Bundesministerium für Bildung und Forschung

PROJECT MESOWAS

A solar-based membrane reactor for hydrogen production

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Synhelion

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DLR

Introduction: The MESOWAS project
Membrane-based solar thermal cycles for the synthesis of green hydrogen

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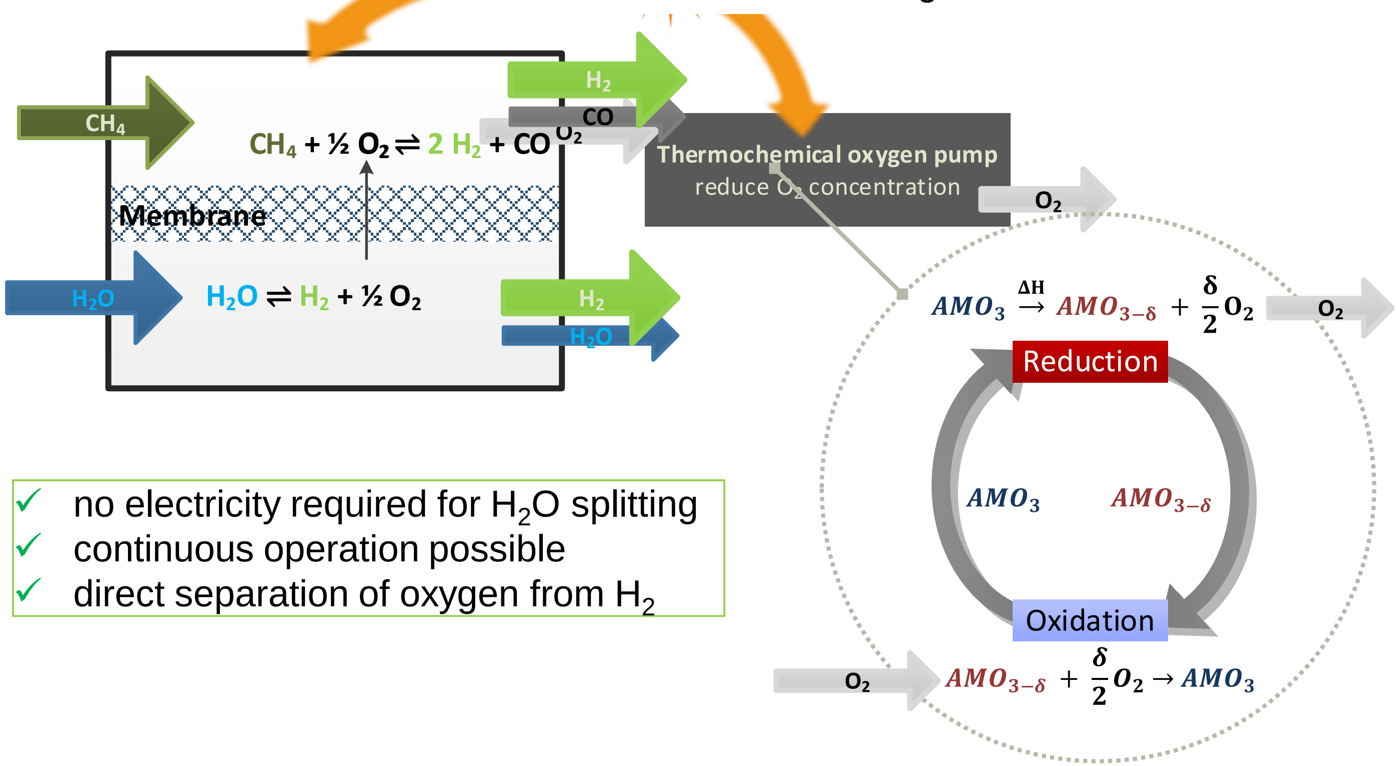
Federal Ministry of Education and Research
Grant: 03SF0648A

Option A: Sweep gas or thermochemical O_2 pump
Option B: Partial oxidation of biomethane or biogas

DLR solar simulator - Cologne



- ✓ no electricity required for H_2O splitting
- ✓ continuous operation possible
- ✓ direct separation of oxygen from H_2

Aim of project:

1. Experimental proof-of-concept of a solar membrane reactor for water splitting
2. Development of membrane
3. Investigation of different approaches to reduce the oxygen concentration on permeate side
4. Potential analysis of membrane technology

Start 01.08.2022
End 31.07.2025

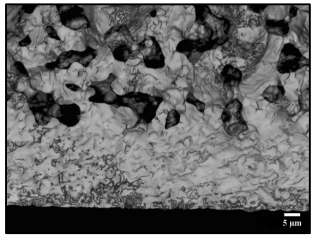
Consortium:

Synhelion JÜLICH Forschungszentrum DLR

MESOWAS: Membranbasierte solarthermische Kreisläufe für die Synthese von grünem Wasserstoff

Agenda

1. Material selection and membrane fabrication



2. Membrane reactor development

3. Solar energy integration

4. Reactor modelling

Material selection

Application conditions

- □ T: 900 °C
- □ $Po_2 < 10^{-6}$ bar

Required properties

- □ Mixed ionic and electronic conductivity
- □ Low chemical expansion
- □ Good stability

Material candidates

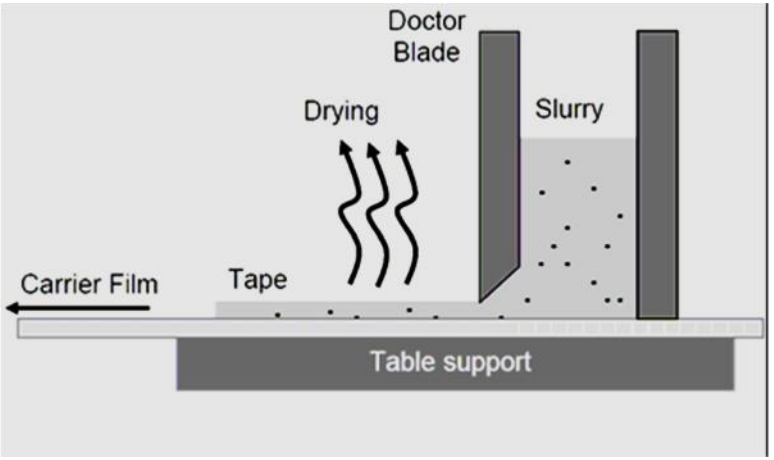
- □ $Ce_{1-x}Gd_xO_{2-\delta}$ (CGO)
- □ $SrTi_{1-x}Fe_xO_{2-\delta}$ (STF)

- Lower chemical expansion from Ti^{4+}(0.605 nm) to Ti^{3+} (0.67 nm) for STF compared to Ce^{4+} (0.97nm) to Ce^{3+} (1.143nm) in CGO
- 25 mol% Fe doping ensure applicable conductivity and structural integrity under low Po_2

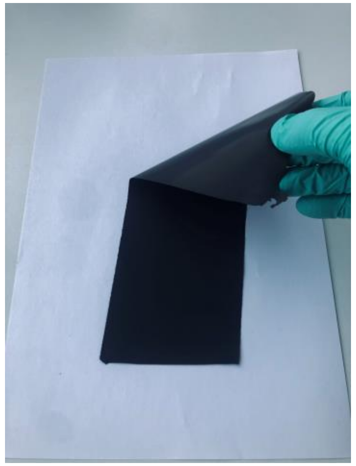
→ **STF** material doped with **25 mol% Fe** is selected

Membrane fabrication and performance

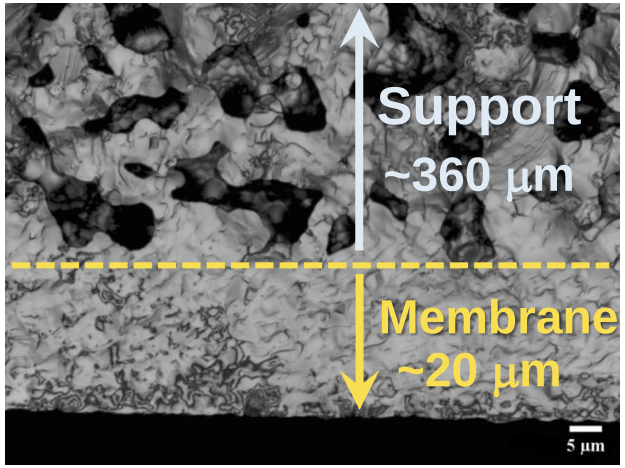
Tape Casting

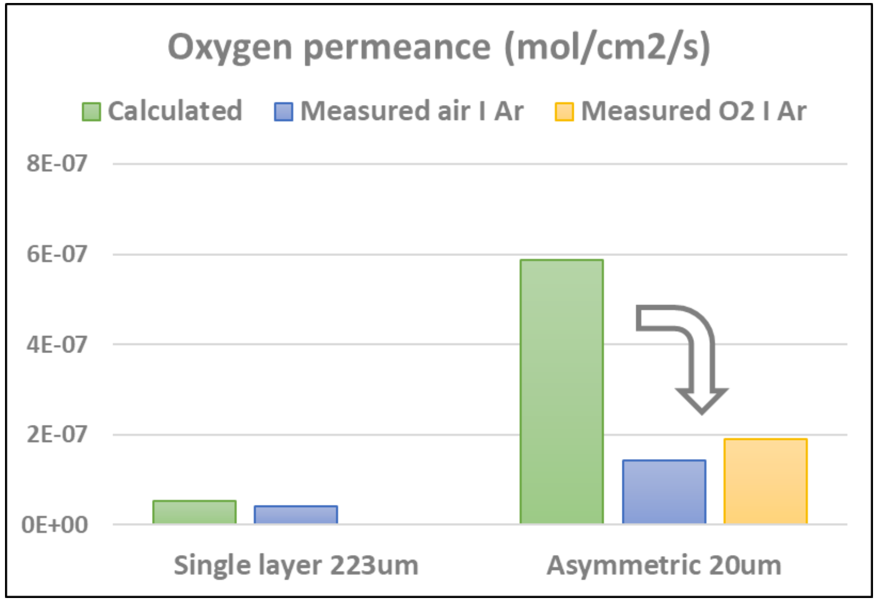


Green Tape



Sintered asymmetric membrane





Bulk transport control:

$$\text{Oxygen Permeance} = -\frac{j_{O_2}}{\int_{P'_{O_2}}^{P''_{O_2}} d\ ln\ P_{O_2}} = \frac{R}{16F^2} \cdot \frac{1}{L} \cdot \sigma_{amb} \cdot T$$

- **Single layer membrane**: the measured value ≈ calculated value, validating the assumption of bulk transport control
- **Asymmetric membrane**: the measured value ≤ calculated value, indicating limiting surface exchange and gas diffusion through the porous support → catalysts required

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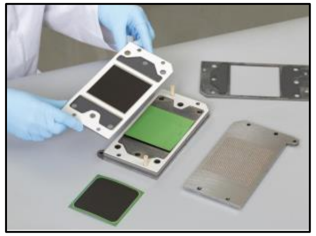
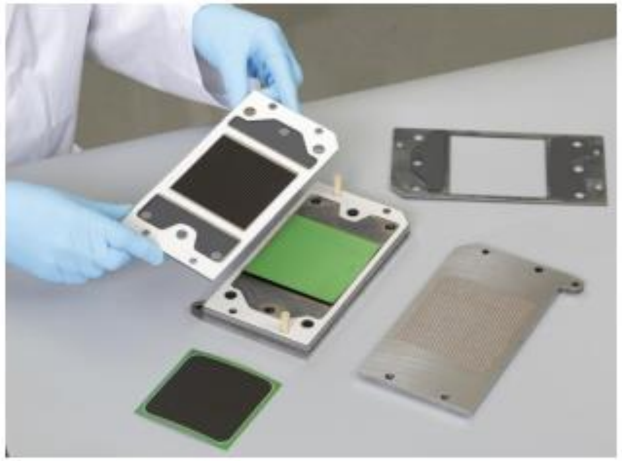
2. Membrane reactor development



3. Solar energy integration

4. Reactor modelling

Reactor design: From F10 Jülich Solid Oxide Electrolysis design to a membrane reactor

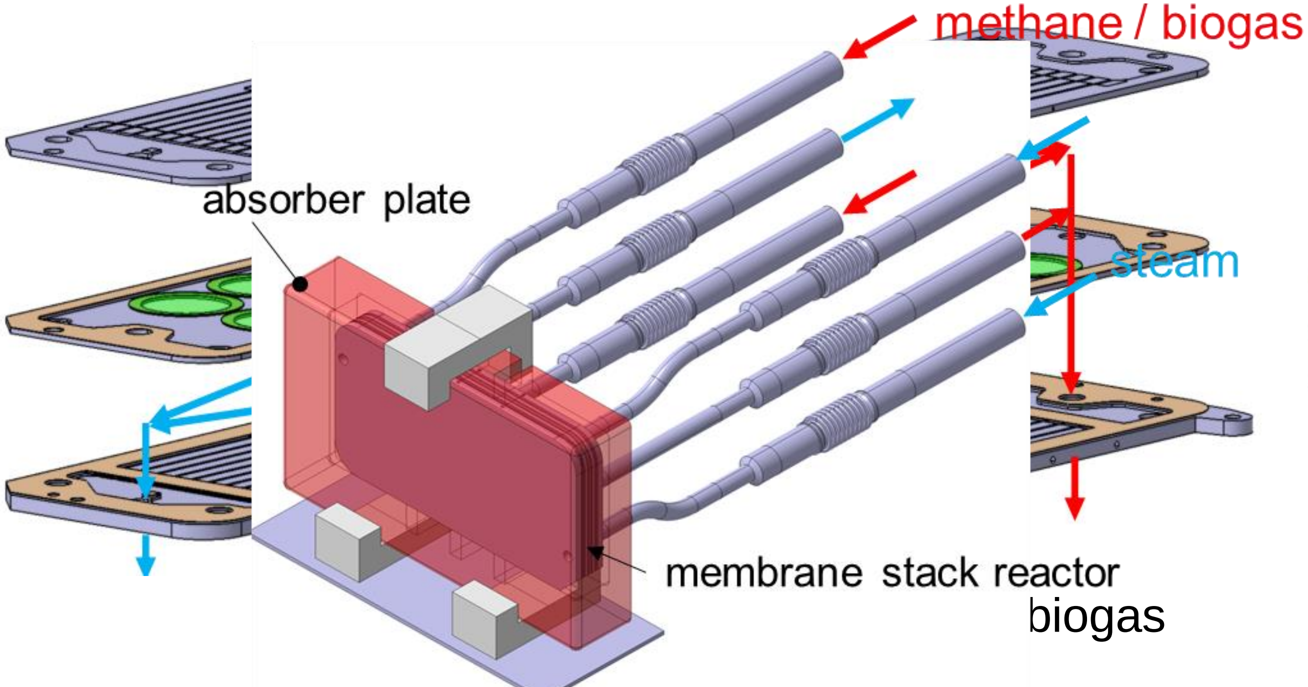


SOC „F10“

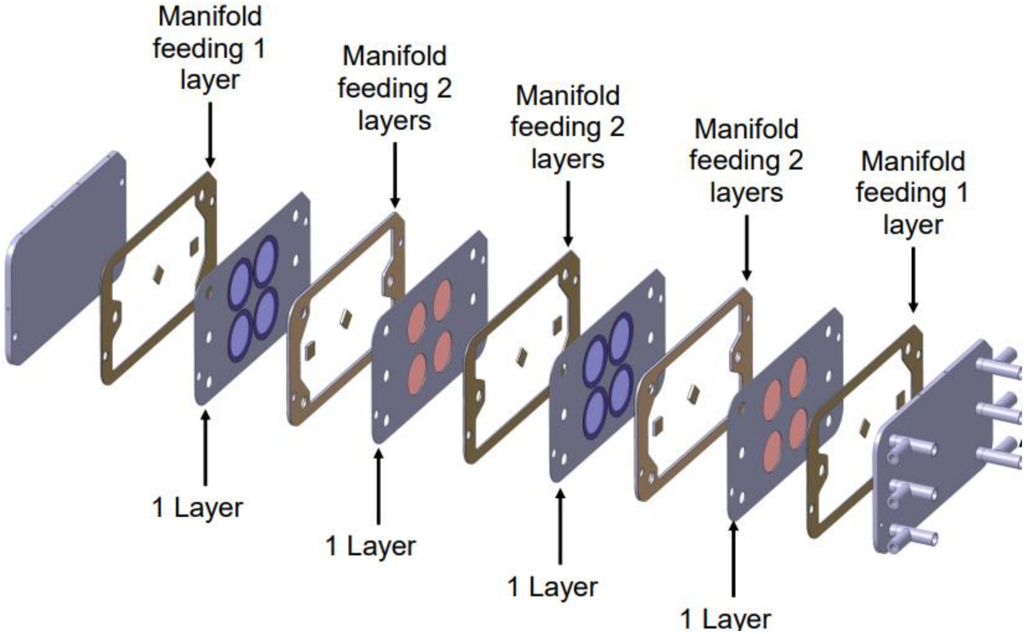
Feasibility of the design:

→ Similar outer envelope can be used; X layer stack footprint: 220 mm x 120 mm **x scalable**
→ Different membrane shapes can be adapted (e.g. circular or rectangular)
→ Shape and type of glass solders can be adapted to membrane and metals of the design
→ Stacks allow scalability of system

Design of membrane reactor
proof-of-concept of the solar membrane reactor (using stacks):



Repeatable layer - partially assembled



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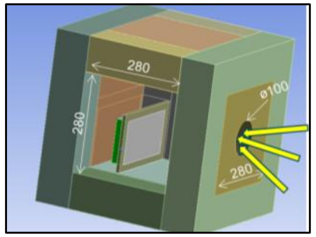
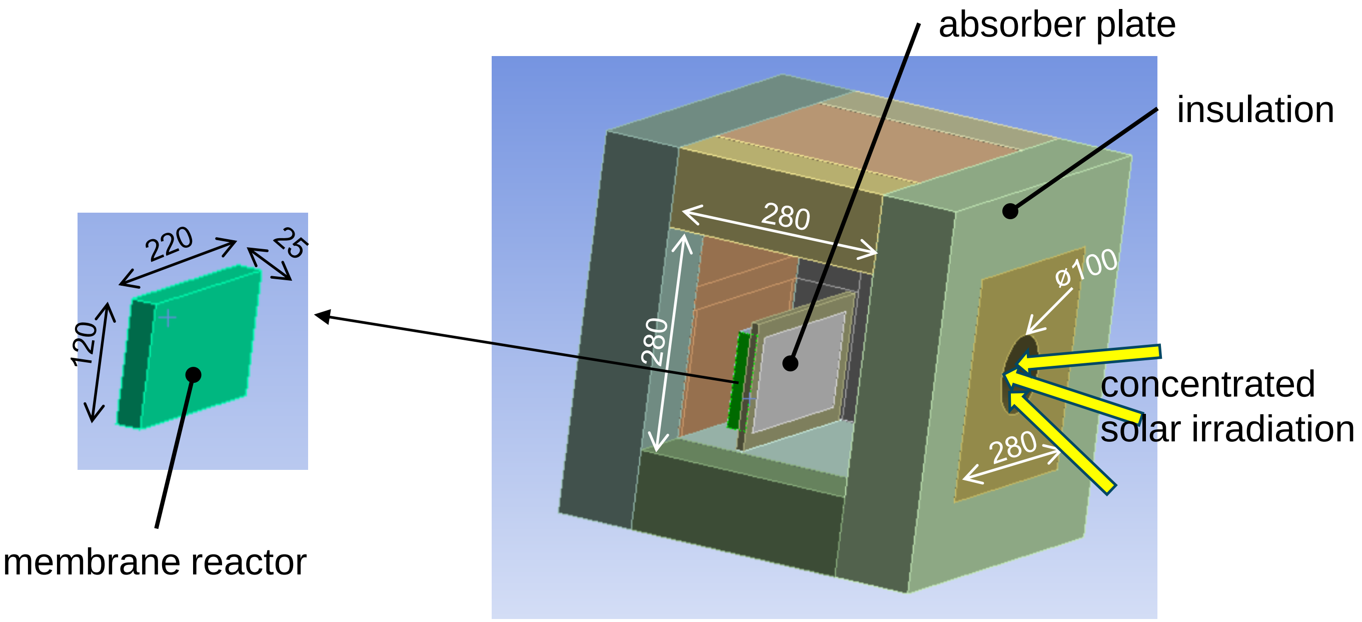


4. Reactor modelling

Solar energy integration

- Membrane reactor stack inside an open insulation „box“
- Concentrated solar energy enters cavity and hits the absorber plate in front of the stack



dimensions in mm

Integration of solar energy

Using intermediate Heat Transfer Fluid (scale up concept analysis)

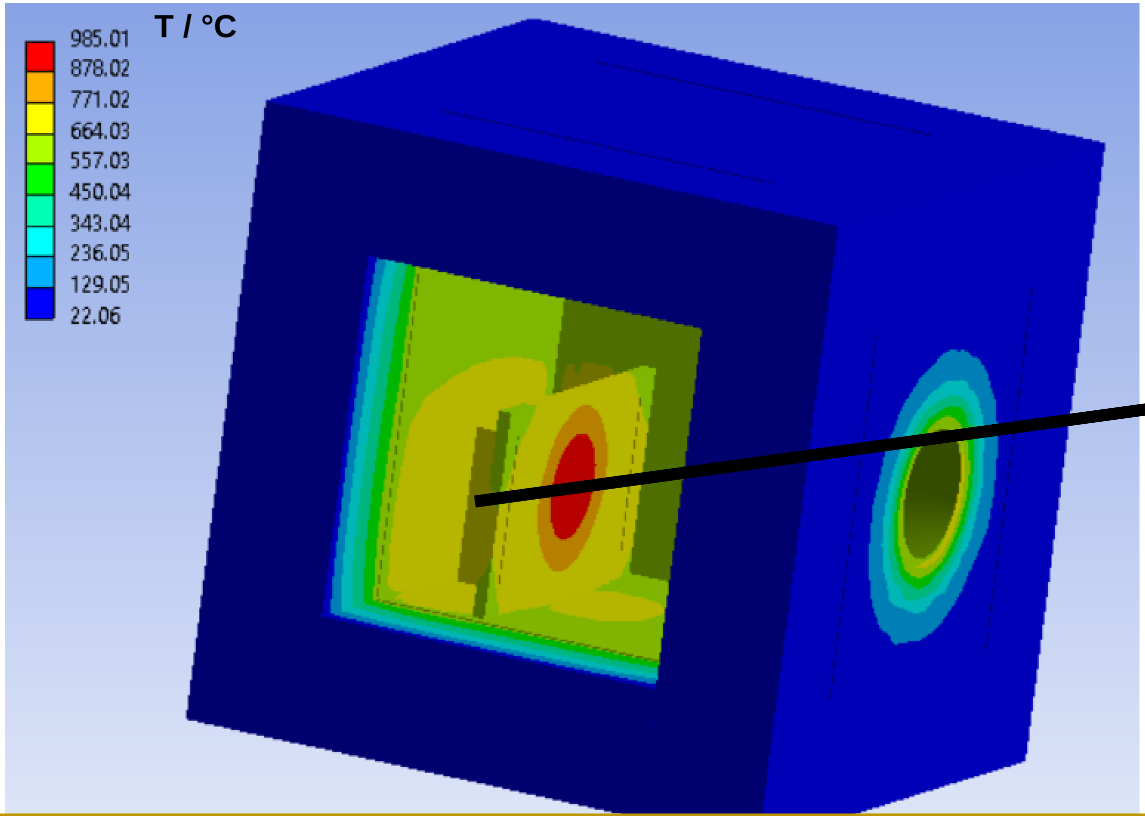
Using indirect irradiation of stack (experiments)

Homogeneous T distribution on membrane reactor

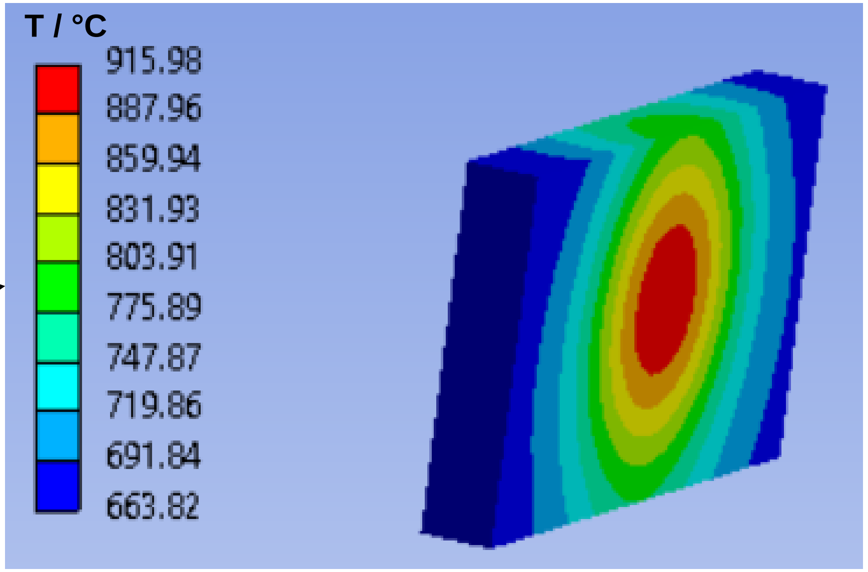
- Temperature for experiments: **(800 – 900 °C)**
- Max. allowable T gradient: **50 K**

Simulations of solar flux distribution on membrane reactor
Material of irradiated plate: steel

T distribution of cavity



T distribution membrane reactor



irradiated plate: steel

- **Hot spot in central part → temperature gradient too large!**

Simulations perfored with Ansys® Academic Research Workbench 2022 R1

Modification of volume of cavity to reach higher temperatures

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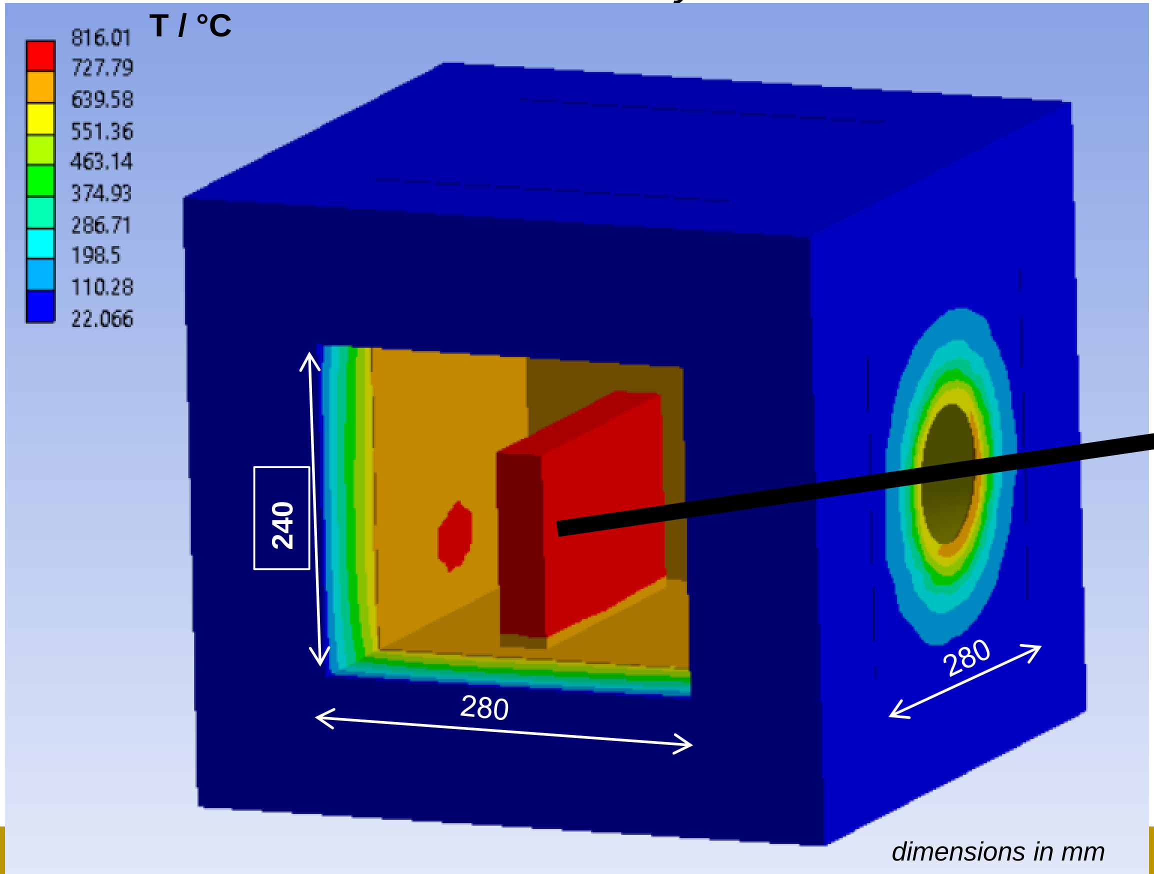
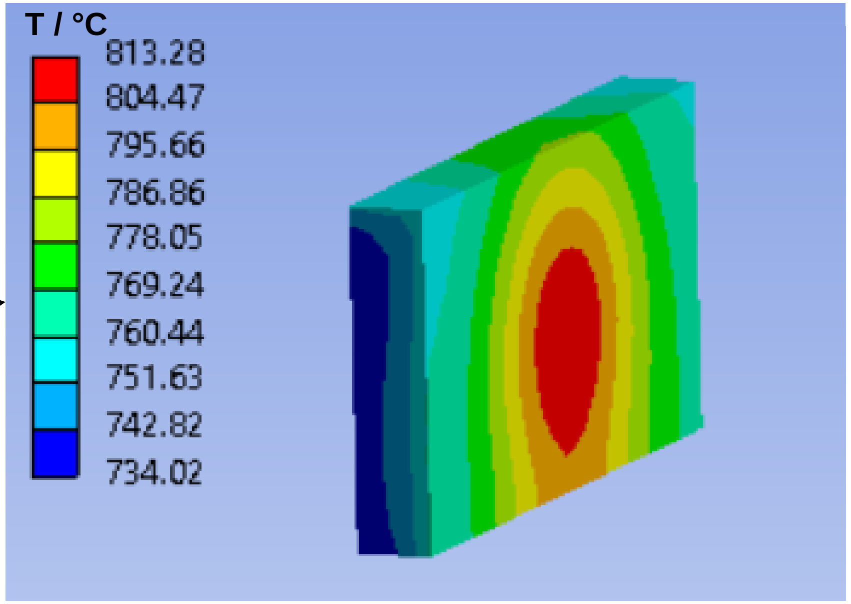
T distribution of cavity



T distribution membrane reactor



irradiated plate: copper

- **High temperature achieved, but T gradient still > 50 K**

Simulations perfored with Ansys® Academic Research Workbench 2022 R1

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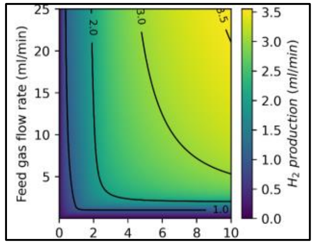


0D – Reactor Modelling

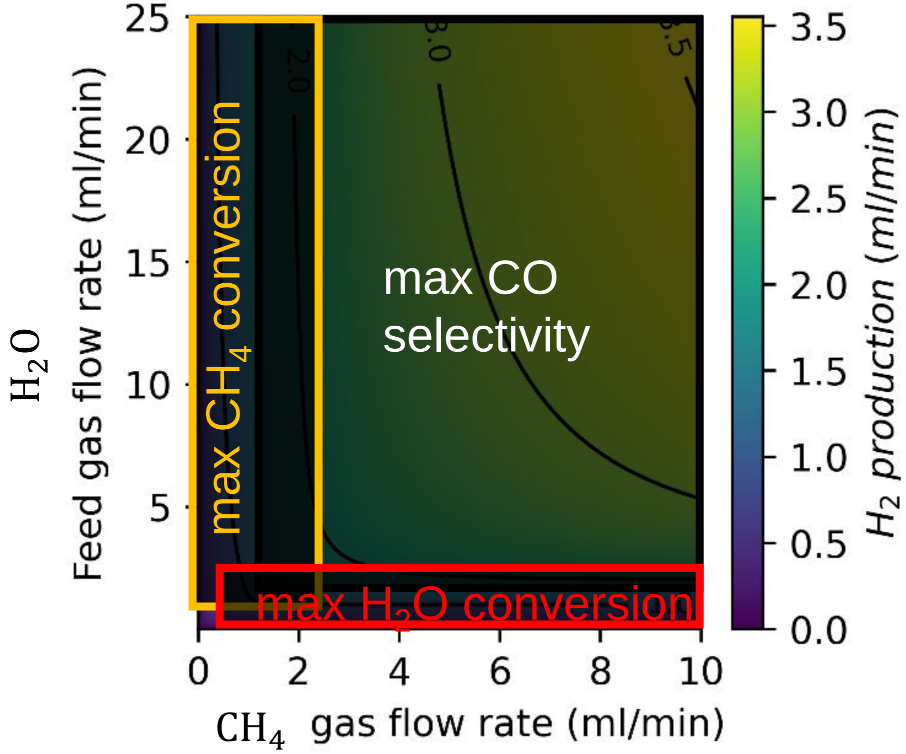
- Development of a 0D model for initial design iterations [1]

Assumptions:

- Chemical equilibrium on both sides
- Infinite fast diffusion in gas phase
- Isothermal

Implementation:

- Coupling of two Gibbs minimization problems by Wagner equation



H_2 production for 1 cm^2 active membrane area

[1] Bittner, K., Margaritis, N., Schulze-Küppers, F., Wolters, J., & Natour, G. (2023). A mathematical model for initial design iterations and feasibility studies of oxygen membrane reactors by minimizing Gibbs free energy. *Journal of Membrane Science*, *685*, 121955.

3D – Reactor Modelling

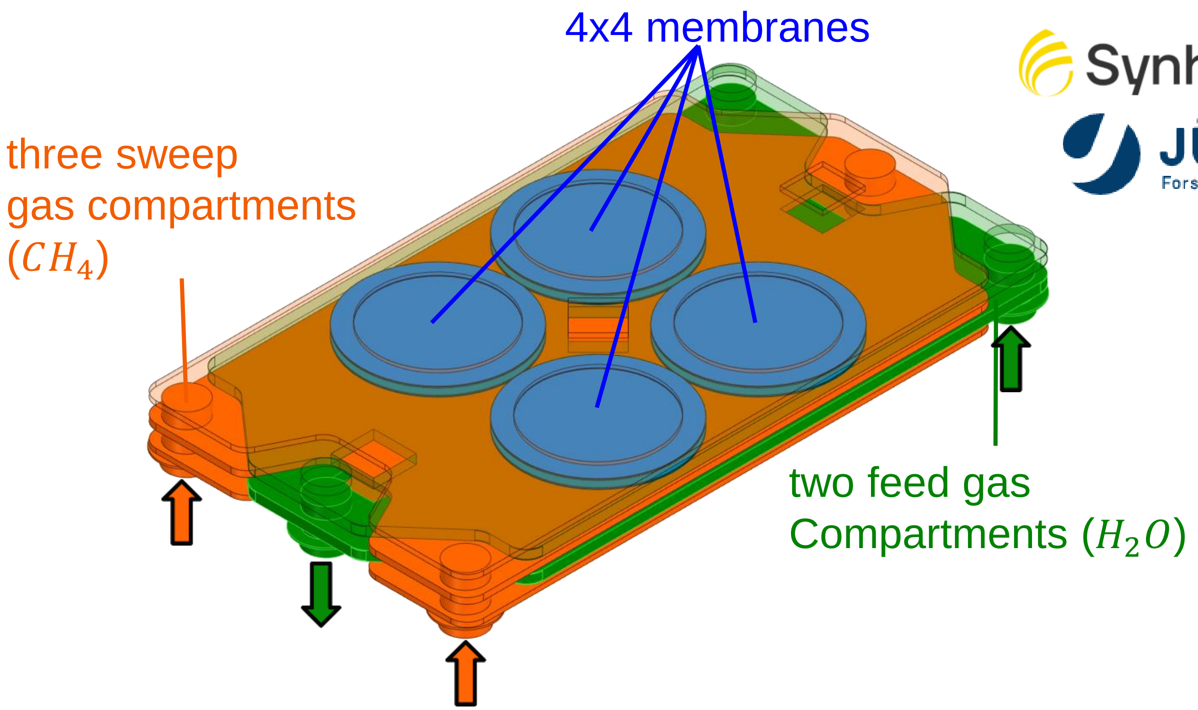
- Development of a 3D model to investigate geometrical effects

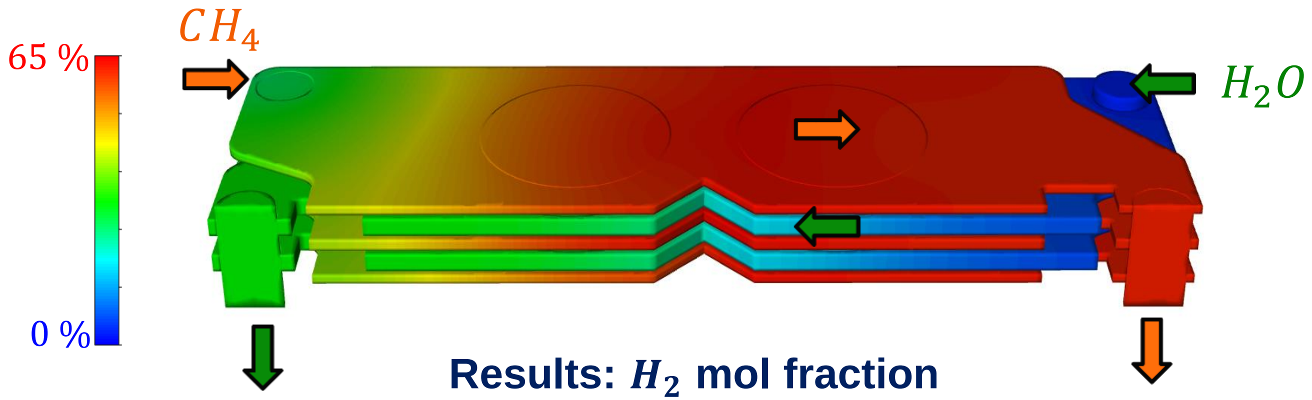
Assumptions:

- Chemical Equilibrium at the membrane surface

Implementation:

- Fluid flow equations are solved using Ansys Fluent
- Surface reactions and oxygen permeation are modelled using User Defined Functions





Results: H_2 mol fraction

Conclusion

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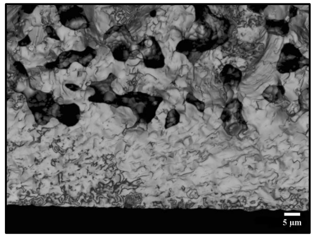
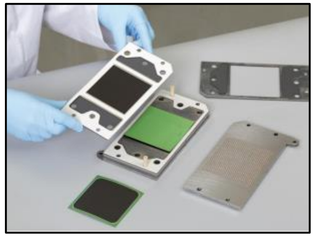
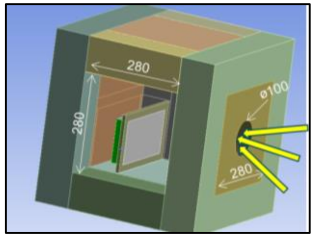
- STF-based membranes with 25 mol% Fe showed best mix of low thermal expansion and ambipolar conductivity for 800 °C – 900 °C and low pO_2 operation.



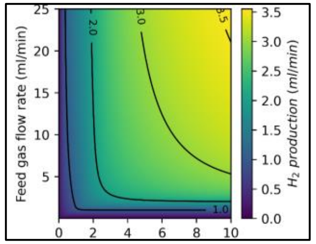
- Design of a first-of-a-kind solar membrane stack reactor.



- Solar energy can cover the energy demand of the reactor, but homogenisation of flux distribution still ongoing.



- 0D and 3D reactor model to identify suitable operation parameters.



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