FE0007632: Novel Inorganic/Polymer Composite Membranes for CO_2 Capture

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Inorganic Materials Science

Materials Science and Engineering

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Outline of this presentation

Bio of the PI

Project goals, scope

Success criteria

Concepts for process, membrane, fabrication

Relevant transport and sorption mechanisms

Development strategy

Hendrik Verweij

MS Chemical Engineering, TU *Delft*, 1975

Philips Research Labs, *Eindhoven* TU, 1975-1991

PhD, Eindhoven TU, 1980

Faculty Inorganic Materials, U of *Twente*, 1992-2000

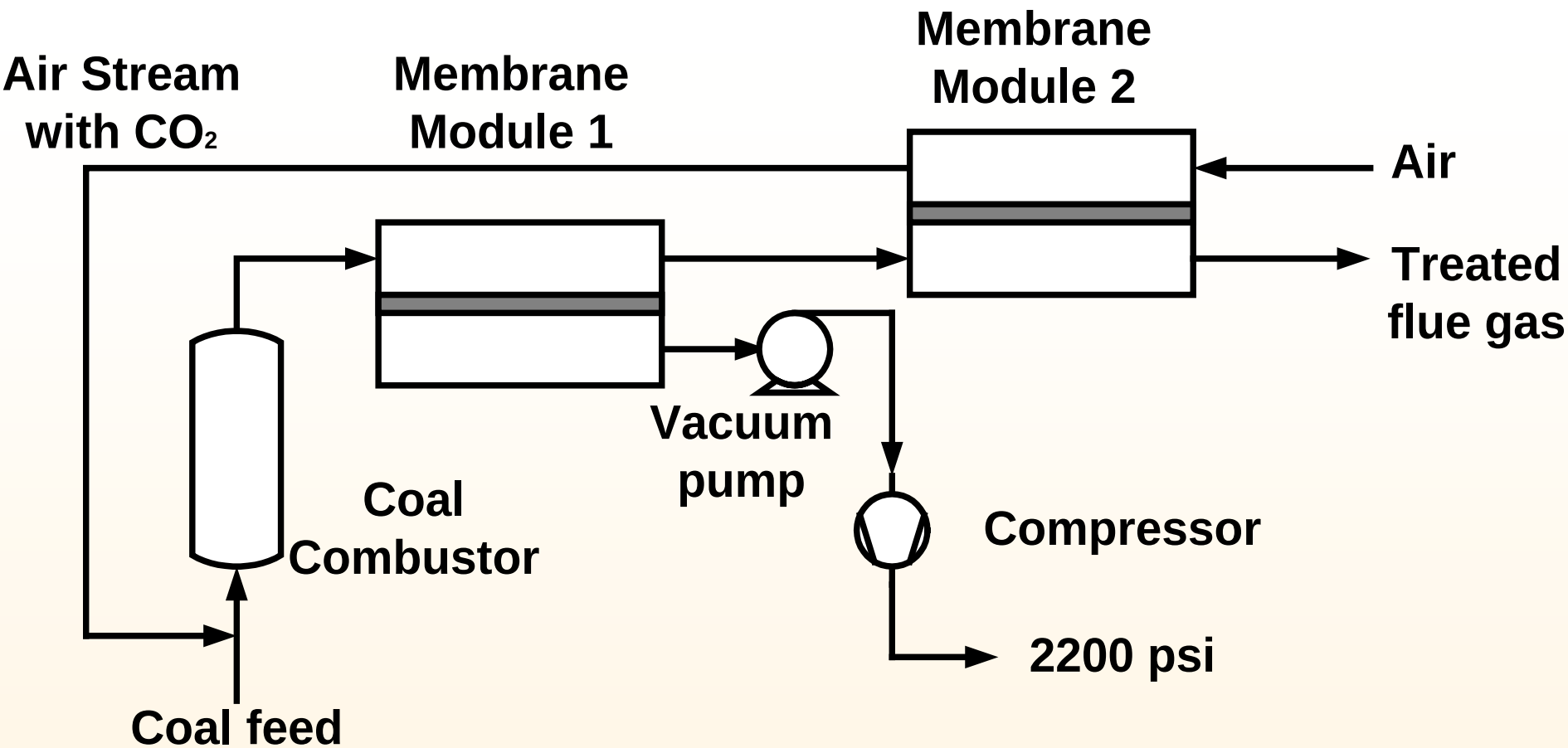
Faculty Ceramic Engineering, OSU, 2001-present

Overall project objectives, conditions

Membrane-based **process for:**

- **Cost-effective capture of** CO_2 **from flue gas:**
  - ◊ 35% **increase of the cost of electricity**
  - ◊ 90% **capture,** 95% **purity at** 150 Atm **total pressure**
  - ◊ **initial calculations based on dry** CO_2/N_2
- ***2 stage process*** **with air sweep:**
  - ◊ combustion [CO_2] = 18.5…25%**; cost optimum at** 22.5%
- **Limits membrane concept to:**
  - ◊ **Mass-manufactured polymer-supported membranes**
  - ◊ **Permeance** >3,000 GPU**; selectivity** >150
    - ♦ 3000 GPU = 9.4 10^{-7} [mol/m^{2}s•Pa])

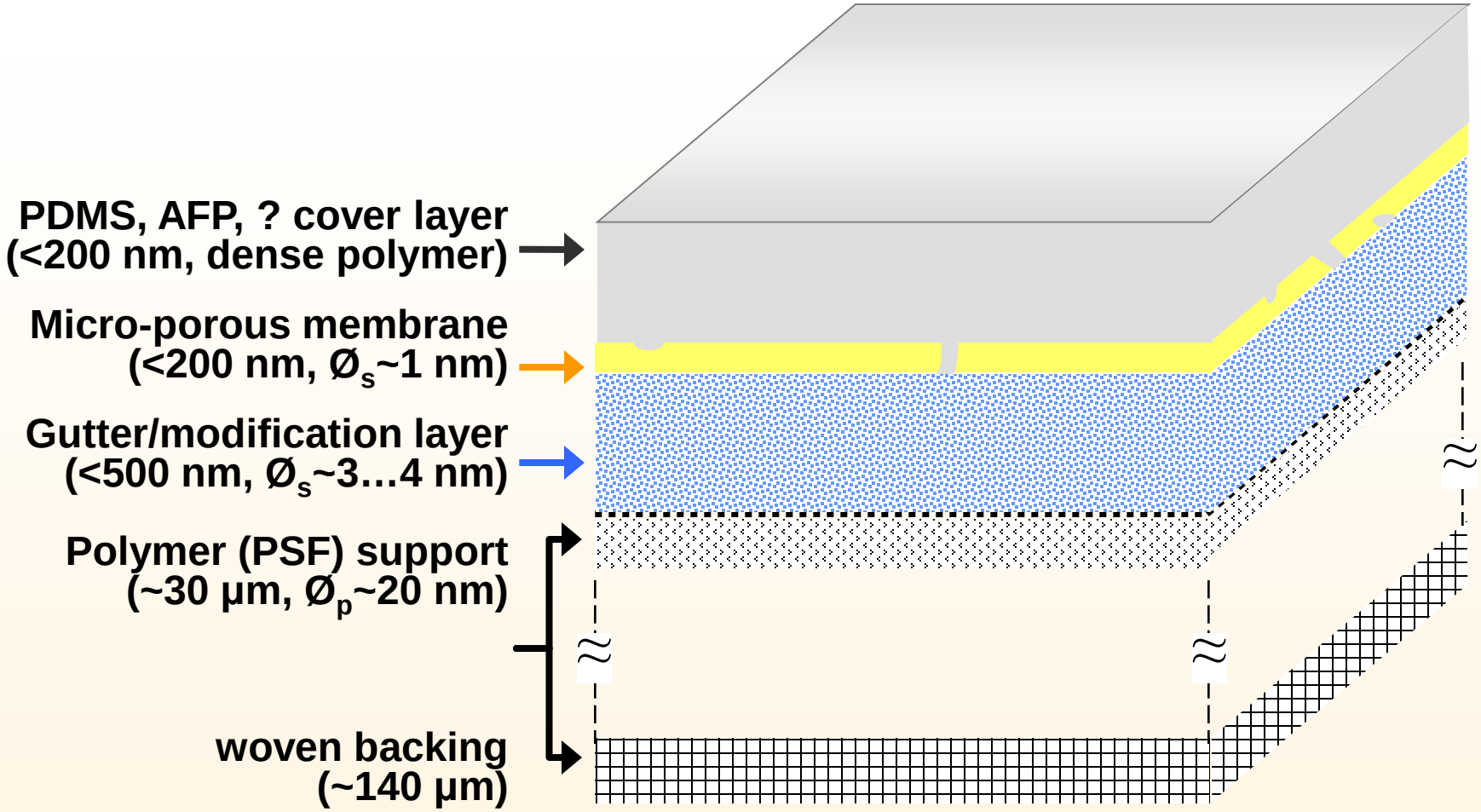
Process concept



Stage 2: fresh air sweep maximizes driving force

Stage 1: high *f*, *α* allows for 10…15 kPa **evacuation**

Supported hybrid membrane concept



Synopsis of project scope

BP1/YR1:

- **Lab scale synthesis, characterization**
  - ◊ **Ceramic supports for quantitative parameters**

BP2/YR2:

- **Lab scale membrane optimization**
- **Bench scale membrane fabrication**

BP3/YR3:

- **Bench scale membrane optimization**
- **Demonstration**

Development guided by systems/costs studies

Detailed success criteria

BP 1:

polymer-supported: $f^{a}_{CO_2}$ = 1000…3000 GPU; α_{CO_2/N_2} = 50…100

ceramic-supported: $f^{a}_{CO_2}$ = 1000…3000 GPU; α_{CO_2/N_2} = 100…200

BP 2:

polymer-supported: $f^{a}_{CO_2}$ = >3000 GPU; α_{CO_2/N_2} = 50…100

ceramic-supported: $f^{a}_{CO_2}$ = >3000 GPU; α_{CO_2/N_2} = 100…200

BP 2:

polymer-supported: $f^{a}_{CO_2}$ = >3000 GPU; α_{CO_2/N_2} = >200

ceramic-supported: $f^{a}_{CO_2}$ = >3000 GPU; α_{CO_2/N_2} = >200

1000|3000 GPU = 3.1 10^{-7}|9.4 10^{-7} [mol/m^{2}s•Pa]

Membrane manufacturing concepts

Cost-effective poly-sulfone (PSF) *support*:

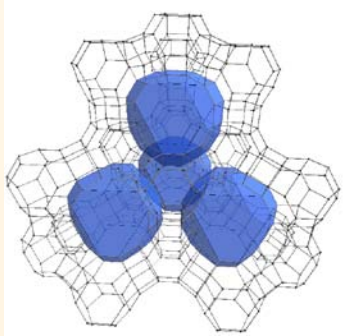
- **Commercially obtained; alternatives available**

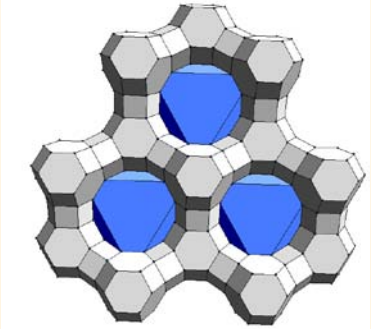
Casting and drying of:

- ***Colloidal dispersions*** **→ dense-packed particles**
- ***Polymer solutions*** **→ homogeneous polymer**

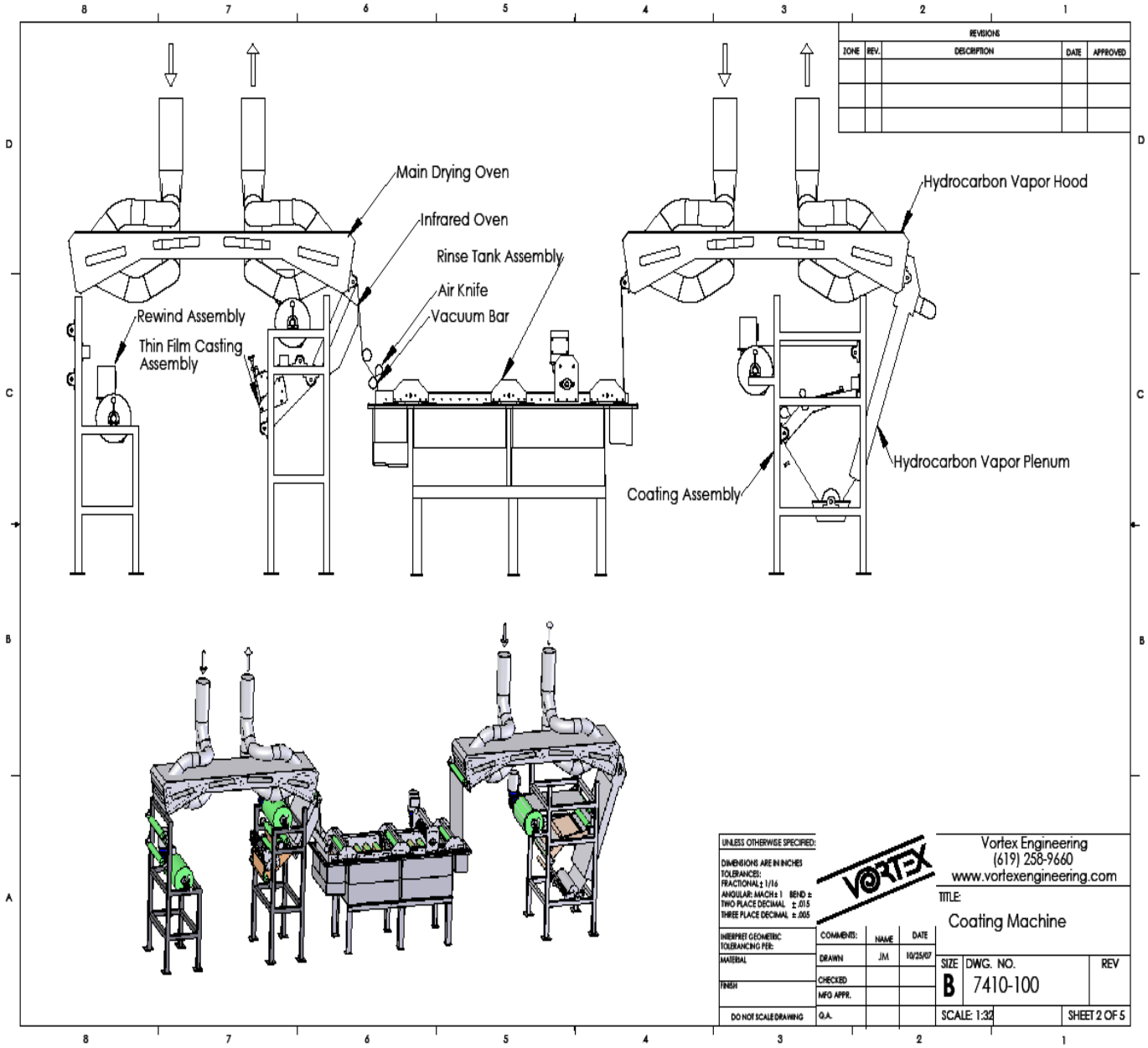
Creating a thin, *micro-porous* layer by:

- **Modification of a meso-porous particle layer**
- **Growth of a ZY particle layer into continuous ZY**
  - ◊ **ZY is Zeolite Y**





Casting machine diagram



Casting machine

Colloidal processing for homogeneity

Precipitation synthesis

Dispersion by:

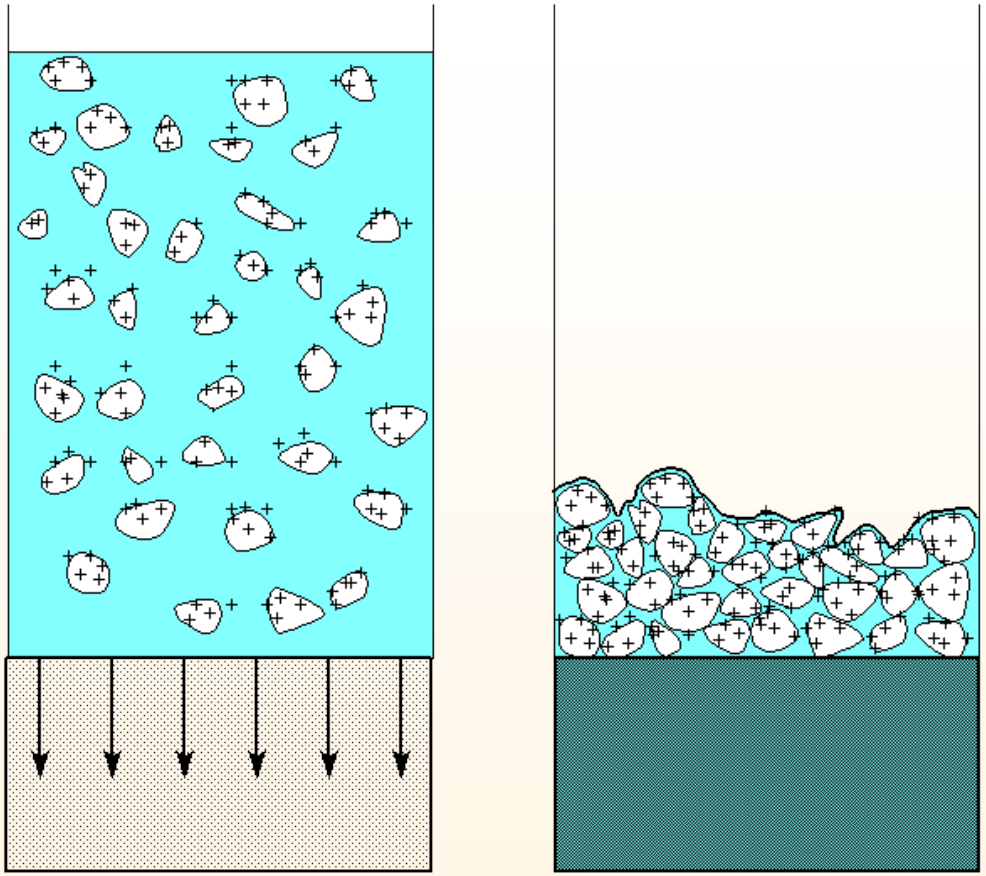
- ◊ **Sonification**
- ◊ **Colloidal stabilisation**

Purification by:

- ◊ **Screening**
- ◊ **Centrifugation**

Consolidation by:

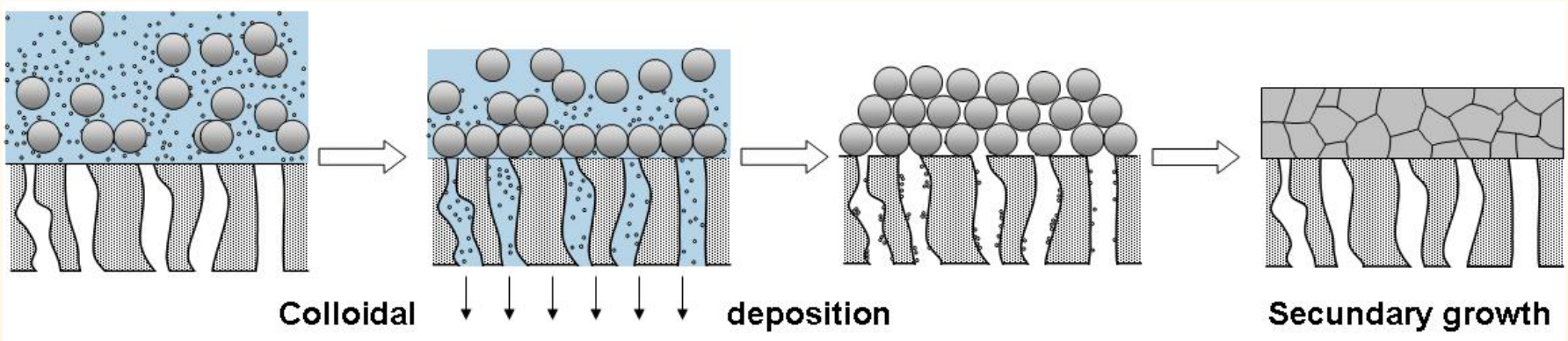
- ◊ **Film coating**
- ◊ **Filtration**



Dry support Wet support

Membrane fabrication with ZY growth

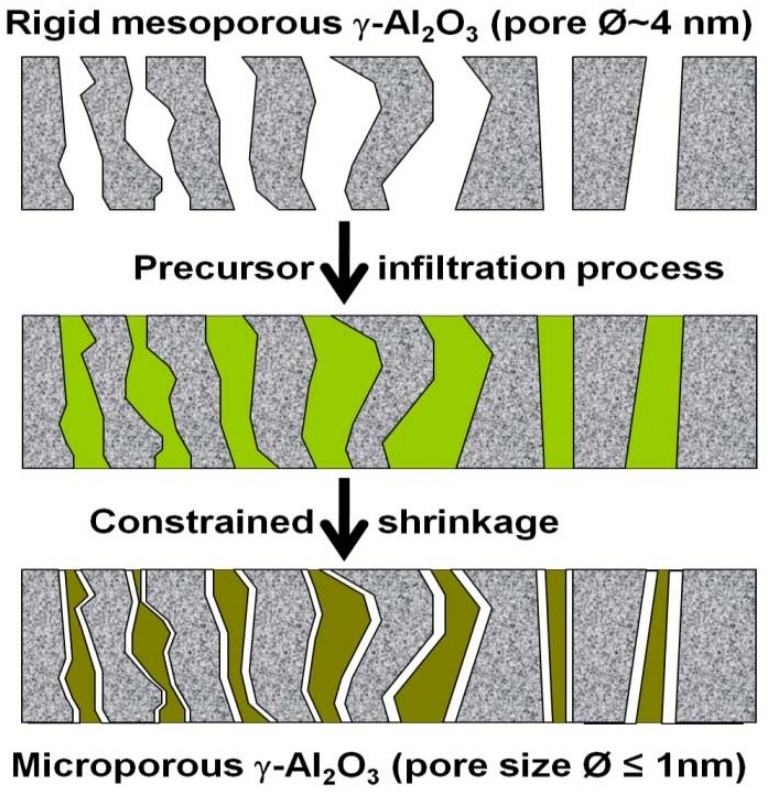
1. **Acquisition of poly-sulfone support**
2. **Application polymer *gutter* layer**
   - ◊ **Resolves the *transition* (spreading) resistance**
3. **Preparation, casting, drying of ZY dispersion**
   - ◊ **Growth of Zeolite Y into a *continuous* layer**



4. **Application of a polymer *cover* layer**
   - ◊ **For protection and defect abatement**

Membrane fabrication with modification

1. Acquisition of poly-sulfone support
2. Application meso-porous oxide particle layer
   - ◊ Acts as gutter layer: provides scaffold
3. Modification of the top meso-porous oxide layer
   - ◊ To form a micro-porous layer in the top part
4. Application of a polymer cover layer
   - ◊ For protection and defect abatement



Fast low-*T* process for inorganic films

Polysulfone ($6.22/m^2)

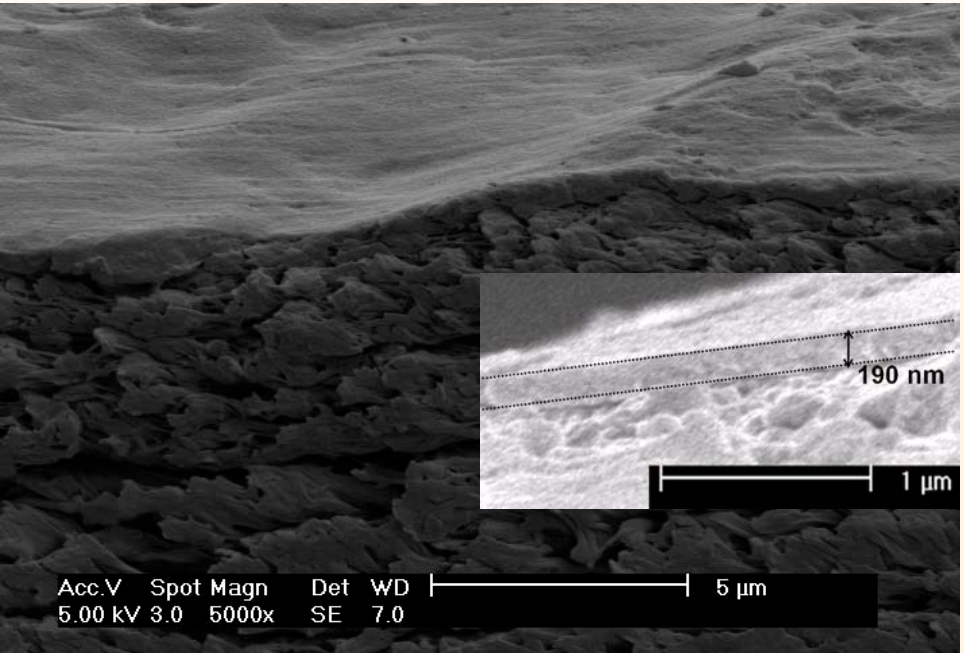
Ceramic supports:

- **Commercial (<**$45K/m^2**)**

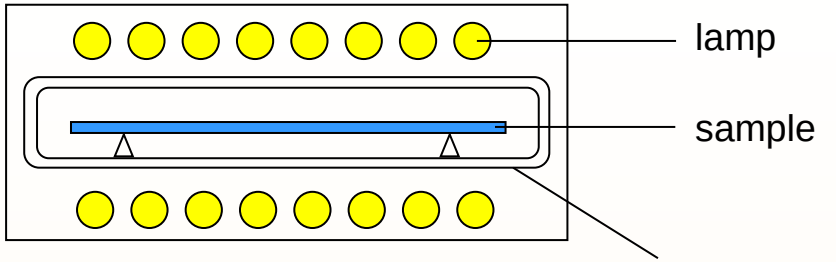
RTP forms γ-alumina @ 400 C; 1′

Polysulfone **remains** <160 C

- SO-Al **bond** → **adhesion**



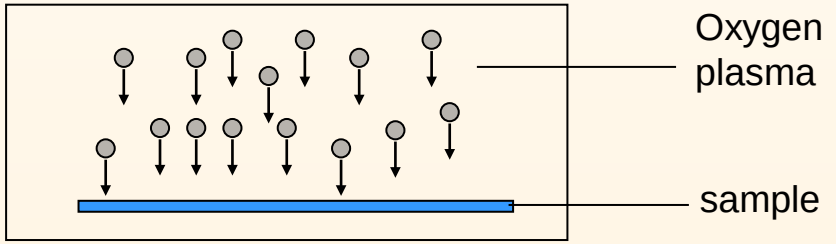
Rapid Thermal Processing



RTP provides an efficient way to heat coating samples with a ramp rate up to 200ºC/s.
Polymer supports remain cool.

Microwave drying

Reactive Ion Etching



RIE helps to remove the organics in the coating and densify the coating at low temperature.

[redacted]: Morphology, phase definition, notations

A:	**exposed apparent membrane area** [m^2]
X:	**membrane thickness** [m]
f|p:	**feed|permeate side** [superscript]
l:	**molar species** [subscript]
g|ℓ|s:	**gas|liquid|solid** [subscript]
c:	**molar concentration** [mol]
p:	**pore** [subscript]
Ø:	**diameter** [m]
ϕ:	**volume fraction;** ϕ_p**: porosity** [-]
τ:	**tortuosity, average transport length/*X*** [-]

: Definitions and notations for transport

n_l: **molar flow** [mol/s]; n_ℓ: **liquid flow** [m^3/s]

j_l: **molar flux,** n_l/A [mol/(m^2s)]

j_ℓ: **liquid flux,** n_ℓ/A [m/s]

p: **pressure** [Pa]; η: **dynamic viscosity** [Pa•s]

f_l: ***molar permeance***, $j_l/\Delta p_l$ [mol/(m^2s•Pa)]

f_ℓ: **mechanical permeance**, $j_\ell \bullet \eta_\ell/\Delta p$ [m]

k_l: **molar permeability,** $f_l \bullet X$ [mol/(m•s•Pa)]

k_ℓ: **mechanical permeability,** $f_\ell \bullet X$ [m^2]

$\alpha^{s}_{l_1,l_2}$: **permselectivity,** f_{l_1} / f_{l_2} [-]

α_{l_1,l_2}: ***true selectivity***, $c^{p}_{l_1} c^{f}_{l_2} \big/ c^{f}_{l_1} c^{g}_{l_2}$ [-]

"Pore" sizes matter for transport

1. $Ø_p > 50$ nm: ***Macro-porous***
2. $2 < Ø_p < 50$ nm: ***Meso-porous***
3. $0.3 < Ø_p < 2$ nm: **Polymer *free volume***
4. $0.3 < Ø_p < 2$ nm: ***Micro-porous***

Transport regimes:

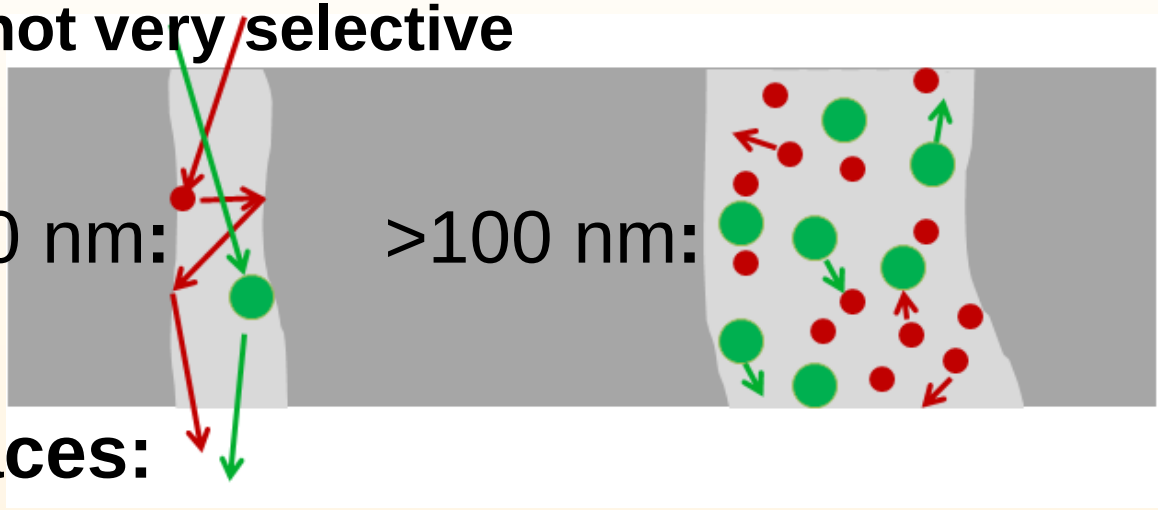
1. **Non-selective *viscous*: defects reduce selectivity**
2. **Slightly selective (*Knudsen* diffusion): defects ibid**
3. **Moderately selective molecular *migration***
4. **Highly selective molecular *exclusion*, *hopping***

Transport regimes

Larger pores:

- ***Viscous*** **transport: very high *k*, not selective**
- ***Ballistic*** **transport:**
  - ◊ ***Specular*****: very high *k*, can be selective**
  - ◊ ***Knudsen*****: high *k*, not very selective**

$Ø_p$ <100 nm: >100 nm:



Smaller pores, surfaces:

- ***Diffusive*** **transport: medium *k*; *α* can be very high**

"Pore" sizes matter for use

1. $Ø_p > 50$ nm: **Macro-porous**
2. $2 < Ø_p < 50$ nm: **Meso-porous**
3. $0.3 < Ø_p < 2$ nm: **Polymer free volume**
4. $0.3 < Ø_p < 2$ nm: **Micro-porous**

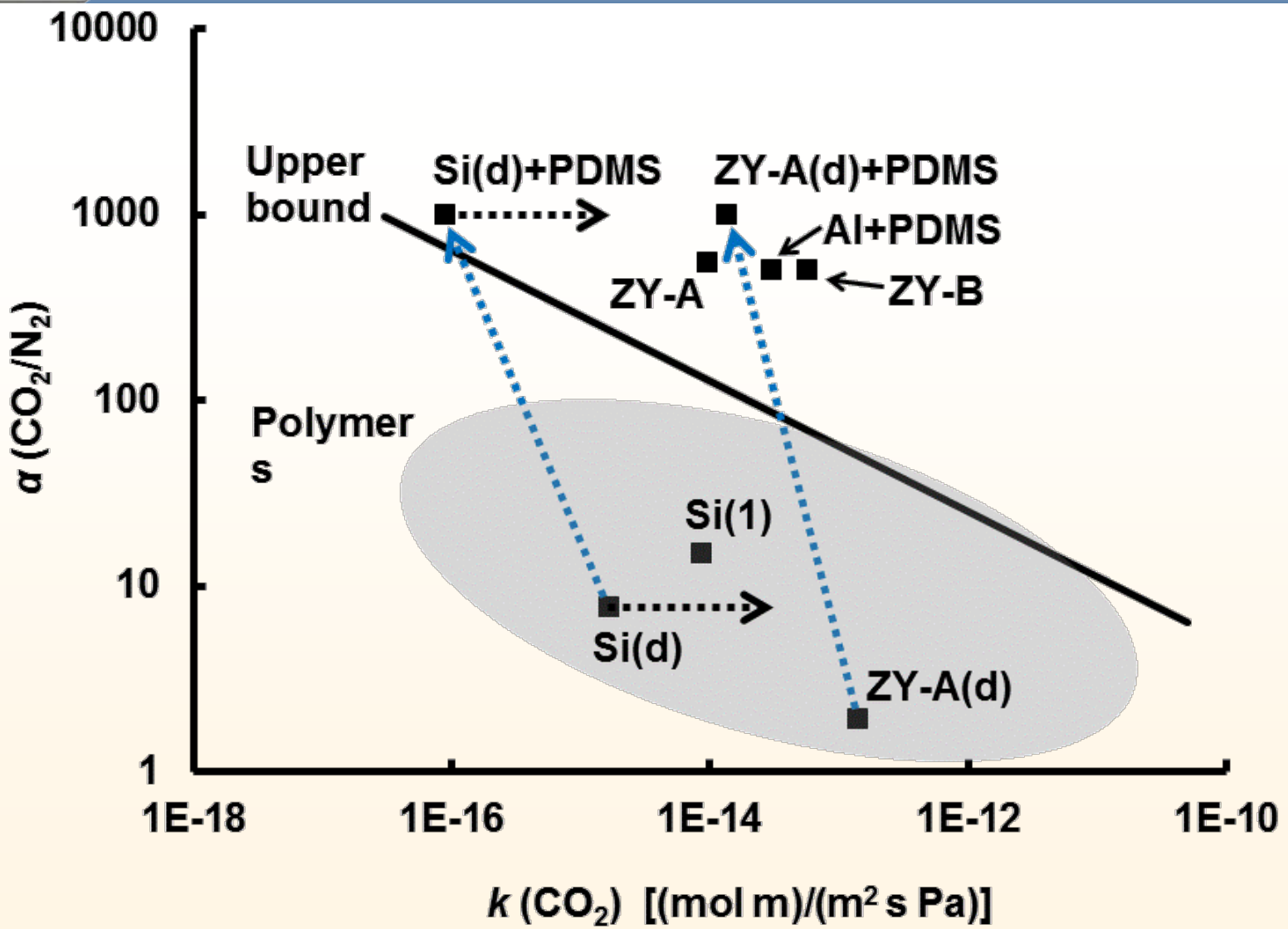
Applications:

1. **Supporting part of PSF, backing layer**
2. **Gutter layer/modification scaffold, ZY seed layer**
3. **Gutter layer between ZY and support, cover layer**
4. **Thin, hence permeable, highly selective layer**

Multi-layer membrane strategy

1. **Macro-porous part PSF: strength, support**
2. **Meso-porous PSF top: pore bridging, deposition**
   - ◊ **All of the above: non-selective, non-resistive: easy**
3. **Gutter layer: to utilize the full membrane *A*rea**
   - ◊ **Can be low-selectivity/must be non-resistive: thin (**1 μm**)**
4. **Micro-porous membrane**
   - ◊ **Highly selective, for high *f*: very thin (**~200 nm**)**
   - ◊ **Very thin → defects more likely: decrease selectivity**
5. **Polymer cover: for protection, defect abatement**
   - ◊ **Can be low-selectivity, must be high permeance: thin**

The membrane must be unusual: Robeson



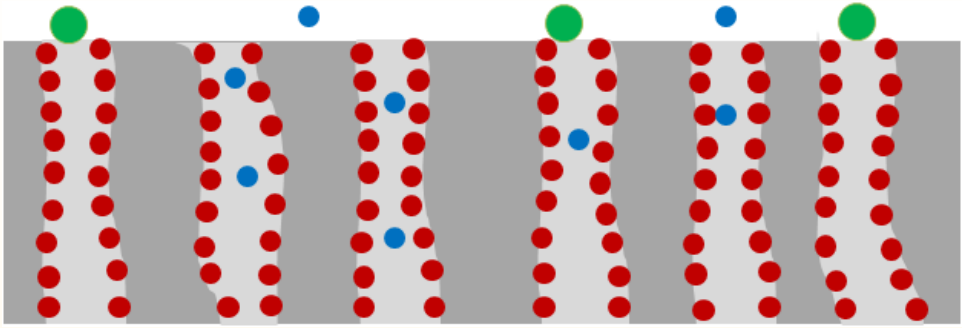
W.V. Chiu et al: J. Membrane Sci., 377 [1-2] 182-190 (2011)

Mechanisms: external size exclusion

α for blocked molecule infinite

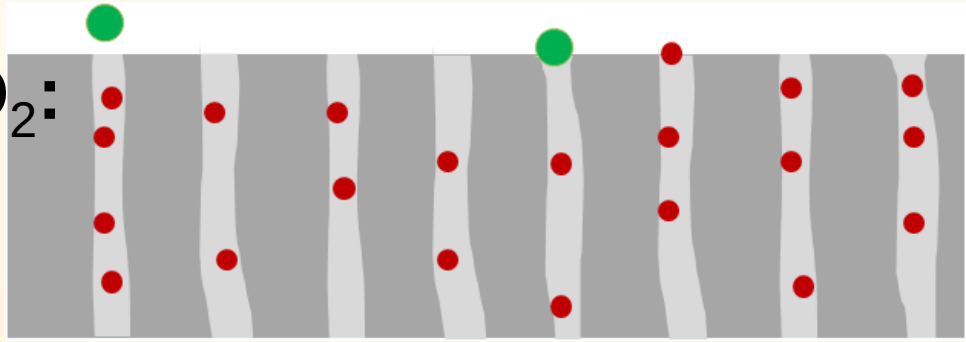
Large micropores: *sorption-induced*:

- **ZY window -** $2\times CO_2$ = 0.16 nm
  - ◊ *k* CO_2 **high**
  - ◊ *k* $N_2 \rightarrow$ **zero**



Compare amorphous SiO_2**:**

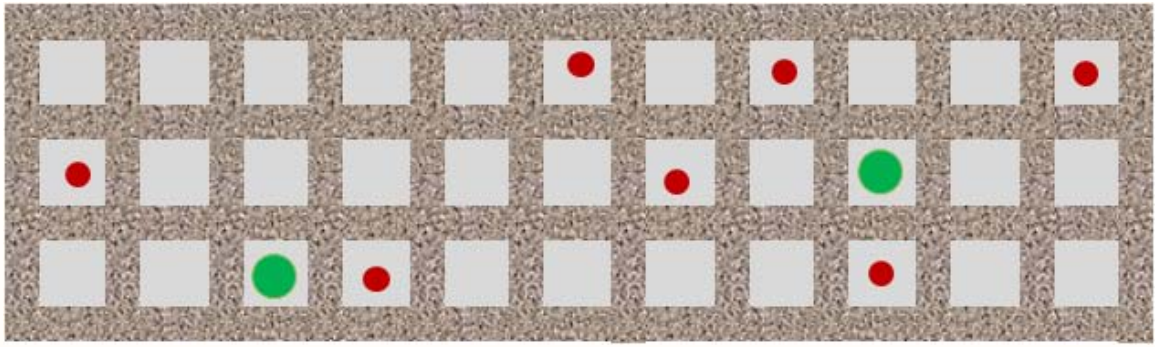
- **Small micro-pores**
- **Permeability low/zero**



Mechanisms: low concentrations (low θ)

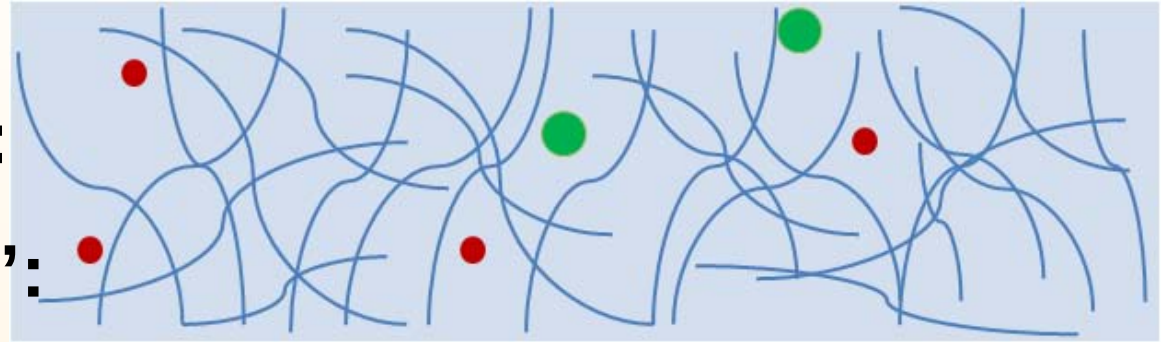
Micro-pore *sites*, surface sites:

- **"hopping"**
- **Selectivity $\rightarrow \infty$**



Compare *polymers*:

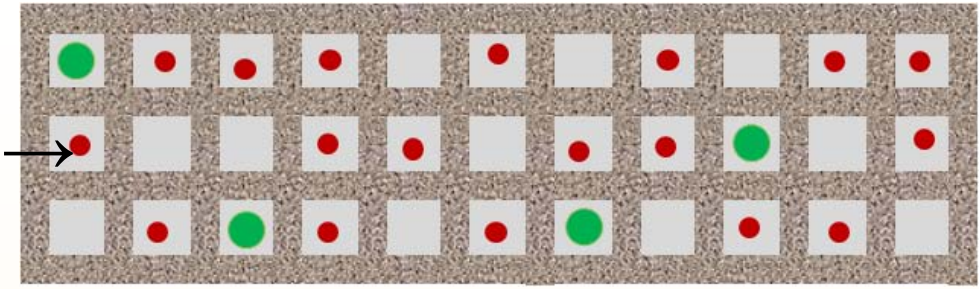
"*Solution-diffusion*":



- **Permeance: trade-of of mobility, b^0, and $\Delta\theta$**
- **Selectivity typically** <50

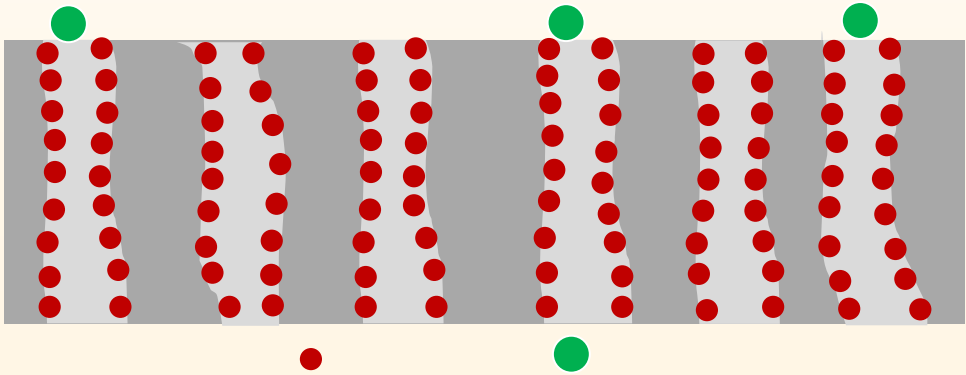
Mechanisms: high concentrations (high θ)

On pore surface or small micropore system →



Diffusion *correlation*:

- N_2 **largely slowed down: *percolative*** CO_2 **network**
- k_{CO_2} **as for single gas**



Very high α likely:

- **combination with size exclusion**

Development strategy

Permeance:

- **Membrane material, thickness, *gutter* layer**
- ***Adjusting* sorption to local conditions**

Selectivity:

- **Membrane material, defect *abatement***
- **Adjusting sorption to local conditions**

Costs:

- **Cheap materials, and fast, continuous production**
- **System studies → membranes, conditions**

Down selection: growth vs modification

Optimized feed, permeate side sorption

High mobility due to surface diffusion

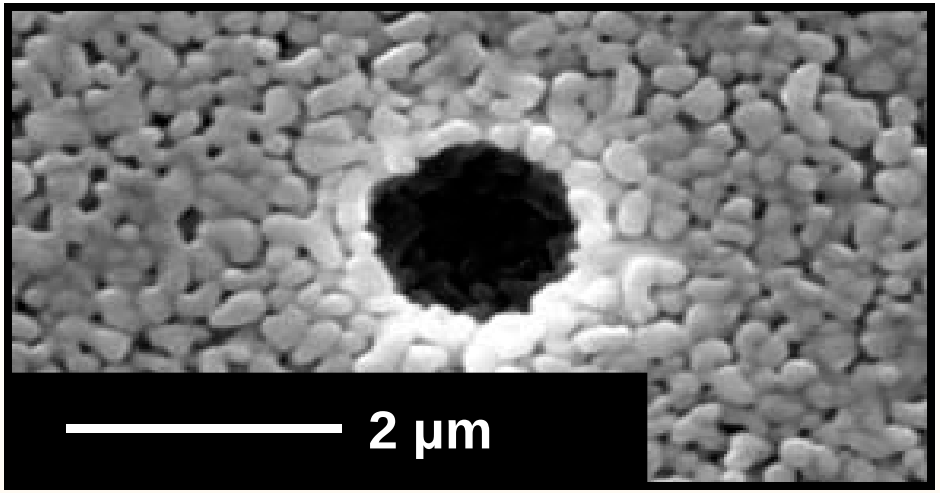
Zeolite Y:

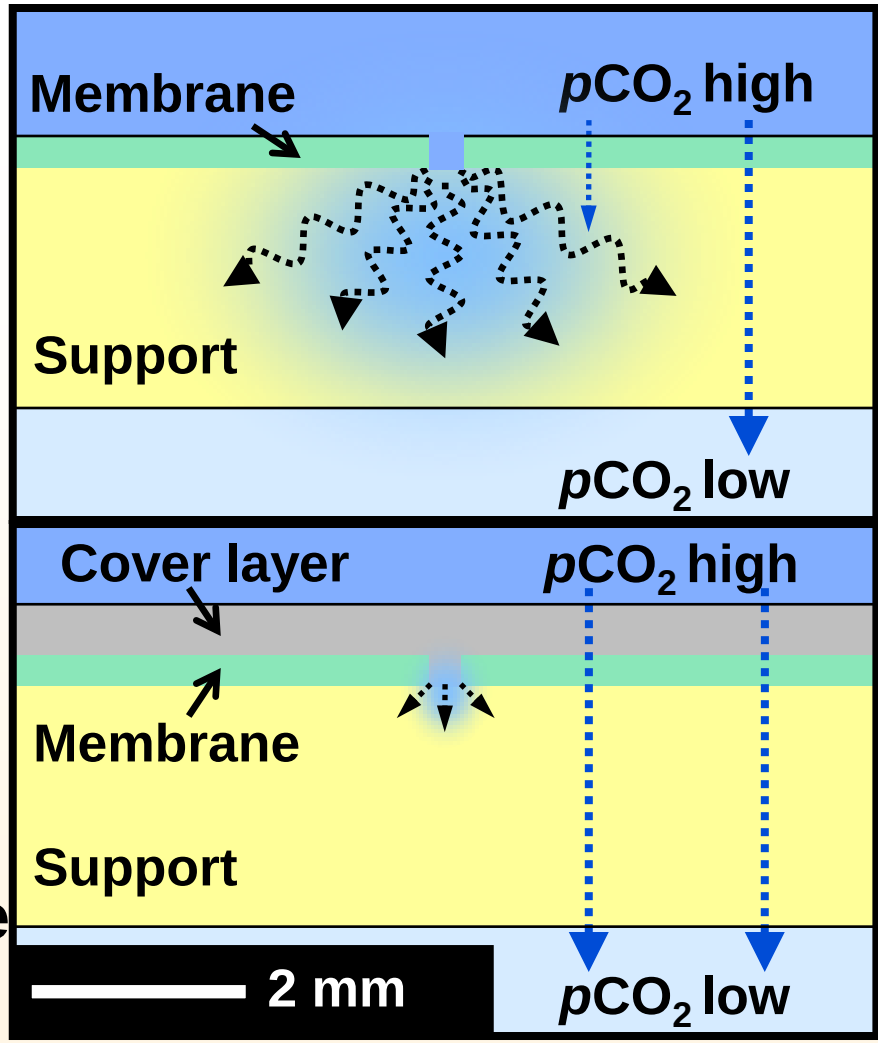
- ◊ **Good *definition*, *tunable* with pore chemistry**
- ◊ **Extreme selectivity, good permeance confirmed**
- ◊ **Growth into continuous layer currently too slow**

Modification method:

- ◊ **Fair definition, tunable with oxide chemistry**
- ◊ **Good selectivity, permeance, fairly reproducible**
- ◊ **Growth is fast enough**

Mitigation for selectivity: cover layer





<1 µm thin membranes:

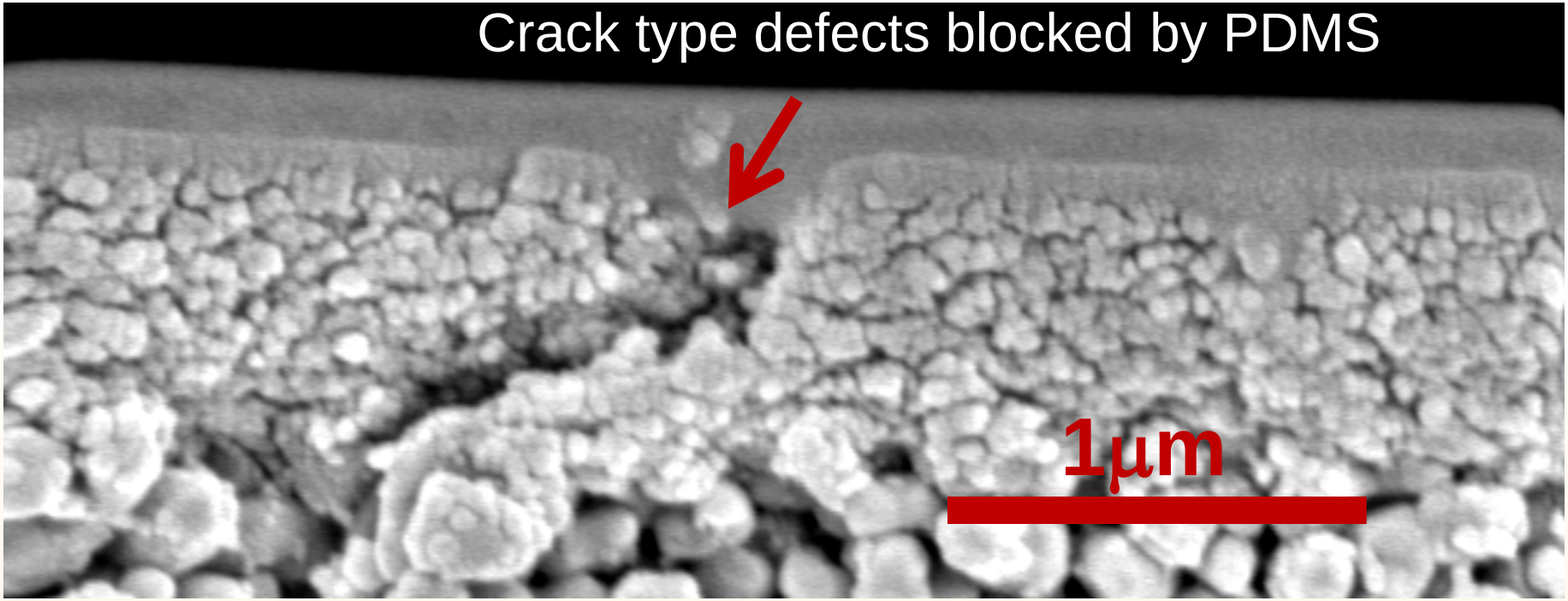
Defects: no selectivity

- **High "spreading" flux**

Cover: permeable, non-selective

- **Abates effect "leaks"**
- **Demonstrated:** γ-alumina**,** SiO_2, zeolites

200 nm thin PDMS, alternatives



Alternatives, backup plan:

- **Amorphous fluoride polymers (**400…450ºC**)**
- **Interfacial polymerization, meso-pore infiltration**

Systems studies

With sub-contractor

Cost+Performance Baseline DOE/NETL-2010/1397

Starting from initial calculations for dry CO_2/N_2:

- **Model implemented in Aspen**
- **Water effects and management added**
- **Finite-element modeling membrane modules**
- ***f*, *α* made dependent on local conditions:**
  - ◊ **Through parameterization of**
    - ♦ **Detailed intrinsic transport characterization**
    - ♦ **Detailed morphology characterization**