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JÜLICH FORSCHUNGSZENTRUM

Oxygen Transport Membrane Modules for Oxyfuel Applications developed in GREEN-CC

AMPEA Workshop

Materials for membranes in energy applications: gas separation membranes, electrolysers and fuel cells

SINTEF, Oslo, NO, Feb 7-8th 2017

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Institute of Energy and Climate Research IEK-1
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GREEN
Graded Membranes for Energy Efficient New Generation Carbon Capture Process
Grant Agreement Number 608524

SEVENTH FRAMEWORK PROGRAMME

Project facts and figures

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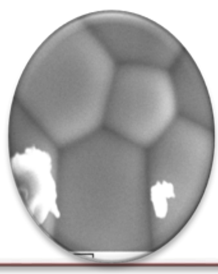
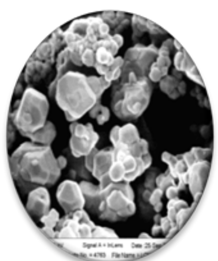
WP1: Membrane

- Materials
- Support
- Assembly
- Modeling



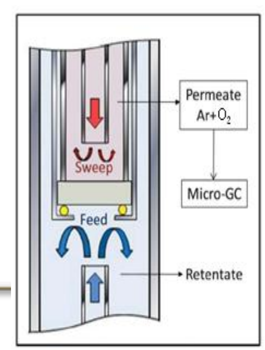
WP2: Catalyst

- Materials
- Modeling
- Application



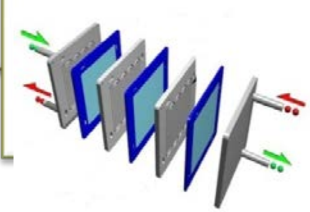
WP3: Application oriented testing

- Stability
- Slip stream in real PP
- Permeation



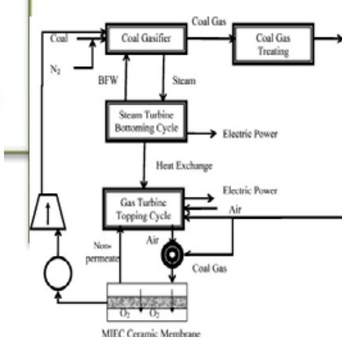
WP4: Proof-of-concept

- Module design
- Membrane assembling
- Test facilities design
- Module testing



WP5: Process Engineering

- Process Simulations
- Scale up rules
- Cost estimations



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Outline

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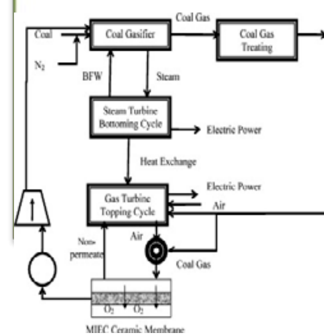
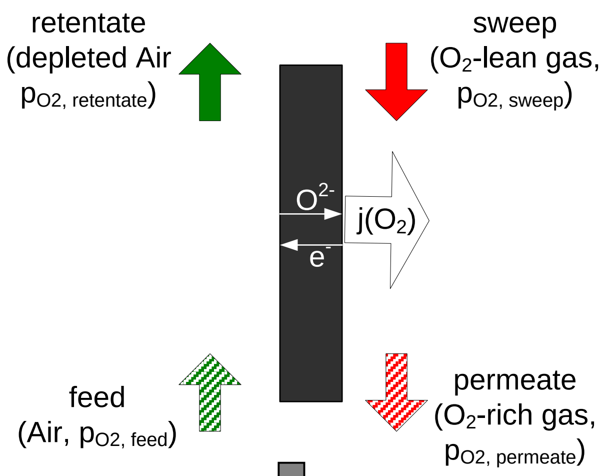
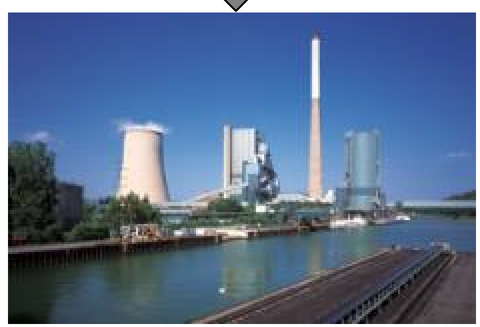


4-end membranes for oxyfuel combustion in industrial applications



Main target: Identifying the **energetic and economic** benefit of an OTM in all 3 process routes **under consideration of realistic boundary conditions**

IGCC



Oxyfuel Power Plant

Oxyfuel Cement

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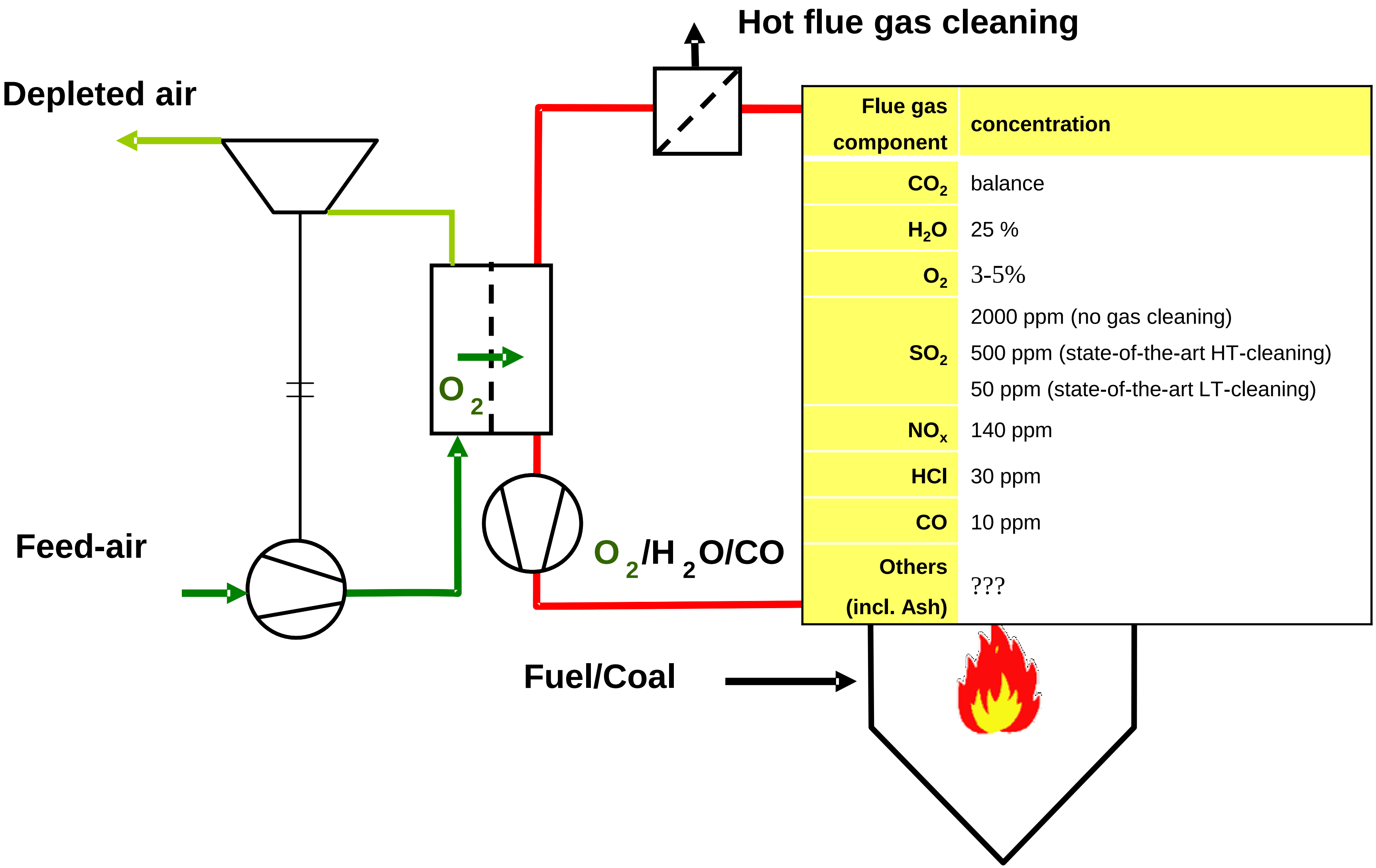
Process conditions
Oxyfuel process - 4-end integration



Flue gas component	concentration
CO_2	balance
H_2O	25 %
O_2	3-5%
SO_2	2000 ppm (no gas cleaning) 500 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)	???

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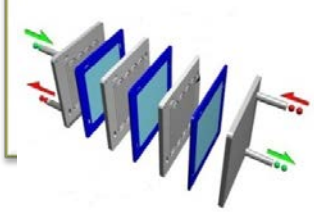

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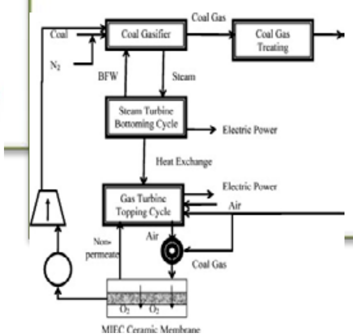

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Module design and operation

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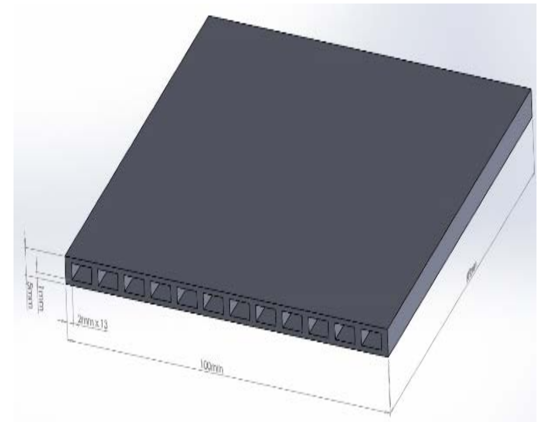
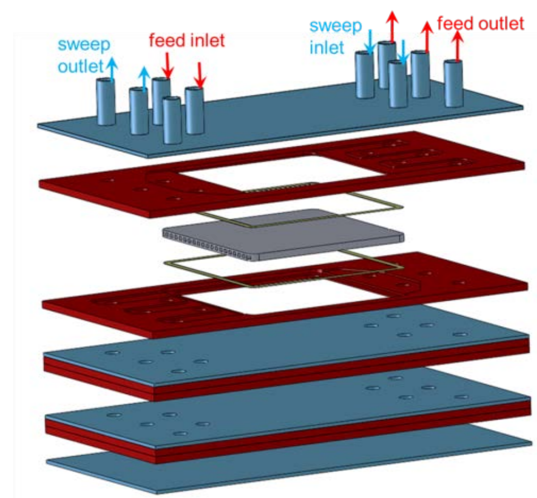
Design and build of a proof- of-concept membrane module

- Planar stack with asymmetric membranes
- Effective area at least 300 cm^2
- 4-end operation



Key issues/activities

- Mechanical stress analysis
- CFD simulation
- Joining techniques for ceramic-ceramic and ceramic-metal joints



Design and build of a pilot loop for module testing
Proof of performance (TRL 4)

- Operating temperature 750 – 900 °C
- Leakage lower than 2%
- **Long term tests (1000 h)** in a synthetic flue gas stream

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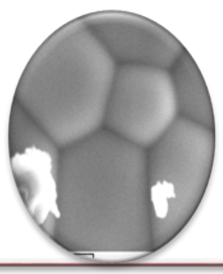

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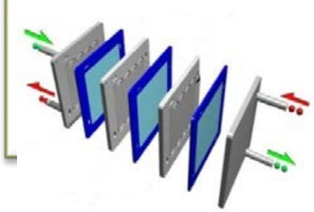

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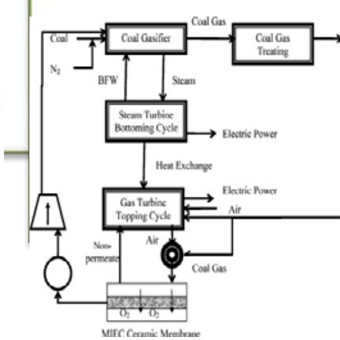

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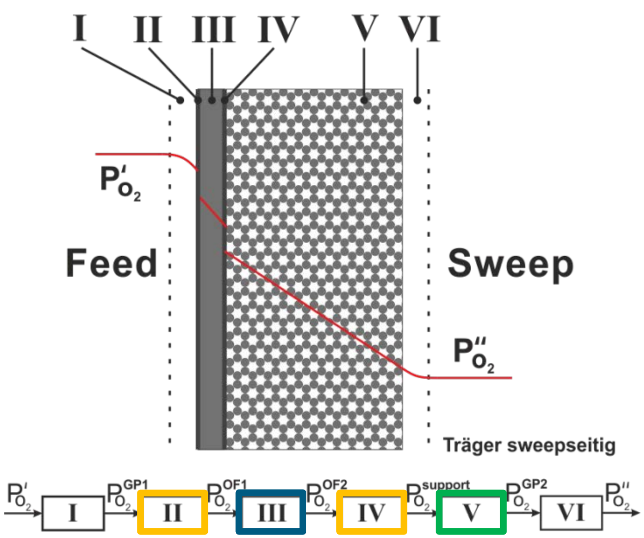
Oxygen Transport in Mixed Conductors



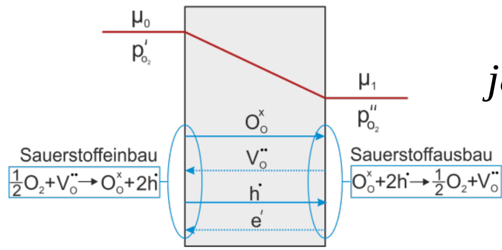
(1)

I & VI	Gastransport
II & IV	Surface Exchange
III	Bulk Diffusion
V	Gastransport in Support

1. Schulze-Küppers, Dissertation Ruhr-Universität Bochum (2010)

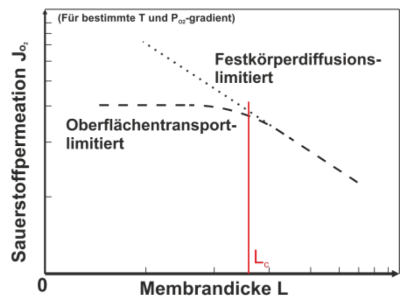
2. Bouwmeester et al. Fundamentals of Inorganic Membrane Science and Technology (1996)

Zone III Bulk diffusion



$$j_{O_2} = -\frac{1}{L}\cdot\frac{RT}{16\cdot F^2}\cdot\frac{\sigma_i\cdot\sigma_e}{\sigma_i+\sigma_e}\cdot\ln\frac{p'_{O_2}}{p''_{O_2}}$$

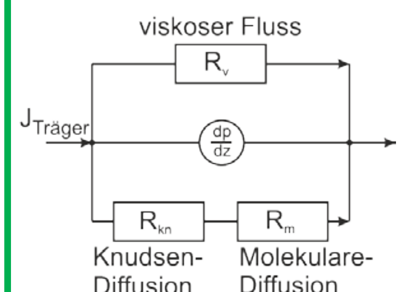
Zone II & IV Surface exchange kinetics



$$j_{O_2} = -\frac{1}{L+2L_c}\cdot\frac{RT}{16\cdot F^2}\cdot\frac{\sigma_i\cdot\sigma_e}{\sigma_i+\sigma_e}\cdot\ln\frac{p'_{O_2}}{p''_{O_2}} \quad (2)$$

$$L_c = \frac{D^*}{k}$$ Characteristic Thickness

Zone V Gas transport in support



$$\underbrace{\nabla_{T,P} x_i + \frac{x_i}{p_{ges}}\nabla p_{ges}}_{\text{driving force}} = \underbrace{RT\sum_{j=1}^{n}\frac{(x_i\vec{J_j} - x_j\vec{J_i})}{P_{ges}D_{ij}}}_{\text{molecular diffusion}} - \underbrace{f_{im}\frac{RT}{p_{ges}}\vec{J_i}}_{\text{Knudsen-Diff. + viscos flow}}$$

driving force — molecular diffusion — Knudsen-Diff. + viscos flow

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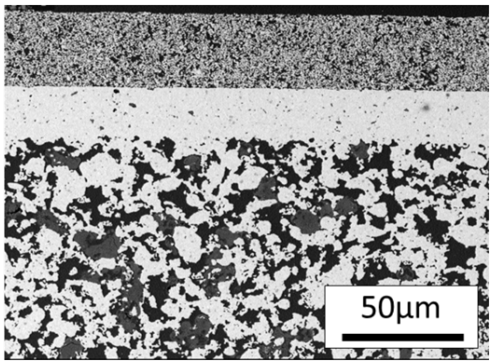
Single phase perovskites



$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (reference)

- ✓ High performance
- ✓ Asymmetric membranes developed
- ✓ Good stability in CO_2
- Limited stability in SO_2

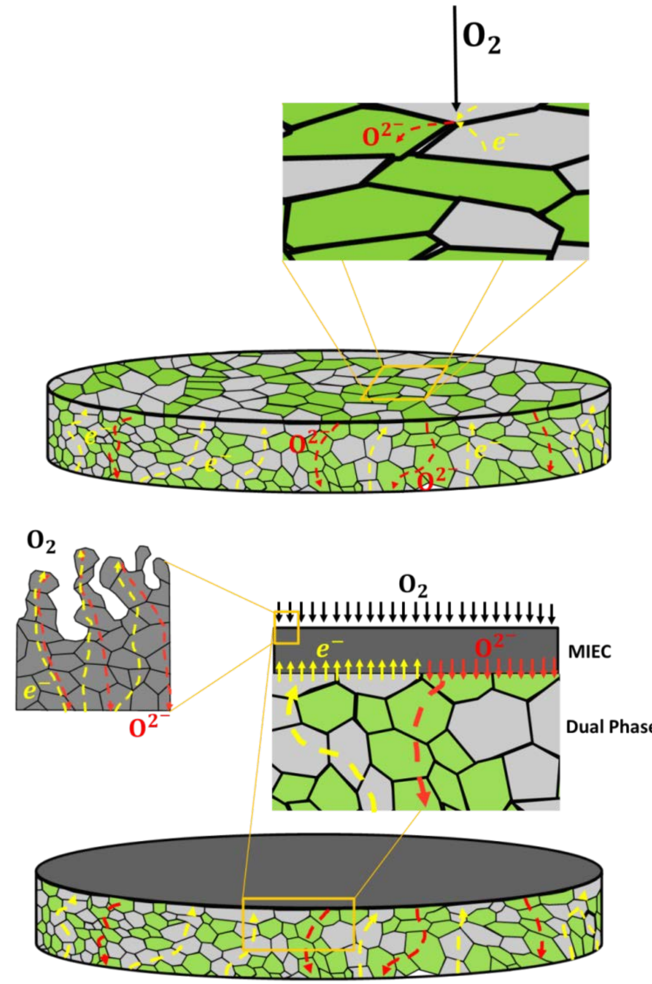
Dual phase composites

Ionic conductor:

- ✓ $Ce_{0.8}Gd_{0.2}O_2$
- ✓ stabilized zirconia

Electronic conductor:

- ✓ $FeCo_2O_4$
- ✓ doped ZnO
- ✓ perovskites



$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ - $FeCo_2O_4$ TEM Analysis

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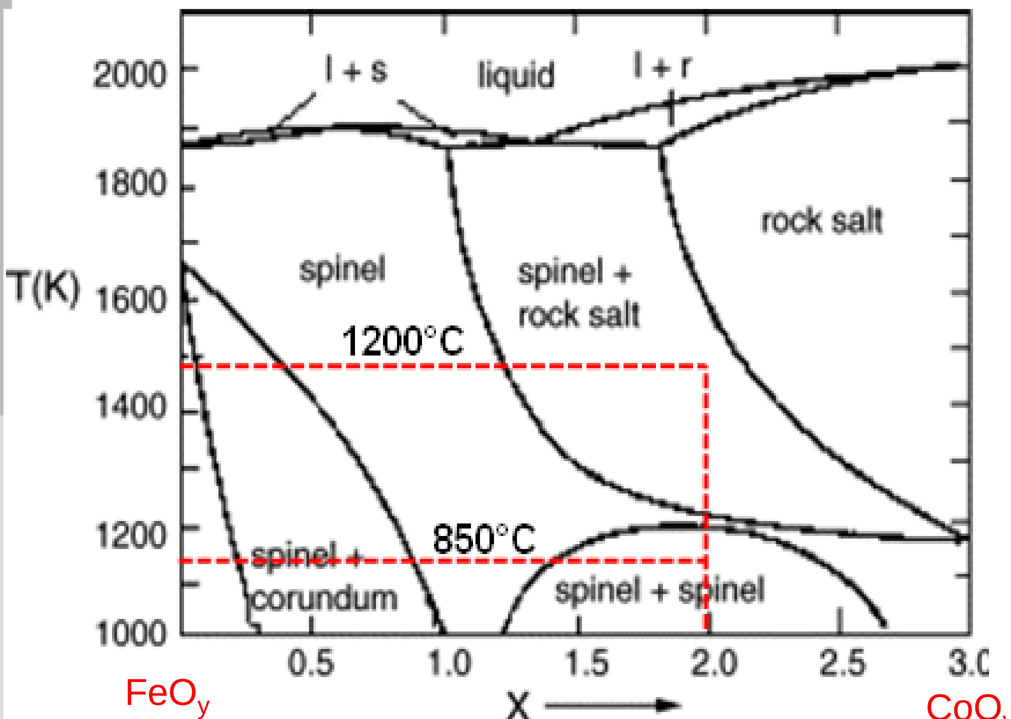
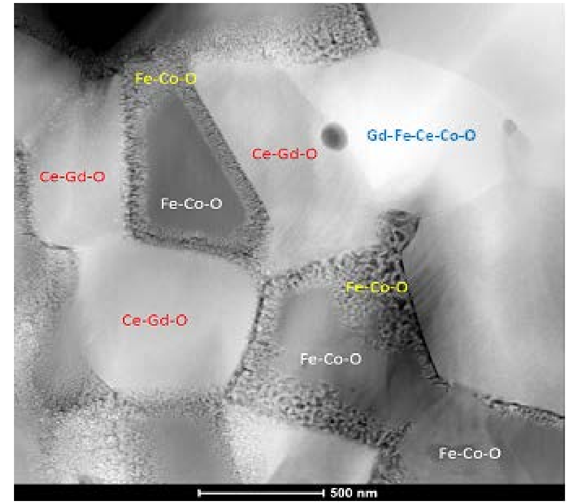
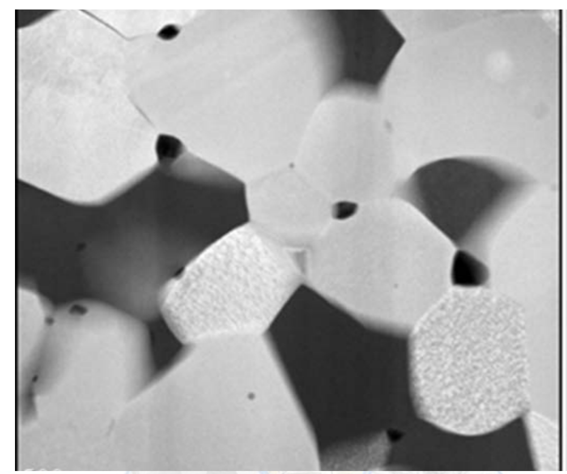
- 3 phases identified:
  - ✓ Ce-Gd-O
  - ✓ Gd-Ce-Fe-Co-O
  - ✓ Fe-Co-O is wrapped in porous O deficient Fe/Co-O phase (with preferential porosity)



Ramasamy et al. J Amer Ceram Soc 99 (2016) 349-355



After optimized sintering cycle



GFE Central Facility for Electron Microscopy RWTHAACHEN

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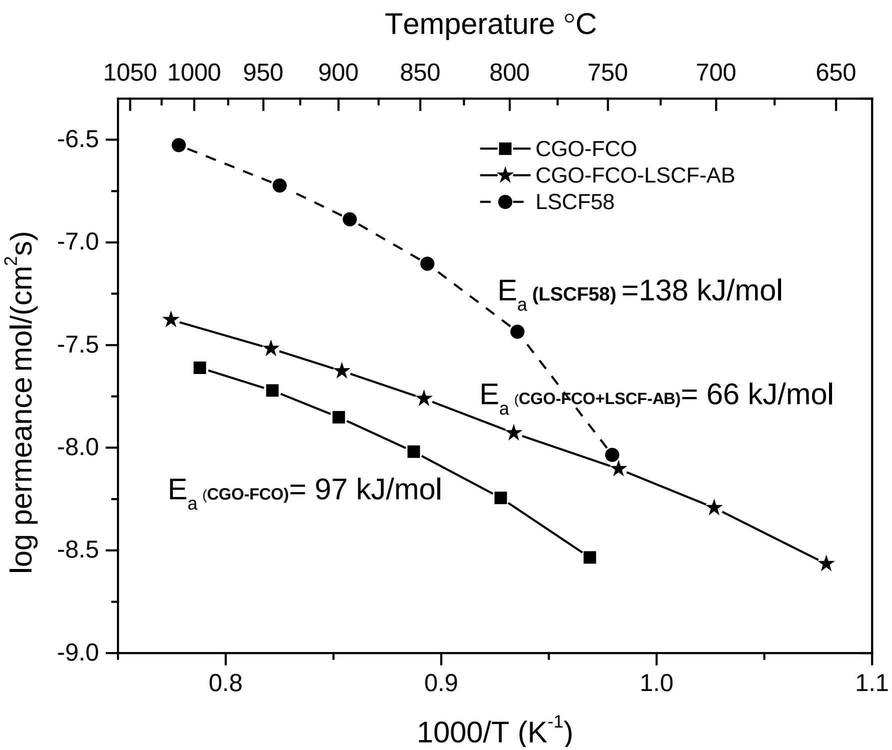
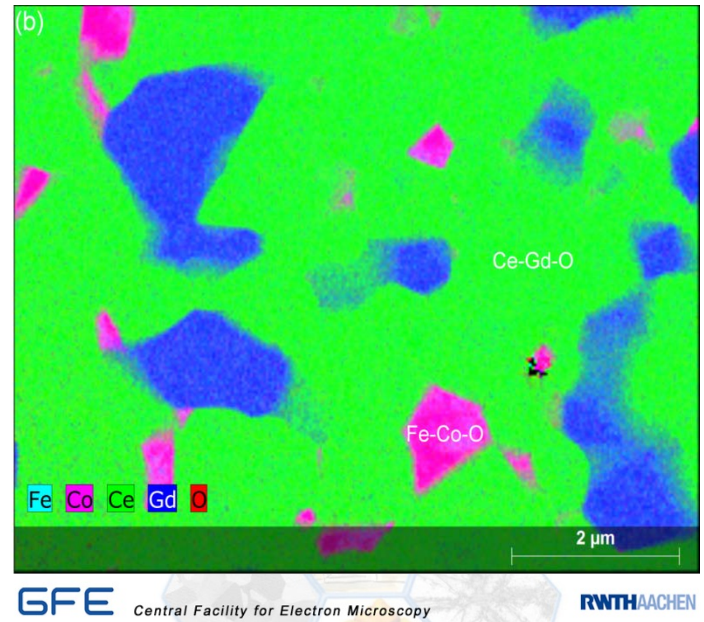
60 wt% $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ - 40 wt% $FeCo_2O_4$





$$permeance = \frac{j_{O_2}}{\ln \frac{p'_{O_2}}{p''_{O_2}}} = \frac{1}{L} \cdot \frac{R}{16 \cdot F^2} \cdot \sigma_i T$$

- Ionic conductivity of CGO is rate limiting if surfaces are activated

approximate composition of the perovskite phase is 15% Ce on A-site, 25% Co on B-site, i.e. $Gd_{0.85}Ce_{0.15}Fe_{0.75}Co_{0.25}O_3$ (GCFCO)

Ramasamy et al. J. Am. Ceram. Soc., 99 [1] 349–355 (2016)

Ramasamy et al. Ceram Sci Eng Proc, ICACC 2016, accepted manuscript

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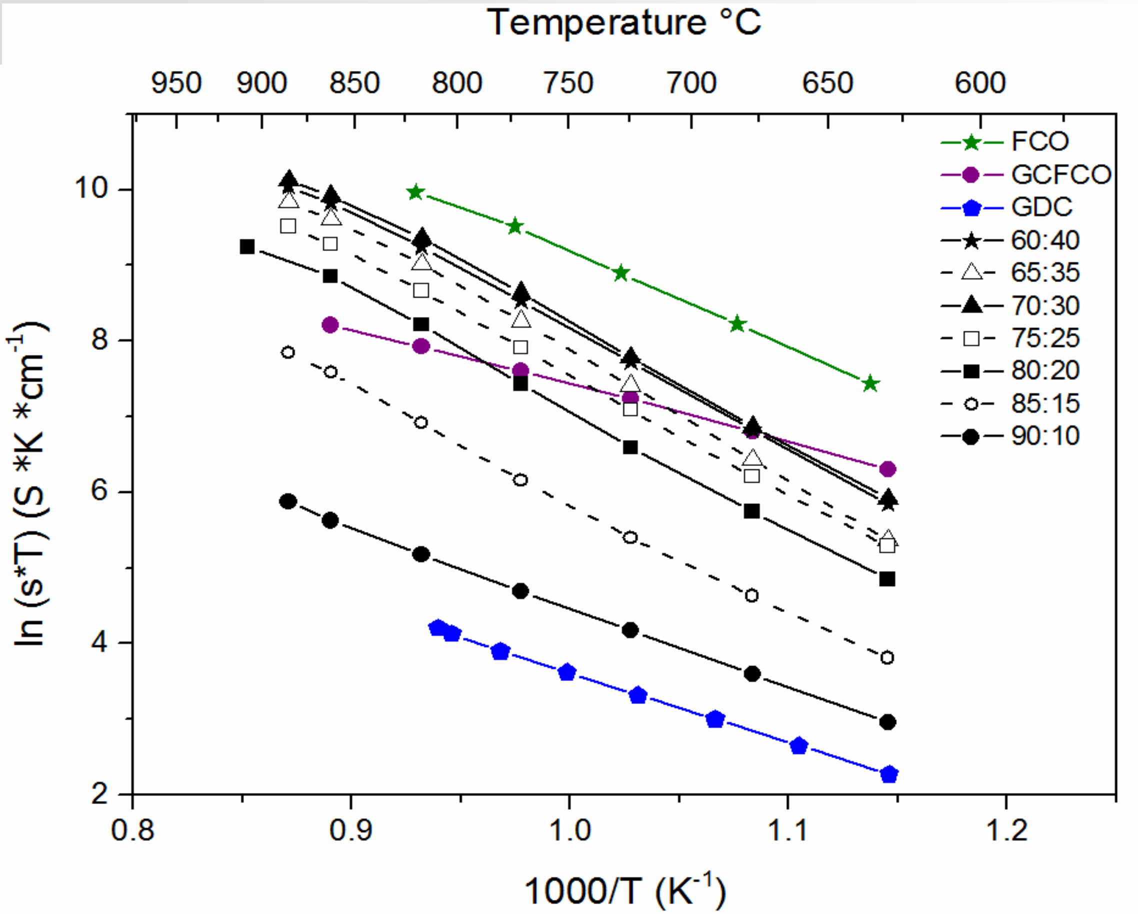
Electrical conductivity



- GCFCO is a pure electronic conductor contributing to ambipolar conductivity
- Electronic conductivity still dominant for 20 wt% spinel content
- Percolating network present in as low as 10 wt% of spinel content

Ramasamy et al. Ceram Sci Eng Proc, ICACC 2016, accepted manuscript

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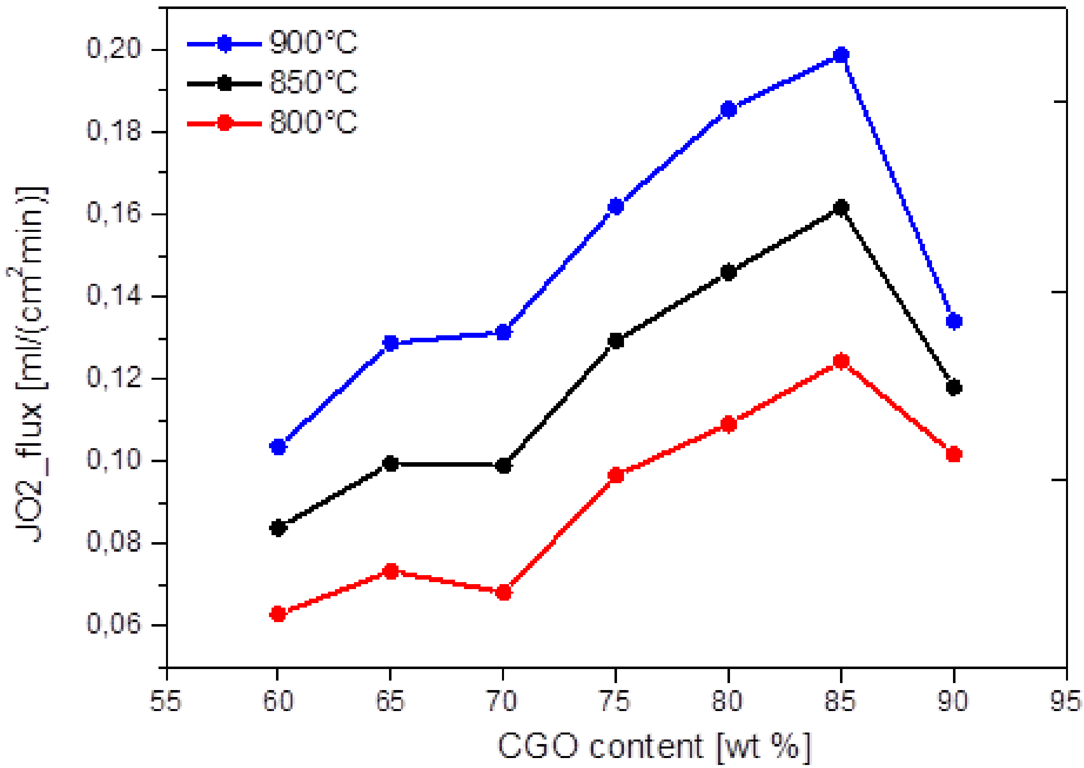
Oxygen permeation rate



CGO-FCO in wt %	CGO-FCO in vol %
60:40	54:46
65:35	59:41
70:30	64.5:35.5
75:25	70:30
80:20	76:24
85:15	81.5:18.5
90:10	87.5:12.5

- Maximum permeation rate achieved using 15 wt% spinel

Ramasamy et al. to be submitted

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Performance of selected OTM materials
LSCF vs 85CGO-15FCO

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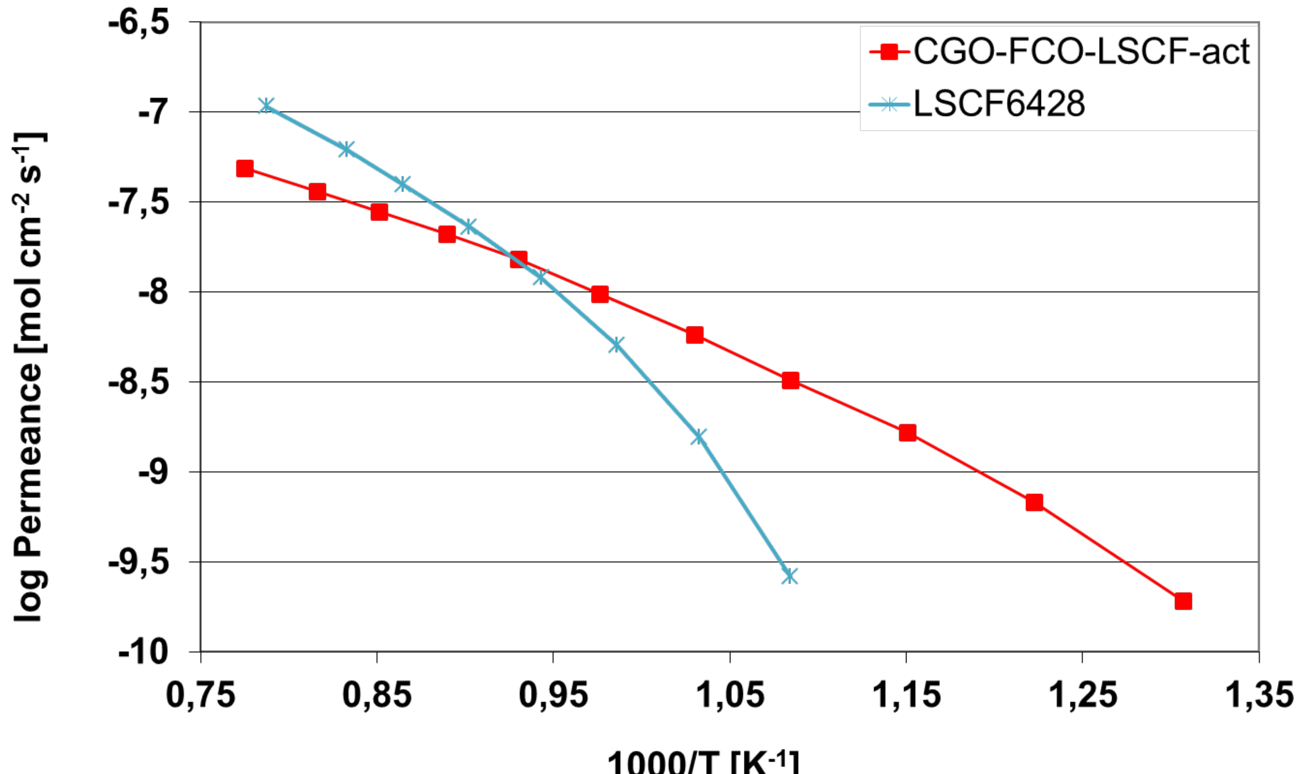

- $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) as reference material and ready for scale up
- Dual phase composites more stable, but less mature. Selection for scale up made for 85 wt% $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ – 15 wt% $FeCo_2O_4$ (CGO-FCO)

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Sequential Tape Casing

Requirements for membranes according to transport Model:

- Thin, defect free membrane layer on a porous support

Tape casting + screen printing:

Tape casting support
(slurry obtaining pore former)

⇩

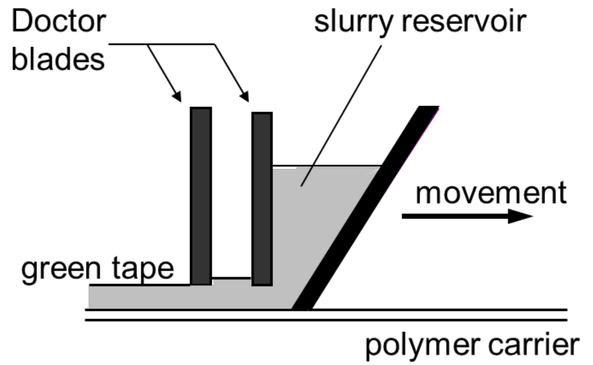
Pre-sintering Support

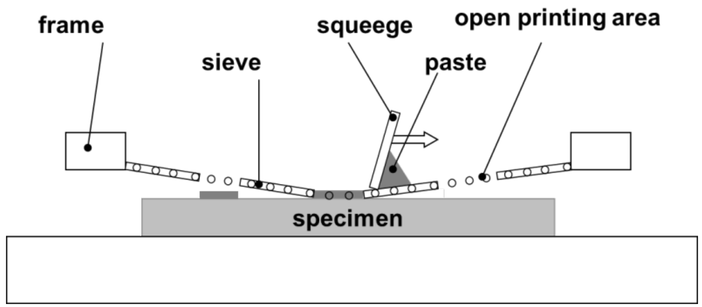
⇩

Screen printing on support

⇩

Composite sintering





Sequential tape casting:

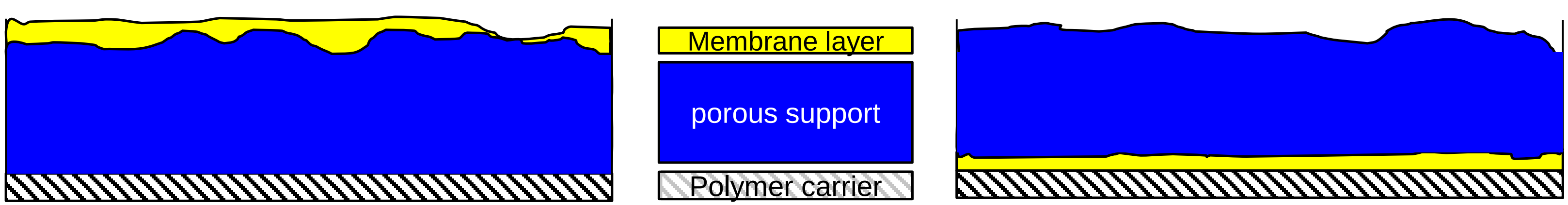
Tape casting Membrane layer
(slurry without pore former)

⇩

Tape casting Support
(slurry containing pore former)

⇩

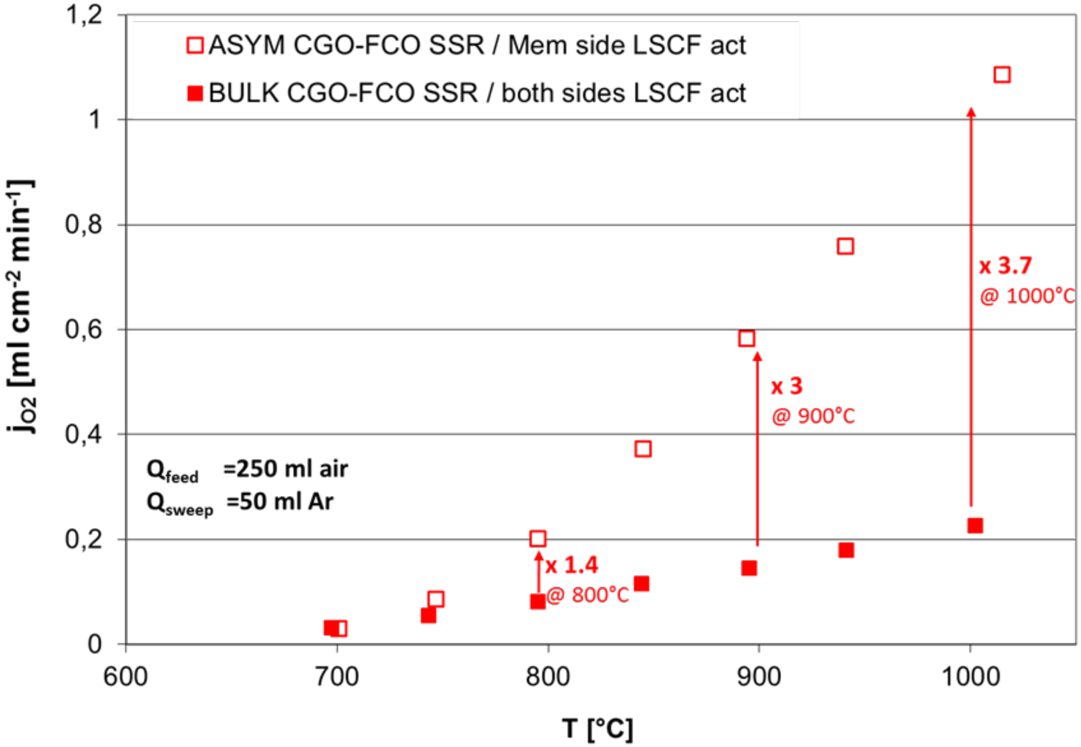
Co-firing
Membrane layer + support

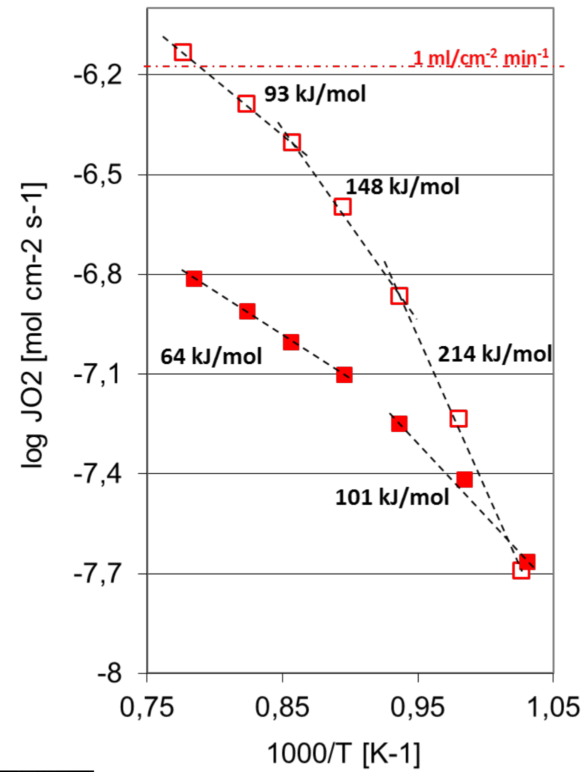


Tape casting + screen printing

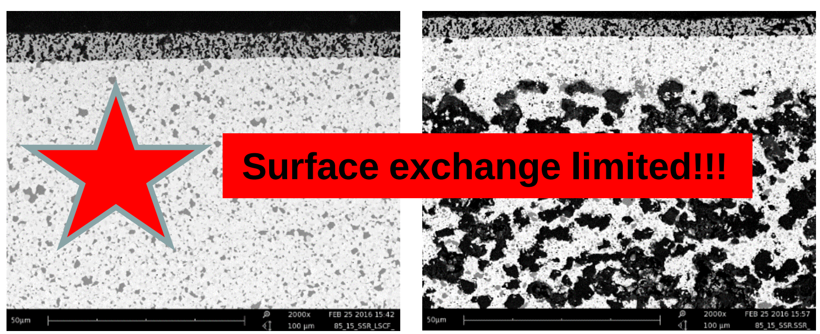
Sequential tape casting

Membrane Development
$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ - $FeCo_2O_4$





Activation layer: 6 µm
Thickness ~ 1000 µm



Activation layer: 5 µm
Membrane layer: 14 µm
Support porosity: 41 %
Thickness ~ 700 µm

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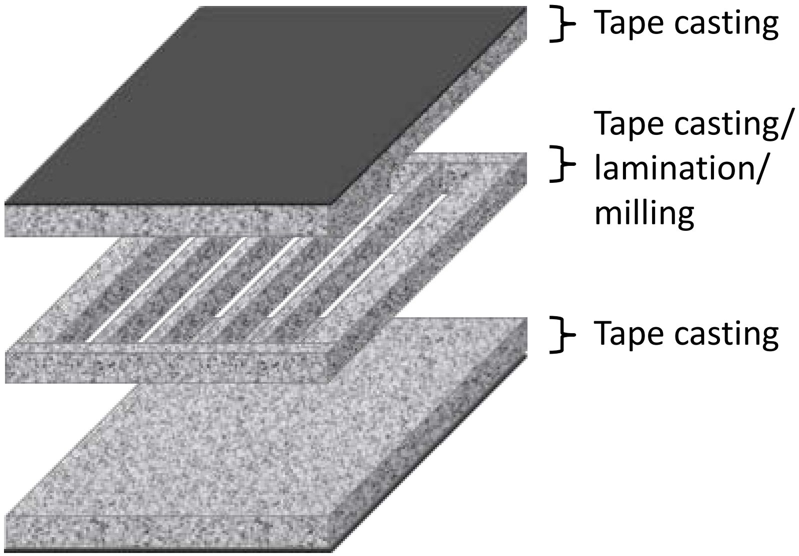
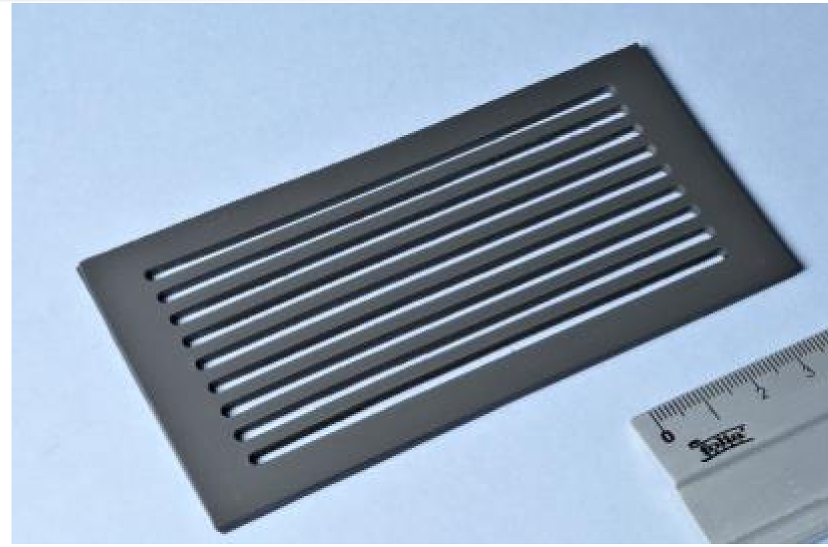
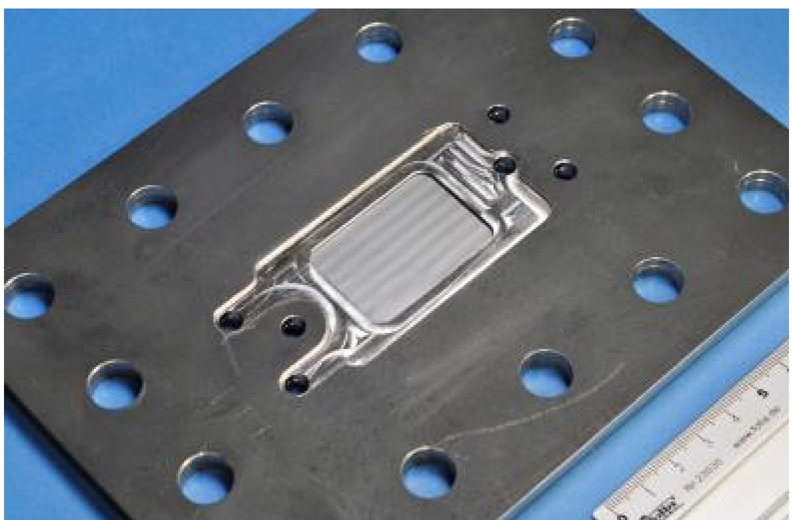
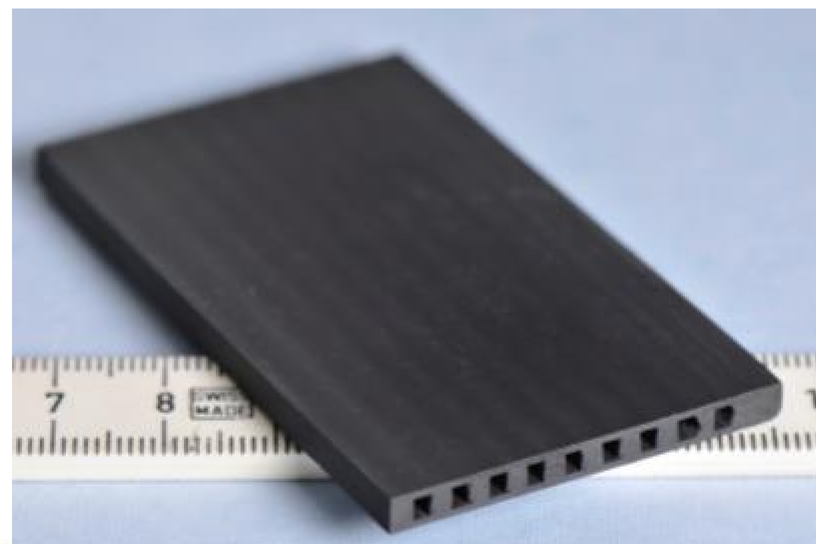
Scale up of LSCF membranes









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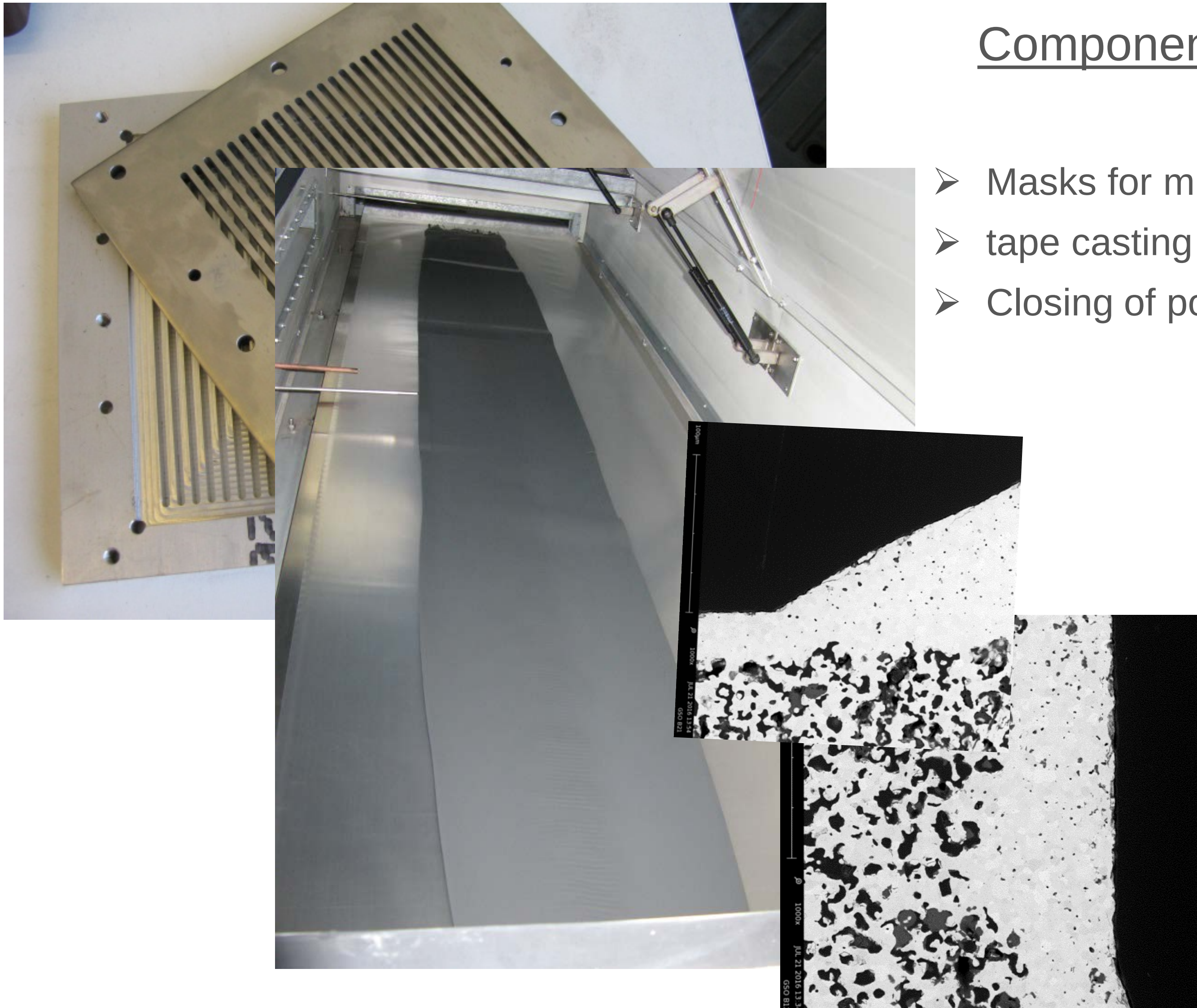
Scale up
LSCF



Component 7 x 10 cm^2

- Masks for milling process
- tape casting in larger scale
- Closing of porous edges

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Acknowledgement

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DTU Danmarks Tekniske Universitet

The University of Queensland Australia

CSIC

Imperial College London

Latvijas Universitāte Anno 1919 University of Latvia

RSE Ricerca Sistema Energetico

RWTH Aachen University

INABENSA

University of Twente.

thyssenkrupp

The Linde Group

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Seventh Framework Programme

THANK YOU FOR YOUR ATTENTION