FE0007632: Novel Inorganic/Polymer Composite Membranes for CO_2 Capture

Hendrik Verweij

July 9, 2012

Inorganic Materials Science

Materials Science and Engineering

THE OHIO STATE UNIVERSITY

Funding and performance dates

Total budget: October 1, 2011…September 30, 2014

- **DOE**: $3,000K; **OSU**: $679K; **ODOD**: $500K

BP1: October 1, 2011…September 30, 2012

- **DOE**: $898K; **OSU**: $219K; **ODOD**: $132K

BP2: October 1, 2012…September 30, 2013

- **DOE**: $958K; **OSU**: $226K; **ODOD**: $181K

BP3: October 1, 2013…September 30, 2014

- **DOE**: $1,144K; **OSU**: $233K; **ODOD**: $187K

Partners

NETL: José D. Figueroa, project manager

OSU:

- ◊ **Hendrik Verweij: Materials Science: PI**
  - ♦ **ceramic synthesis, transport, structure analysis**
- ◊ **Prabir K. Dutta: Chemistry: Co-PI**
- ◊ **Winston W.S. Ho: Chemical Eng.: Co-PI**
  - ♦ **polymer synthesis, module fabrication, testing**

Gradient Technologies:

- ◊ **Stephen J. Schmit: Chemical Eng.: Systems**

AEP:

- ◊ **Daniel M. Duelmann: Consultant for plant operation**

Trisep Corporation

- ◊ **Peter A. Knappe: Consultant for manufacturing**

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**
- ***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

Permeance is CO_2 flux/pressure difference

Selectivitity is for CO_2 w.r.t. N2

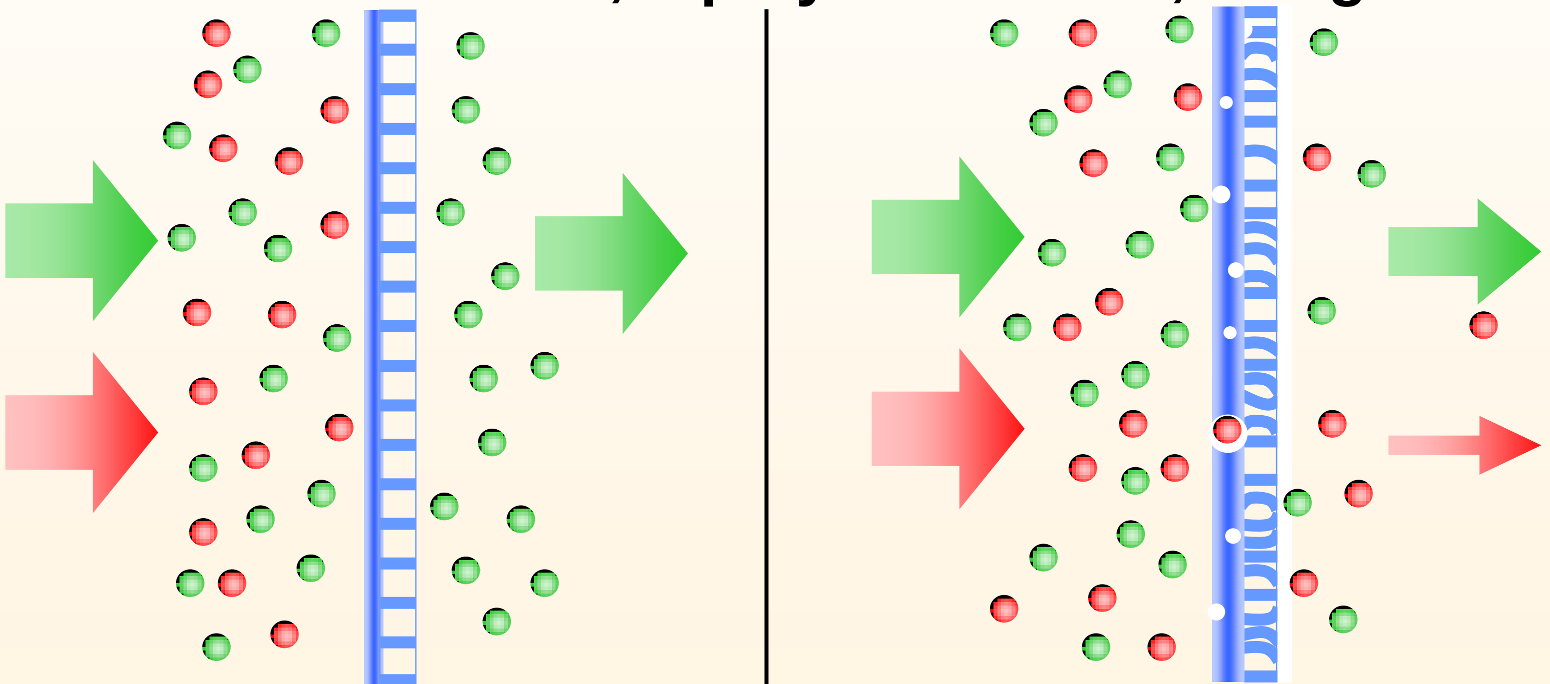
Ideal vs real membrane separation

Ideal membrane separation: isothermal → free!

kinetic gas permeance: <10^8 GPU; **selectivity (α): <**∞

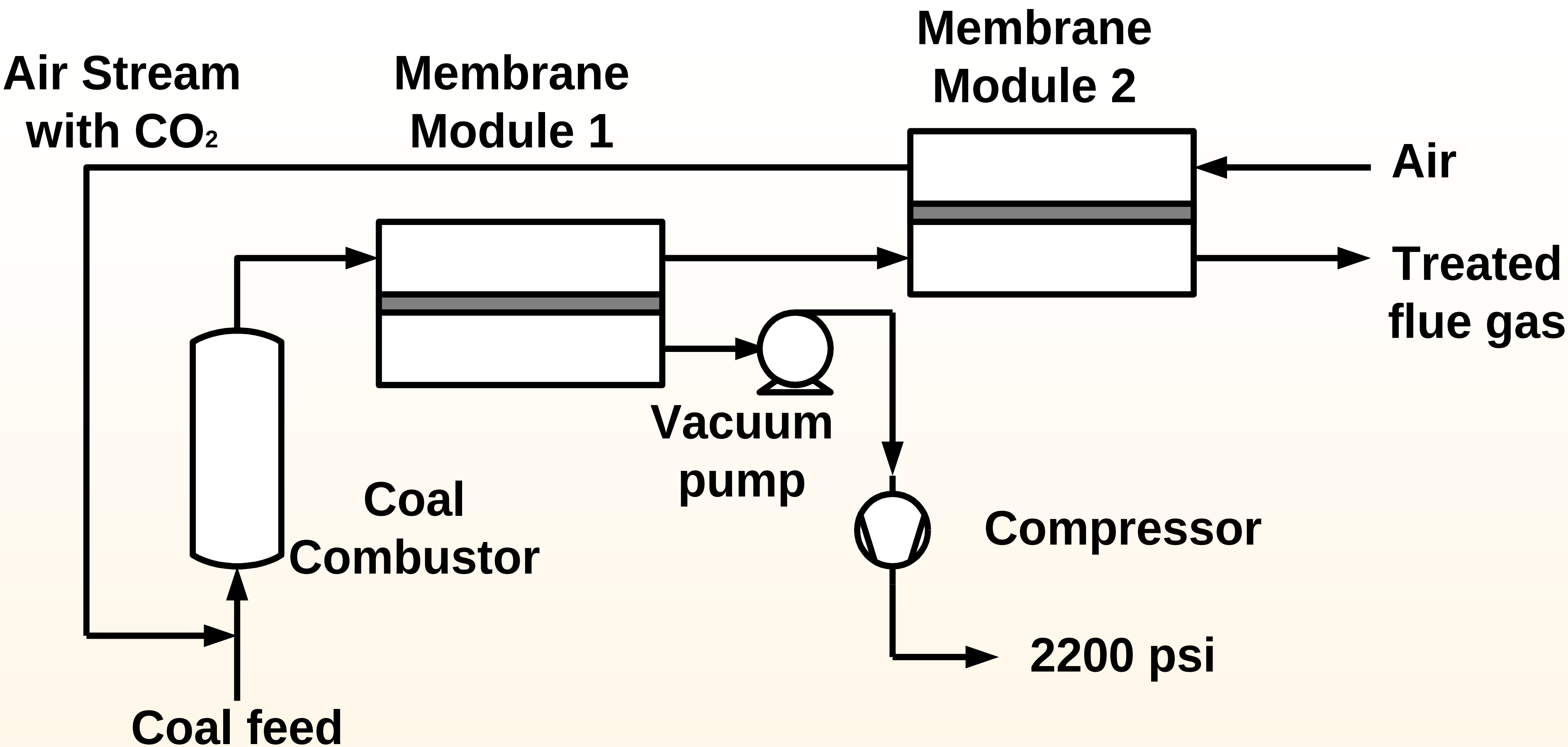
capillary condensation: <10^7 **GPU; selectivity (α):** <50

diffusion: <10^5 GPU; α **polymers:** <100; **inorganics:** <∞



thin, selective permeable | thick, less selective, defects

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

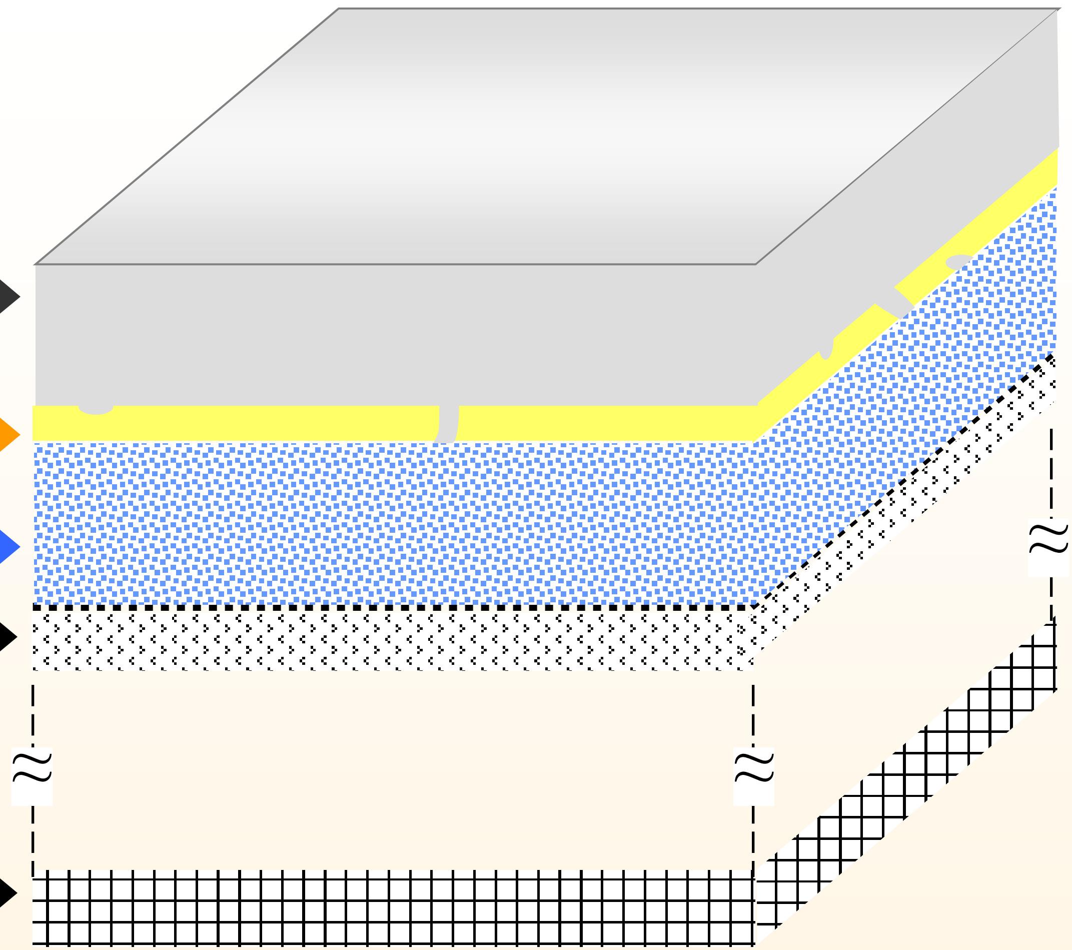
Defect abatement cover layer
(*X* = <200 nm**, dense polymer)**

Micro-porous membrane
(*X* = <200 nm**,** Ø$_p$ = <1 nm**)**

Gutter/modification layer
(*X* = <500 nm**,** Ø$_p$ = 3…4 nm**)**

Polymer support
(*X* = ~30 µm**,** Ø$_p$ = 20-1000 nm**)**

woven backing
(*X* = ~200 µm**)**



X **= thicknes;** Ø$_p$ **= pore diameter**

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

Baselines and success criteria

For 50% CO_2 **on good, resistive ceramic supports:**

- **Zeolite Y:** *f* = 500 GPU**;** *α* > 100
- **Modified** γ-alumina**:** *f* = <3000 GPU**;** 50 < *α* < 150

Success criteria for polymer supports:

- **BP 1:** *f* = 1000…3000 GPU **with** *α* = 50…100**.**
- **BP 2:** *f* = >3000 GPU **with** *α* = 50…100**.**
- **BP 3:** *f* = >3000 GPU **with** *α* = >200

Ceramic **supports: characterization, parametrization**

BP1 work plan synthesis

1. **Smooth, highly permeable ceramic support** ☑
2. **Cover layer permeance** >3000 GPU ☑
3. **Crack-free inorganic layers on polymer** ☑
4. **Ceramic intermediate on polymer** >3000 GPU ☑
5. **Selection polymer support:** PES 100…1000 kD ☑
- PES **is polyethersulfone**
6. **Formation** zeolite Y **(selective material) <**15' ☑
7. **Building a mini-module** ☑
8. **Introducing the selective layer:** $\alpha > 15$ ☐

Common characteristics of deposition

(Precipitation synthesis)

Dispersion by:

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

Purification by:

- **Screening, centrifugation**

(Support pre-treatment by):

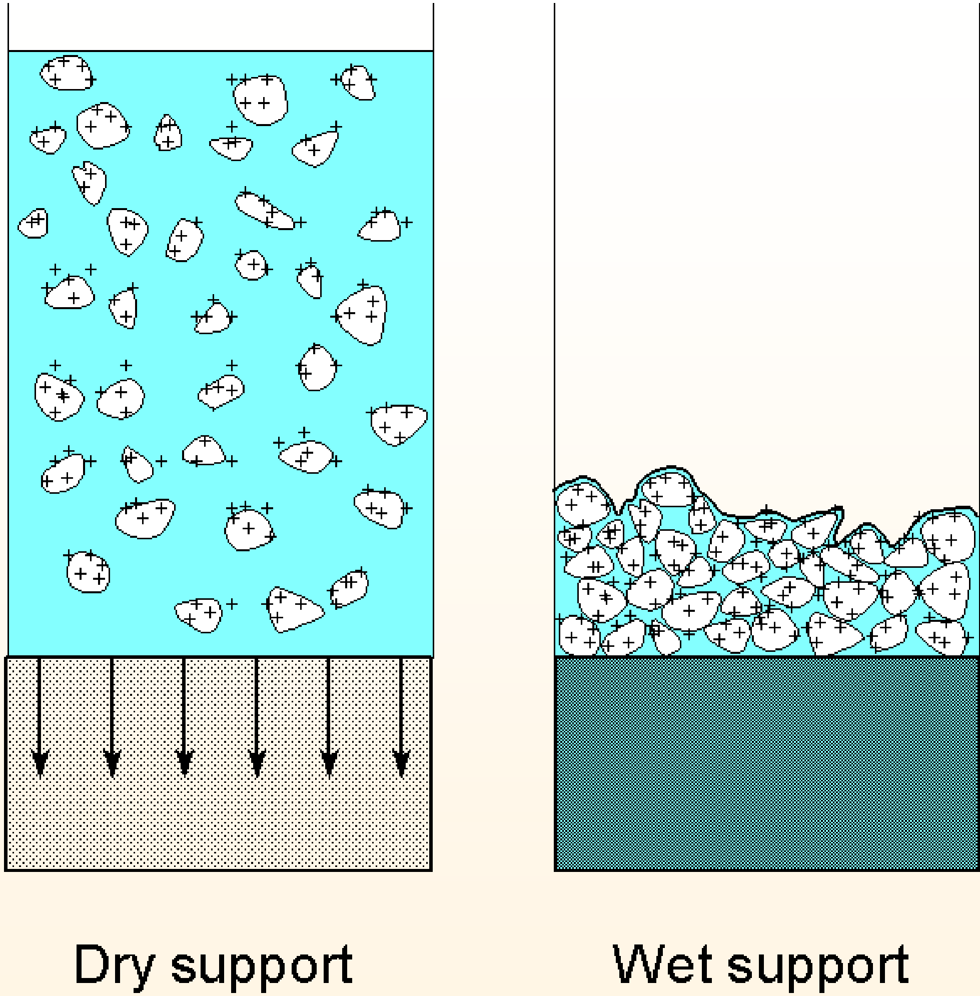
- **Reactive ion etching**

Deposition by:

- **Film coating, filtration**

Consolidation by:

- **Drying, rapid heating**



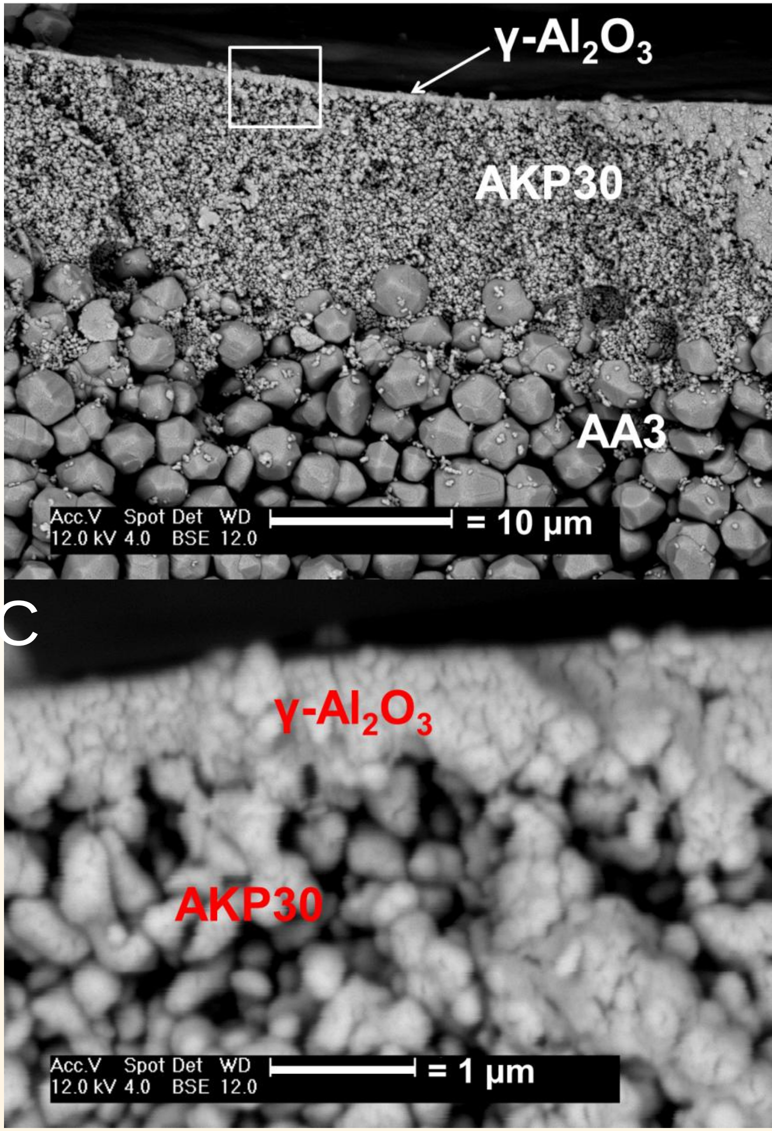
Highly permeable ceramic support

For membrane deposition and transport studies

Colloidal casting, sintering of:

- 2 mm AA3**:** 3 μm α-Al_2O_3 1400 C
    - ◊ **ground and polished**
- 11 μm AKP30**:** 0.3 μm α-Al_2O_3 950 C
- 300 nm γ-alumina**;** $Ø_p$=4 nm
    - ◊ **Boehmite, calcined at** 600 C

Permeance = 11,000 GPU



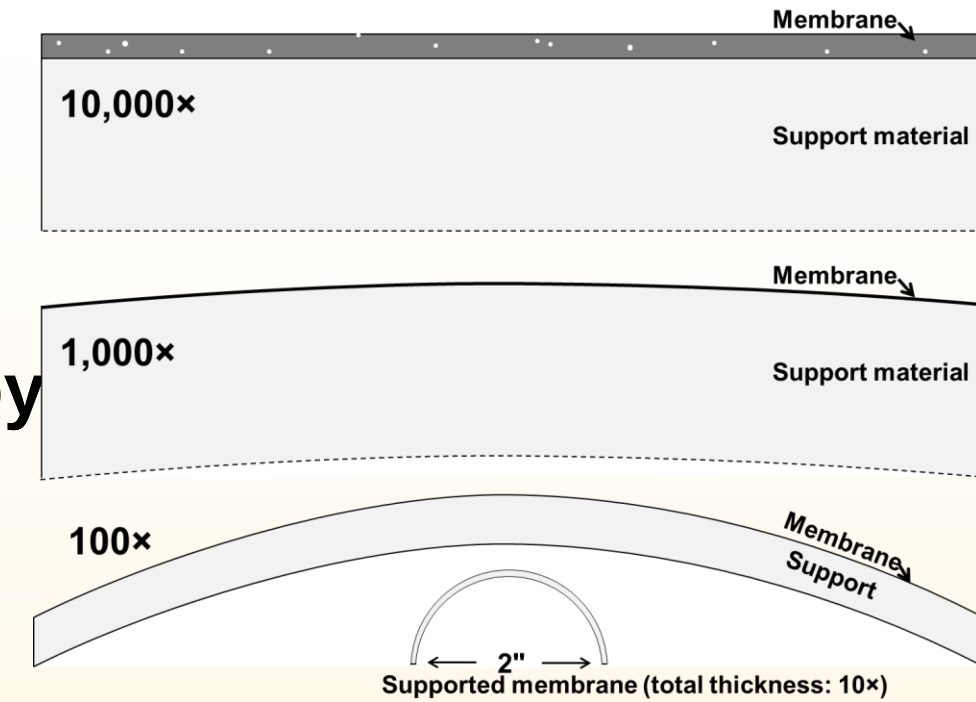
Crack-free ceramic layers on polymers

Most cracks caused by:

- **Excessive stretching**
- **Drying particle layers**

Drying cracks avoided by

- **Improving adhesion**
- **Improving spreading**
- **Decreasing thickness**
- **Increasing packing**
- **Internal lubrication**



Highly permeable ceramics on polymer

Permeable porous inorganic layers as intermediate layers and modification scaffolds

1000 kD polyethersulphone polymer supports:

- **highly permeable; thermally stable up to** 150…200 C**.**

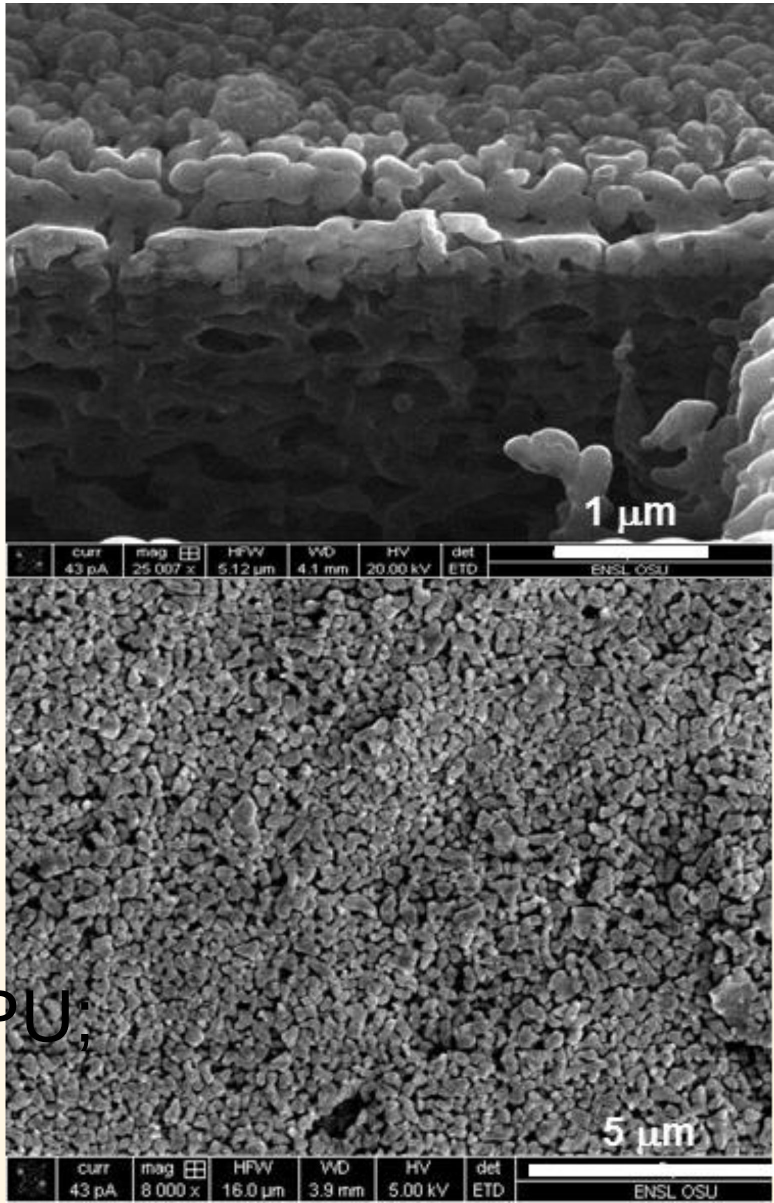
Colloidal casting, drying of:

- 420 nm AKP30**:** 0.3 μm α-Al_2O_3

Without cover: $f_{CO_2} > 4000$ GPU

With ~1 μm PDMS: $f_{CO_2} = 650$ GPU;

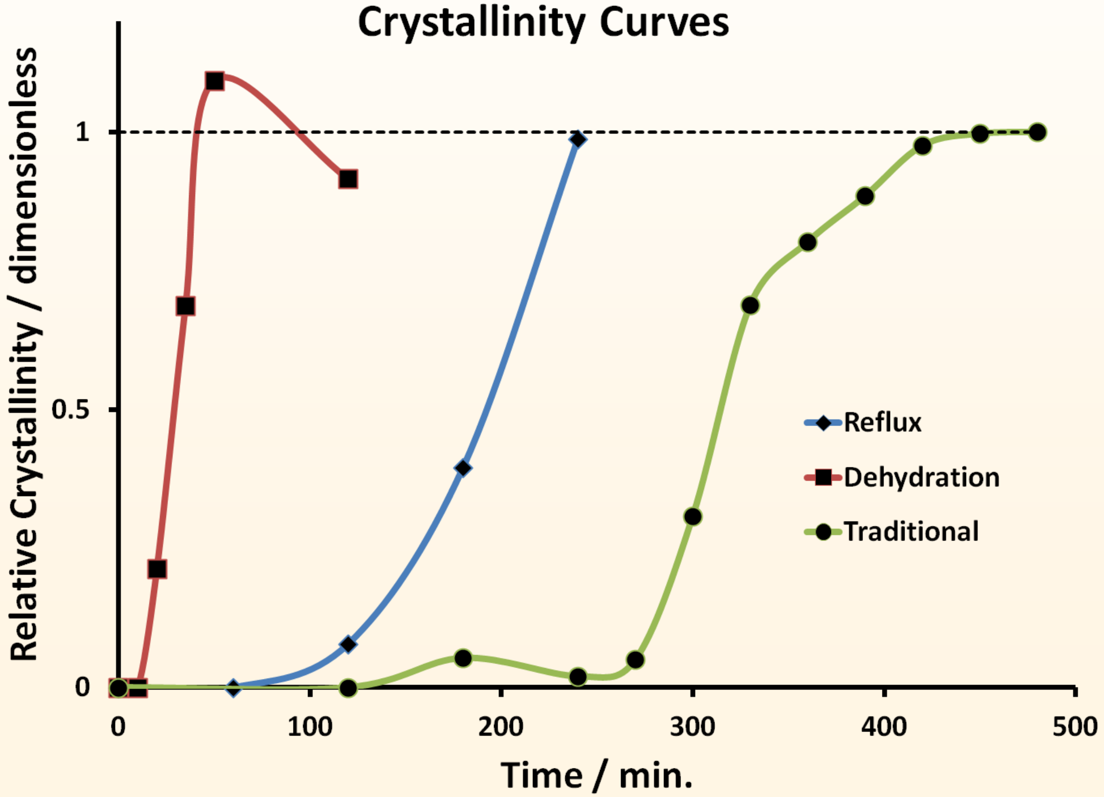
$\alpha_{CO_2/N_2} = 6.4$



Zeolite Y growth process accelerated

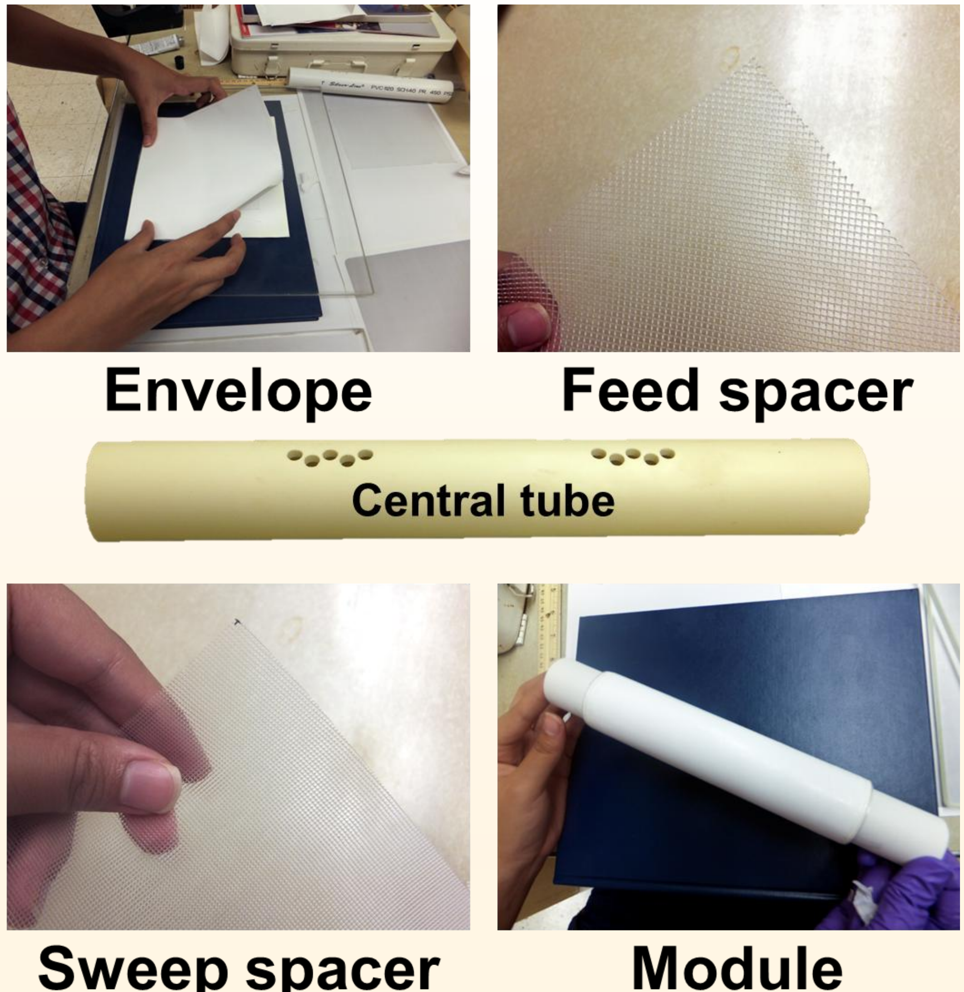
Zeolite Y: one of the potential selective materials

- **Commercial growth times:** >>2 h **($10B market)**
- **For membrane deposition:** <16 min **required**
- **New dehydration method:** <15 min



First module (non-selective demo)

Spiral-wound with 1 µm polydimethylsiloxane on 400 nm porous α-Al_2O_3 on 1000 kD polyethersulfone



BP1 work plan characterization, systems

Characterization:

1. Electron microscopy of 2D FIB cross-sections ☑
2. High-pressure sorption, dehydration studies ☑
3. Membrane transport at flue gas conditions ☑
4. Contact-less characterization by ellipsometry ☑

System studies:

1. Preliminary OSU model in Aspen ☑
2. Implementing water management ☐
3. Implementing detailed membrane transport ☐

Electron microscopy of FIB cross-sections

Electron-transparent films;

“perfect” 2D cross-sections

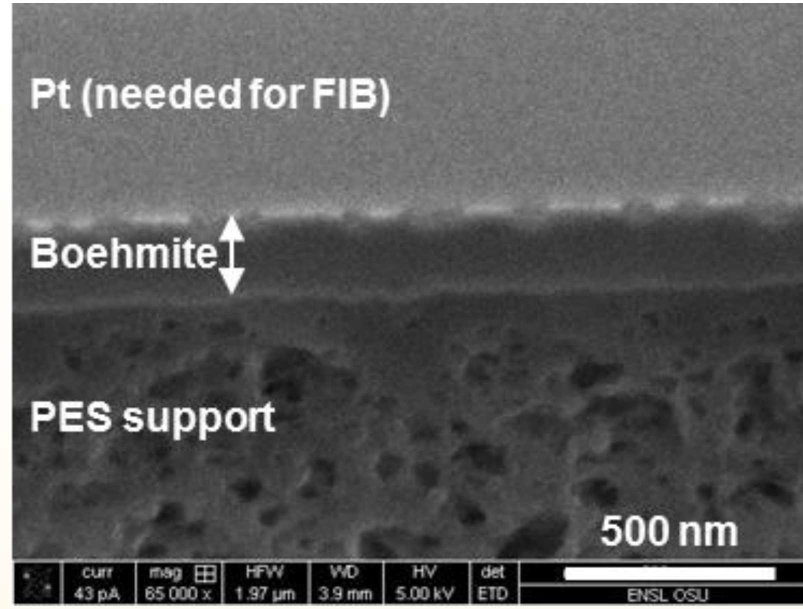
- **for structure analysis**

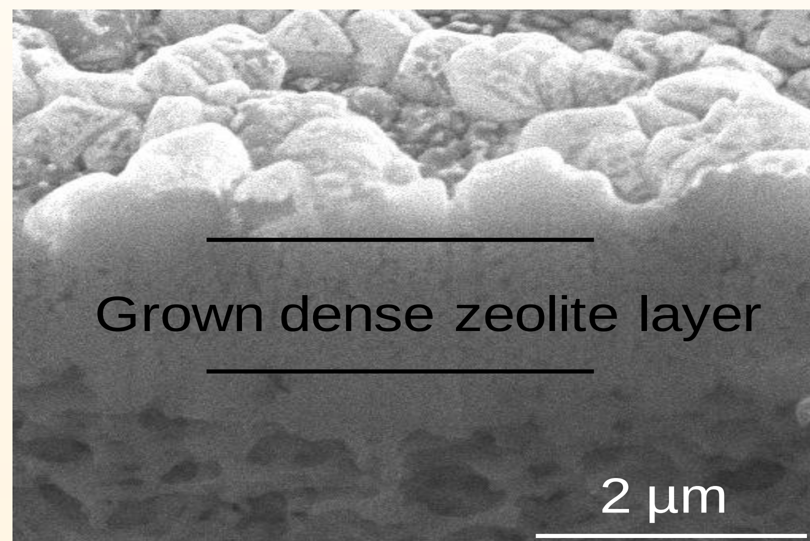
Porous polymers difficult:

- **instability, charging**

Improvements:

- **modern equipment**
- **developing operator skill**
- **application thick Pt layers**

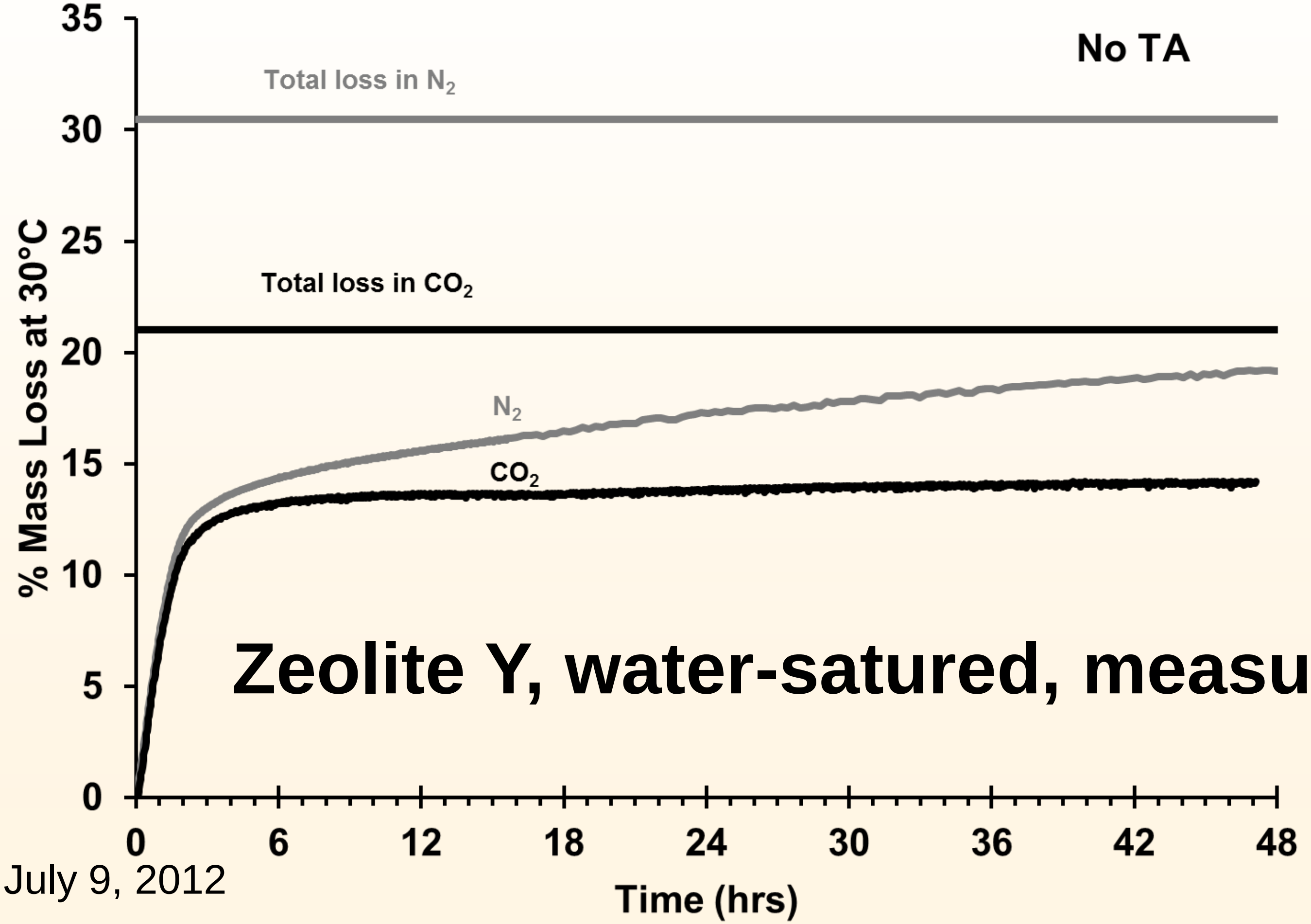




High pressure thermo-gravimetry

Sorption isotherms for transport studies

Confirmation that CO_2 is active in water exchange



Zeolite Y, water-satured, measured at 30°C

Spectroscopic ellipsometry

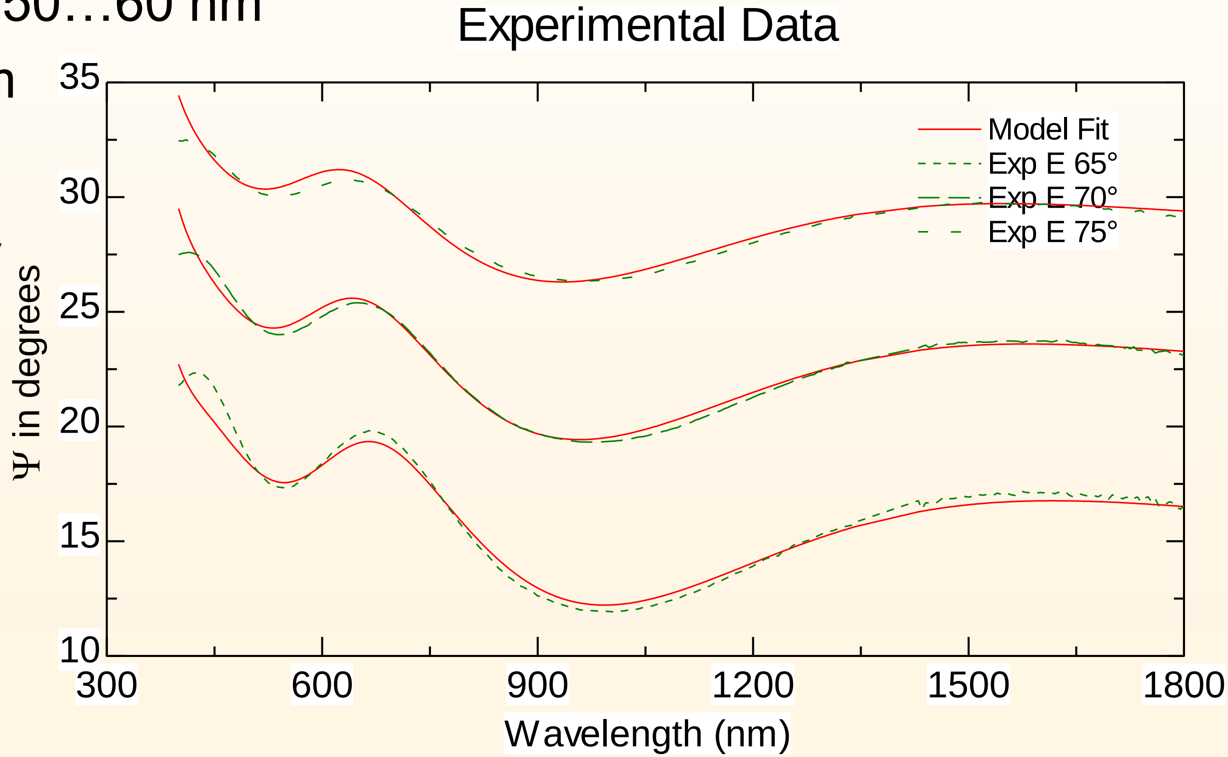
Thickness, contactless during synthesis & use

Composition from refractive index

AKP30 α-Al_2O_3 **on** 1000 kD **polyethersulfone:**

- **Thickness** 410…430 nm
- **Surface roughness** 50…60 nm
- **Intermix** 50…100 nm
- *n* = 1.39

Shows the quality of deposition



Plans for BP1 completion

Growth of thin, selective zeolite Y layers

Selective modification alumina layers

Optimization/automation layer depositions

Experimental design synthesis, pore activation

Competitive H_2O/CO_2 **sorption studies**

Transmission Electron Microscopy FIB films

Ellipsometry of membrane activation/activity

Continuation system studies