IONIC CONDUCTING CERAMIC MEMBRANES

From Laboratory to Market

18.10.2019 I W. A. MEULENBERG, S. J. HARBOE, W. DEIBERT, M.E. IVANOVA, F. SCHULZE-KÜPPERS, S. BAUMANN

UNIVERSITY OF TWENTE.

JÜLICH Forschungszentrum

Outline –
Ionic Conducting Cells – From Laboratory Scale to Market

- Potential applications of **mixed ionic** electronic conductors
- Development strategies and microstructures
- From membrane button cell to industrial relevant size – manufacturing challenges
- Planar module designs
- Cost evaluation – examples OTM for carbon capture in a oxyfuel cement plant and SOFC

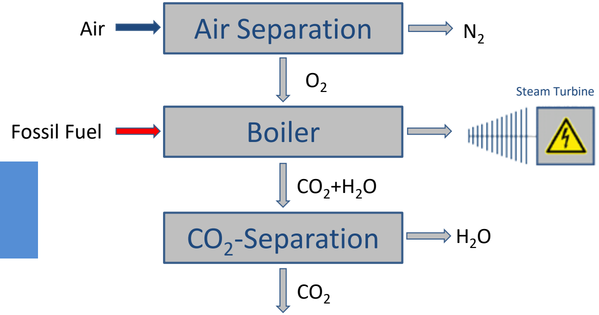
- This lecture shows concepts and is not focussed on a single material

Applications of Mixed Ionic Electronic Conductors

Gas Supply

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

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



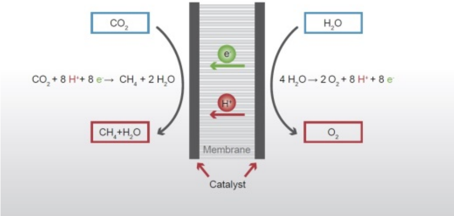
Oxyfuel Combustion

Membrane Reactors

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

CO_2 Utilisation
Commodity Chemicals /
Chemical Energy Carriers
Environmental Applications

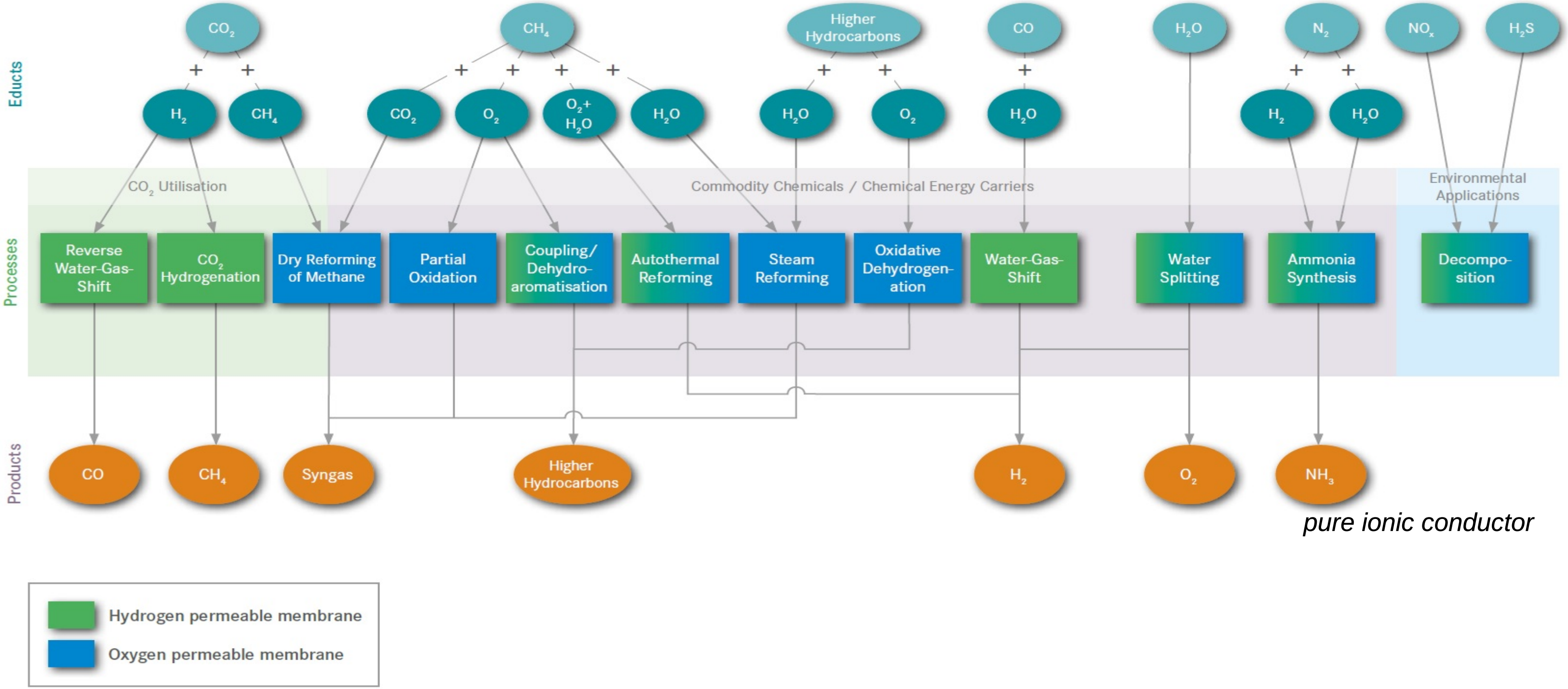
$$CO_2 + 4\ H_2 \rightarrow 2\ H_2O + CH_4$$



Methane Synthesis

Potential Applications of Membranes in Catalytic Membrane Reactors (CMR)

CO_2-Utilisation, Chemical Energy Carriers, Environmental Applications



pure ionic conductor

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

Potential Applications of Membranes in Catalytic Membrane Reactors (CMR)

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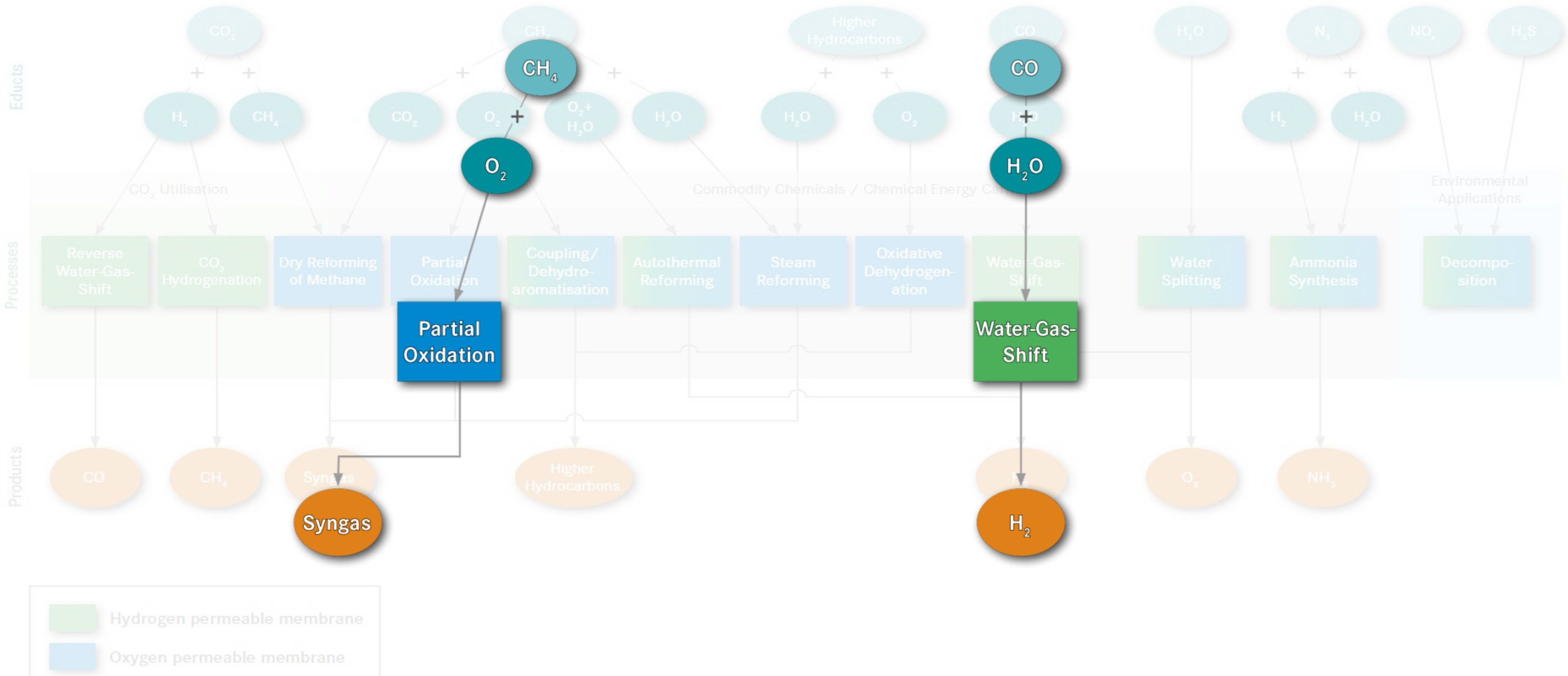


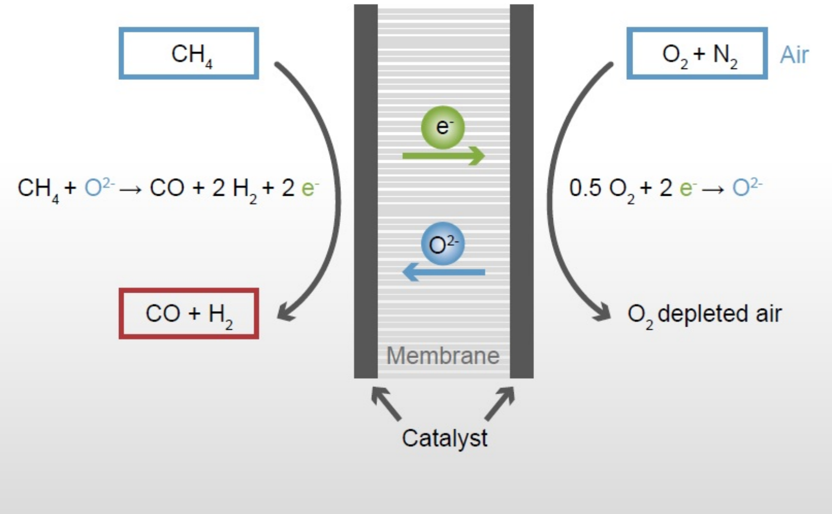
W. Deibert, M. E. Ivanova, S. Baumann, O. Guillon, W. A. Meulenberg
Journal of Membrane Science (2017)

Exemplary Catalytic Membrane Reactors

Catalytic Partial Oxidation of Methane
Production of Syngas

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

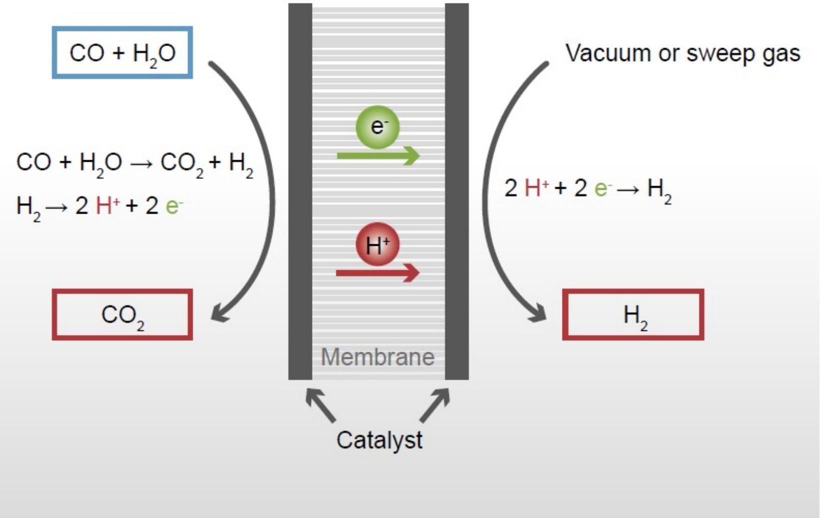
T = 900 °C, catalyst: Ni



Water-Gas Shift Reactor
Separation of Pure Hydrogen

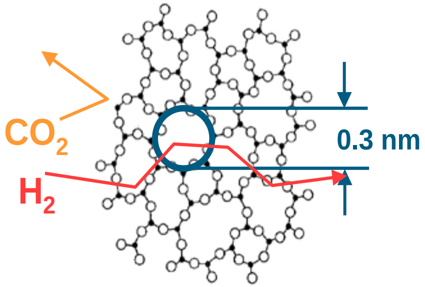
Reaction: **$CO + H_2O \rightarrow CO_2 + H_2$**

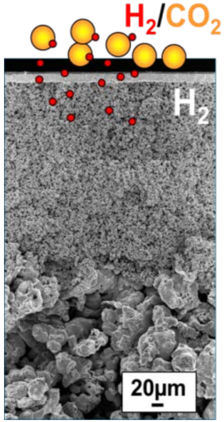
T = 550-900 °C



Ceramic Gas Separation Membranes

Microporous Membranes

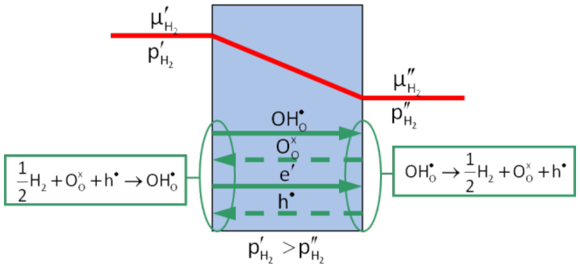


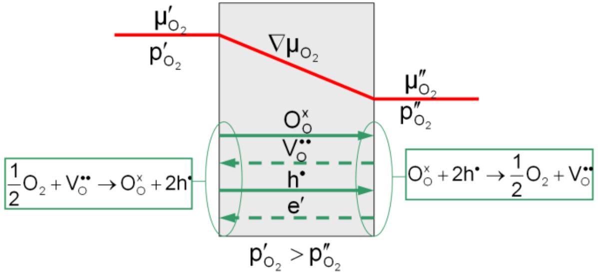


SiO_2 Top layer

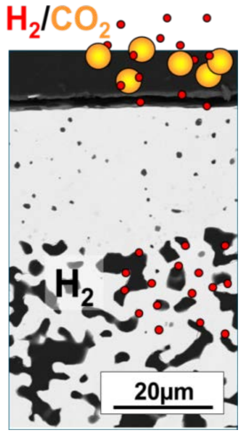
T ≈ 200°C

Dense Mixed Ion-Electron Conducting Membranes



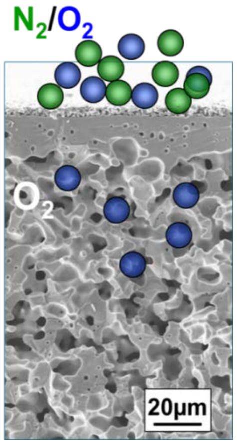


$La_{6-x}WO_{12-\delta}$

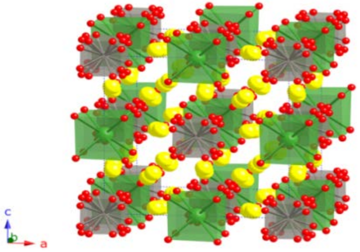
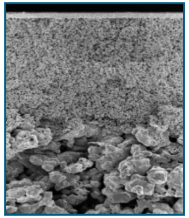
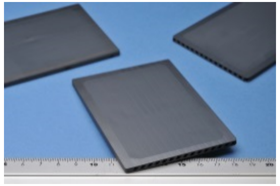


T = 400-900°C

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



Development Strategy and Challenges

Materials Development	Microstructuring	Component Manufacturing
 	 	 
• high ionic / electronic conductivity • stability in aggressive environment • thermal stability • compatibility • low cost material • availability of materials	• thin films for high performance • porous catalytic layers • low polarisation in support • no deformation of membrane • no delamination of single layers • thermomechanical stability	• adjustment of sintering steps • module design and sealing • no deformation of membrane • thermomechanical stability • fast, scalable and low cost processing technologies

Manufacturing Steps

e.g. Sequential tape casting and screen printing

Tape cast support
(slurry containing pore former)

⇩

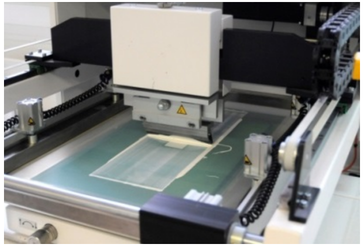
Pre-sintering of support

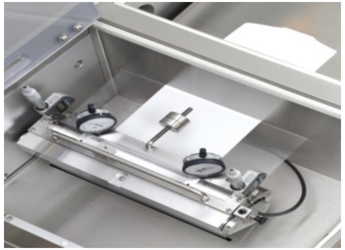
⇩

Screen printing on support

⇩

Co-sintering





Tape cast membrane layer
(slurry without pore former)

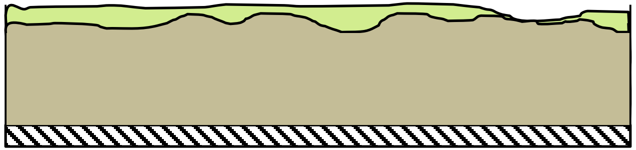
⇩

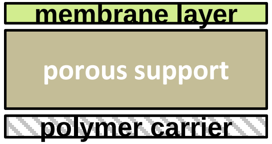
Tape cast support
(slurry containing pore former)

⇩

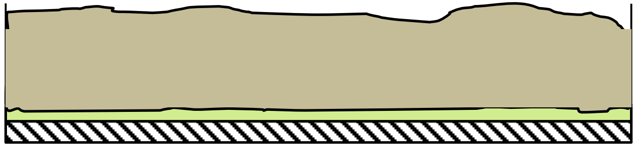
Co-sintering

Tape casting + screen printing





Sequential tape casting



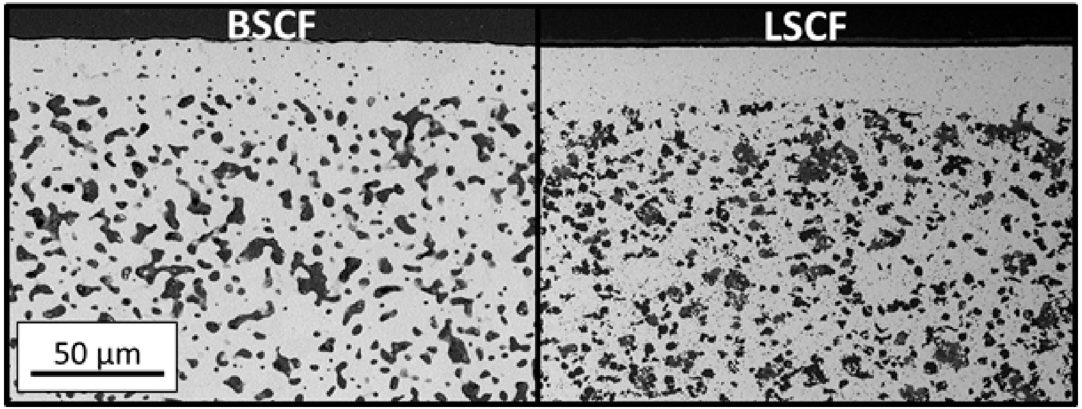
Similar Membrane Microstructure

….with different materials

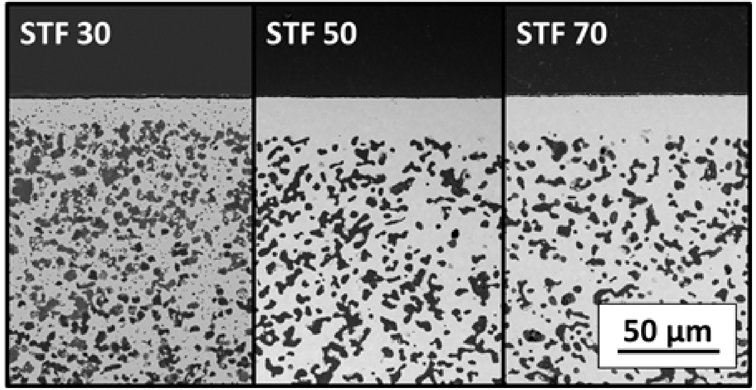
- Tape cast membranes with thicknesses between 15 and 30 µm
- Comparable porosity

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

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



$SrTi_{1-x}Fe_{x}O_{3-\delta}$

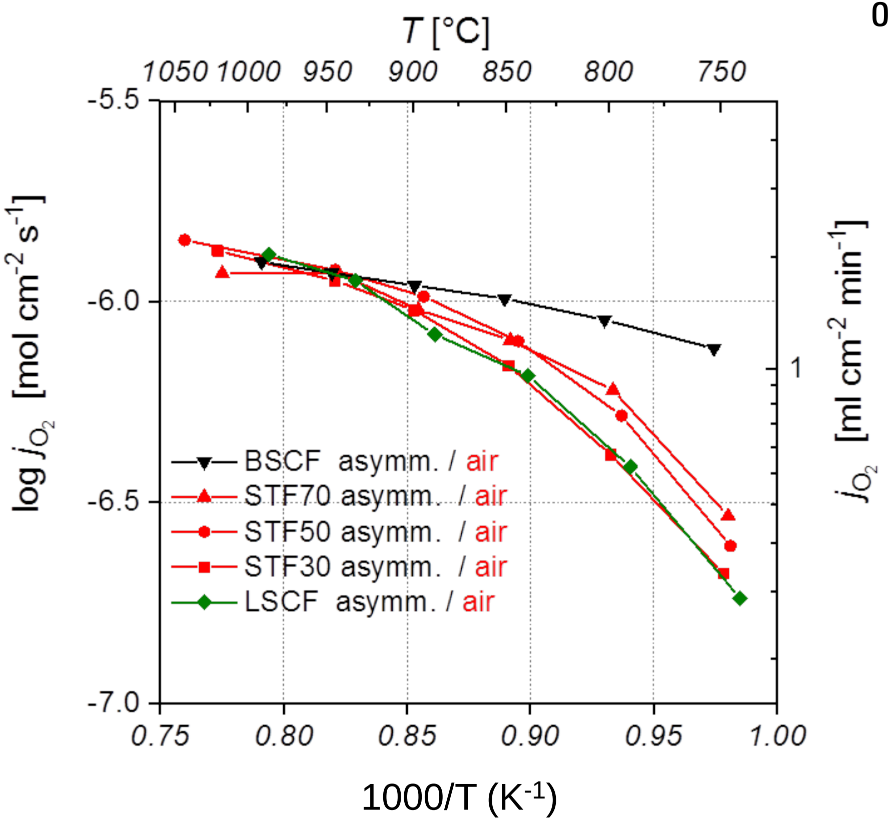


	Thickness Membrane (µm)	Porosity Membrane (%)	Porosity Support (%)
STF30	14	< 5	38
STF50	20	< 1	25
STF70	22	< 1	27
BSCF	25	< 5	26
LSCF	30	< 1	30

Similar Membrane Microstructure

….with different materials

- At high temperature flux nearly independent from material
- Polarisation effect in support

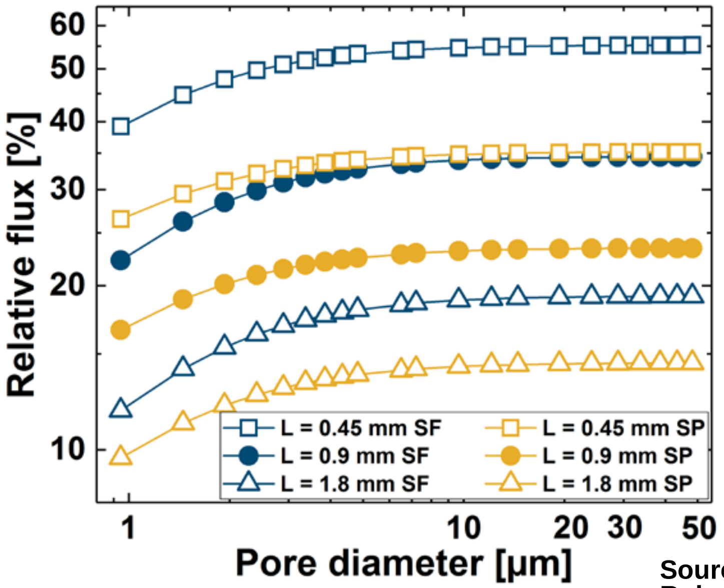


Polarisation depends on:

- Thickness
- Open porosity
- Pore diameter and shape
- Tortuosity
- Gas species

Modelling: Understanding the Limitations

Flux relative to thin bulk membrane

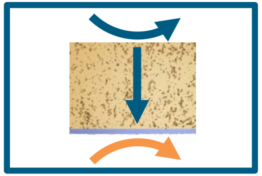


Large effect of substrate thickness

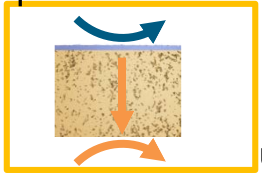
Small pores limit transport

Source: Unoako Unije and Robert Mücke

Support on feed side



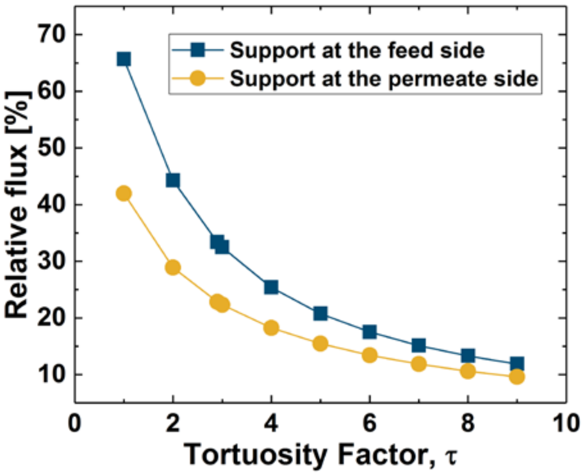
permeate side



U. Unije et al., *J. Membr. Sci.*, (2017)

Effect of tortuosity

Straighter pores significantly better



Effect of pore shape

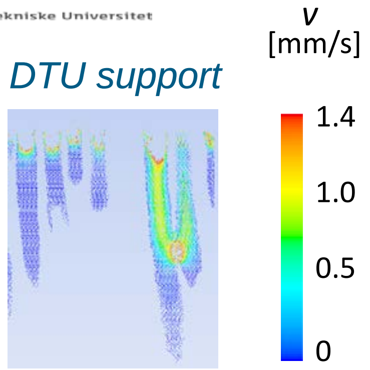
CFD / Fluent

µCT data phase inversion tape casting

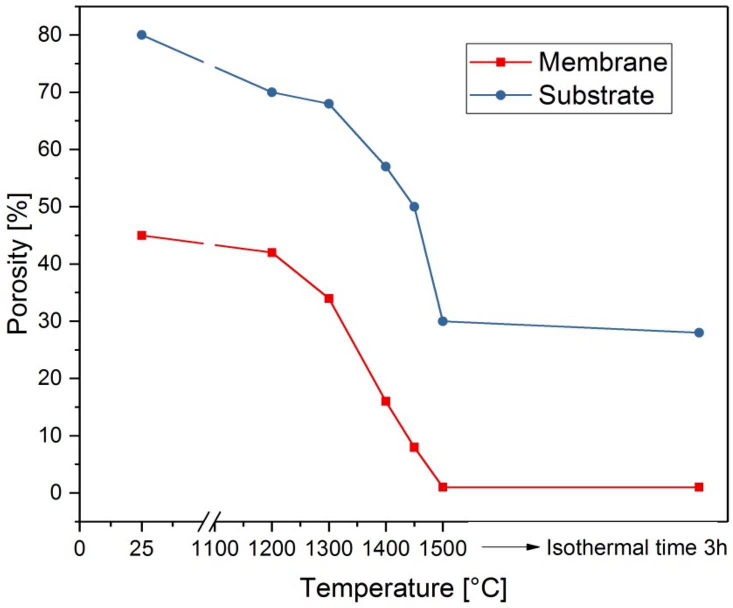
DTU Danmarks Tekniske Universitet

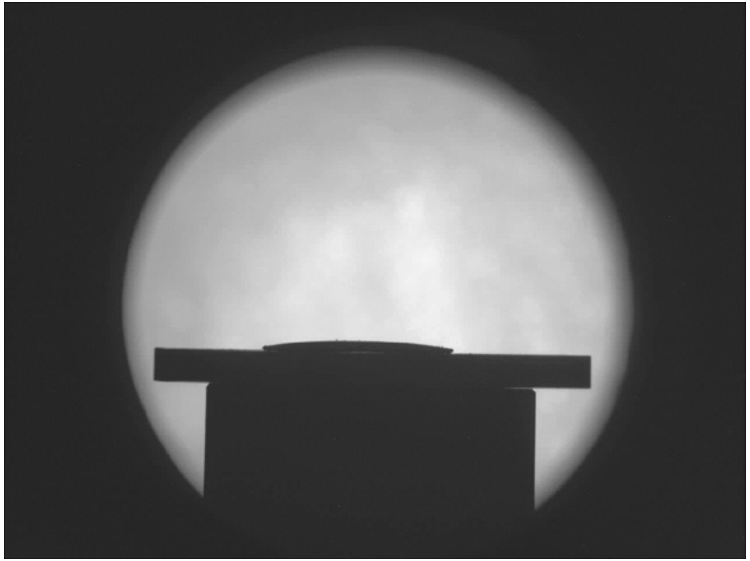
DTU support

U-shaped pores enhance flow velocity



Co-Sintering of Membrane and Support





Modelling of sintering behaviour possible

Video made by Kwati Leonhard in Jülich

Temperature above 1450°C is required for full densification of thin membrane

Curvature rate proportional to the difference in free sintering rates

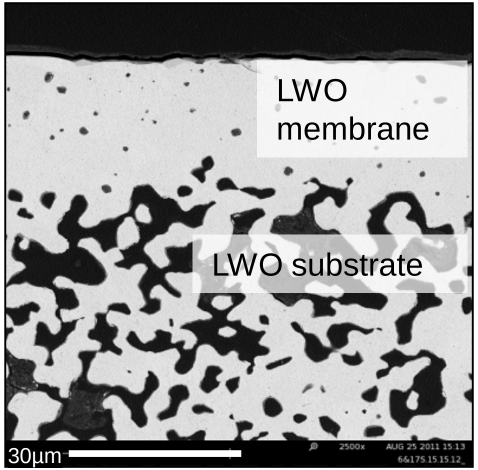
O. Guillon et al. Woodhead Pub. 2010

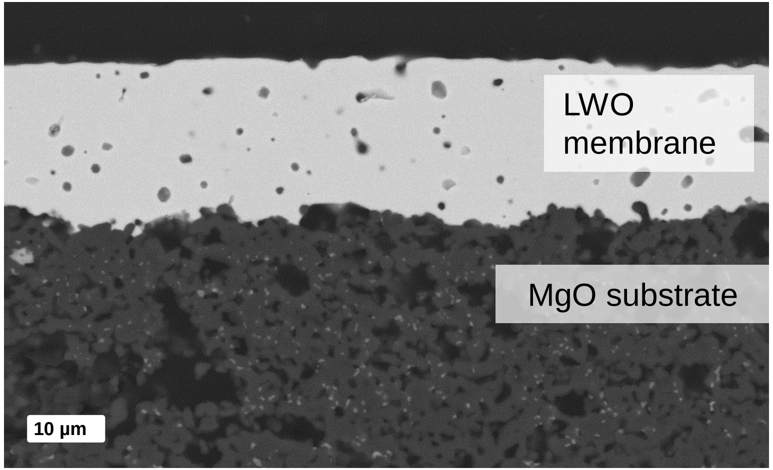
Manufacturing of Asymmetric Membranes

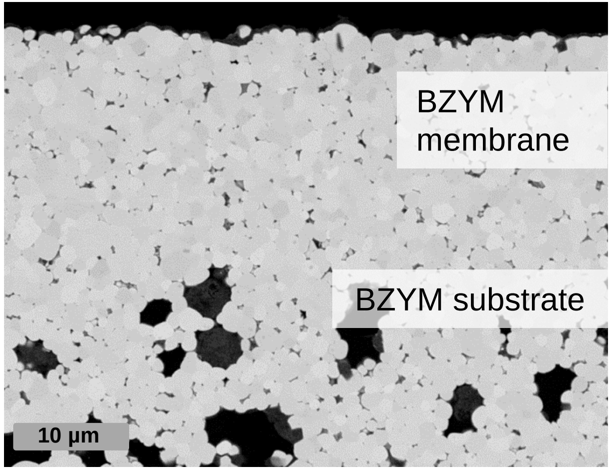
Successful Materials Combinations

$La_{6-x}WO_{12-\delta}$ (LWO)

$BaZr_{0.8}Y_{0.15}Mn_{0.05}O_{3-\delta}$

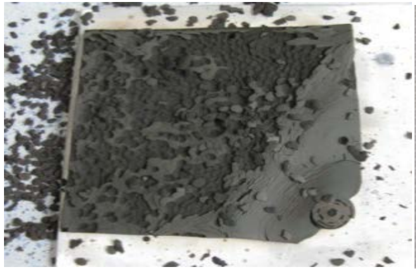




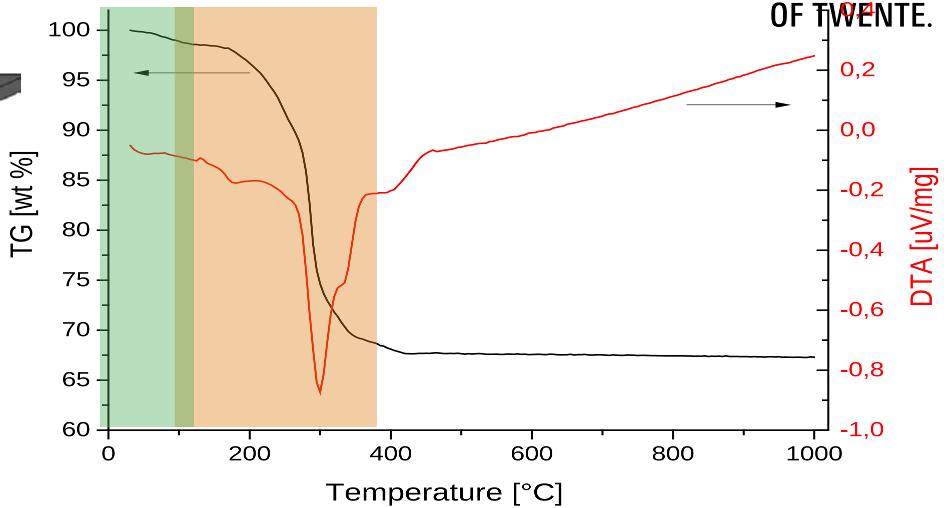


W. Deibert, Journal of Membrane Science (2015)
W. Deibert, Journal of European Ceramic Society (2017)

Scale-Up of Membrane Components



P. Niehoff et al., American Ceramic Society Bulletin, (2015)



Evaporation of residual solvents and melting of plasticisers and binder

Pyrolysis of organic components
- Plasticisers
- Binder
- Starch (pore former)

Scale-Up of Membrane Components

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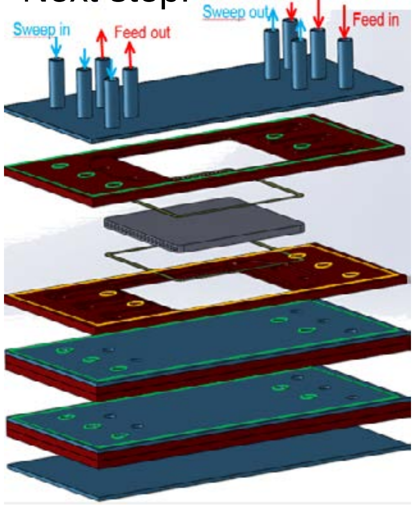
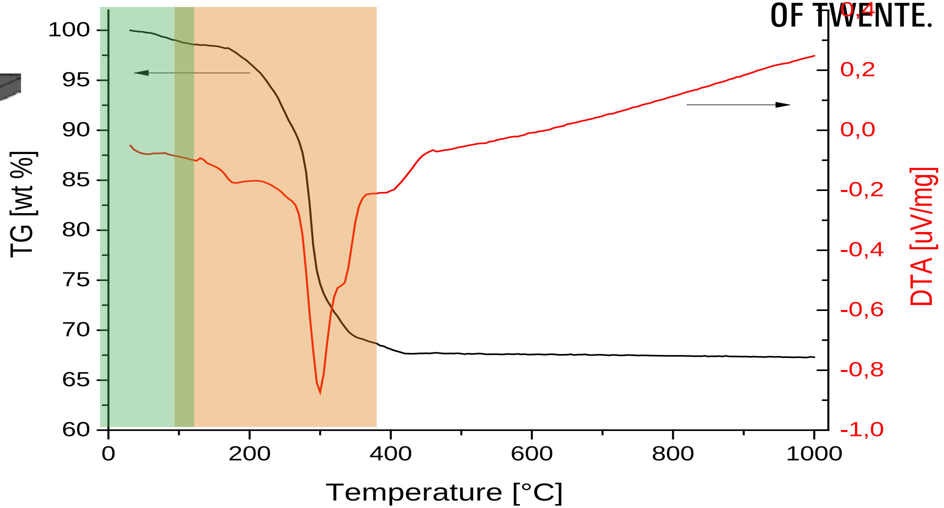
Next step:





Evaporation of residual solvents and melting of plasticisers and binder

Pyrolysis of organic components
- Plasticisers
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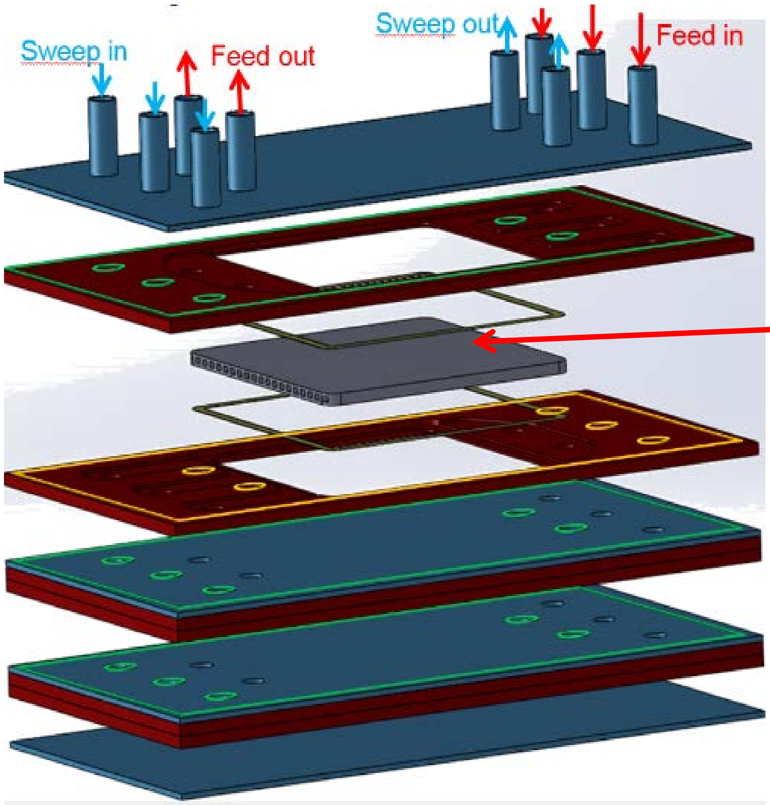
P. Niehoff et al., American Ceramic Society Bulletin, (2015)

Simulation-Supported Module Design

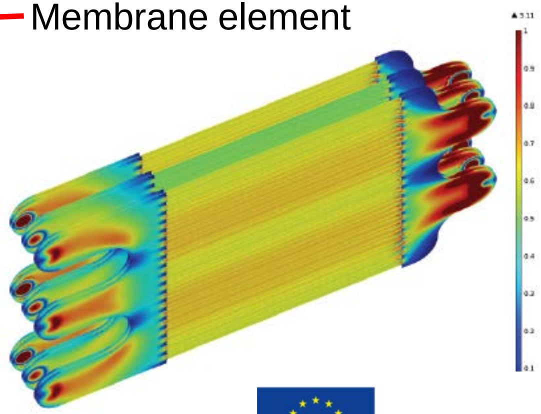
GREEN-CC Project (Coordination: W. A. Meulenberg)



Key issues/activities

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

Membrane element



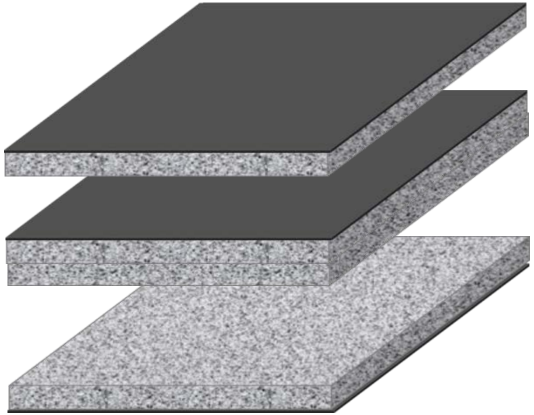
CFD modelling shows homogeneous velocity distribution of air flow

GREEN
Graded Membranes for Energy Efficient New Generation Carbon Capture Process
Grant Agreement Number 608524
SEVENTH FRAMEWORK PROGRAMME

Development of Membrane Components

Lamination of single tapes

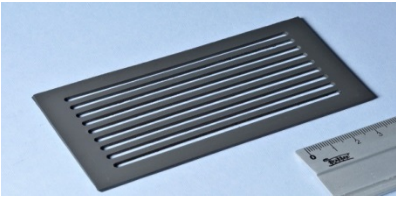
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$

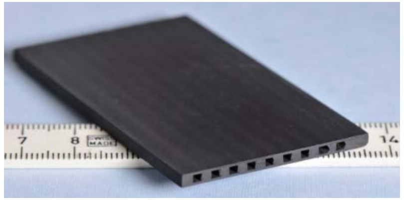


} Tape casting

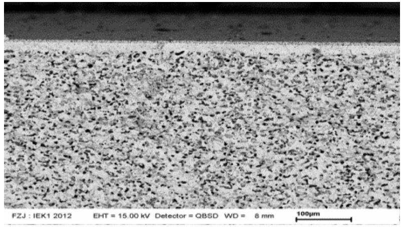
} Tape casting/
cutting or milling

} Tape casting

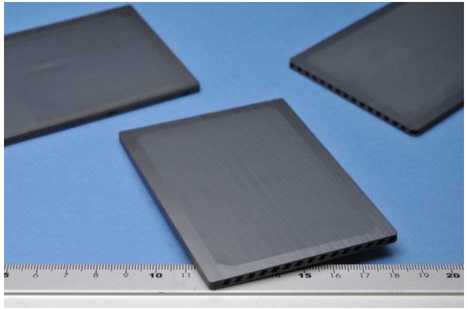


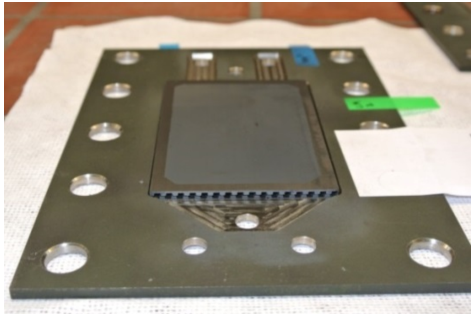


Size: 4 x 7 cm^2



Assembling of OTM Module:
Dec. 2017, Area: 420 cm^2





Size: 7 x 10 cm^2

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Cost estimation of the prototype membrane

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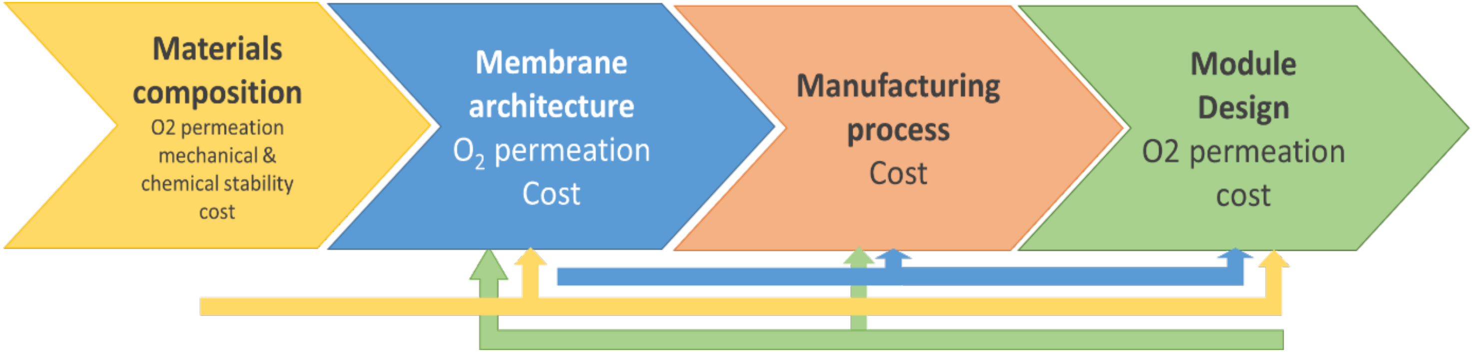
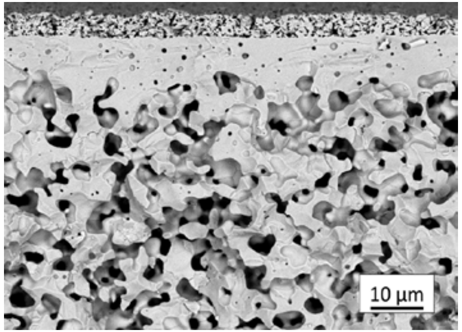
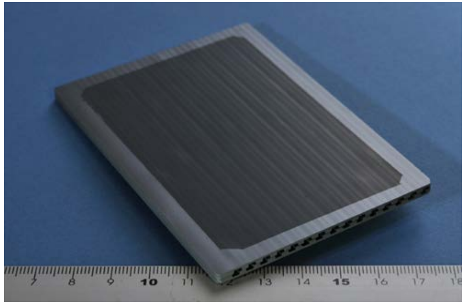


Batch / Amount [kg]	Price [€/kg]
10 - 50	430
51 - 100	390
101 - 500	290
501 – 1.000	260
1.001 – 10.000	210
10.001 – 50.000	150 - 180
50.001 – 100.000	100 - 130

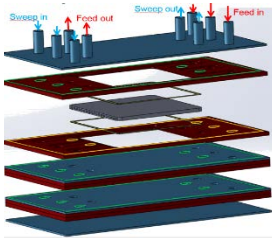
Powder Price of LSCF in dependence of amount of delivery
Source Solvay Flour





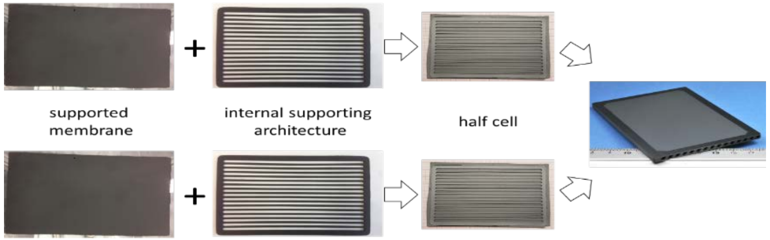
Cost estimation of the prototype membrane

Slurry preparation
Tape casting
Shaping (cutting/punching)
Lamination membrane + interlayer „hal-fcell“
Sintering of half-cells
Combining two half-cells to a membrane component
Ironing
Leak-test
Reworking (e.g. cutting, grinding,…)

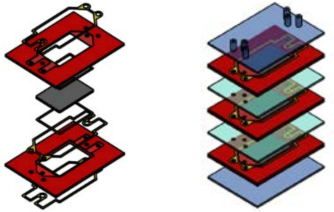


$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)

- membrane material costs: ceramic material cost is 700 €/m^2
- membrane-manufacturing costs: 4200 €/m^2



- costs for the housing and sealing: 11500 €/m^2



Calculated by Sonja Paul, AVT RWTH Aachen

- total membrane module costs: 16400 €/m^2
- ➢ drastically decrease is expected for a commercial module design

large potential for cost reduction

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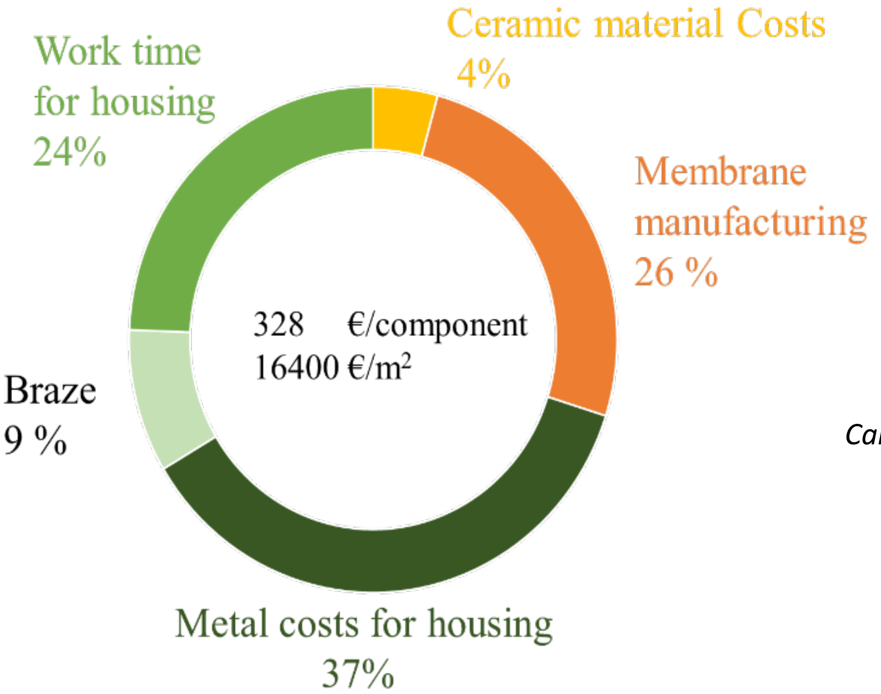
Cost estimation of the prototype module



Calculated by Sonja Paul, AVT RWTH Aachen

Graded Membranes for Energy Efficient New Generation Carbon Capture Process
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Cost estimation of the prototype membrane

	Oxyfuel Power Plant	Cement Plant
Product costs:		
OTM (without membrane)	9.87 c€/kWh$_{el}$	7.41 €/t
Cryogenic ASU	11.85 c€/kWh$_{el}$	11.29 €/t
Plant Capacity	623.4 MW$_{gross}$ (OTM)	3,000 t/d
Oxygen demand	99 kg/s	8,8 kg/s
Average oxygen flux	0.9 Nml/min cm^2	0.9 Nml/min cm^2
Membrane area (for LSCF)	~500.000 m^2	~44 000 m^2
Membrane lifetime:		
35 years	1050 € per m^2	3367 €/m^2
4 years	120 € per m^2	385 €/m^2
	Power plants should be a long-term application	Since the cement industry is price sensitive these supplementary costs have to be forced by governmental regulation

Calculated by Sonja Paul, AVT RWTH Aachen

Graded Membranes for Energy Efficient New Generation Carbon Capture Process
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Cost reduction potential

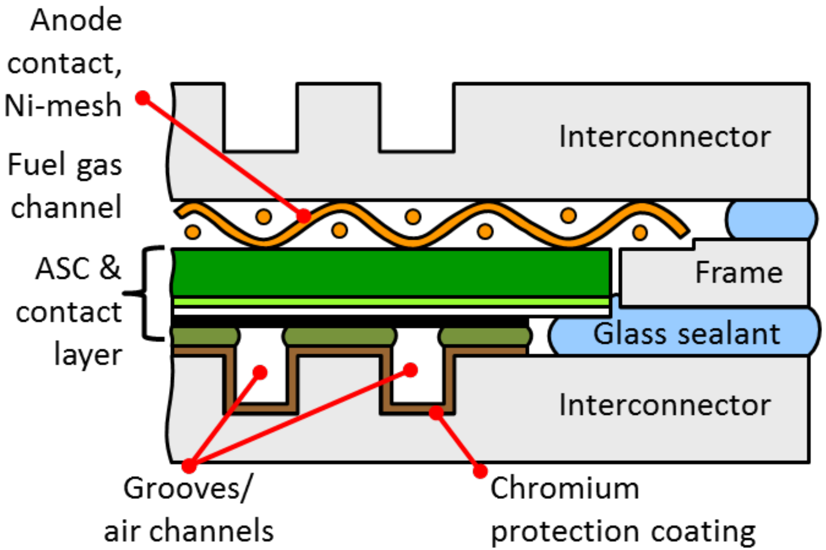
Material:
- Using cheap support materials (ZrO_2, MgO, etc…..)

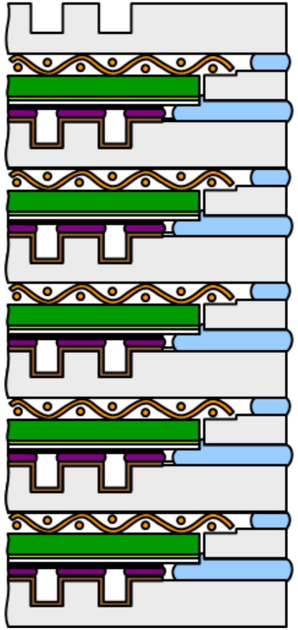
Membrane unit:
- Reduction of manufacturing steps or using of other routes (e.g. extrusion, 3D-Printing)
- Using of advanced sintering methods, e.g. FAST

Housing:
- Using of cheaper steels or ceramics - MIEC membrane does not require conductive housing material
- Using of cheap sealants

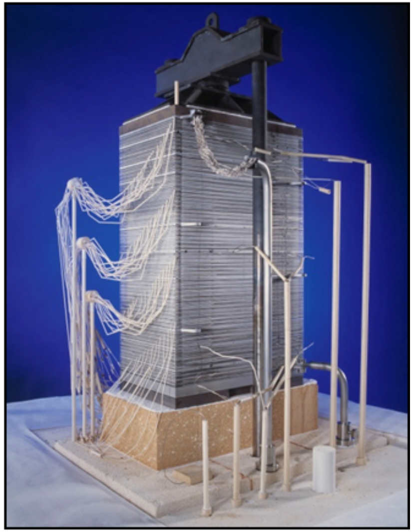
Overall:
- Long life means low cost / Lifetime more important than performance /
- Continuous operation must be guaranteed

Stack components Jülich design





Repeating units



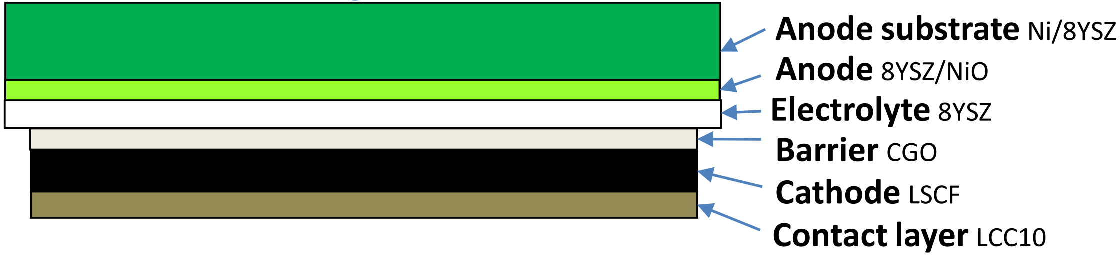
Drawings: Martin Bram

Photo: Ralf-Uwe Limbach

supplied by Norbert Menzler and Siri Harboe

Two different Jülich stack designs

Anode supported cells

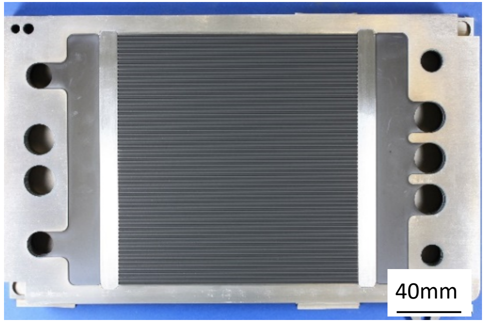


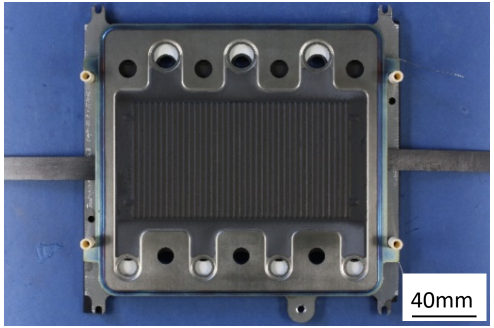
1: Stationary design ($T_{op.}$~700°C) : P_{el} / A = 0.37 W/cm^2

- Alloy Crofer22APU, thicker plates
- Machined by milling & creep feed grinding

2: Light-weight design (Top.~770°C) : P_{el}/A=0.25 W/cm^2

- Alloy Crofer22H thinner sheets
- Hydroforming





supplied by Norbert Menzler and Siri Harboe

Photos: ZEA-1

Harboe et al., Manufacturing Cost Model for Planar 5 kWel SOFC Stacks at Forschungszentrum Jülich, International Journal of Hydrogen Energy (subm. 2019)

SOFC manufacturing cost model

SOFC stacks scale-dependent processing-lines evaluated

Material costs
net demands, scraps, price

Machine costs
machine cycle time, CAPEX depreciation, maintenance

Labor costs
duration of manufacturing, labor rate

Energy cost
duration of machines in use, energy demand and price

$\sum$ = Direct costs

- Costs of SOFCs manufacturing
- Costs: Pros & cons of stack designs
- Costs reduction R&D aspects

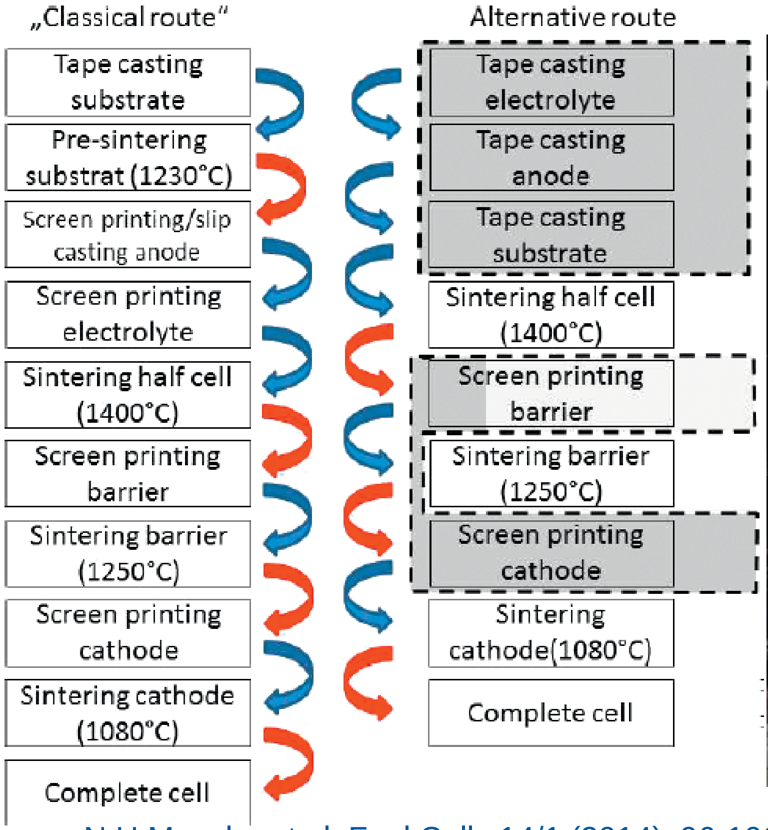
supplied by Norbert Menzler and Siri Harboe

Harboe et al., Manufacturing Cost Model for Planar 5 kWel SOFC Stacks at Forschungszentrum Jülich, International Journal of Hydrogen Energy (subm. 2019)

Scale-up possibilities- example Solid Oxide Cells

JÜLICH Forschungszentrum

UNIVERSITY OF TWENTE.



N.H.Menzler et al. Fuel Cells 14/1 (2014), 96-106

JuCast 3-500: Sequential tape caster with three casting heads

Differences MIEC Membrane - SOFC

Membrane unit and materials:

- Only membrane layer and support required, sometimes also active surface layer
- No requirements regarding electrical conductivity for support, cheap ceramics can be used
- Reaction catalyst required

Housing and interconnect/gas separators:

- Using of cheaper steels or ceramics possible compared to SOFC
  MIEC membrane does not require conductive interconnect material
- Using of different sealants including metals are possible

Operation:

- Pressure controlled instead of power controlled (higher pressure and reaction harder to control)
- Often more aggressive environment
- No electricity required

Thank you for your attention