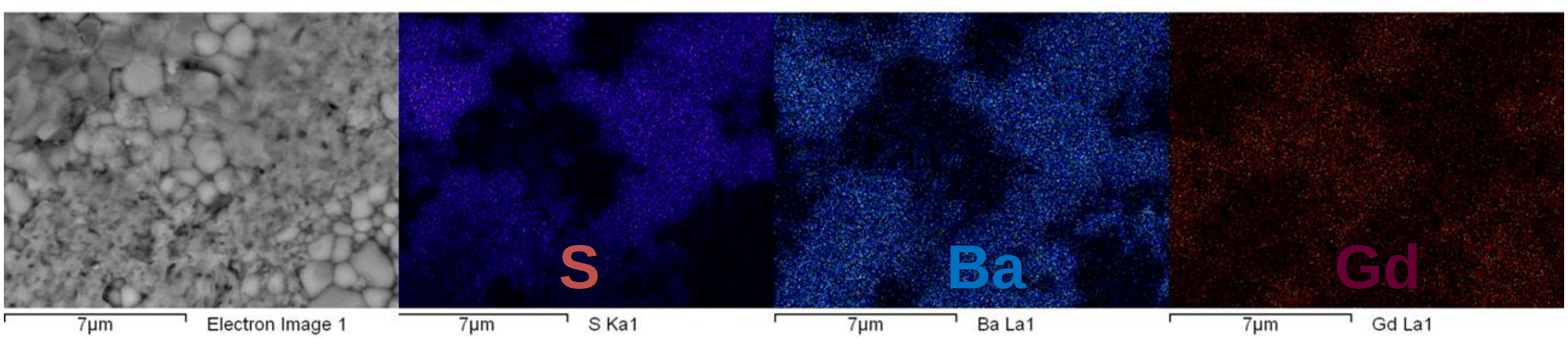
SEM-EDS and XRD (still in progress)

- **No** alterations on the **morphology** and **micro-structure** of the **bulk** on **BCZ20Y15-GDC15** samples.
- Bulk of the single-phase precursors: **Y_2O_3** in **BCZ20Y15** and reduced layer and **cracks** on the **GDC15**.
- XRD patterns do not present peaks of **byproducts (Rietveld refinement in progress).**
- **Surfaces** of **BCZ20Y15-GDC15** samples treated at **600C and 700 C** have **few alteration products related to BCZ20Y15 phase** (EDS detected S only in some areas and it is not always related with Ba).

BCZ20Y15-GDC15 POST 24h in 2000ppm H_2S @ 700C



BCZ20Y15-GDC15 surface mapping after 24 h in 2000 ppm H_2S at 600 °C



Conclusions

- **BCZY15-MDC15 50:50** and **60:40 composites membranes** demonstrated good chemical stability under different **syngas/H_2 atmospheres**, in particular compared to single-phase precursors: no carbonates were detected, the microstructure of the samples do not present alterations or cracks.

- **EIS** measurements under **2000 ppm H_2S** show that at 600C and 700C the total conductivity of the **BCZ20Y15-GDC15 50:50** membrane decreases. From **SEM-EDS** investigations, this decrease is ascribed to **few alterations products containing S** observed **only** in **some** regions of the composite surfaces (S is not detected in all the areas investigated). In few of these areas, **S is related to the Ba** suggesting an alteration of the perovskite phase while in other regions the trend is unclear and the S is spread "randomly".

- **BCZ20Y15-GDC15 membrane** demonstrated relatively good tolerance to H_2S considering that the concentration in operating conditions is at the level of tens ppm.

- The results indicate that the alteration process involves **the surface** (bulk appear unaltered) → more detailed study of the phenomena by surface analysis (in situ analysis?)

Acknowledgements

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KIT
Karlsruhe Institute of Technology

THANK YOU FOR YOUR ATTENTION!!