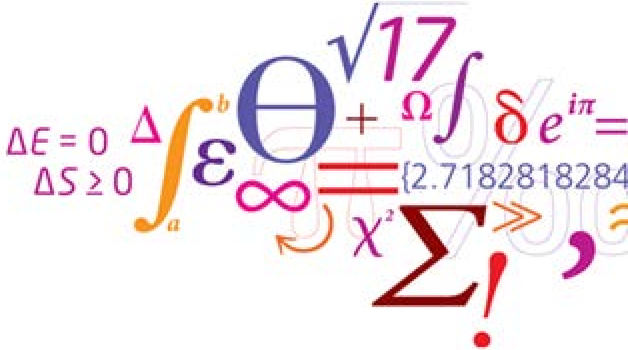
Graded Membranes for Energy Efficient New Generation Carbon Capture Process
Grant Agreement Number 608524

Long-Term Stability of Oxygen Transport Membranes in simulated Flue Gas Environments

– Lesson learned in the GREEN-CC Project-

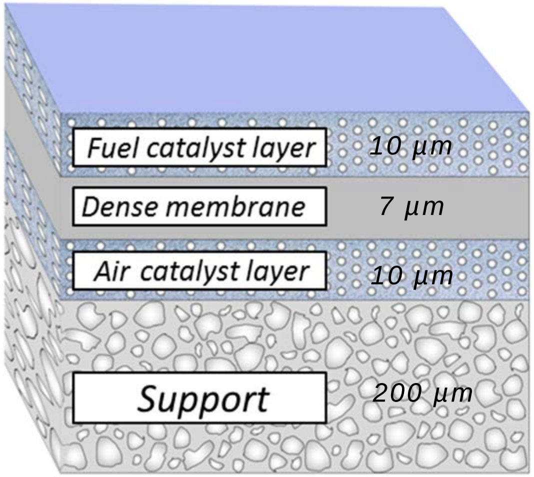
Ragnar Kiebach, ***Stéven Pirou****, Jonas Gurauskis, Vanesa Gil, Martin Søgaard, Peter Vang Hendriksen, Andreas Kaiser, Peter Stanley Jørgensen, Simona Ovtar, Julio Garcia-Fayos, Jose M. Serra*

DTU Energy Conversion
Department of Energy Conversion and Storage



08 February, 2017 – Oslo, AMPEA workshop: "Materials for membranes in energy applications: gas separation membranes, electrolysers and fuel cells"

Manufacturing process : 10Sc1YSZ-$MnCo_2O_4$ (70-30 vol. %)



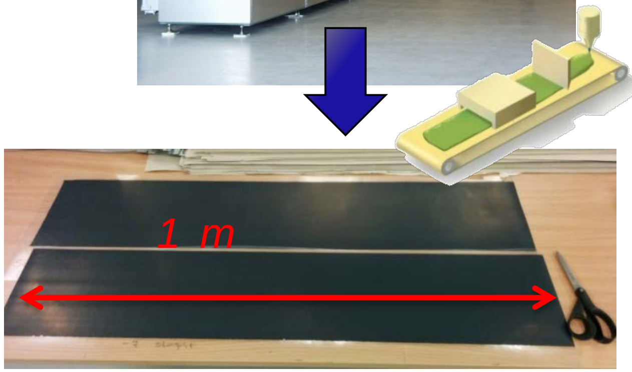
$(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ **(8YSZ)**

10Sc1YSZ + $MnCo_2O_4$ (70-30 vol.%)

$(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ **(8YSZ)**

$(Y_2O_3)_{0.03}(ZrO_2)_{0.97}$ **(3YSZ)**
+ 20 vol% Al_2O_3

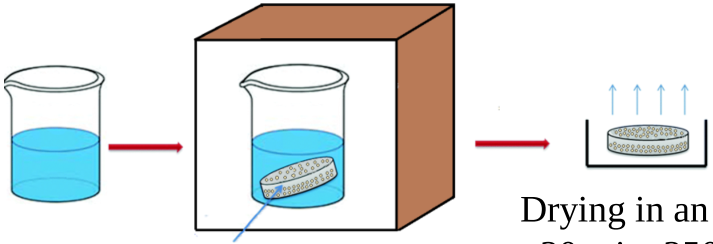
1. Tape Casting



Tape of 10Sc1YSZ – $MnCo_2O_4$

<u>Development of asymmetric membranes by 4 steps</u>:

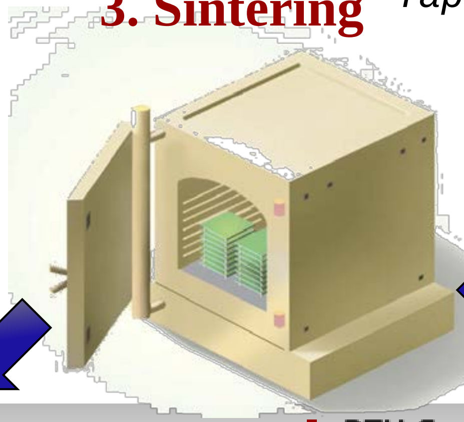
4. Application of catalysts
$Gd_{0.2}Ce_{0.8}O_{2-\delta}$ (GDC)/ $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ (LNC)



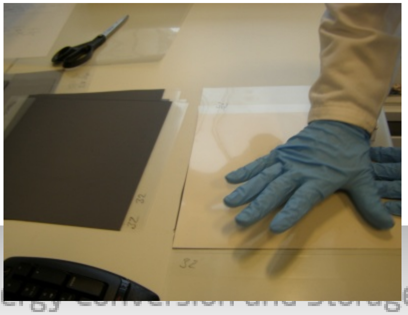
Immersion membrane in aqueous solution **3 min** in vacuum chamber

Drying in an oven: 30 min, 350° C

3. Sintering

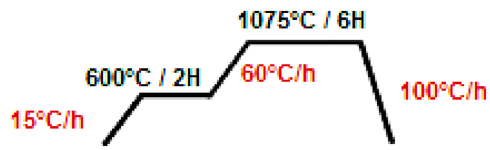


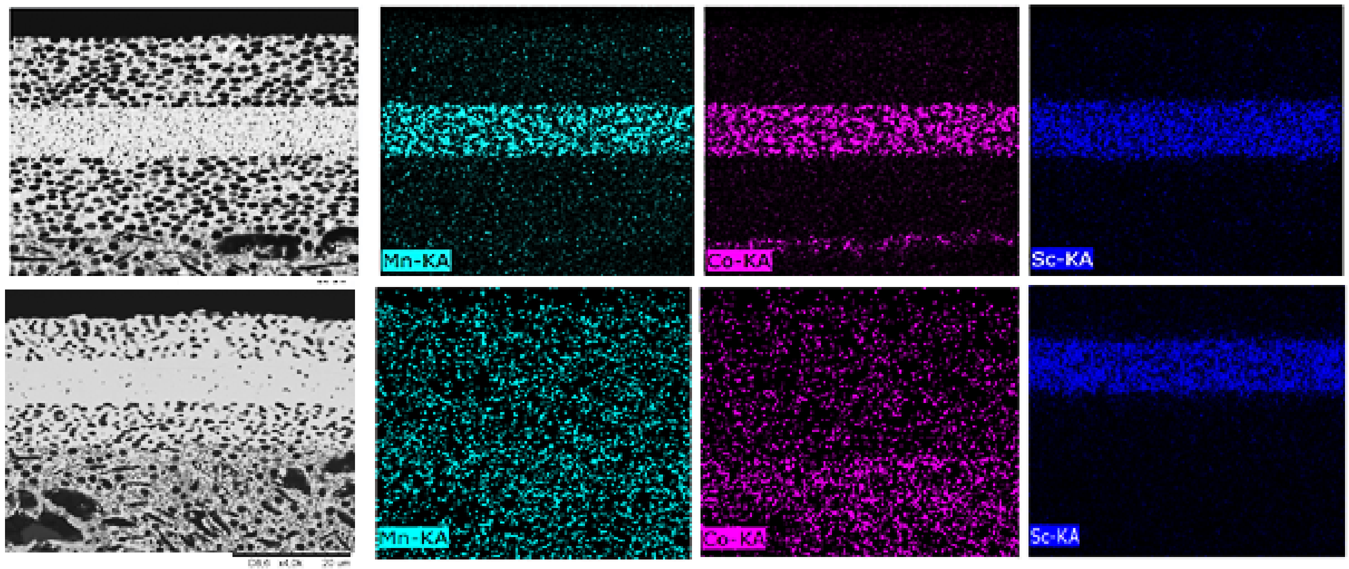
2. Lamination

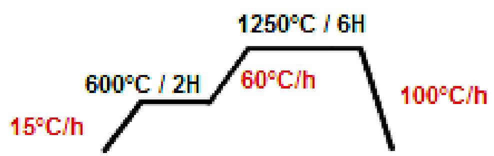


Manufacturing process : Two-step sintering

Conventional sintering:

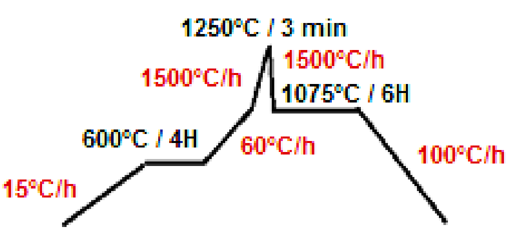


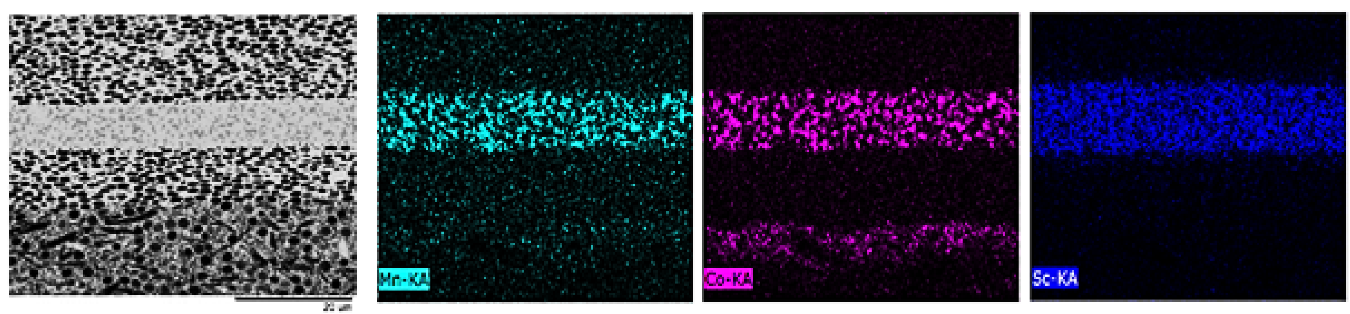




❖ Loss of Mn and Co

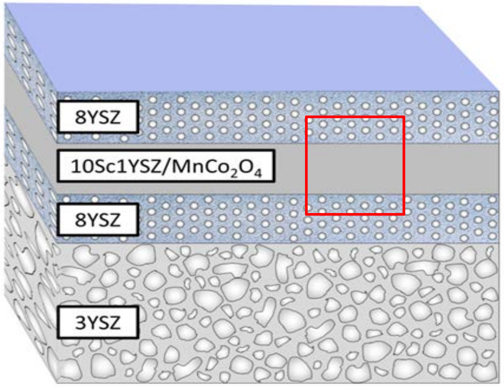
Two-step sintering:



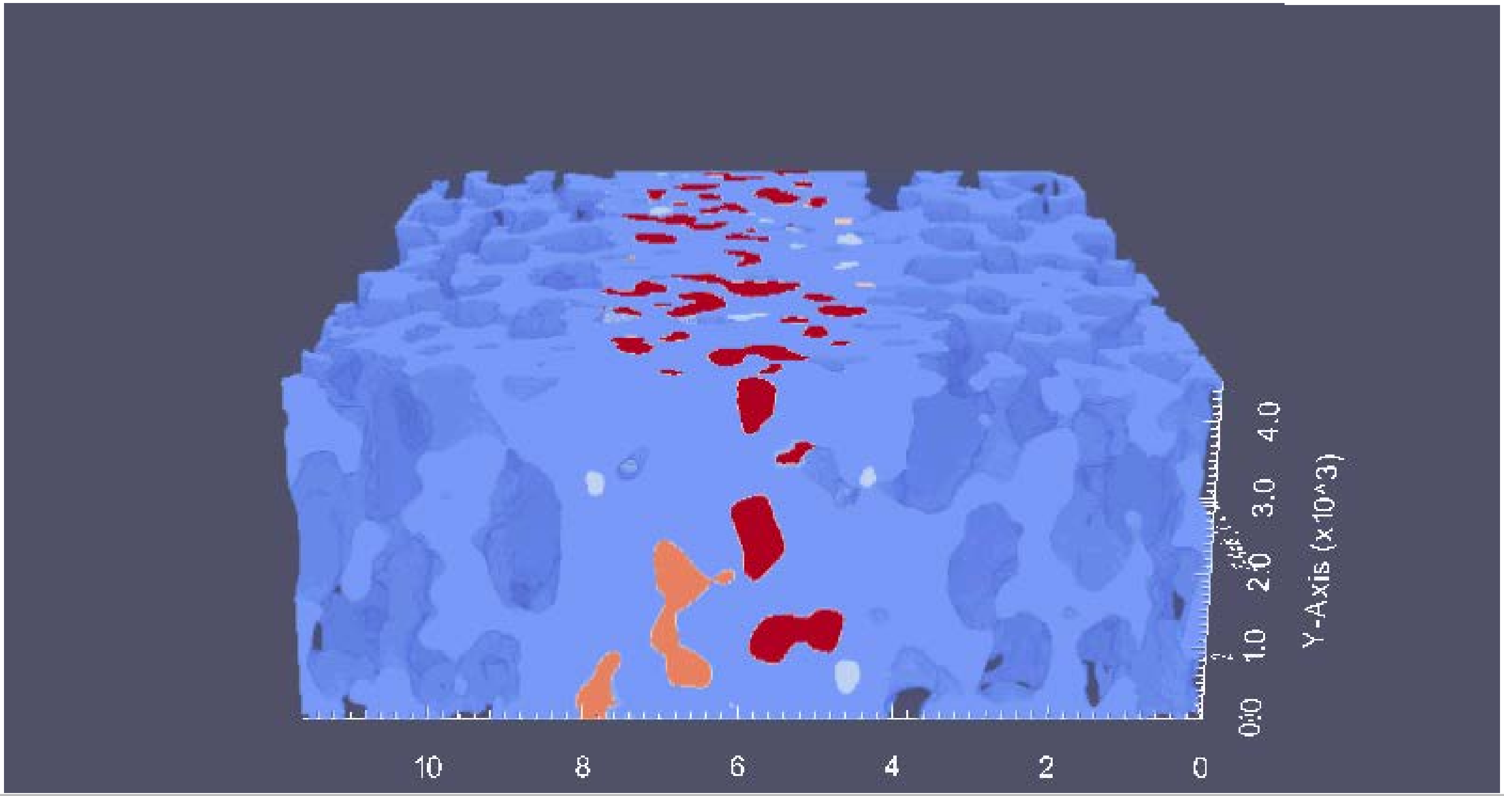


❖ Thin membrane layer (7 µm)
❖ Good adhesion of the membrane layer on interlayer
❖ Two-step sintering → dense layer + 30 vol% of $MnCo_2O_4$

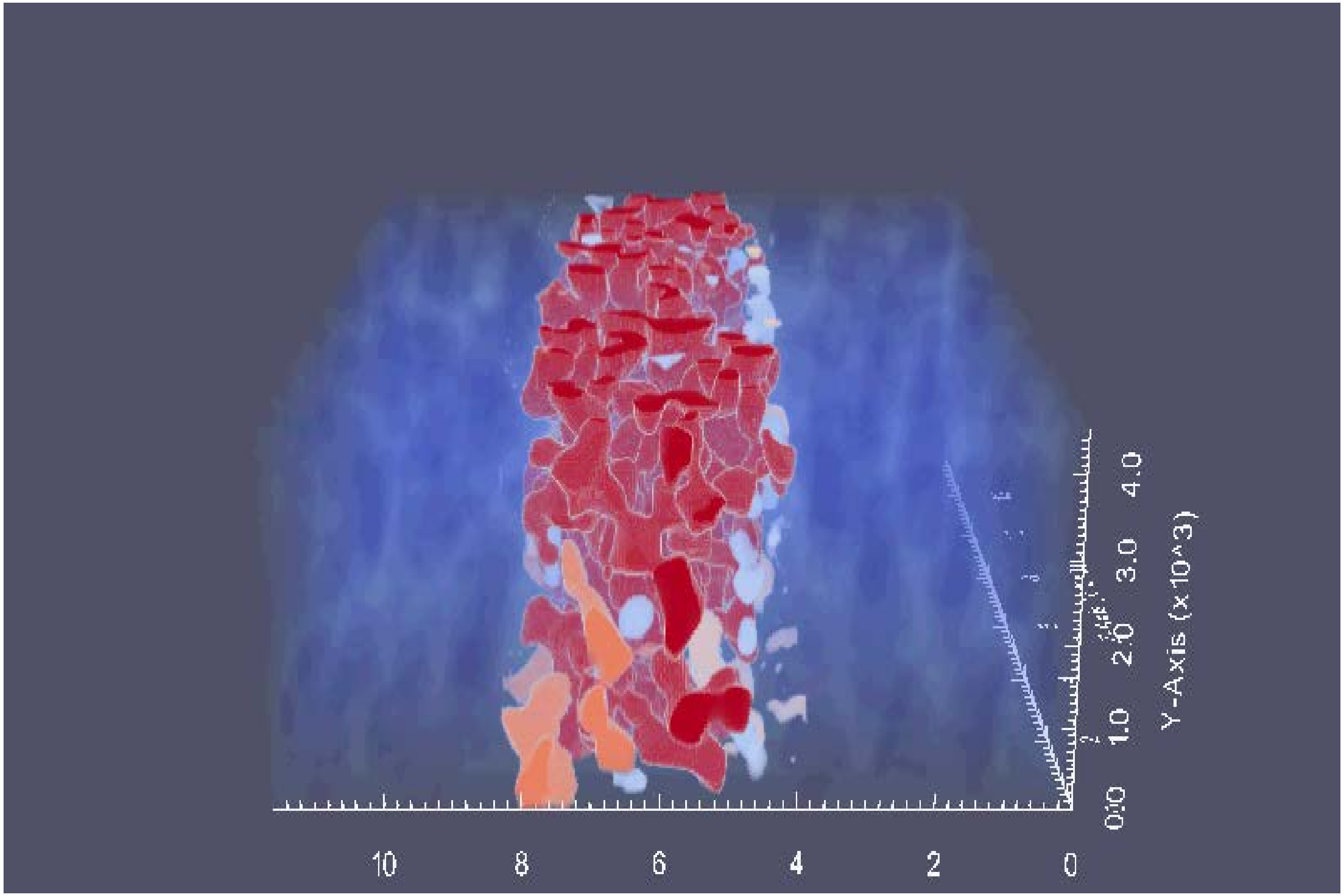
3D reconstruction of 10Sc1YSZ-$MnCo_2O_4$



Focused ion beam-scanning electron microscopy analysis

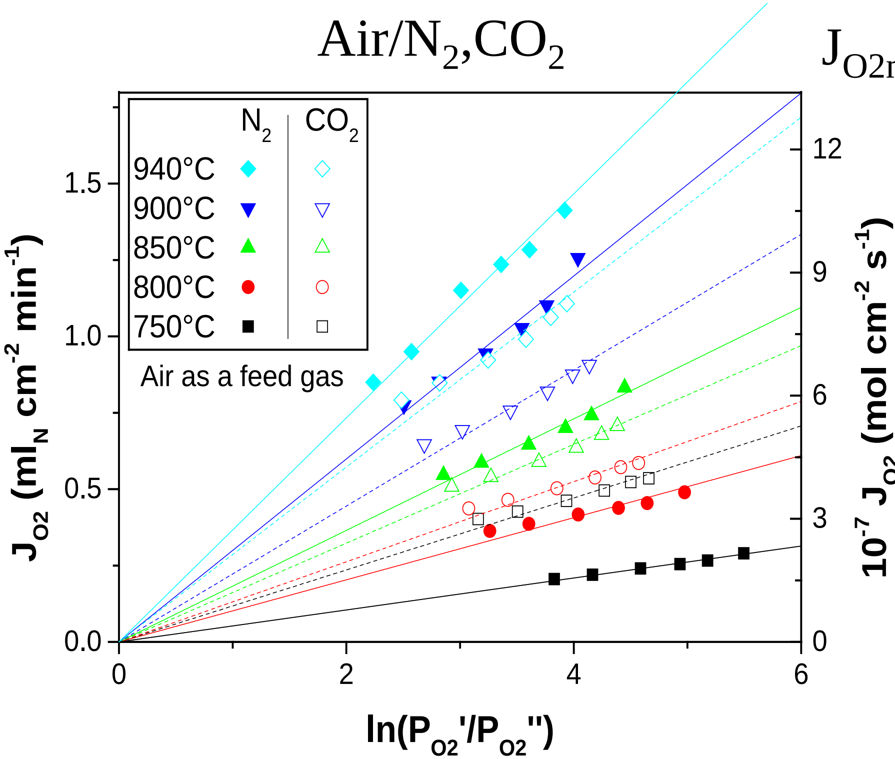


3D reconstruction of 10Sc1YSZ-$MnCo_2O_4$



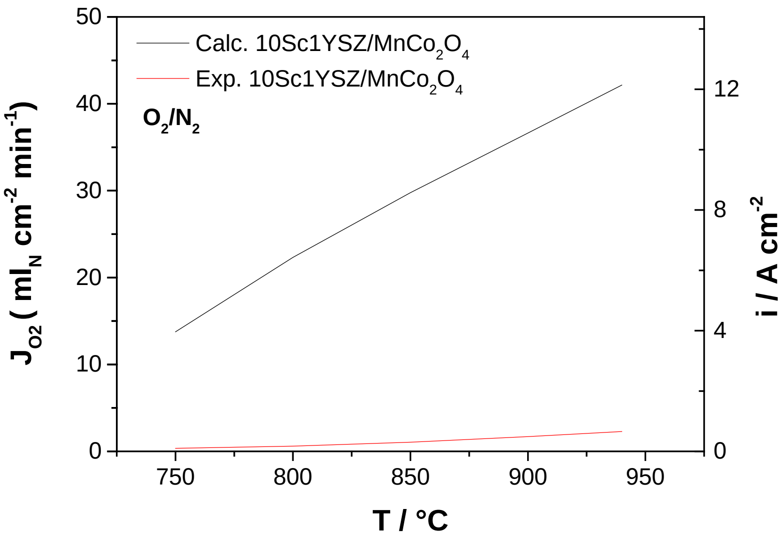
90 % of the MCO grains are connected to both sides of the dual-phase layer.

Oxygen permeation test: 10Sc1YSZ-$MnCo_2O_4$ (70-30 vol%)



J_{O2max} : **1.4 ml_N cm^{-2} min^{-1}** (at 940 °C in air/N_2)

2.3 ml_N cm^{-2} min^{-1} (at 940 °C in O_2/N_2)

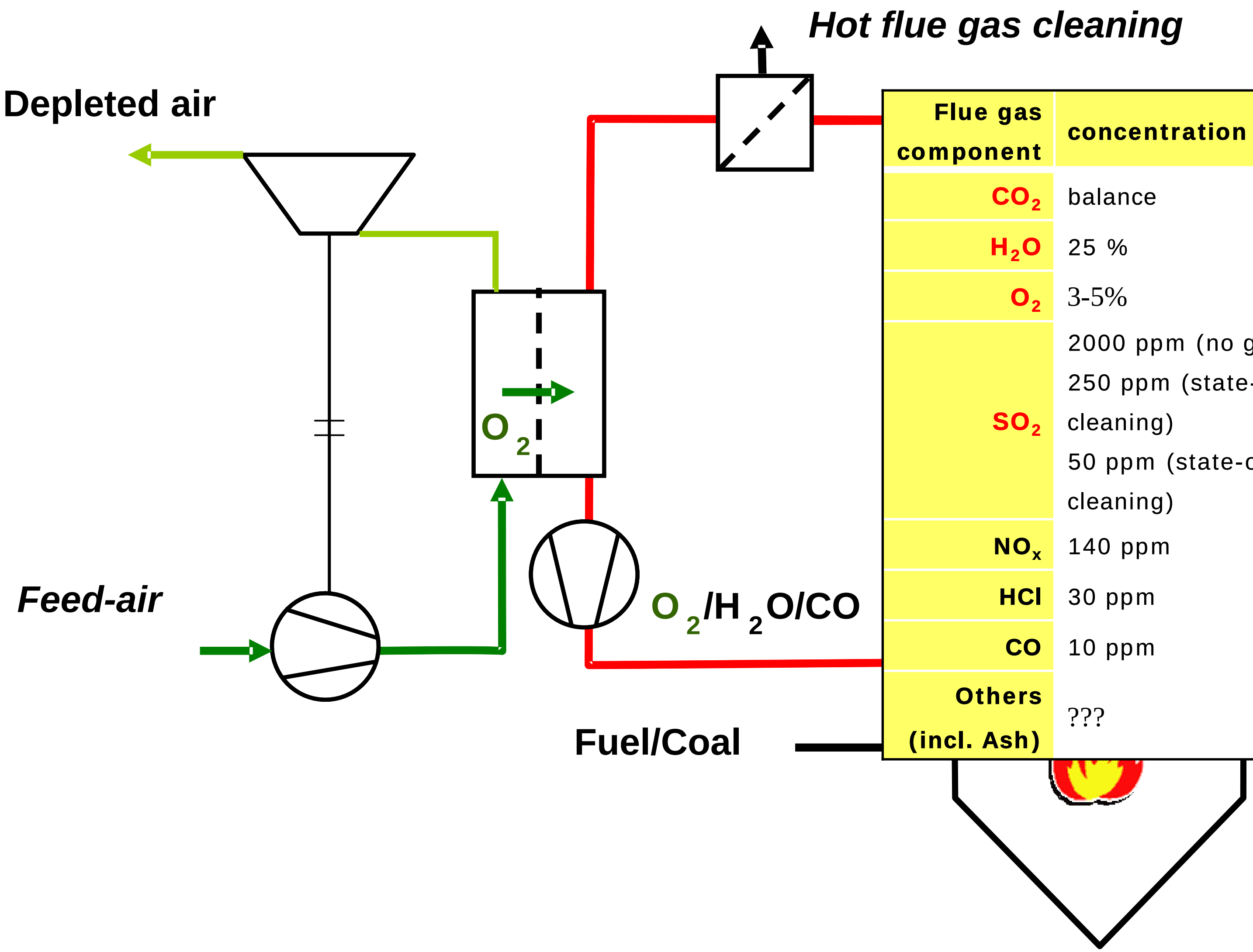


Materials	T (°C)	L (µm)	Gas pO_2'/pO_2''	J_{O2} (ml cm^{-2} min^{-1})	Ref
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	1000	70	Air/Ar	12.2	[1]
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	950	30	Air/Ar	4	[2]

[1] Ultrahigh oxygen permeation flux through supported $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes. S. Baumann et al. J. Mem. Sc. ***2011*** *377, p198-205*

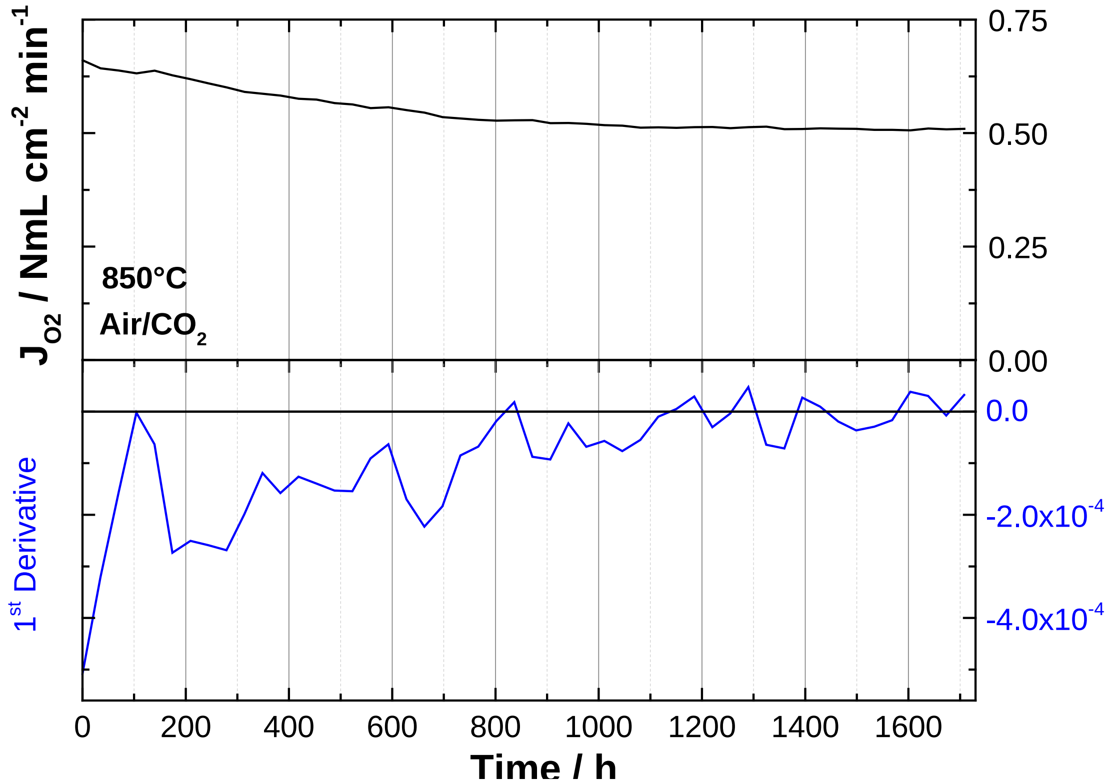
[2] Oxygen permeation through tape-cast asymmetric all-$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membranes. J.M. Serra et al. J. Mem. Sc. ***2013*** *447, p297-305*

Process conditions Oxyfuel process - 4-end integration



Flue gas component	concentration
CO_2	balance
H_2O	25 %
O_2	3-5%
SO_2	2000 ppm (no gas cleaning) 250 ppm (state-of-the-art HT-cleaning) 50 ppm (state-of-the-art LT-cleaning)
NO_x	140 ppm
HCl	30 ppm
CO	10 ppm
Others (incl. Ash)	???

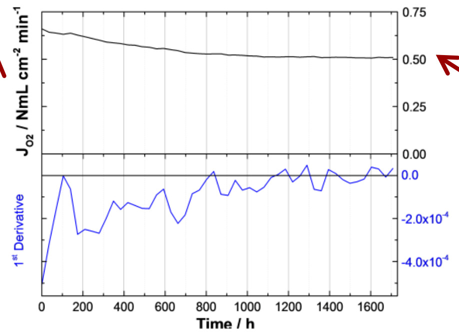
Stability test in CO_2: 10Sc1YSZ-$MnCo_2O_4$

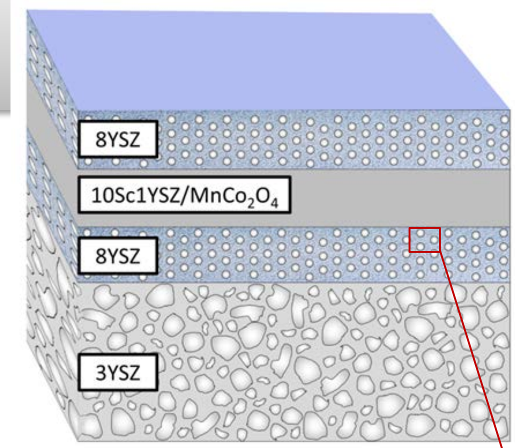


Observations

- **From 0 to 1730 h:** -22.7 % of J_{O2}.
- J_{O2} is **stable after 1100 hours.**
- Performance drop probably due to the degradation of functional layers (GDC/LNC).

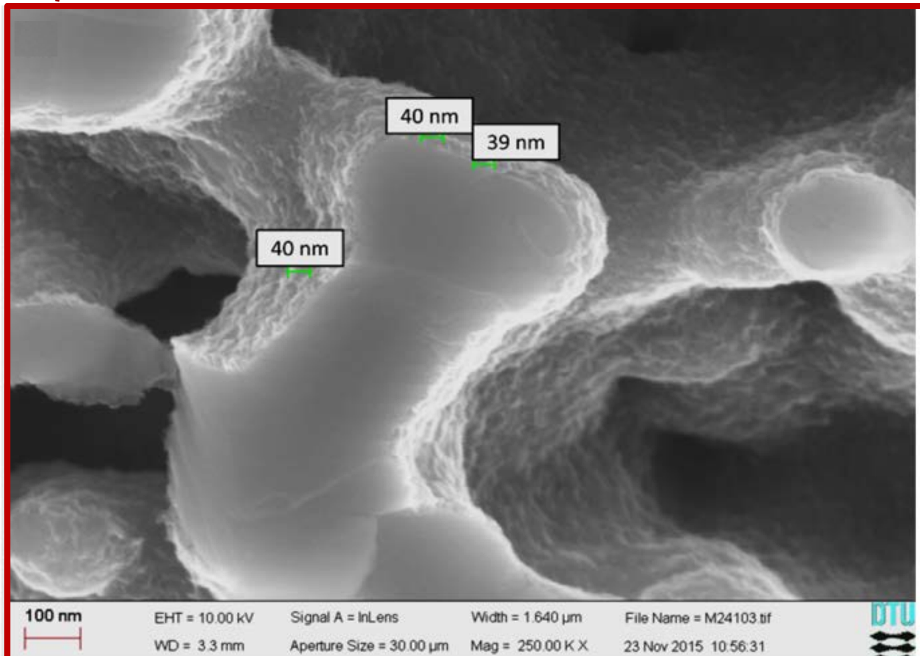
Degradation mechanism

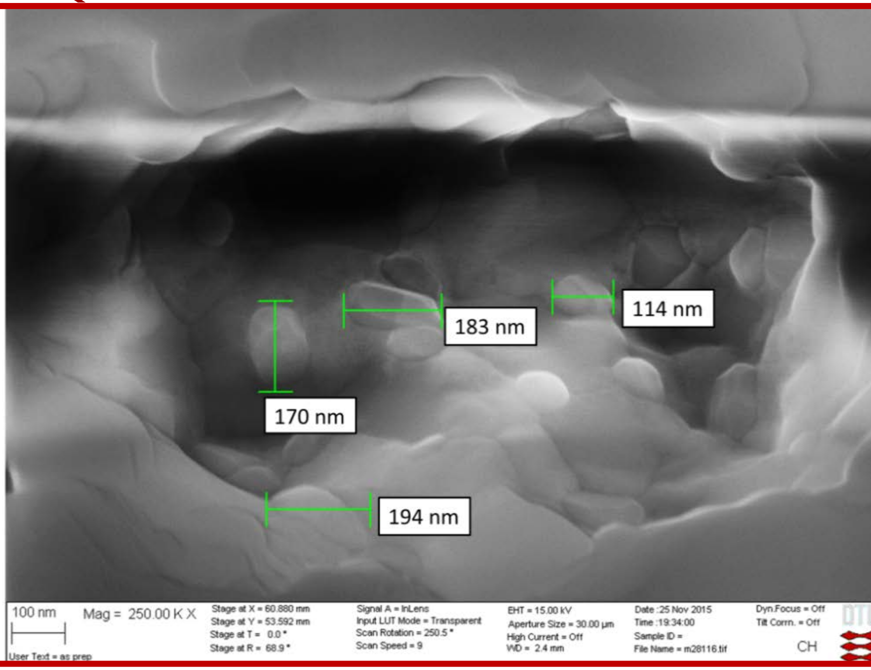




t = 0

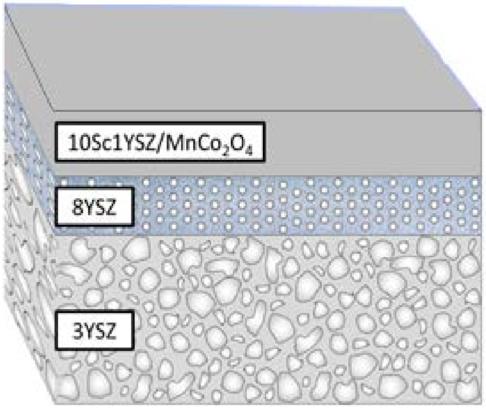
t = 1730 hours

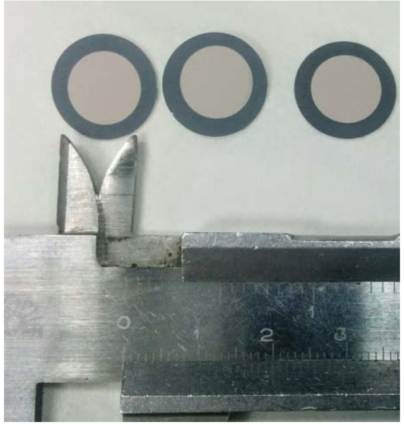




Particles size 4 times higher after test = ↘ surface area = degradation catalysts activity

Experimental work performed in co-operation with ITQ





Stable in CO_2 + SO_2?

1- SO_2 stability tests: 7 days under 250 ppm SO_2, 5% O_2, rest CO_2 (wet conditions) at 850° C

2- Oxygen permeation tests: Using different backbones ((i) 8YSZ, (ii) ScYSZ-$MnCo_2O_4$, (iii) NFO-CTO) , atmospheres: Ar, CO_2, SO_2+CO_2, Ar

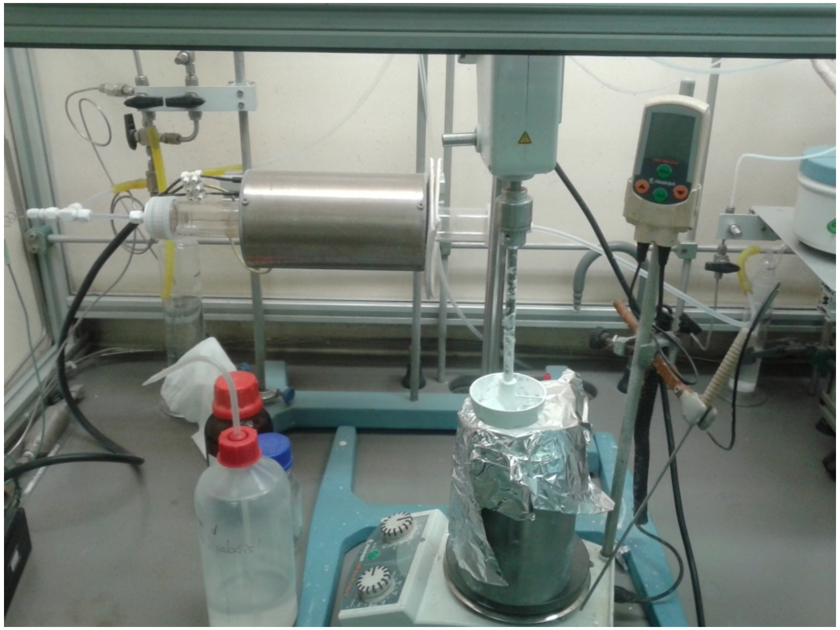
Stability test in realistic power plant conditions (SO_2/CO_2/H_2O)

- Samples: - 1 bare membrane: **3YSZ/8YSZ/10Sc1YSZ-MCO**
  - 1 membrane coated by 8YSZ: 3YSZ/8YSZ/10Sc1YSZ-MCO/8YSZ

The samples were **not infiltrated** by catalysts

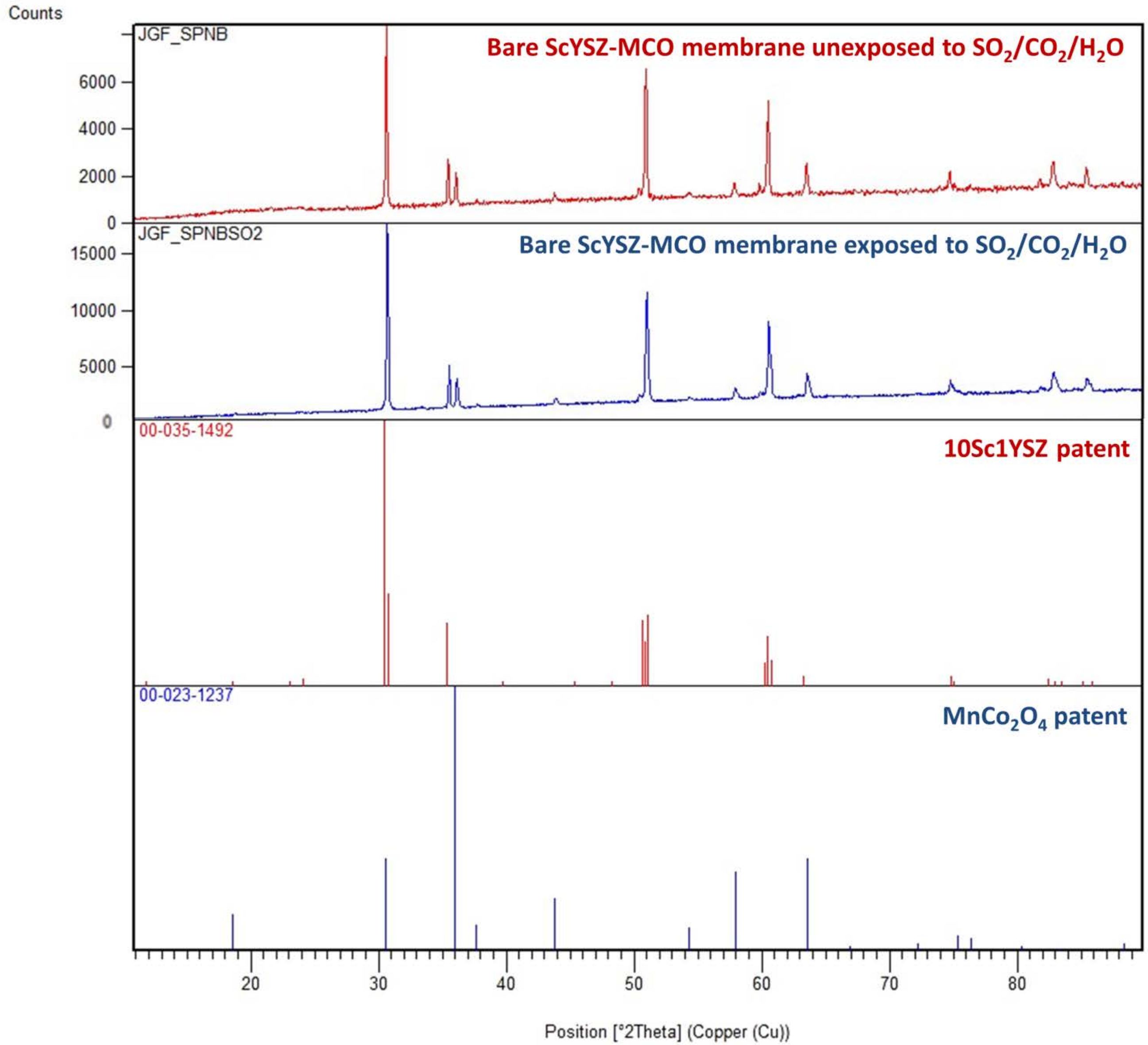
- Conditions: T° = 850° C
  Duration= 7 days (168 h)
  Atm: 250 ppm SO_2, 5% O_2, 3% H_2O, rest CO_2

- Analyses: XRD, SEM



XRD analysis

- Sample: 3YSZ/8YSZ/10Sc1YSZ-MCO – no backbone – no catalysts

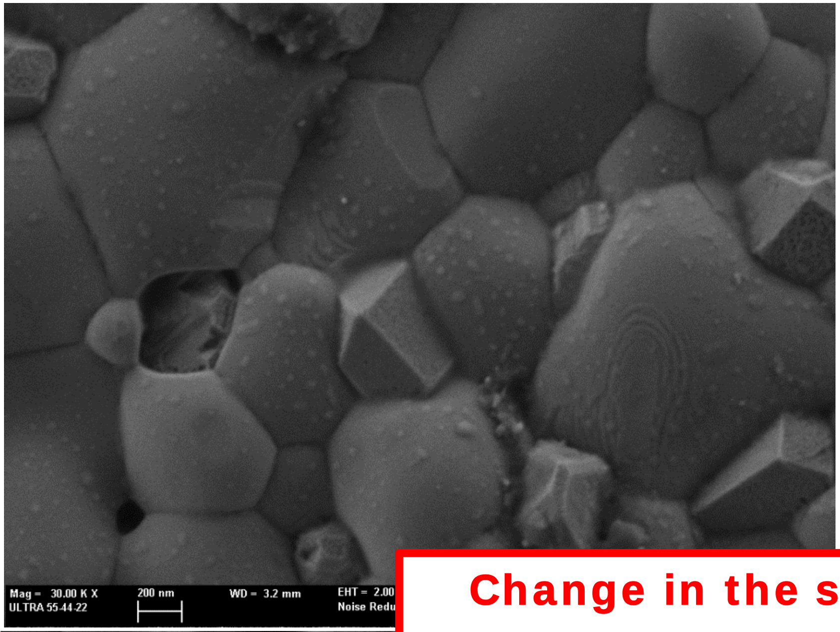


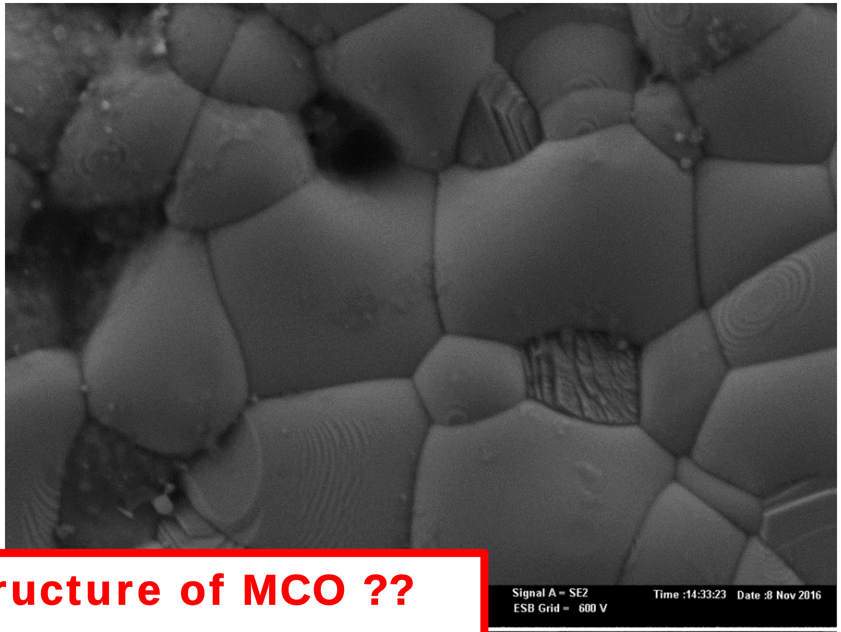
SEM analysis

Sample: 3YSZ/8YSZ/10Sc1YSZ-MCO

Tested membrane

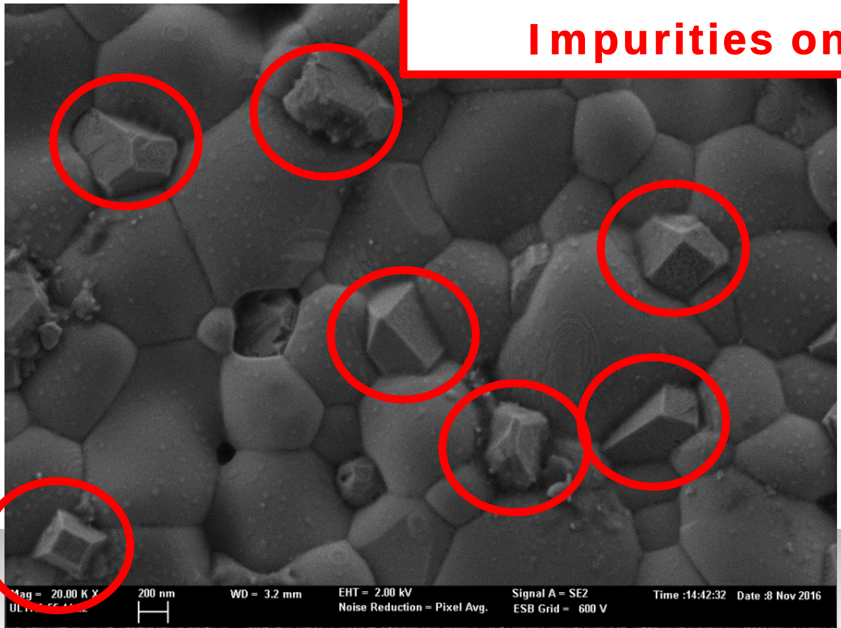
Untested membrane

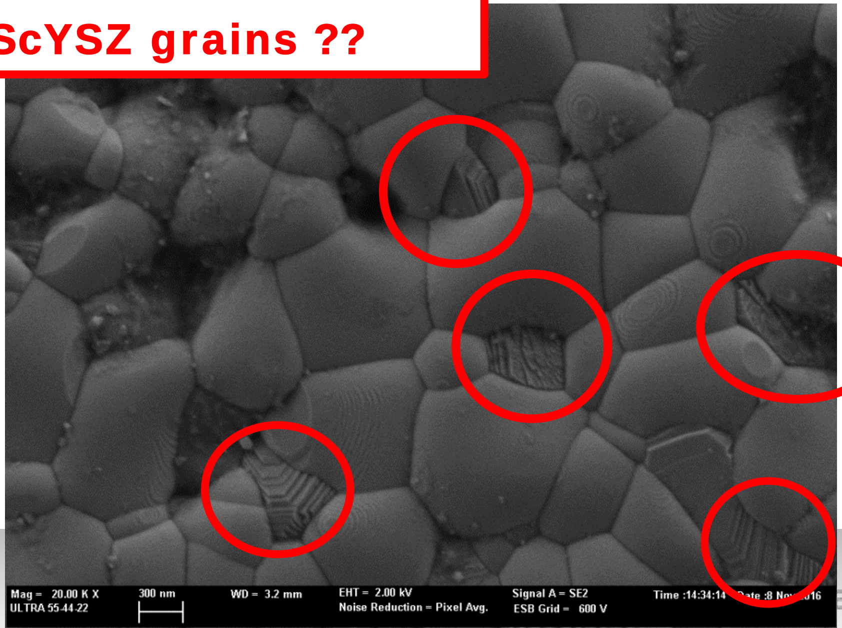




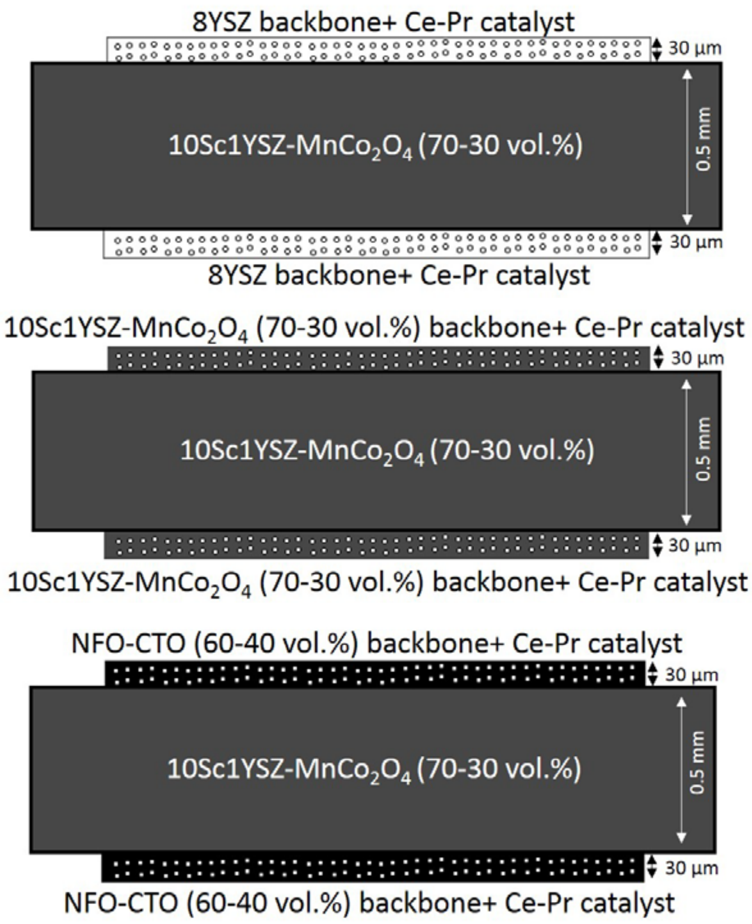
Change in the structure of MCO ??

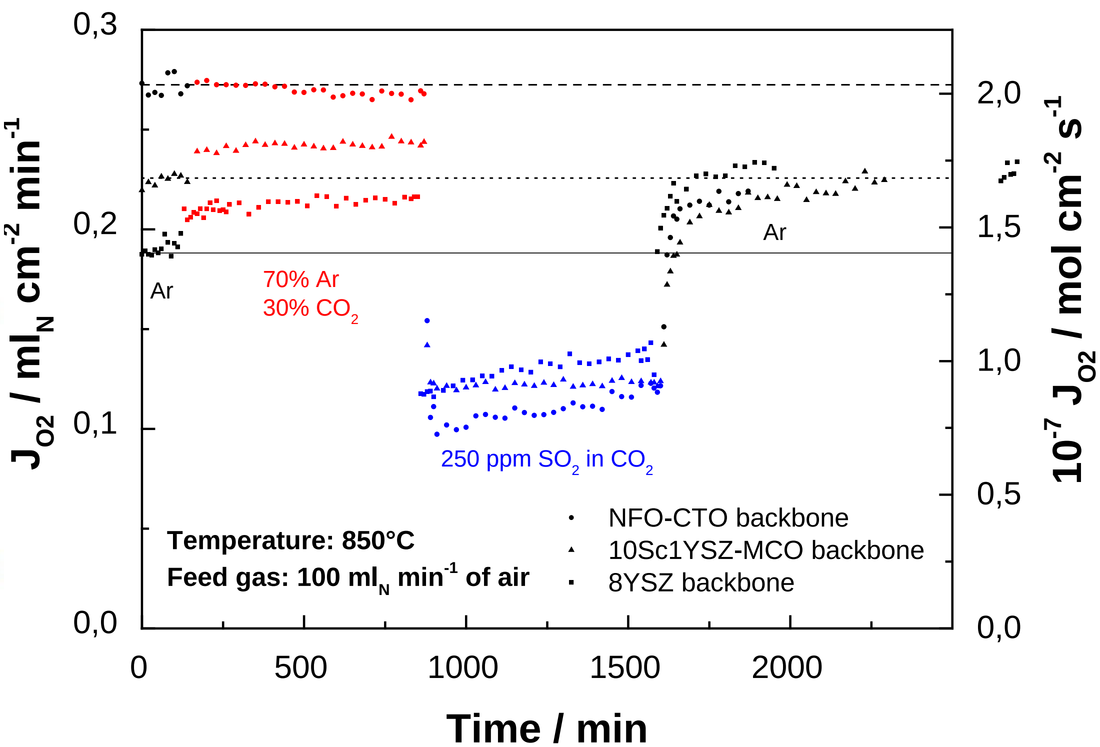
Impurities on ScYSZ grains ??





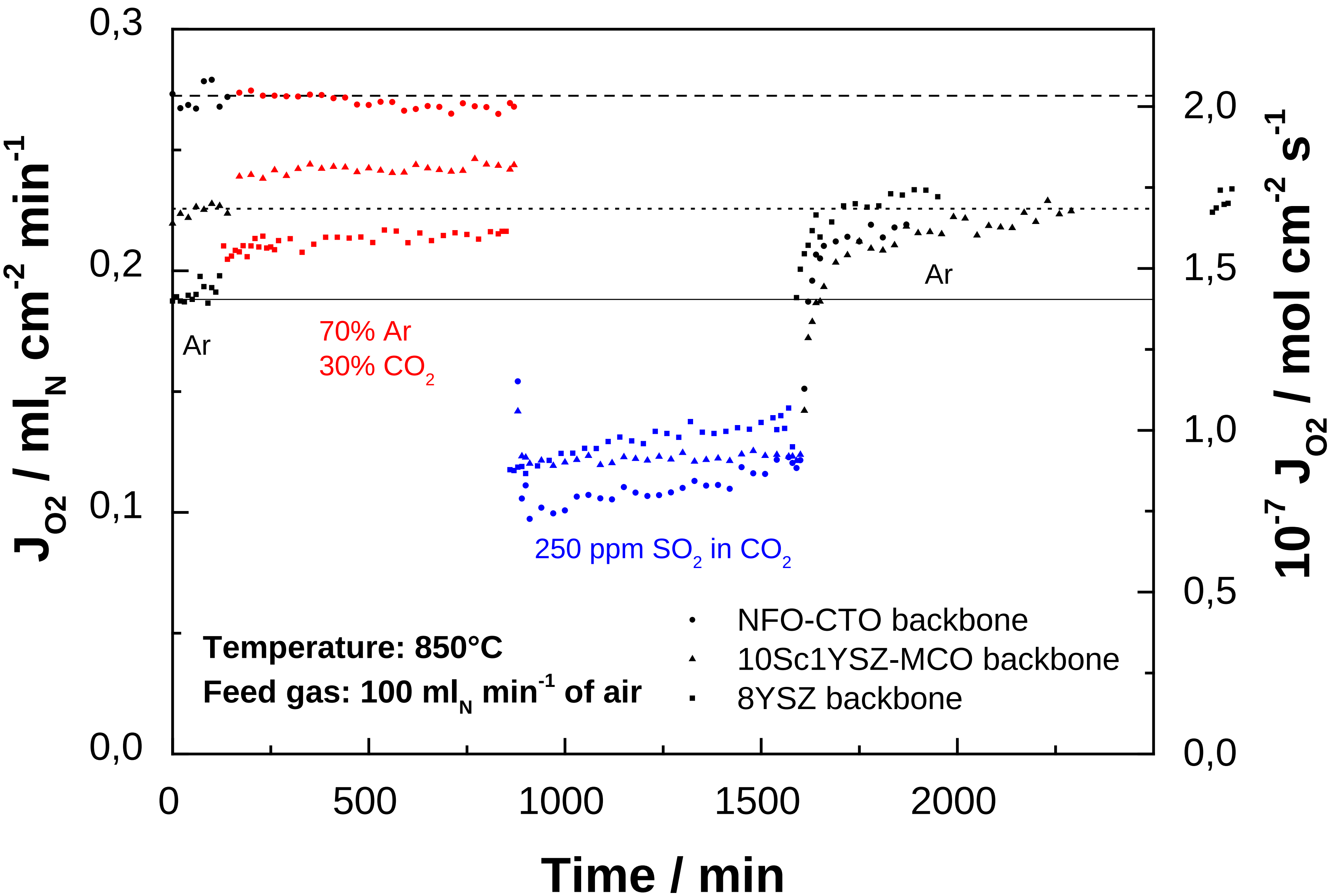
Oxygen permeation tests on 0.5 mm thick pellets

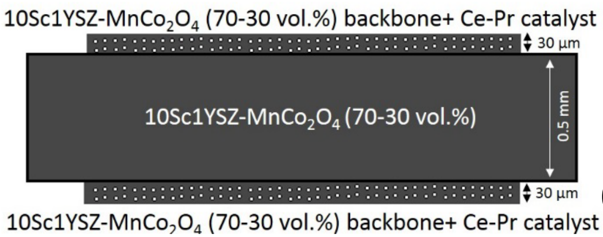




Same membrane (500 um), variation in catalyst layers

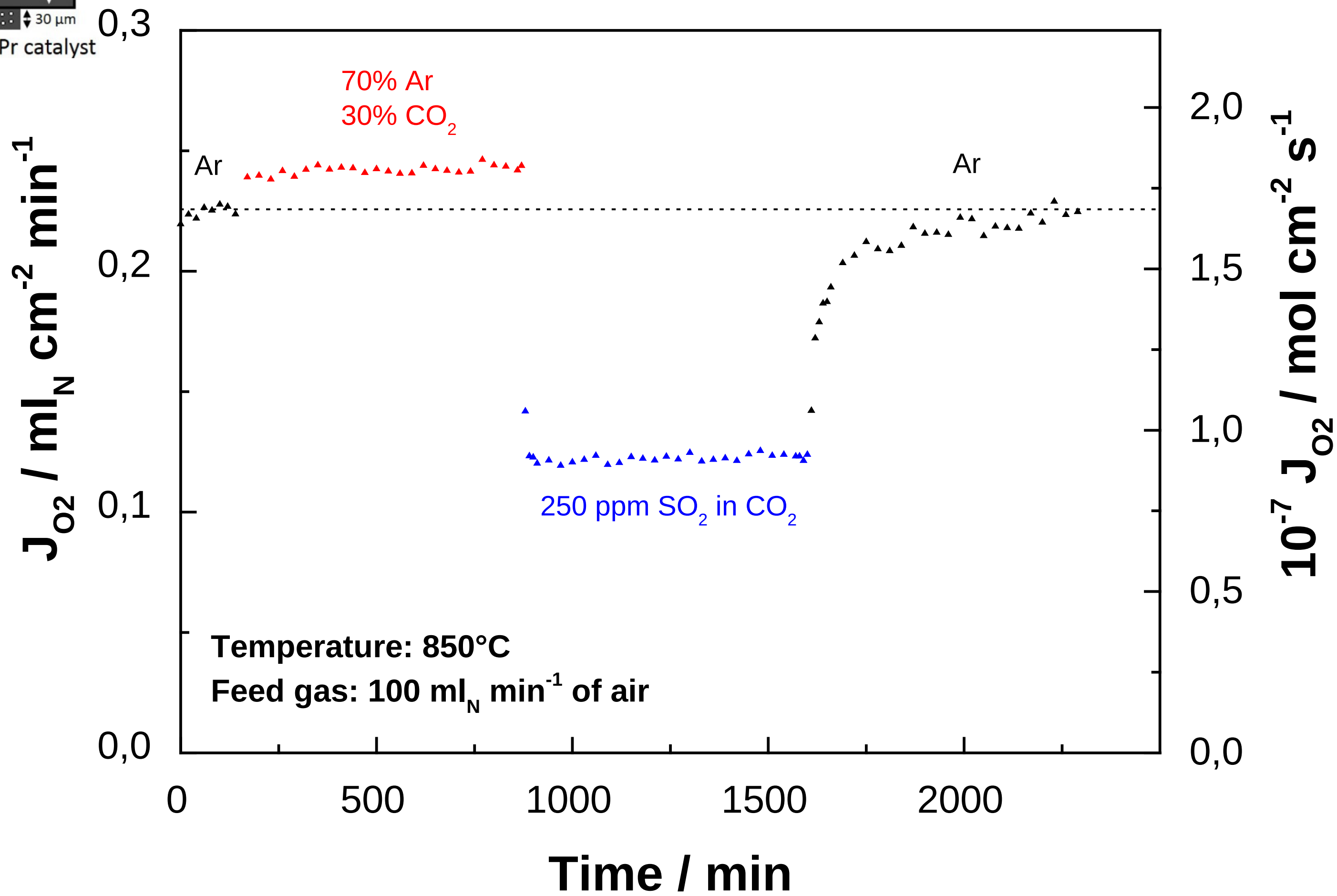
Oxygen permeation tests on 0.5 mm thick pellets





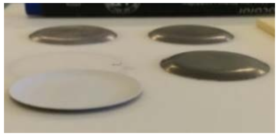
10Sc1YSZ-MnCo$_2$O$_4$ (70-30 vol.%) 1mm thick pellet with ***10Sc1YSZ-MnCo$_2$O$_4$ (70-30 vol.%)*** *porous backbone*

- *Steady Performance*
- *Full recovery!!!*

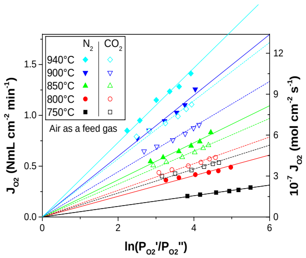


Conclusions & Outlook

Conclusions

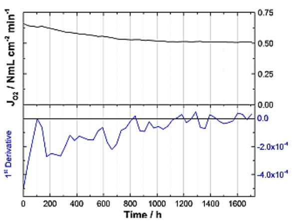


❖ **Two-step sintering** → Successful development of dual phase $10Sc1YSZ/MnCo_2O_4$ asymmetric membranes

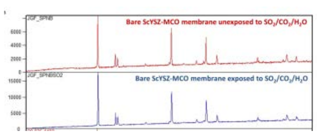


❖ **Promising performances** → 1.41 ml_N min^{-1} cm^{-2} (940 °C - air/N_2)

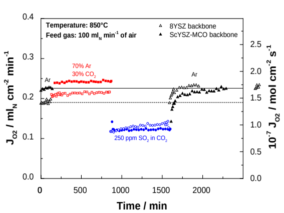
2.3 ml_N min^{-1} cm^{-2} (940 °C - O_2/N_2)



❖ **Stable performance under CO_2**



❖ **ScYSZ-$MnCo_2O_4$ stable in SO_2 containing atmospheres**



❖ **Test on pellets – Limited performances**

Acknowledgements

Funding

Graded Membranes for Energy Efficient New Generation Carbon Capture Process
Grant Agreement Number 608524

SEVENTH FRAMEWORK PROGRAMME

Colleagues

S. Pirou

P. V. Hendriksen

V. Gil

J. Gurauskis

P. S. Jørgensen

S. Ovtar

A. Kaiser

M. Søgaard

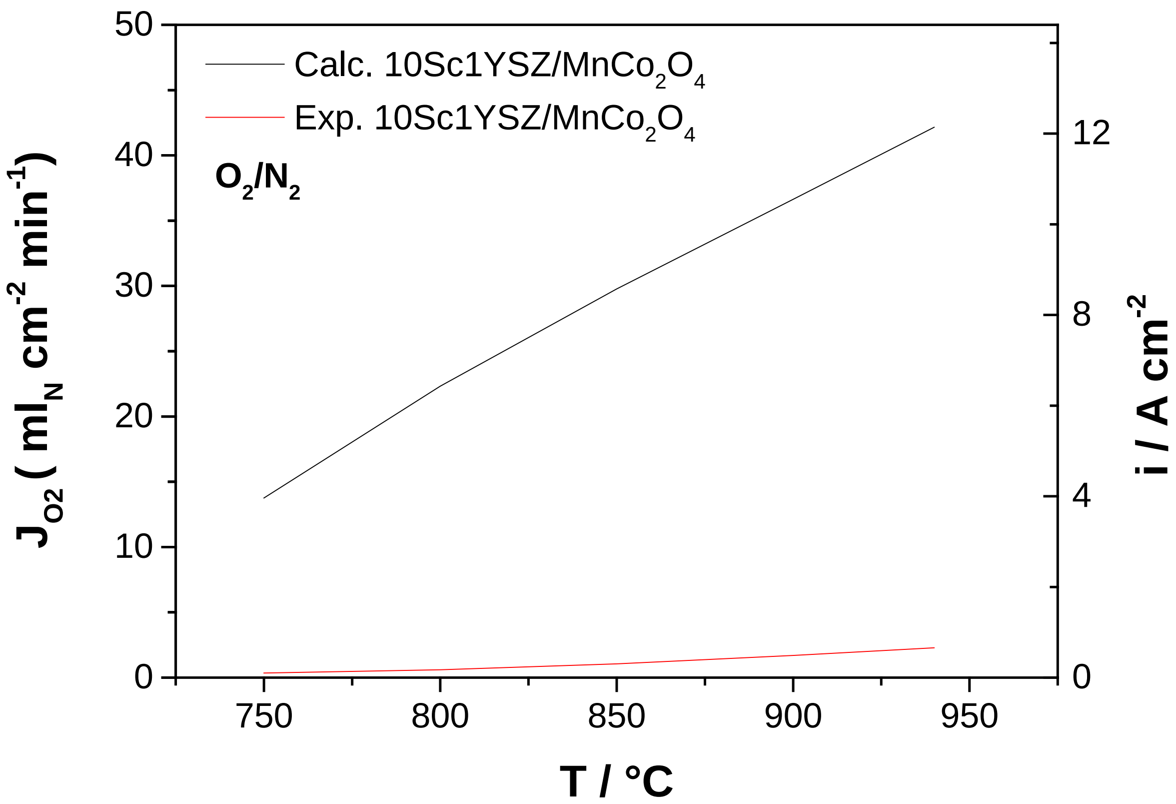
ITQ

Julio Garcia-Fayos

Jose M. Serra

Thank you for your attention !

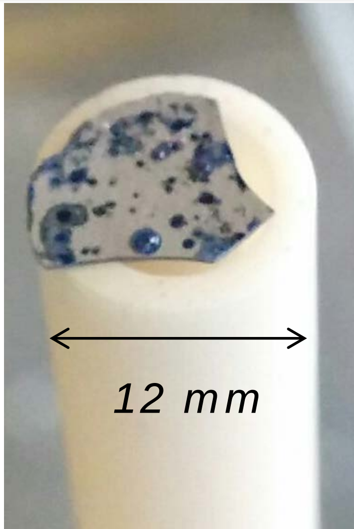
Theoretical flux



$$i = \frac{RT}{4F}\frac{(\alpha\sigma_{ion,ScSYZ} + \beta\sigma_{ion,MCO})}{t}\ln\left(\frac{p'}{p''}\right)$$

Alfred Junio Samson , Martin Søgaard, Peter Vang Hendriksen. (Ce,Gd)O2δ-based dual phase membranes for oxygen separation. Journal of Membrane Science 470 (2014) 178–188

Post-mortem analysis

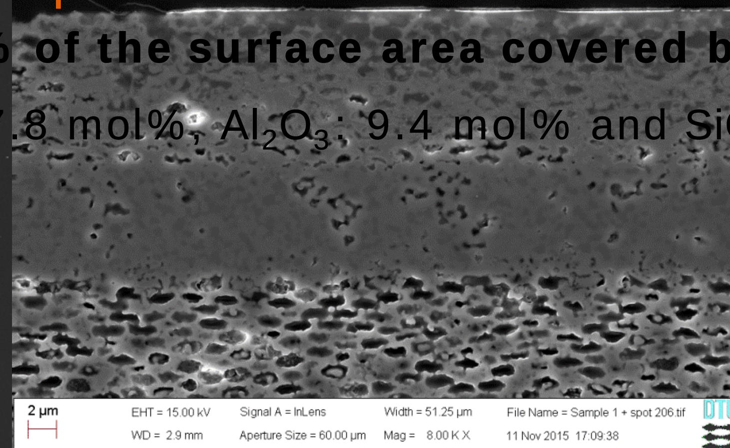


Membrane's picture after test (Anode side CO_2/N_2)

~ 40-50 vol.% of the surface area covered by NAS impurities

(NAS, Na_2O: 17.8 mol%, Al_2O_3: 9.4 mol% and SiO_2: 72.8 mol%)

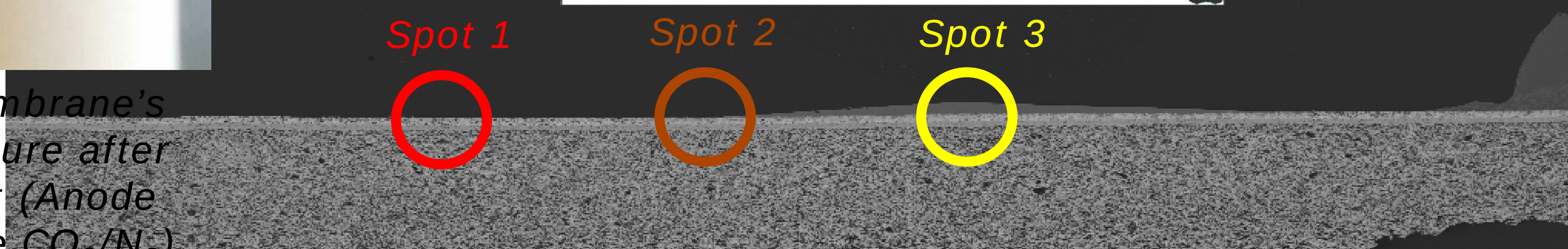
Spot 2



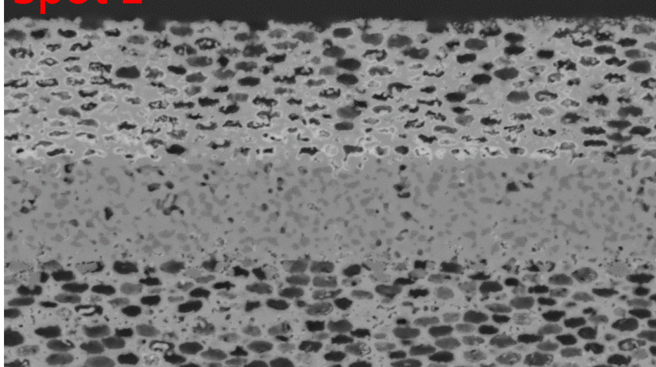
8YSZ + NAS impurities

10Sc1YSZ + $MnCo_2O_4$

8YSZ



Spot 1

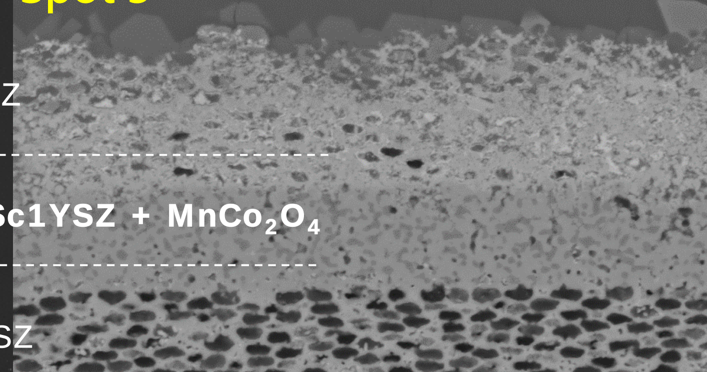


8YSZ

10Sc1YSZ + $MnCo_2O_4$

8YSZ

Spot 3



NAS impurities

8YSZ + NAS impurities

10Sc1YSZ + $MnCo_2O_4$

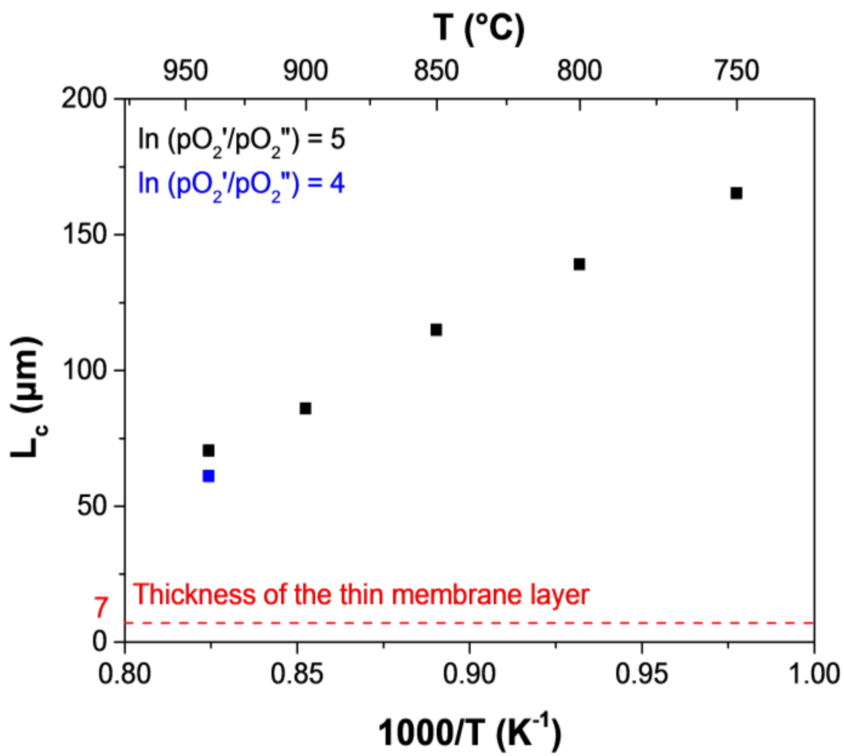
8YSZ

Oxygen flux through ScYSZ-$MnCo_2O_4$ (70-30 vol.%) membranes could be ~2 times higher without the impurities from the sealing material!

Main limitation: Surface-exchange kinetics

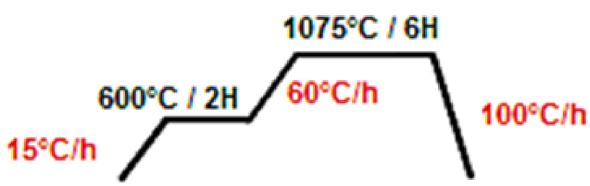
Characteristic membrane thickness:

- $$J_{O_2} = -\frac{1}{1+(\frac{2L_C}{L})}\frac{RT}{16F^2L}\int_{P''O_2}^{P'O_2}\frac{\sigma_{el}\sigma_{ion}}{\sigma_{el}+\sigma_{ion}}(pO_2)d\ln pO_2$$



Conventional sintering Vs Two-step sintering

Conventional sintering



Two-step sintering