CERAMIC GAS SEPARATION MEMBRANES FOR THE USE IN CCSU

12.03.2021 I WILHELM A. MEULENBERG, STEFAN BAUMANN, OLIVIER GUILLON

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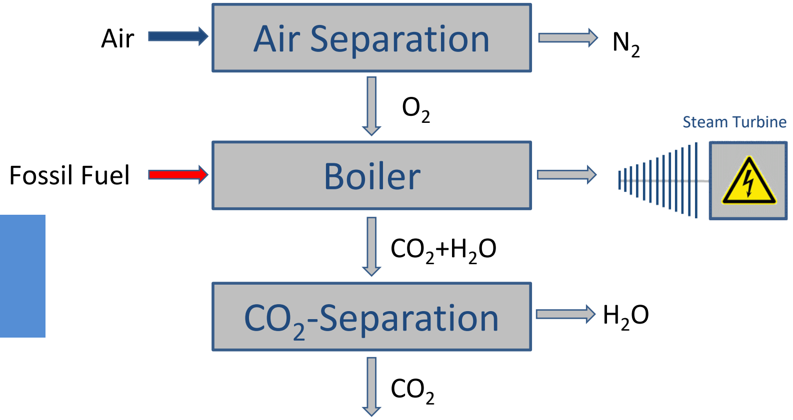
Applications of Mixed Ionic Electronic Conductors

Gas Supply

Power Plants, Cement Industry (GREEN-CC), Glas Industry, Steel Industry, Medical, etc.

Separation of single gases
e.g. O_2, H_2, CO_2



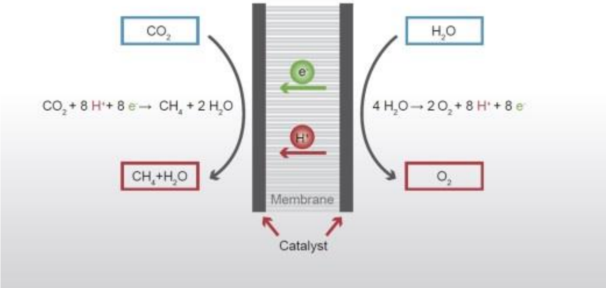
Oxyfuel Combustion

Membrane Reactors

Syngas-Production, Methanation, Dehydration, Water Gas Shift Reaction, etc.

CO_2 Utilisation
Commodity Chemicals /
Chemical Energy Carriers
Environmental Applications

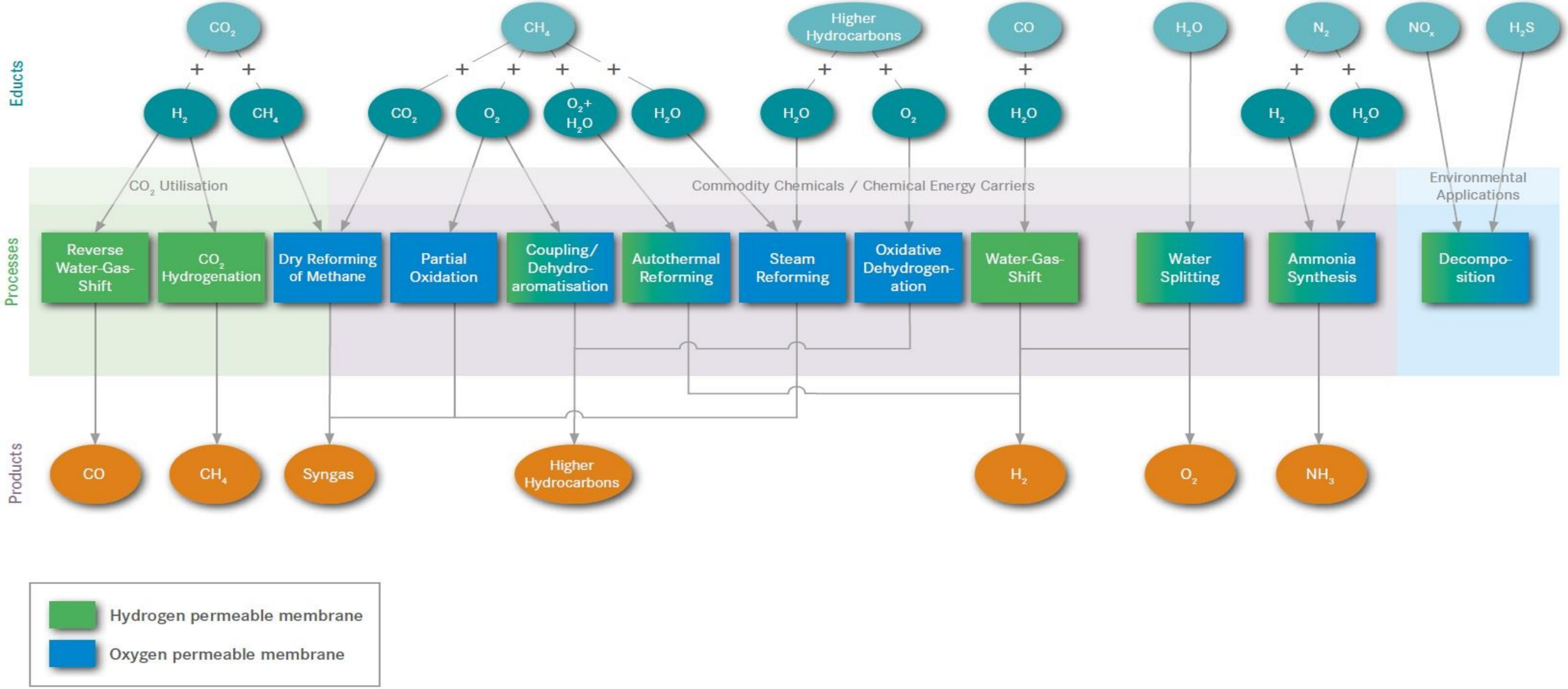
$CO_2 + 4\ H_2 \rightarrow 2\ H_2O + CH_4$



Methane Synthesis

Potential Applications of Membranes in Catalytic Membrane Reactors (CMR)

CO_2-Utilisation, Chemical Energy Carriers, Environmental Applications



W. Deibert, M. E. Ivanova, S. Baumann, O. Guillon, W. A. Meulenberg
Journal of Membrane Science (2017)

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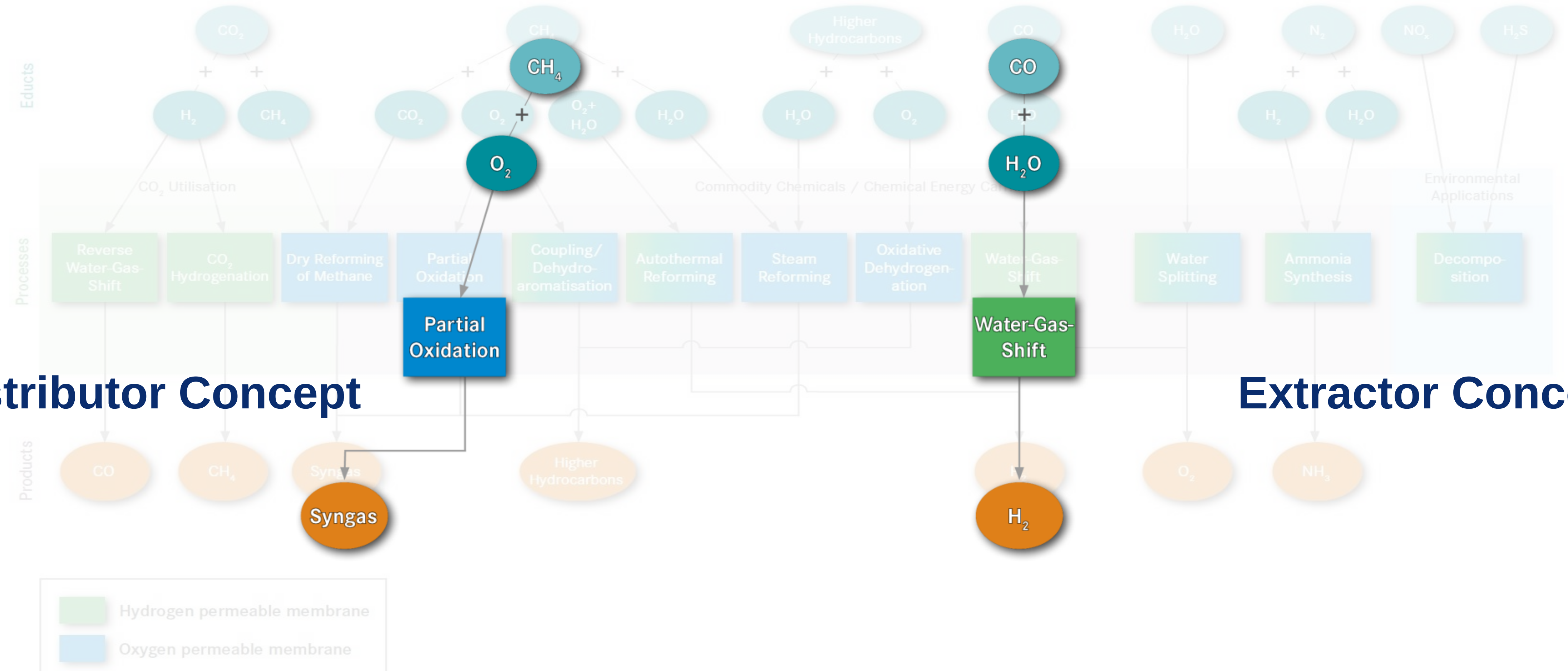


Distributor Concept

Extractor Concept

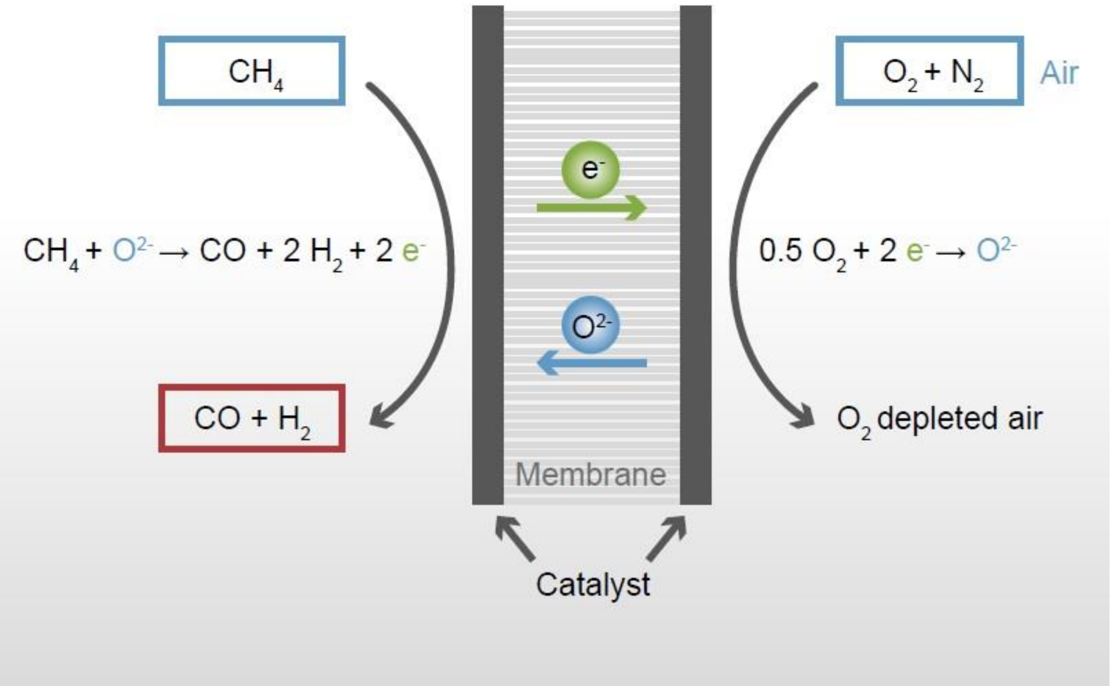
W. Deibert, M. E. Ivanova, S. Baumann, O. Guillon, W. A. Meulenberg
Journal of Membrane Science (2017)

Examplary Catalytic Membrane Reactors

Catalytic Partial Oxidation of Methane
Production of Syngas

Reaction: **$CH_4 + 0.5\ O_2 \rightarrow CO + 2\ H_2$**

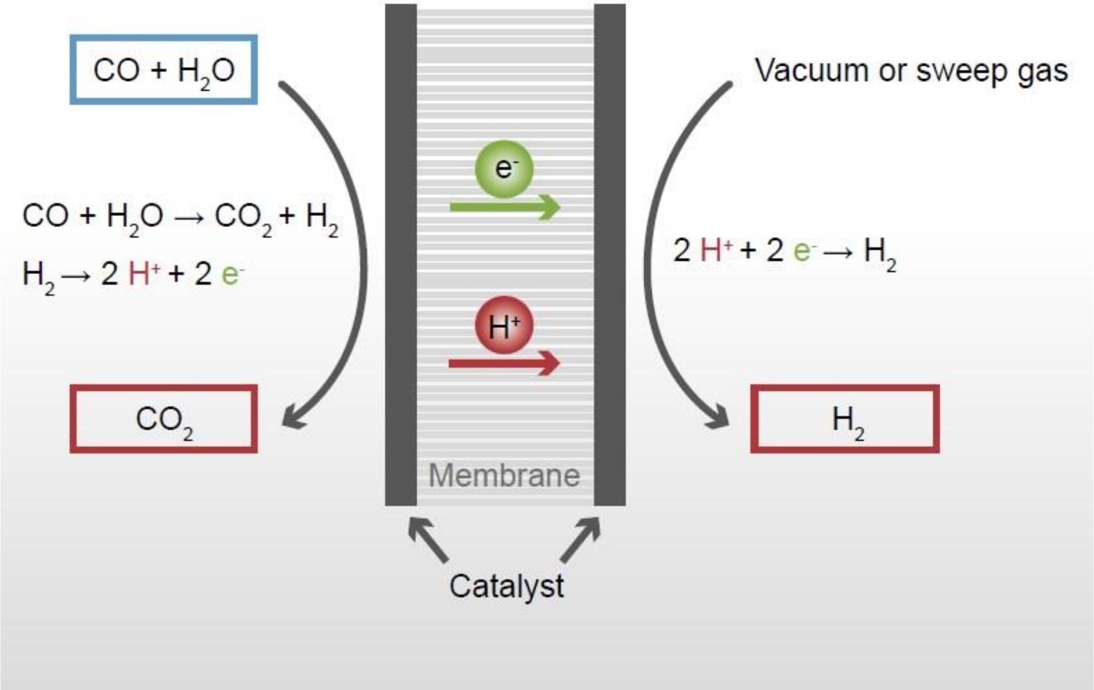
T = 900 °C, catalyst: Ni



Water-Gas Shift Reactor
Separation of Pure Hydrogen

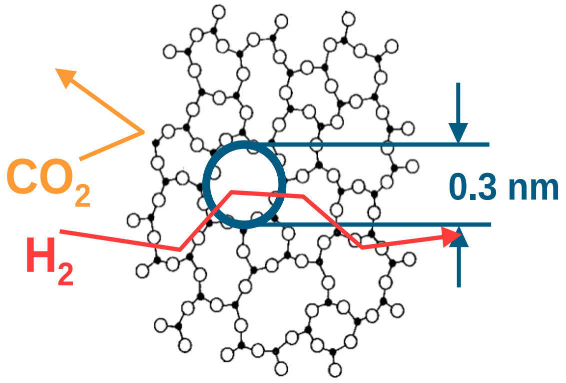
Reaction: **$CO + H_2O \rightarrow CO_2 + H_2$**

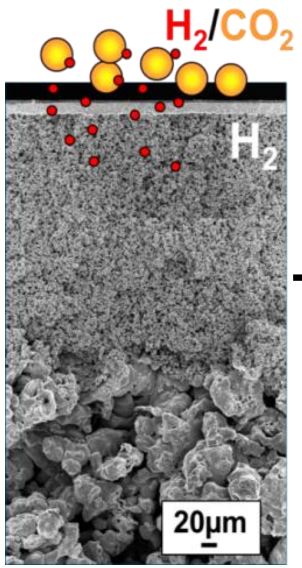
T = 550-900 °C



Gas Separation Membranes

Microporous Membranes

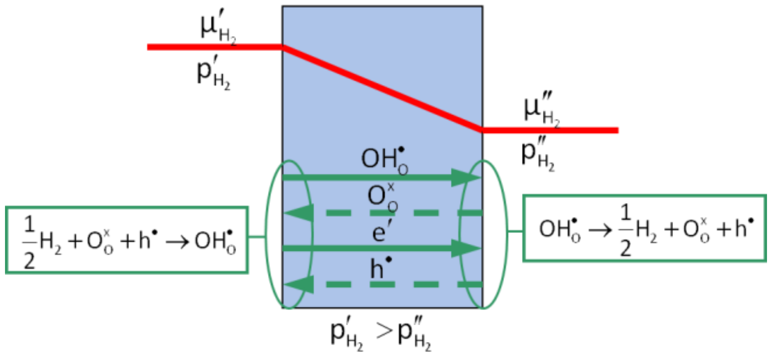


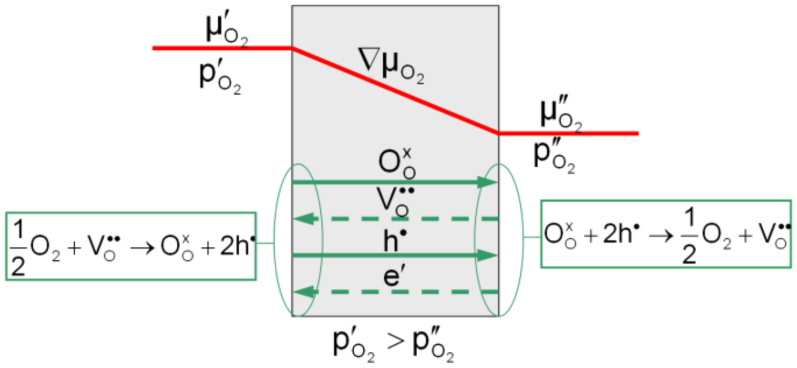


SiO_2 Top layer

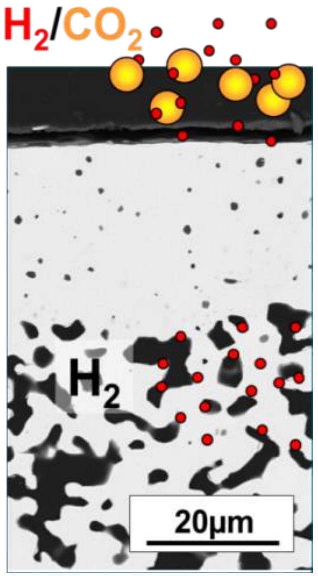
$T \approx 200°C$

Dense Mixed Ion-Electron Conducting Membranes



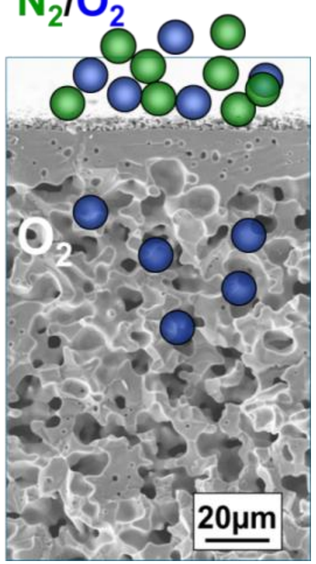


$La_{6-x}WO_{12-\delta}$



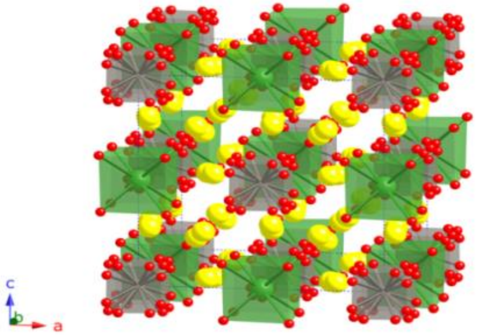
T = 400-900°C

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$



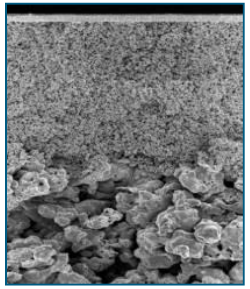
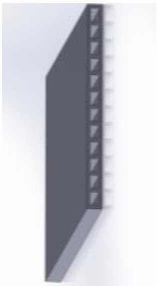
Development Strategy and Challenges

Materials Development



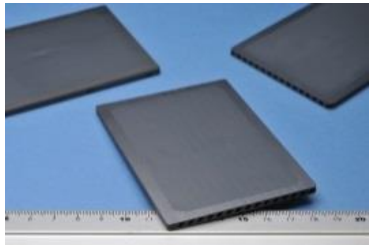

- high ionic / electronic conductivity
- stability in agressive environment
- thermal stability
- compatibility
- low cost material
- availiability of materials

Microstructuring

- thin films for high performance
- porous catalytic layers
- low polarisation in support
- no deformation of membrane
- no delamination of single layers
- thermomechanical stability

Component Manufacturing

- adjustment of sintering steps
- module design and sealing
- no deformation of membrane
- thermomechanical stability
- fast, scalable and low cost processing technologies

Scientific work packages

GREEN-CC Project (EU - FP7)

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 Simulation
- Integration Scenario
- Cost Estimations

Imperial College London

DTU Danmarks Tekniske Universitet

CSIC

RWTH AACHEN UNIVERSITY

LATVIJAS UNIVERSITĀTE ANNO 1919 UNIVERSITY OF LATVIA

RSE Ricerca Sistema Energetico

THE UNIVERSITY OF QUEENSLAND AUSTRALIA

UNIVERSITY OF TWENTE.

ThyssenKrupp

THE LINDE GROUP

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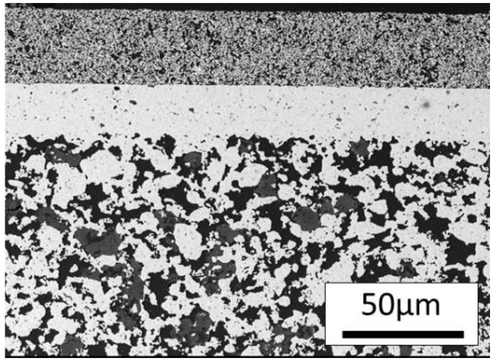
Graded Membranes for Energy Efficient New Generation Carbon Capture Process
Grant Agreement Number 608524

SEVENTH FRAMEWORK PROGRAMME

Selected Materials

Two Route Strategy

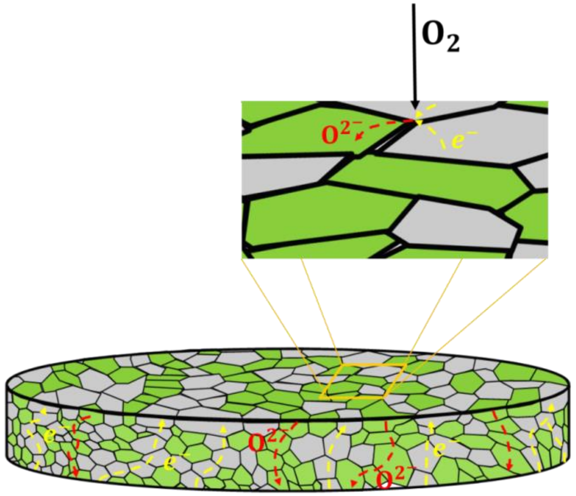
Single phase perovskites

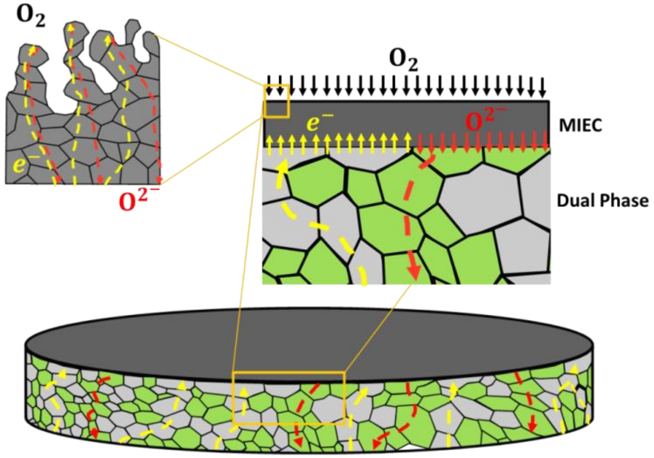


$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$
(reference)

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

Dual phase composites





Ionic conductor:
- ✓ Doped ceria
- ✓ stabilized zirconia

Electronic conductor:
- ✓ Spinels
- ✓ doped ZnO
- ✓ perovskites

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Composite Oxygen Transport Membranes

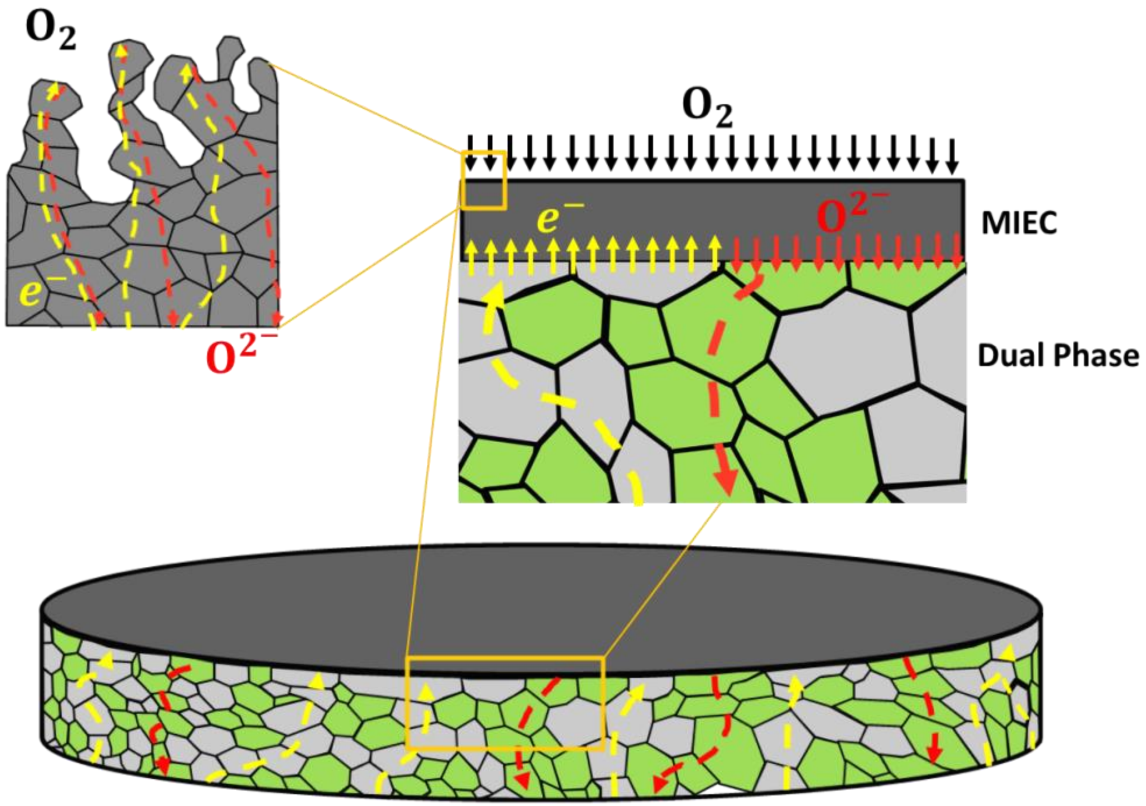
Cer-Cer Composite Concept

- Ionic conductor: $Ce_{0.8}Gd_{0.2}O_{2-d}$ (**CGO**)
  Electronic conductor: $FeCo_2O_4$ (**FCO**)

- Surface activation necessary even at high membrane thicknesses due to short length of triple phase boundaries (**TPB**)

- Surface activation (lab conditions):
  $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (**LSCF**)

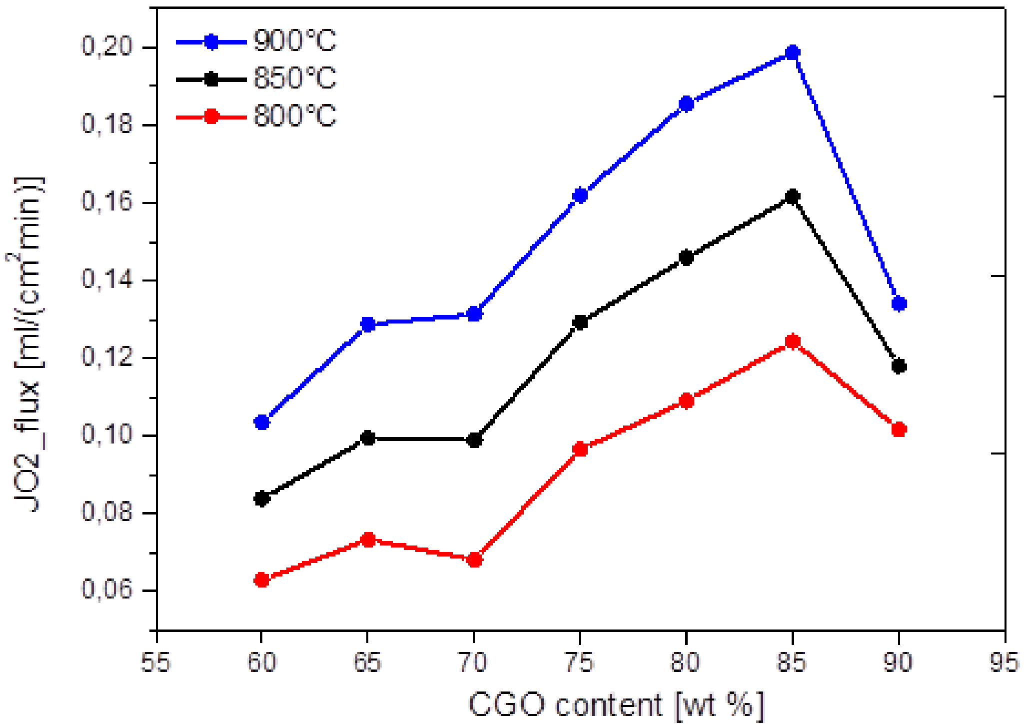
- Surface activation (in application):
  composite porous backbone infiltrated with tailored catalysts

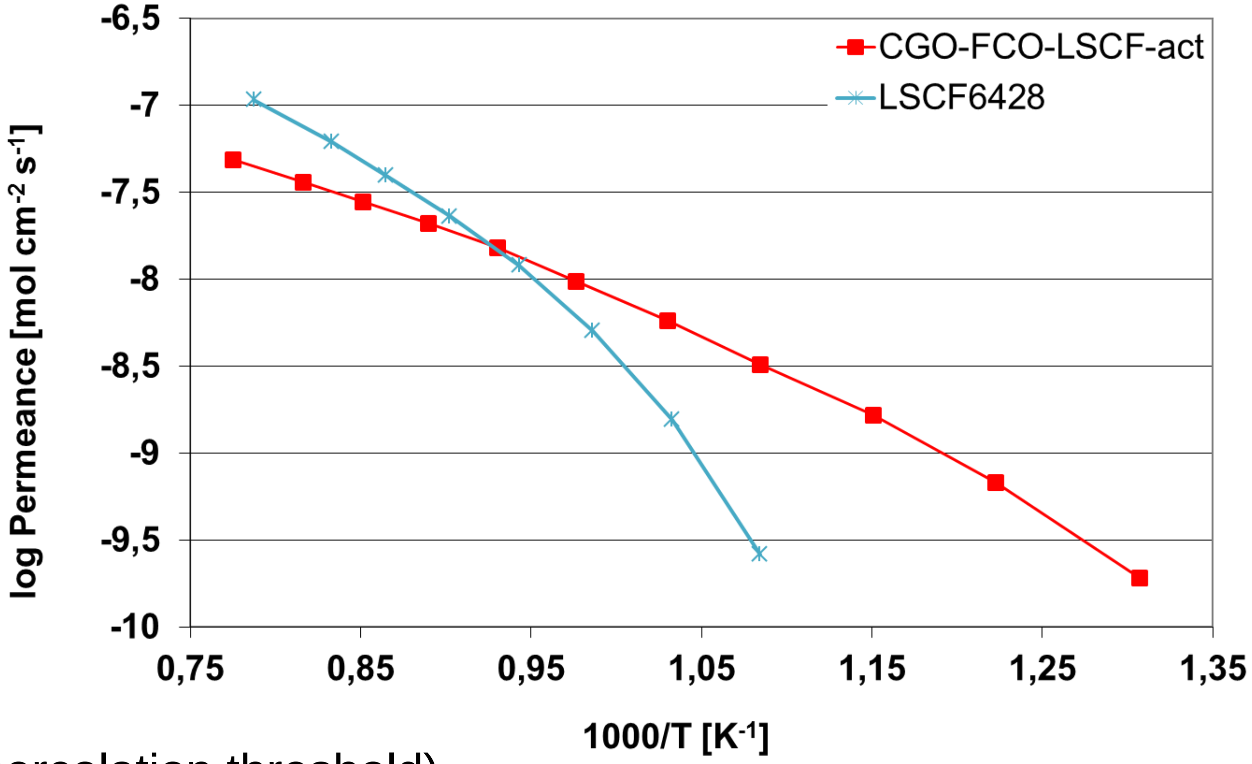


M. Ramasamy et al., J Amer Ceram Soc (2016)

Selected Materials

Dual Phase Composite, e.g. CGO-FeCo2O4





- Maximum performance at 85wt% CGO (above percolation threshold)
- Performance equal to LSCF @800-850 °C
- Stability in CO_2 and SO_2 (cf. WP3)

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Dual Phase OTM

Stability in Acid Gases (SO_x)

- 85:15 wt%-ratio **non-activated**

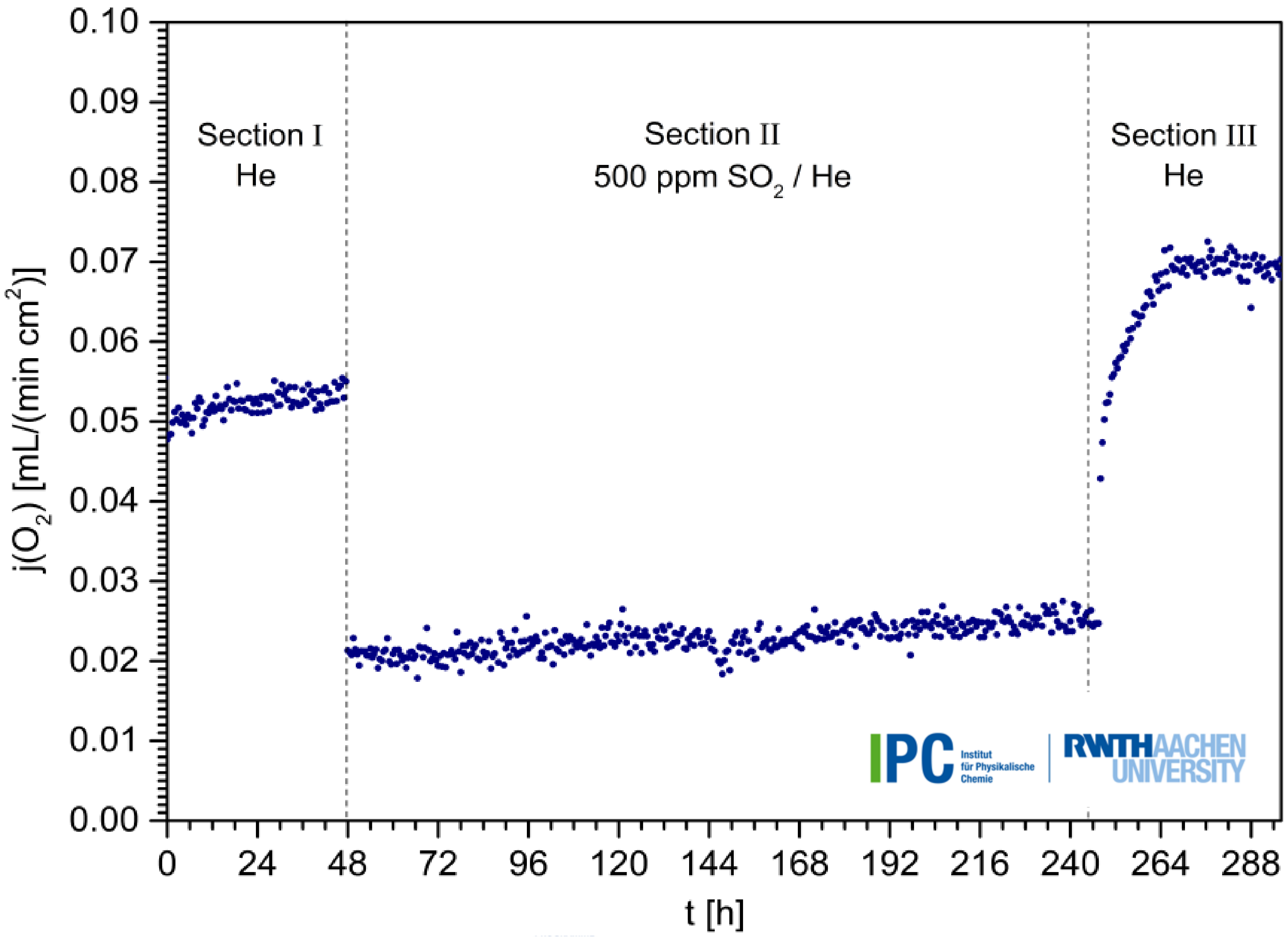
  → low permeation rates
  → surface exchange sensitive

- **Instantaneous drop** of permeation rate
- **Stable performance** in 500 ppm SO_2
- **full flux recovery**
- Post-test analysis confirmed **no sulphate** formation

→**competitive adsorption**

- Slight increase in performance due to **surface roughening**

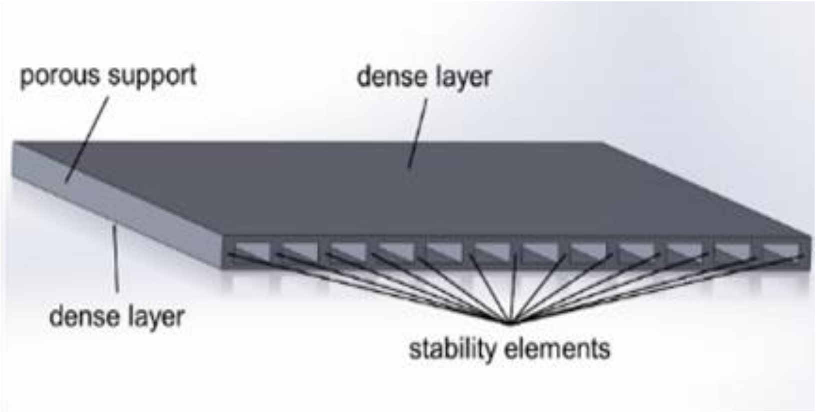
M. Ramasamy et al. J Membr Sci (2017)



Objectives Proof of Concept

Design and build of a membrane module

- Planar stacks with asymmetric membranes
- Effective area at least 300 cm^2
- 4 end operations



Proof of performance

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

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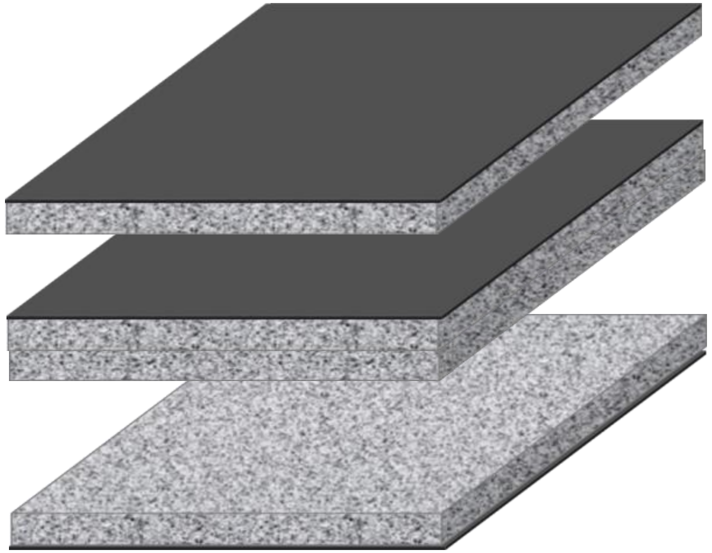
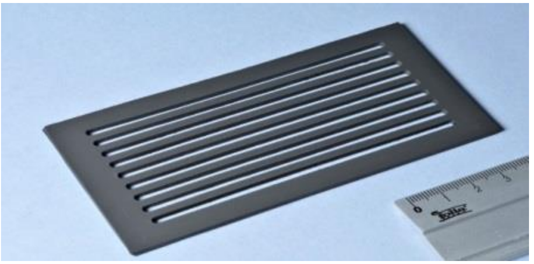
Development of Membrane Components

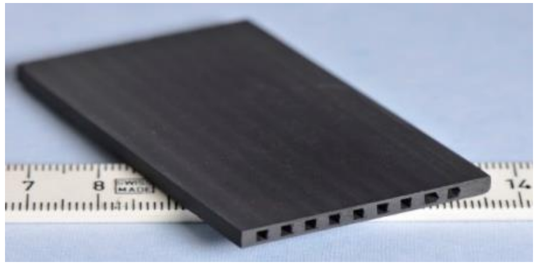
Lamination of single tapes

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$

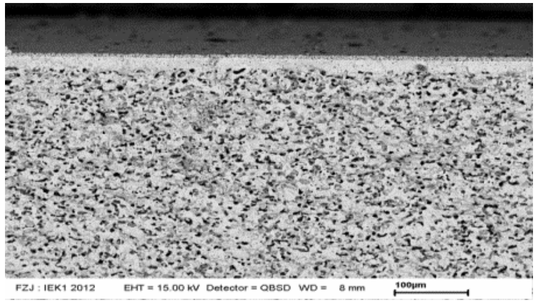


- Tape casting
- Tape casting/ cutting or milling
- Tape casting

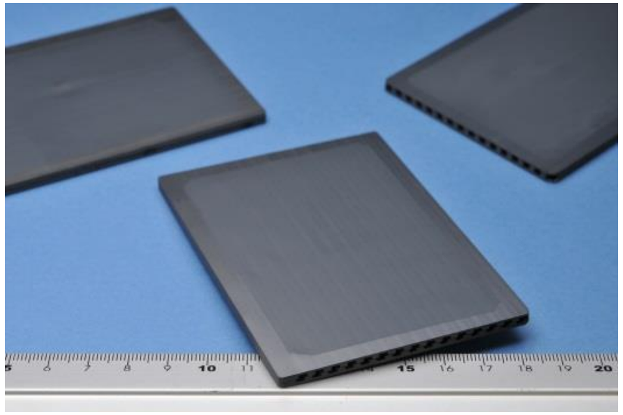


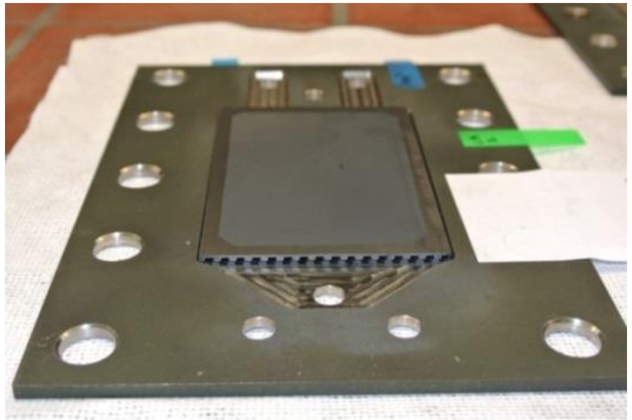


Size: 4 x 7 cm^2



Assembling of OTM Module:
Area: 420 cm^2





Size: 7 x 10 cm^2

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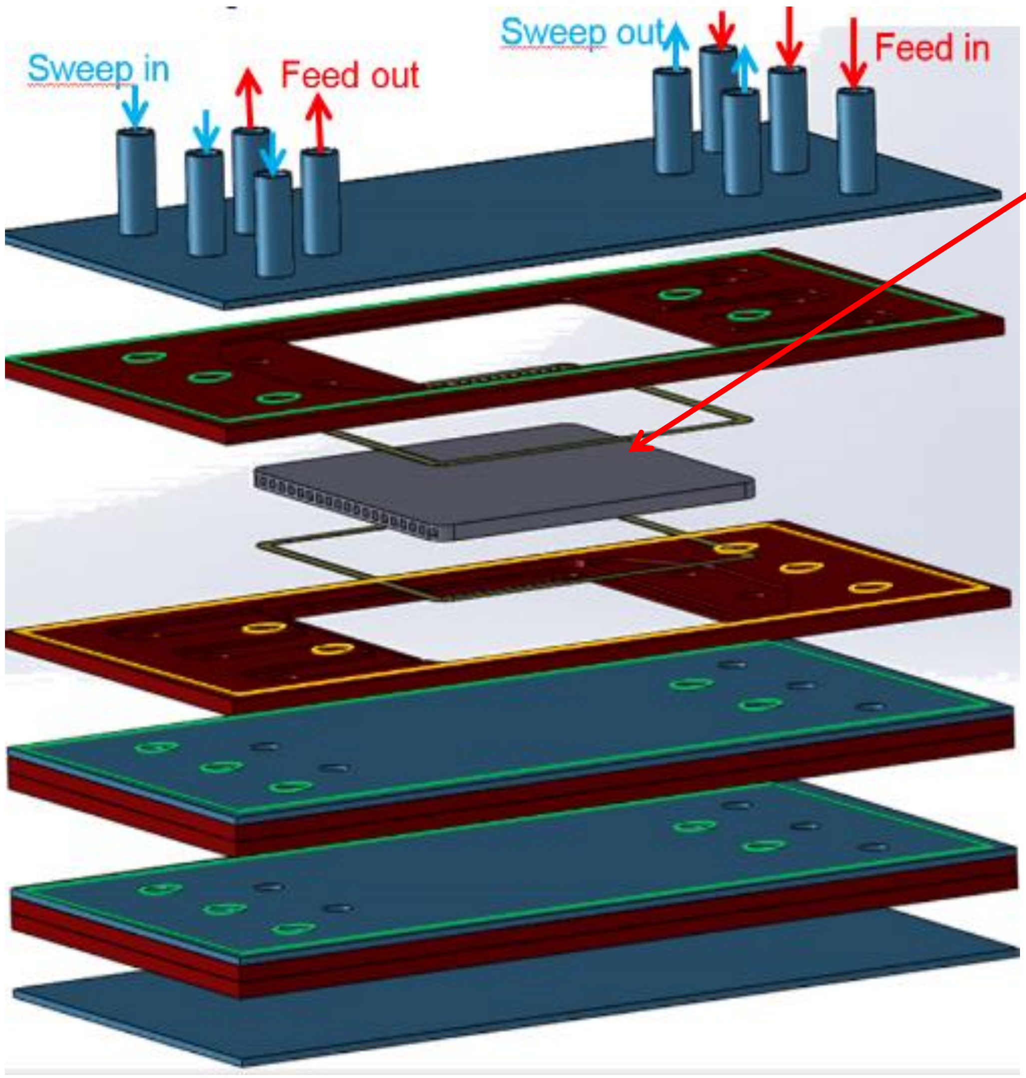
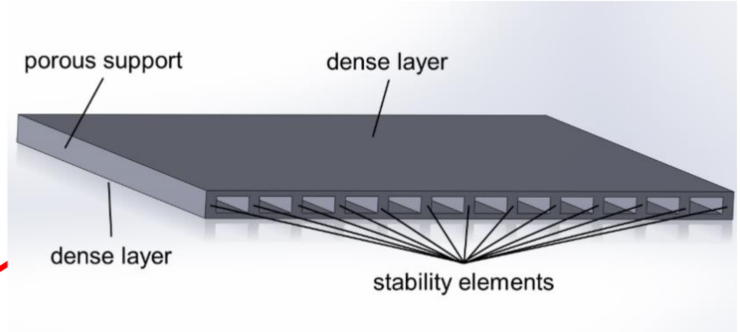
Simulation-Supported Module Design

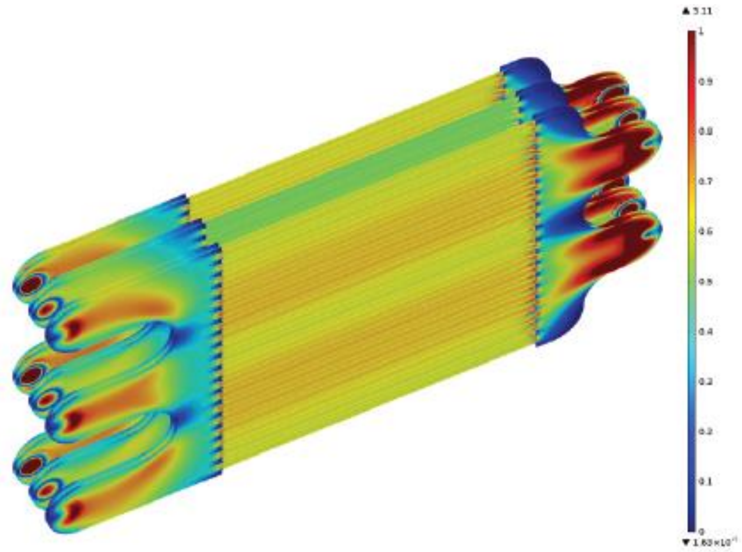




Membrane element

Key issues/activities

- Mechanical stress analysis
- Homogeneous gas flow
- Joining techniques for ceramic-metal materials



CFD modeling shows homogeneous velocity distribution of air flow

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Thank you for your attention