# From polymer to membrane: development of thin-film composite membranes

BioCoMem


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**26.06.2023**

Institute of Membrane Research


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1

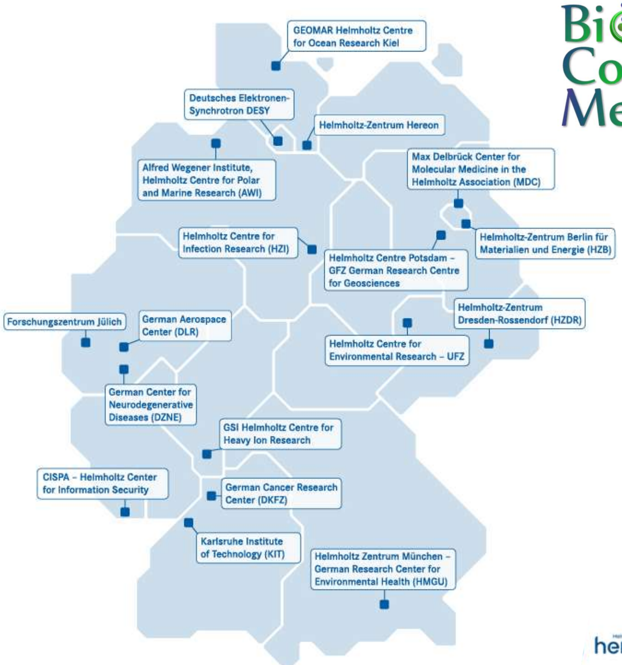
## Helmholtz Association
18 Centers and their Funding

HELMHOLTZ
SPITZENFORSCHUNG FÜR GROSSE HERAUSFORDERUNGEN

Total Budget 4.8B €

70% Federal/State | 30% Third Party

90% Federal | 10% State

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2

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## 15 Institutes

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**Helmholtz Research Programme: Information**
- Institute of Active Polymers
- Institute of Hydrogen Technology
- Institute of Material and Process Design
- Institute of Materials Mechanics
- Institute of Material Systems Modeling
- **Institute of Membrane Research**
- Institute of Metallic Biomaterials
- Institute of Surface Science
- Institute of Photoelectrochemistry

**Helmholtz Research Programme: Earth & Environment**
- Institute of Carbon Cycles
- Institute of Coastal Environmental Chemistry
- Institute of Coastal Ocean Dynamics
- Institute of Coastal System Analysis and Modeling
- Climate Service Center Germany (GERICS)

**Helmholtz Research Programme: Matter**
- Institute of Materials Physics





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3

# Institute of Membrane Research: R&D in membrane gas separation technology

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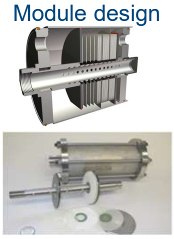
**Lab. scale investigations**
- Polymer synthesis
- Polymer modification
- Permeation behaviour

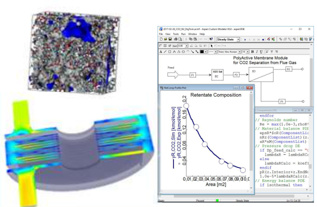
**Pilot scale membrane production**

**Pilot plants**

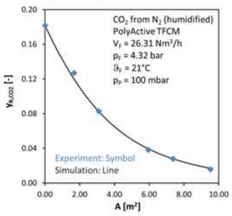
**Module design**



**Modelling and simulation**



**Comp. pilot plant/simulation**



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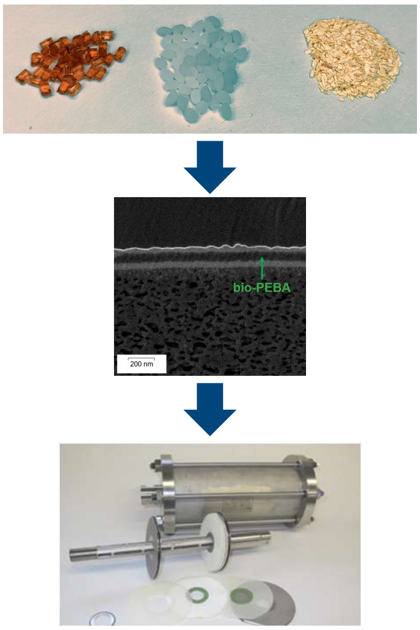
4

## Hereon's role within BioCoMem project

- **Objectives**:
  - ✓ Development of thin-film composite membranes (**TFCMs**) with **bio-based polyether-block-amide (PEBA) copolymers** as **selective layer** materials
  - ✓ Manufacture of **membrane modules**
  - ✓ Intended application → **$CO_2$ separations**:
    - Post-combustion flue gas treatment
    - Natural gas upgrading
    - Biogas upgrading






5

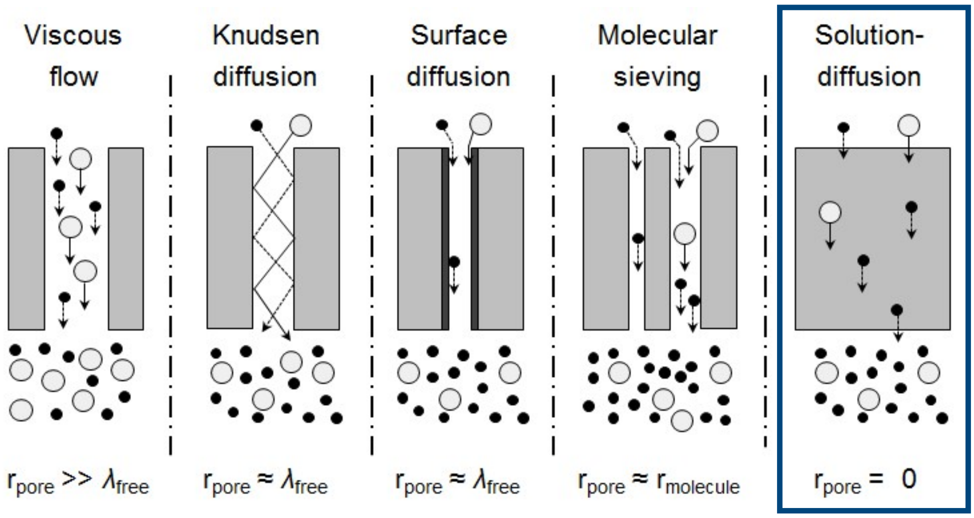
## Methodology for the development of a TFCM

1. General characteri-zation of polymer
2. Choice of optimal solvent
3. Determi-nation of **intrinsic** GS properties of **dense films** (*time-lag*)
4. Prepa-ration of TFCMs in lab scale
5. Morpho-logical character-rization (SEM)
6. Characteri-zation of GS performance of **TFCMs** (*pressure increase)*
7. Upscaling of TFCMs fabrication
8. Reproduci-bility and quality control



6

## Gas separation membranes: transport mechanisms




$\lambda_{free}$: mean free path of molecule





## Solution-diffusion mechanism of transport in polymers

Gas permeation through a nonporous polymer membrane is usually described using a solution–diffusion model

$P_i = D_i S_i$ Equation postulated by Graham (1866)

$$1\ Barrer = 1 \cdot 10^{-10} \frac{cm^3(STP) \cdot cm}{cm^2 \cdot s \cdot cmHg}$$

$$P_i = P_{i0} e^{-E_{P_i}/(RT)} \quad [cm^3(STP) cm\ cm^{-2}\ s^{-1} cmHg^{-1}]$$

$$D_i = D_{i0} e^{-E_{D_i}/(RT)} \quad [cm^2\ s^{-1}]$$

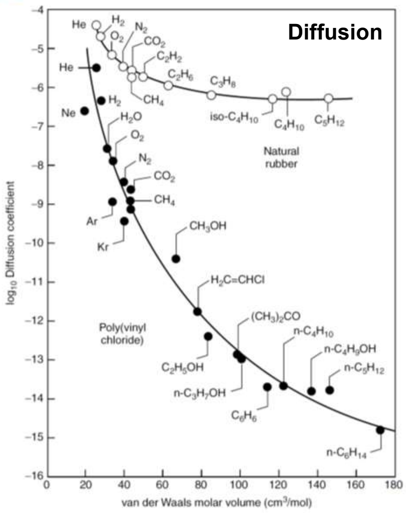
$$S_i = S_{i0} e^{-\Delta H_{S_i}/(RT)} \quad [cm^3(STP)\ cm^{-3}\ cmHg^{-1}]$$

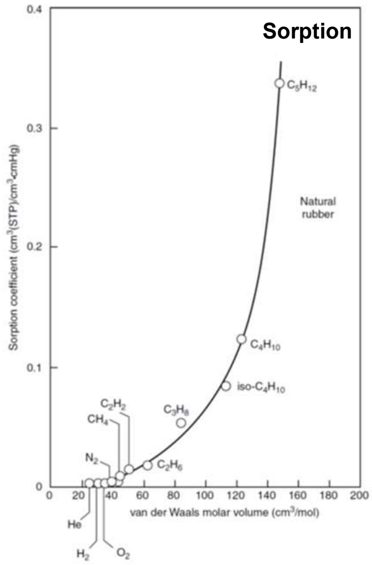
$P_{i0}$, $D_{i0}$, $S_{i0}$ → Pre-exponential factors
$E_{Pi}$, $E_{Di}$ → Activation energies
$\Delta H_{Si}$ → Enthalpy of solution of the penetrant *i*

Ideal Selectivity: $$\alpha_{ij} = \frac{P_i}{P_j} = \frac{D_i}{D_j} \cdot \frac{S_i}{S_j}$$

Example:
**Permeability** coefficient for polymer $P_{gasX}$ = 100 Barrer and **selective layer thickness** = 100 nm
→ membrane **Permeance** $L_{gasX}$ = 2.736 $m^3$(STP) $m^{-2}$ $h^{-1}$ $bar^{-1}$ = 1000 GPU

## Gas diffusion and sorption in polymers depend on penetrating molecule nature and size



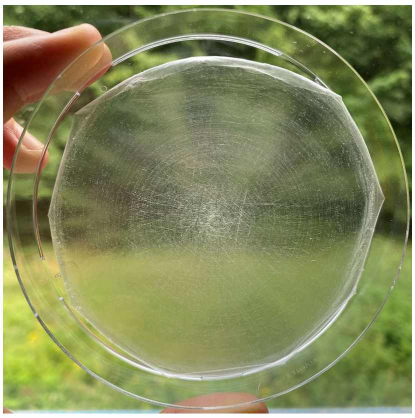




9 F. Gruen, *Experimenta* **3**, 490 (1947)
G.J. van Amerongen, *J. Appl. Phys.* **17**, 972 (1946)

9

## Preparation of polymer dense films via solution casting

1. Preparation of polymer solution in chosen solvent
2. Filtering of homogeneous solutions
3. Pouring of solutions in leveled Teflon® molds
4. Drying solvent out under slow $N_2$ flow
5. Drying film under vacuum
6. Weight, density, thickness determination

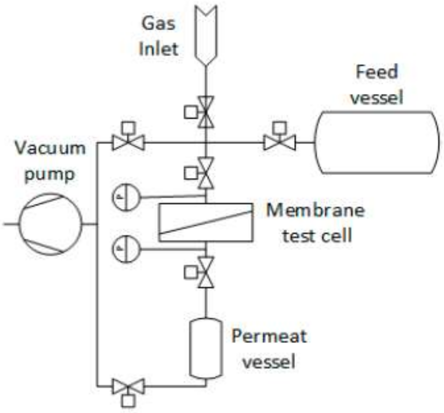


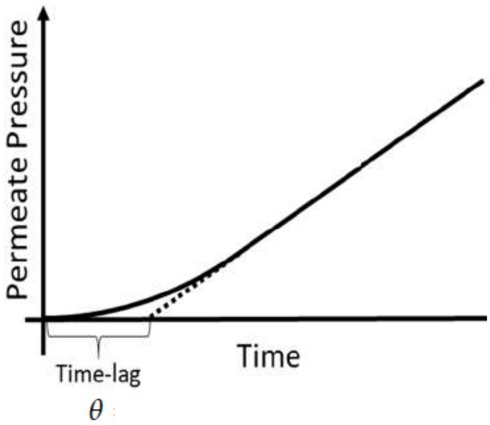
10 From polymer to membrane: development of thin-film composite membranes

10

## Determination of intrinsic gas transport parameters: the „time-lag“ method

- Constant volume, variable pressure measurement principle
- Feed/permeate pressure ratio >100 ensures correct diffusion coefficient determination (±3%)
- Permeate volume calibration accuracy of ±0.5% for permeability and solubility determination with accuracy of at least ±3%




$$\theta = \frac{l^2}{6D_{eff,i}}$$

$$P_{eff,i} = \frac{N_i l}{A_m \Delta p_i}$$

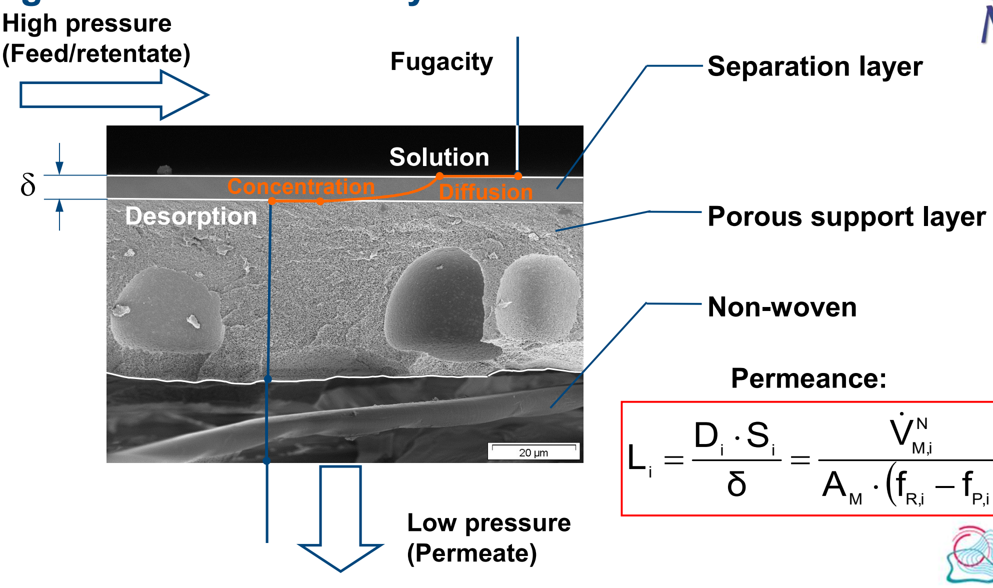
$$P_{eff,i} = D_{eff,i} S_{eff,i}$$

* Weigelt et al. (2018).





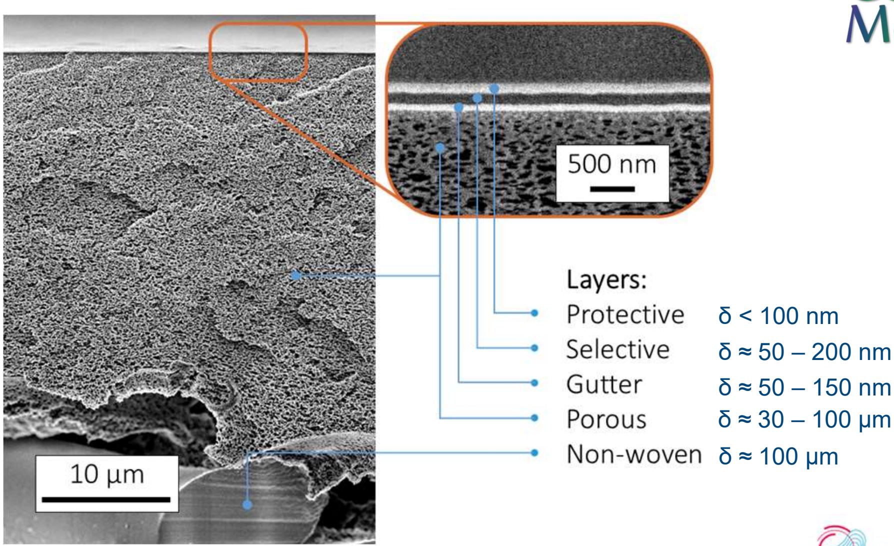
## Solution-diffusion mechanism and practical membranes: battle against the selective layer thickness




Permeance:

$$L_i = \frac{D_i \cdot S_i}{\delta} = \frac{\dot{V}^N_{M,i}}{A_M \cdot (f_{R,i} - f_{P,i})}$$

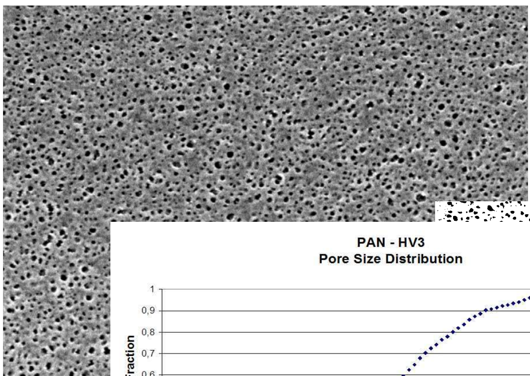
## TFCM: main components



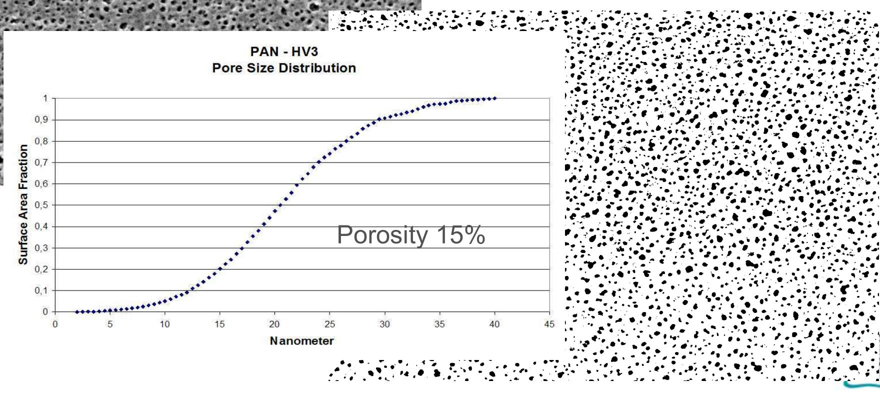



13

## TFCM: surface of porous support



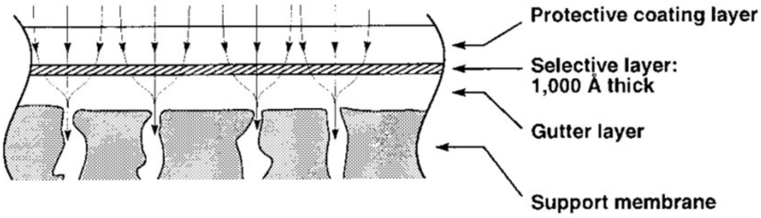
PAN porous membrane (ultrafiltration) on
PEI non-woven support
Highly durable: stable up to 100 bar
Disadvantage for TFCM: low surface porosity




15

## PDMS gutter layer membrane: basis of a good TFCM

**Properties:**
- < 150 nm thickness
- $N_2$ - permeance 2.5 $Nm^3m^{-2}h^{-1}bar^{-1}$
- highly cross-linked
- solvent resistant
- good adhesion due to additives

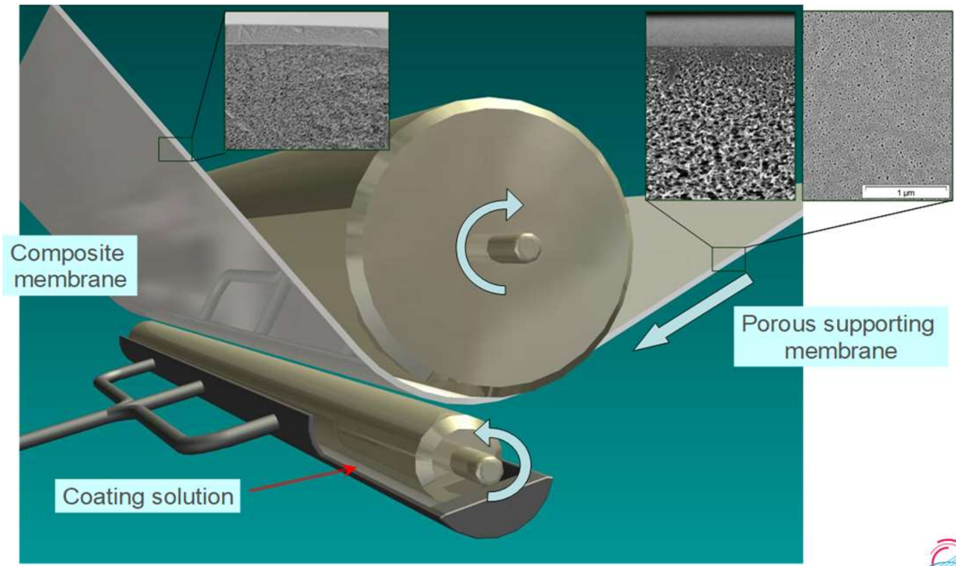



I. Cabasso, K.A. Lundy, 1986
R.W. Baker, Ind. Eng. Chem. Res. 41 (2002) 1393–1411.



16

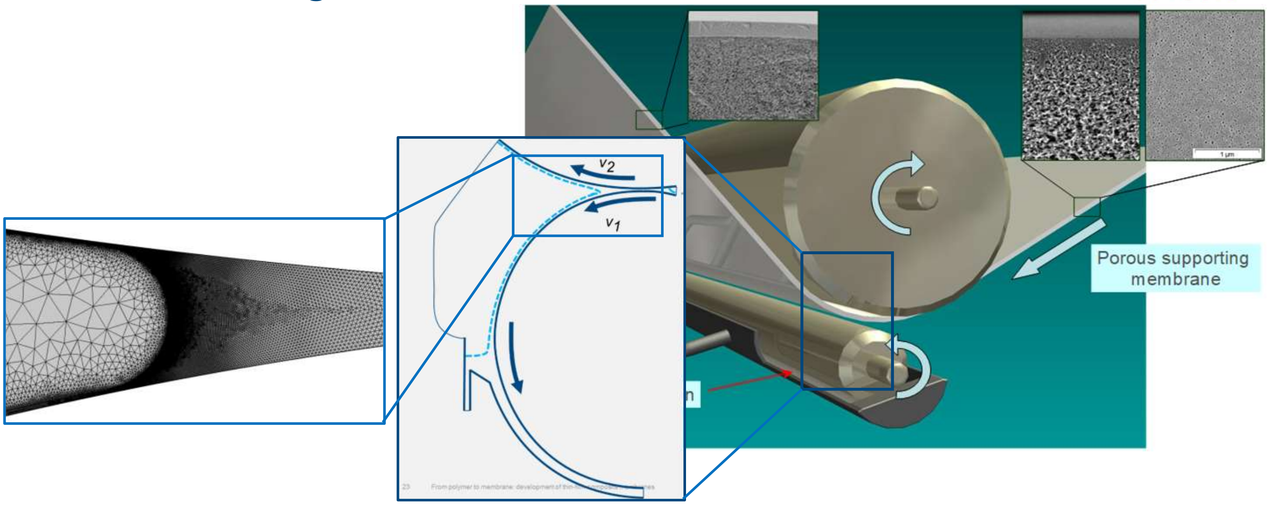
## TFCM production: deposition of selective layer






17

## Mathematical modelling of processes occurring in meniscus during TFCM formation



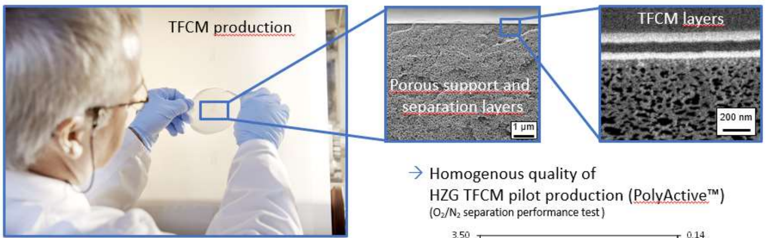

F. Brennecke *et al.*, JMS, 2022





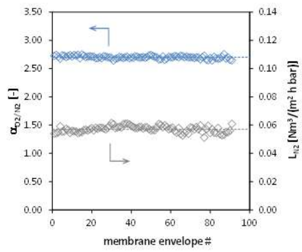
## Asymetric membrane preparation methods

Pilot scale membrane coating facility for thin-film composite membranes (TFCM)



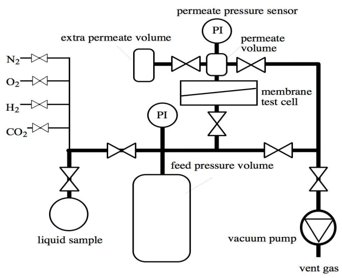

→ Superior properties can be transferred to 100 m² scale

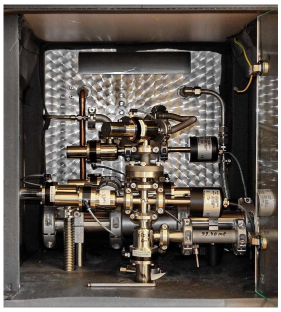
→ Homogenous quality of HZG TFCM pilot production (PolyActive™)
($O_2/N_2$ separation performance test)

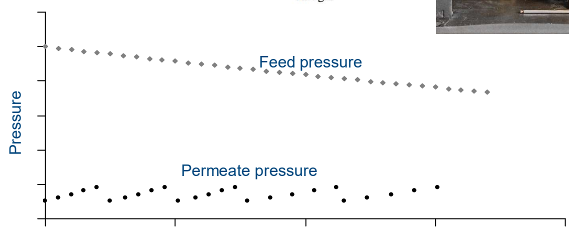


## Pressure increase method for determining permeances

- Automated evaluation of permeation behaviour of single gases
- Determination of temperature dependency
- Consideration of swelling influence
- Fundamental data for permeation modelling



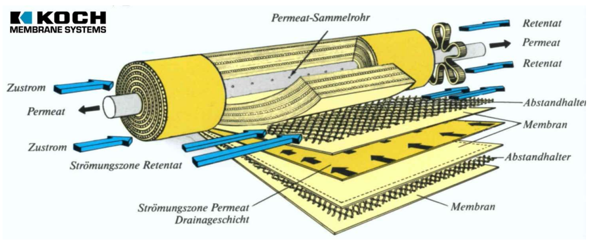



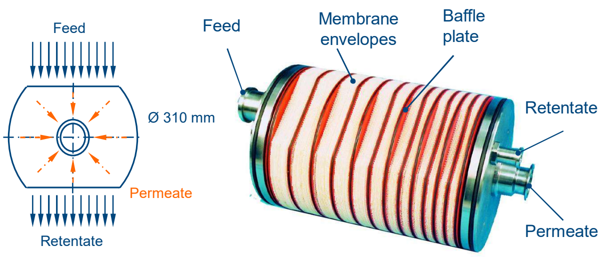




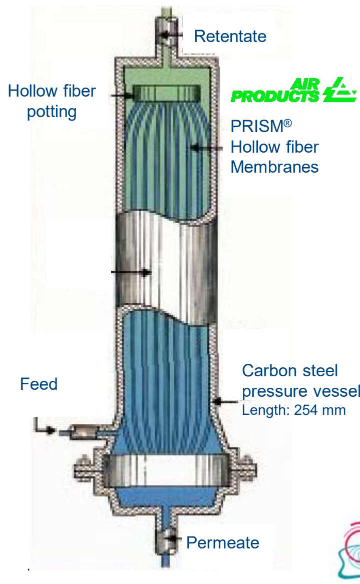

20

## Membrane module design




Hereon's Envelope Type Module






21

# Envelope type membrane modules

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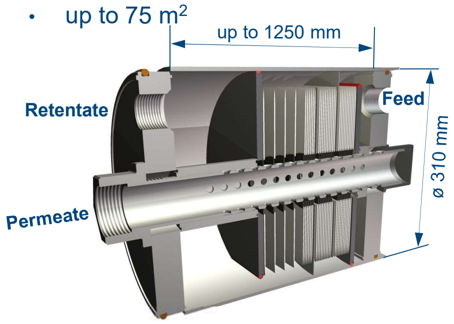
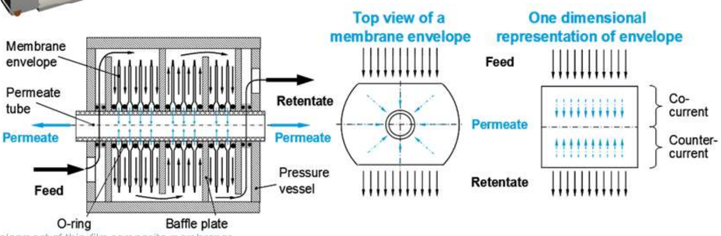
## Standard module

- up to 75 $m^2$




**Pilot** **Standard** **High pressure**

## Model



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# PA11-*b*-PEO TFCM

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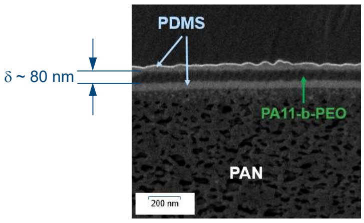
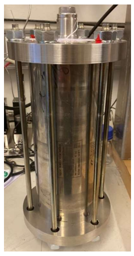
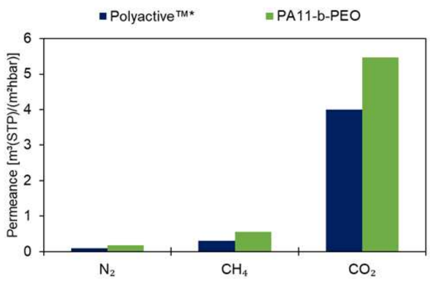
Membrane cross-section

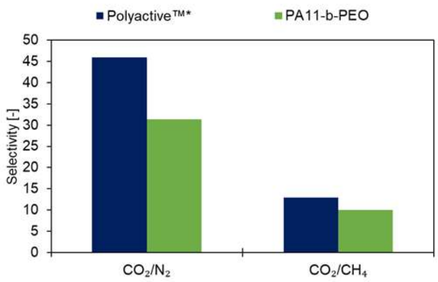



Membrane envelopes

Membrane module






| $CO_2$ transport in bio-PEBA at 30°C | |
|---|---|
| P [Barrer] | 165 |
| L [GPU] | 2000 |



[*] Brinkmann et al., Engineering, Vol. 3, Issue 4, Pages 485-493 **(2017)**

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## Summary

→ TFCMs can be produced from both glassy and rubbery polymers, offering the possibility to use the same supports for various selective layers and thus utilize previously developed technological solutions of membrane packing into the membrane module

→ Multilayer membrane design gives developer flexibility in a material choice. Each layer is serving a specific task: mechanical stability, permeate drainage, smooth support, selectivity, protection

→ TFCMs require extremely small amount of selective material per $m^2$ of membrane opening the way for experimental polymers and other materials into the practical applications

→ The Institute of Membrane Research of Helmholtz-Zentrum Hereon has extensive experience in membrane technology from selective polymer synthesis to pilot scale separation process design



24

# Thank you for your attention!

In case of questions please contact us:
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25