FE0007632: Novel Inorganic/Polymer Composite Membranes for CO_2 Capture

PI: Winston Ho, Professor
Department of Chemical & Biomolecular Engineering
Department of Materials Science and Engineering

Co-PI: Prabir Dutta, Professor
Department of Chemistry
The Ohio State University

Subcontractor: Steve Schmit, Director of R&D
Gradient Technology

2013 NETL CO_2 Capture Technology Meeting
Pittsburgh, PA, July 8 – 11, 2013

Funding and Performance Dates

- **Total Budget: 10/01/2011 – 05/31/2015**
  DOE: $3,000K; OSU: $679K; ODOD: $500K

- **BP1: 10/01/2011 – 05/31/2013**
  DOE: $899K; OSU: $351K

- **BP2: 06/01/2013 – 05/31/2014**
  DOE: $958K; OSU: $131K; ODOD: $277K

- **BP3: 06/01/2014 – 05/31/2015**
  DOE: $1,144K; OSU: $197K; ODOD: $223K

Project Organization and Roles

Ohio State University

- Technical lead
- Concept development and execution
- Novel membrane synthesis/characterization
- Membrane scale-up/continuous fabrication
- Process demonstration
- Cost calculations

Winston Ho and Prabir Dutta

DOE NETL

Project Manager

José Figueroa

Gradient Technology

- System, cost analysis
- EH&S analysis

Steve Schmit

TriSep Corporation

- Consult on continuous membrane fabrication

Peter Knappe

AEP

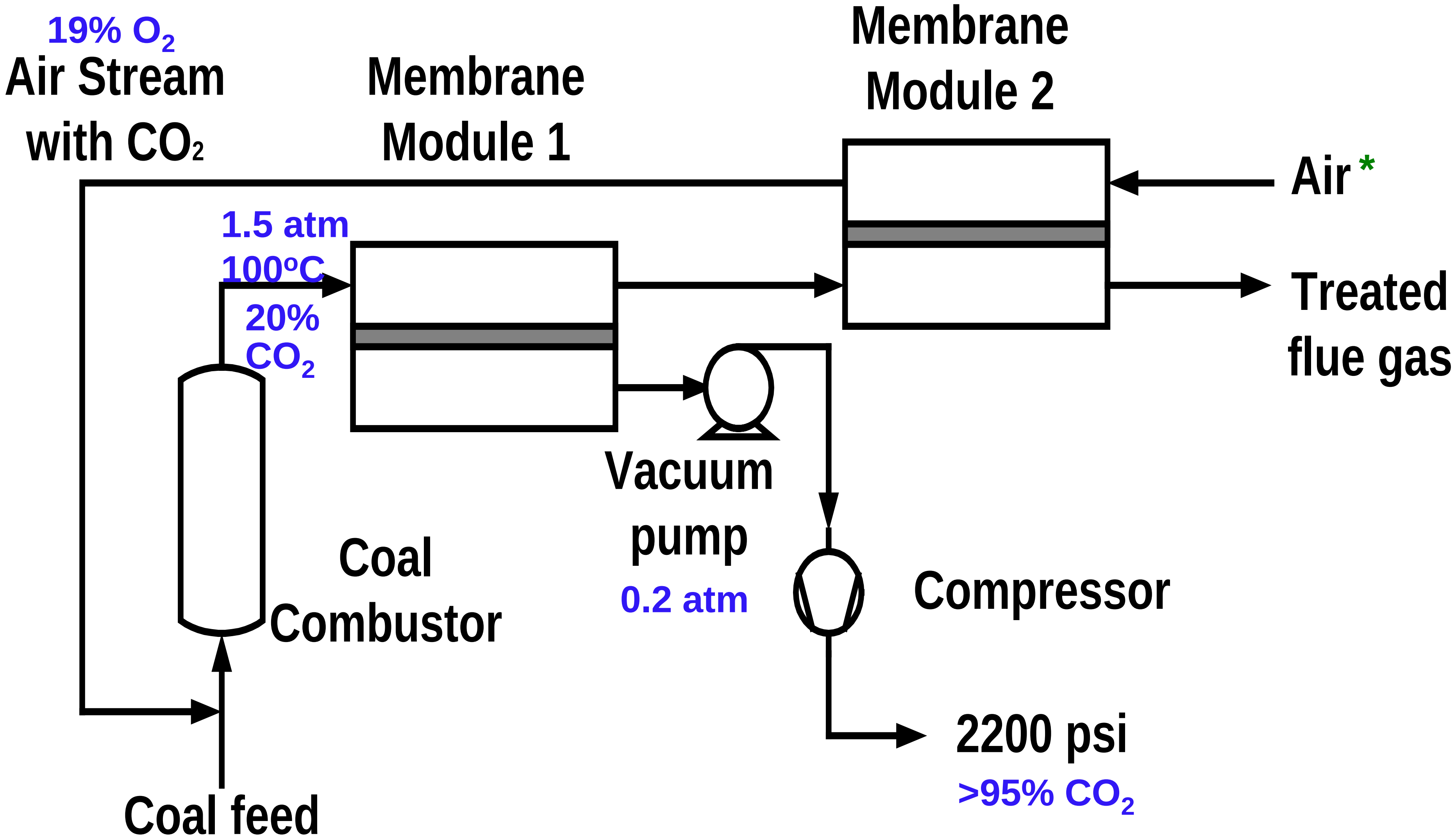
- Consult on plant integration, demonstration and EH&S

Dan Duellman

Project Objective

- **Develop cost-effective design and manufacturing process for new membrane modules that capture CO_2 from flue gas with <35% COE increase and <$40/tonne CO_2**
- **BP1**
    - Bench scale membrane synthesis, characterization, downselection, and gas separation performance
    - Preliminary techno-economic analysis
- **BP2**
    - Bench scale membrane synthesis, characterization and gas separation performance to continue
    - Continuous membrane fabrication
    - Membrane module testing in lab (CO_2, N_2, MOISTURE)
    - Update techno-economic analysis
- **BP3**
    - 3 prototype modules for testing with simulated flue gas
    - Update techno-economic analysis
    - EH&S evaluation report will be developed

Process Proposed for CO_2 Capture from Flue Gas in Coal-Fired Power Plants



*Air Sweep first used by MTR

Membrane Approaches

- **Two Composite Membrane Approaches**
  - All Inorganic composite membrane
  - Zeolite-Y/Polymer composite membrane
    - \+ Amino based cover layer
    - \+ Non-Amino based cover layer

Current Project Success Criteria

- **BP1**
  - **For polymer support:**
    1000 GPU Permeance with Selectivity = 50
  - **For ceramic support:**
    1000 GPU Permeance with Selectivity = 100

Current state-of-the-art 2000 GPU, selectivity = 50

- **BP2**
  - **For polymer support:**
    1500 – 2000 GPU Permeance with Selectivity = 50 – 75
  - **SO_2 effects on membrane (1 – 50 ppm), determine stability of amine membrane with time (100 hours), define limits (24 hours) if polishing unit fails**

- **BP3**
  - **For polymer support:**
    2500 – 3000 GPU Permeance with Selectivity = 100 – 150

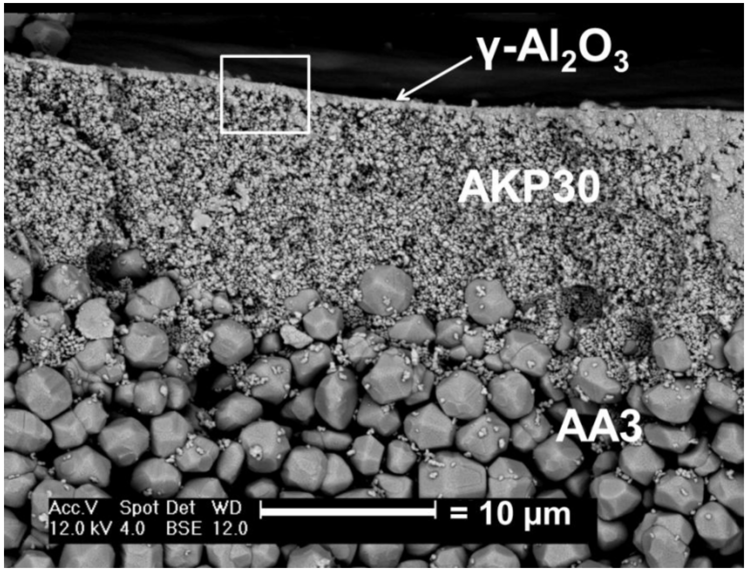
Budget Period 1

- **Two Types of Inorganic Selective Layers Investigated**
  - Alumina
  - Zeolite-Y

- **Alumina Selective Layer on Two Supports**
  - Alumina Selective Layer on Ceramic Support
  - Alumina Selective Layer on Polymer Support

All Inorganic Composite Membrane

- **Highly permeable ceramic support prepared**
- **Rapid modification method of γ-alumina did not give adequate performance (separation factors <10)**
- **Low selectivity due to**
  - **Defects, Cracks**
- **Difficult to scale-up**
  - **Inorganic support**
- **Continuous fabrication**
  - **Not suitable**
  - **High cost**



- **Overall results led to down selection (October 2012) of Zeolite-Y/Polymer composite membrane**

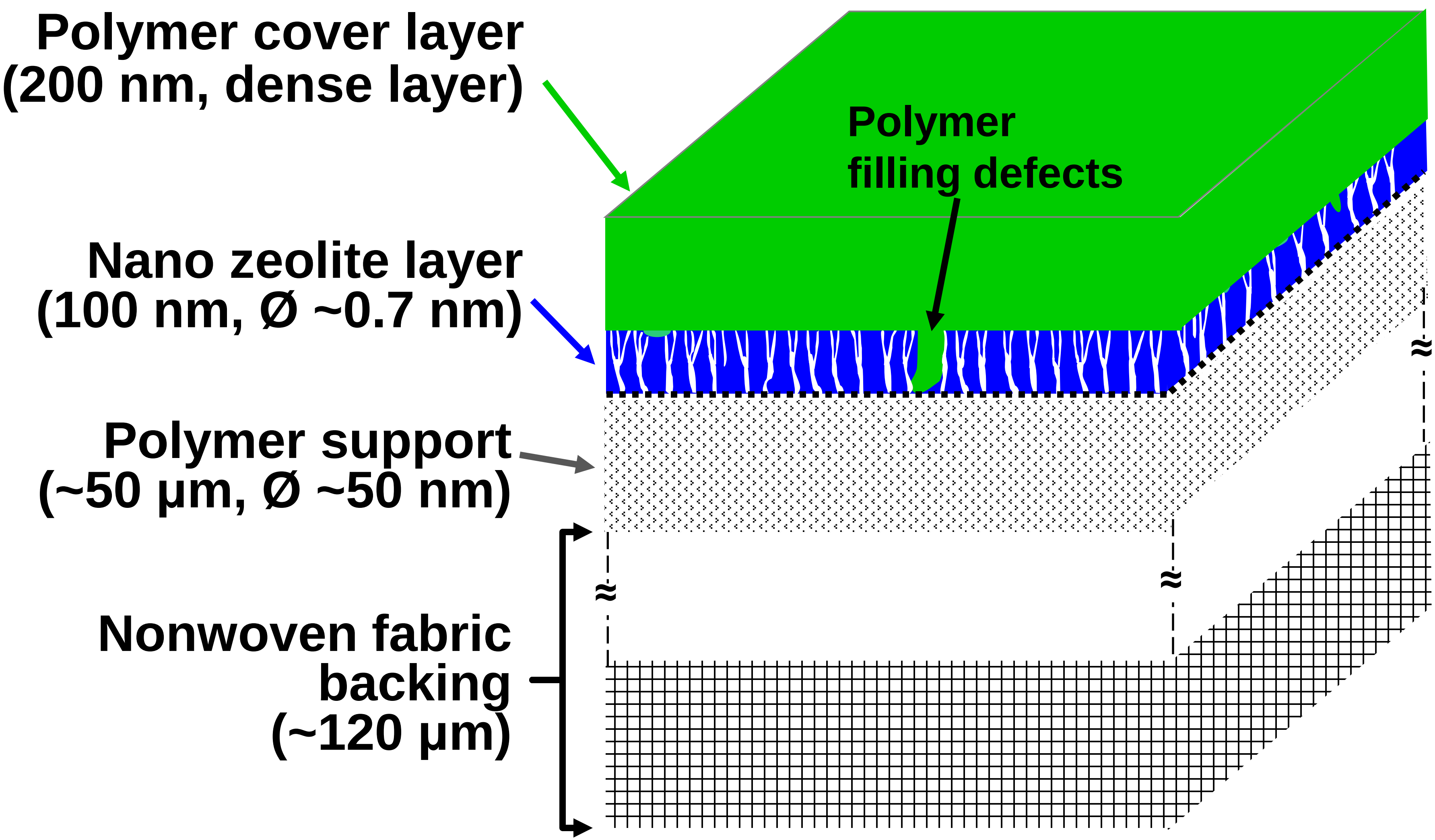
Zeolite-Y/Polymer Composite Membranes

- Zeolite-Y has good affinity to CO_2

- Two Polymer Strategies
  - Amine cover layer
  - Non-amine cover layer

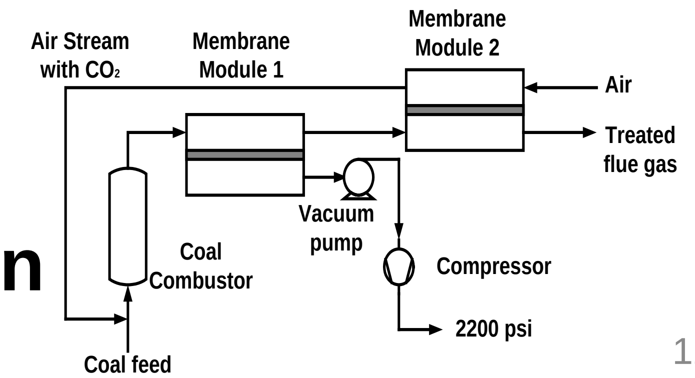
- Polymer support
  - Suitable for continuous fabrication
  - Low processing cost

Inorganic/Polymer Composite Membrane to Capture High Inorganic Performance and Low-Cost Polymer Processing

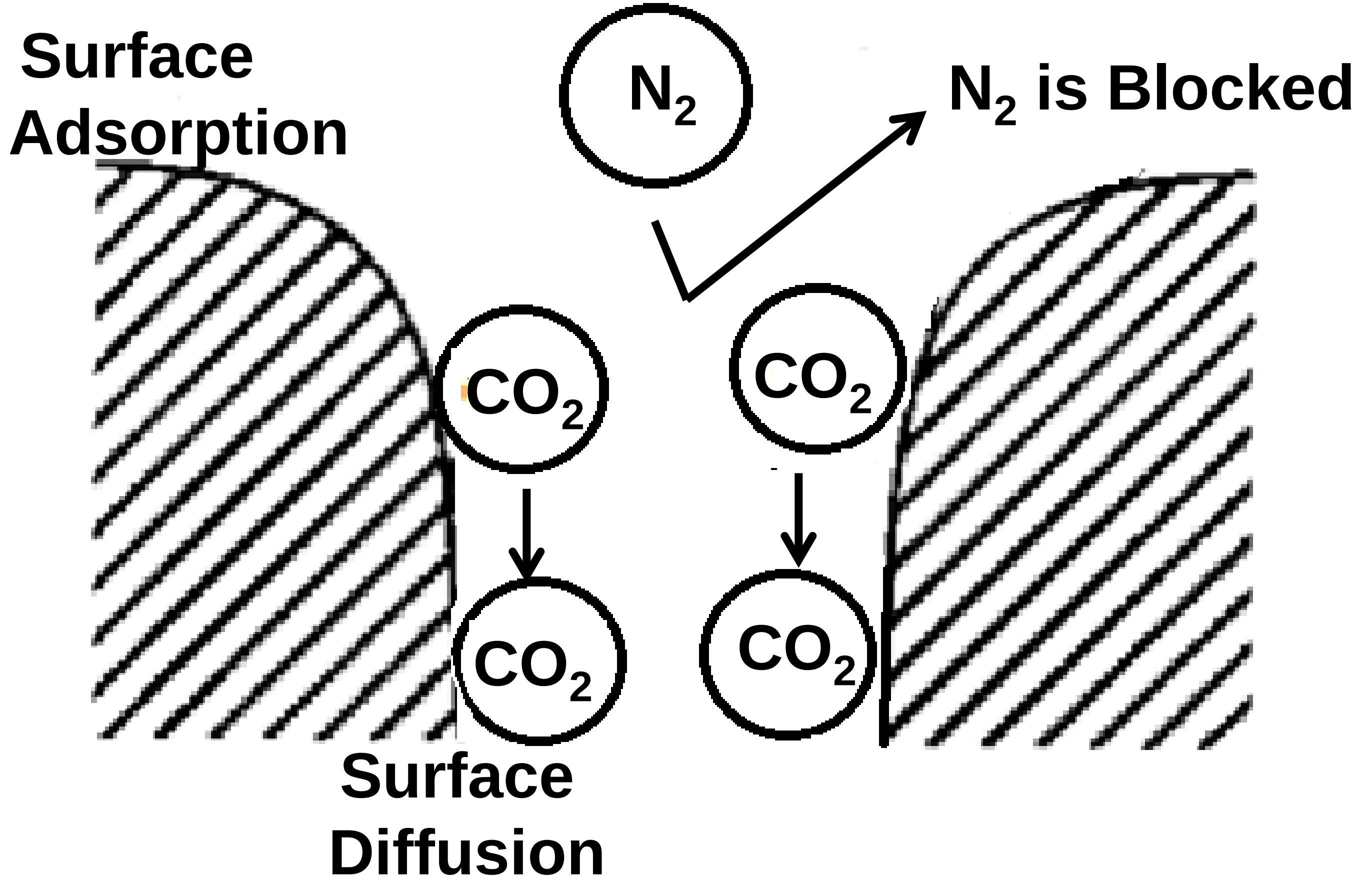


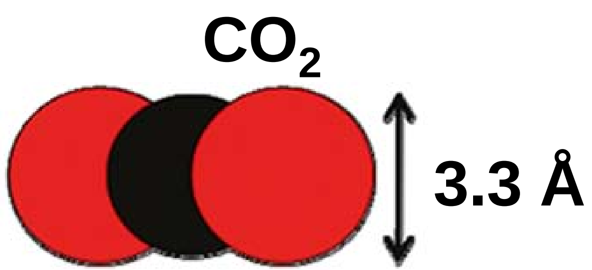
BP1 Accomplishments

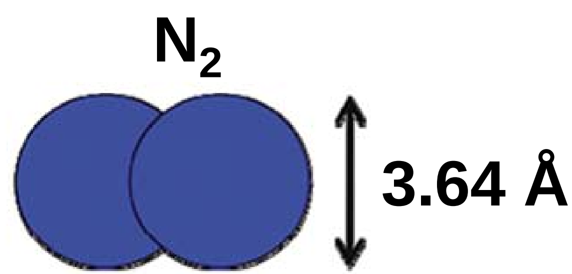
- **Zeolite/amine polymer composite membranes showed 1100 GPU with ~800 selectivity**
  - Achieved BP1 target of 1000 GPU & 50 selectivity
- **Significant Membrane Synthesis Improvements**
  - Including discovery of rapid zeolite synthesis (< 1 hour) for continuous membrane fabrication
  - Ceramic/polymer spiral-wound membrane element exhibited at 2012 NETL meeting; Zeolite/polymer element also rolled successfully
  - Ceramic membrane processing also improved (20 min in lieu of 43 hours), but membrane performance poor
  - Two polymer approaches, amine and non-amine membranes demonstrated
- **Preliminary techno-economic calculations (1100 GPU and >200 selectivity) showed ~46.0% COE increase and ~\$27.7/tonne CO_2**
  - Techno-economic model published
- **Proposed membrane process eliminates cryogenic distillation** (compare to competition)



Transport Mechanism through Zeolite





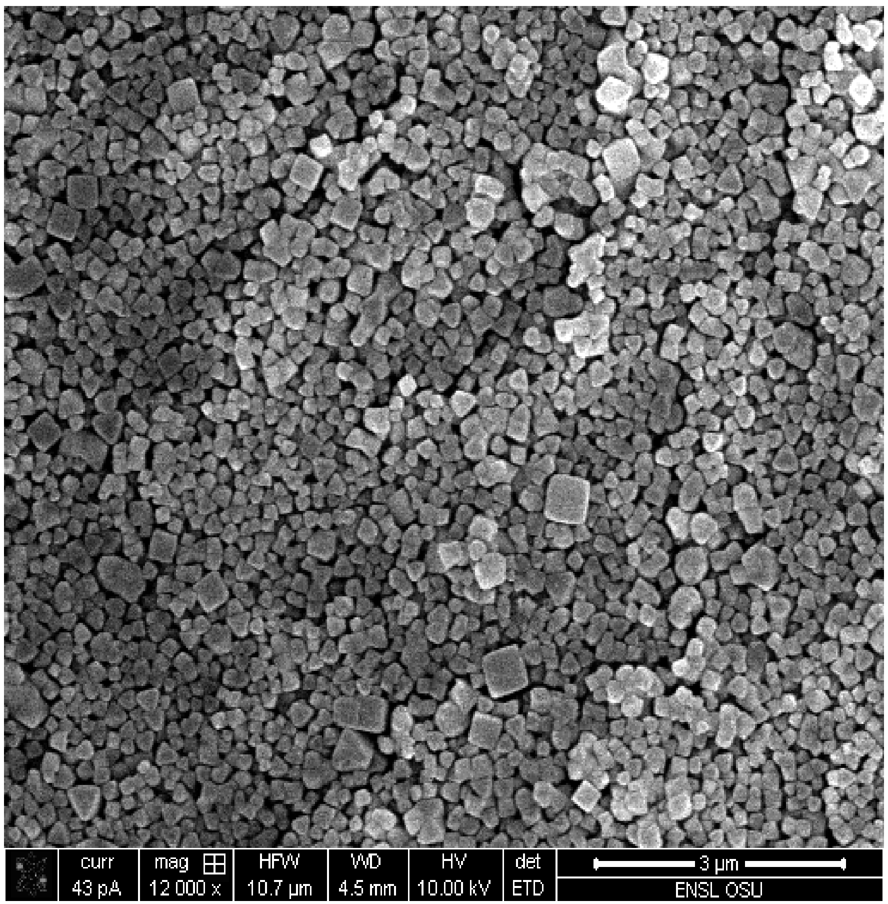


$Q_{CO_2} = -13.67 \times 10^{-40}$ C m^2

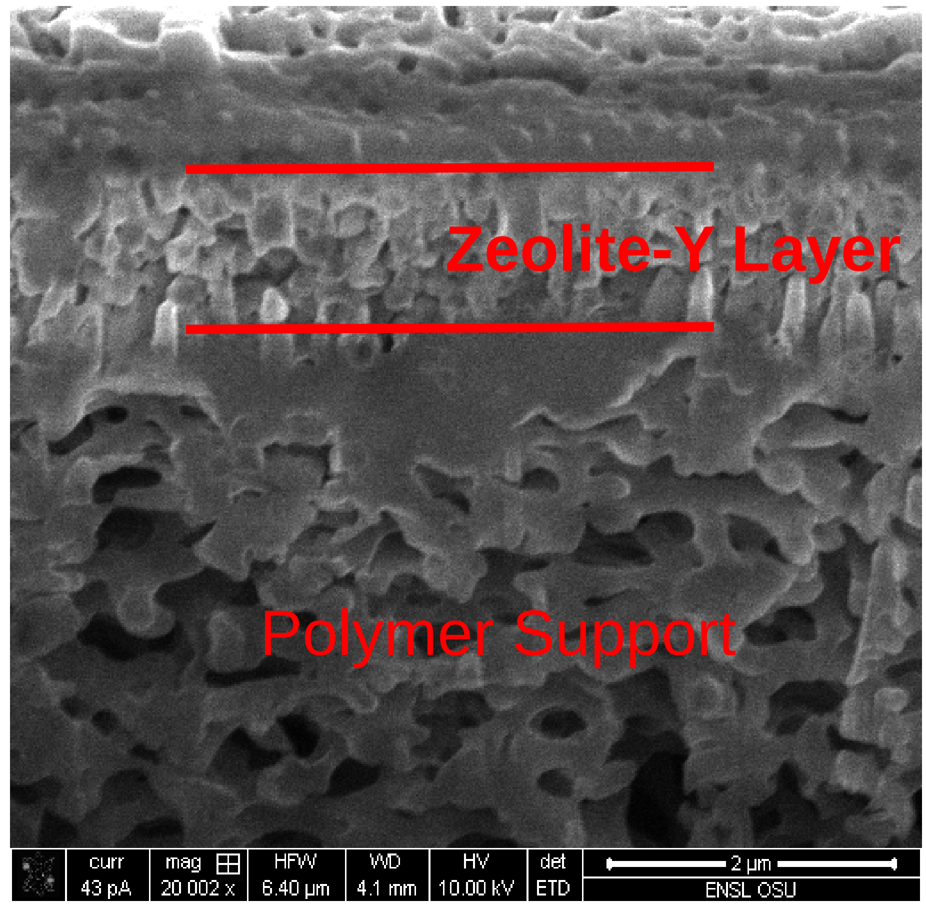
$Q_{N_2} = -4.67 \times 10^{-40}$ C m^2

Zeolite Nanoparticles Deposited on Polymer Support Successfully

Top View



Cross-section

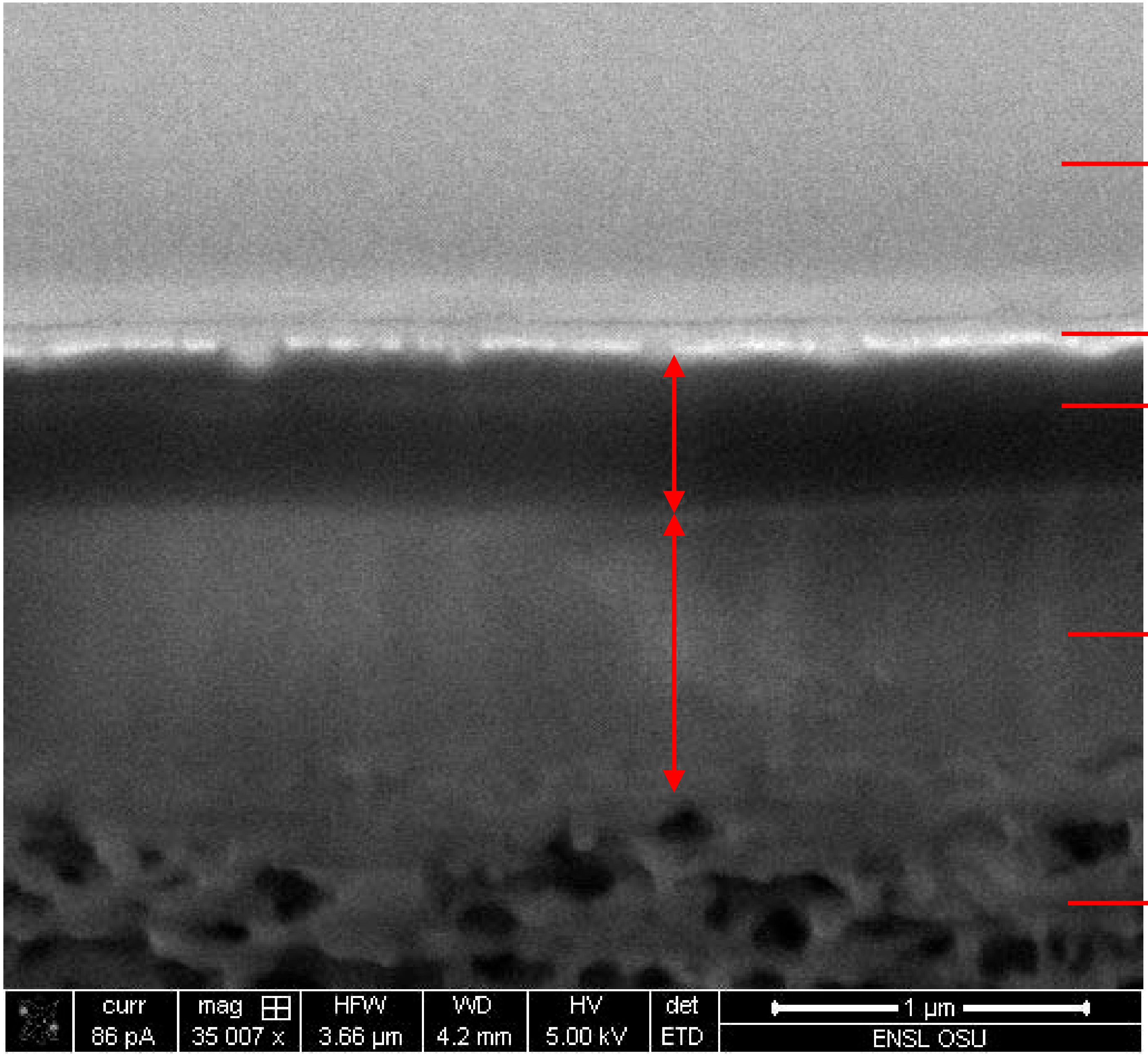


Two Cover Layer Approaches for Zeolite/ Polymer Composite Membranes

- **Amine cover layer**
- **Non-amine cover layer**

Amine/Zeolite Seed Layer/Polymer Support

Platinum and gold used to provide conductivity for focused ion beam microscopy



Pt deposition for better conductivity

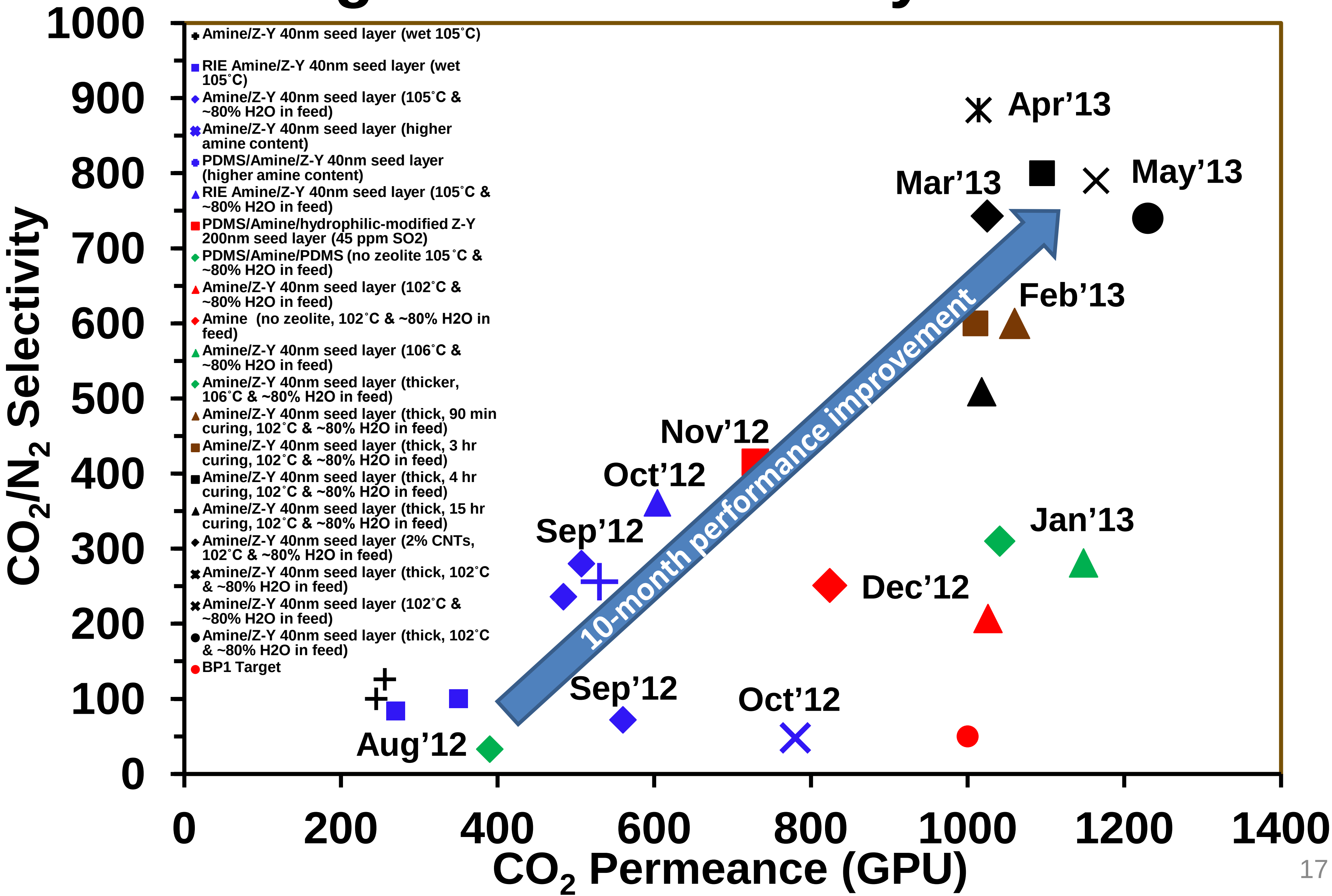
Gold coating

Amine cover layer ~ 500 nm

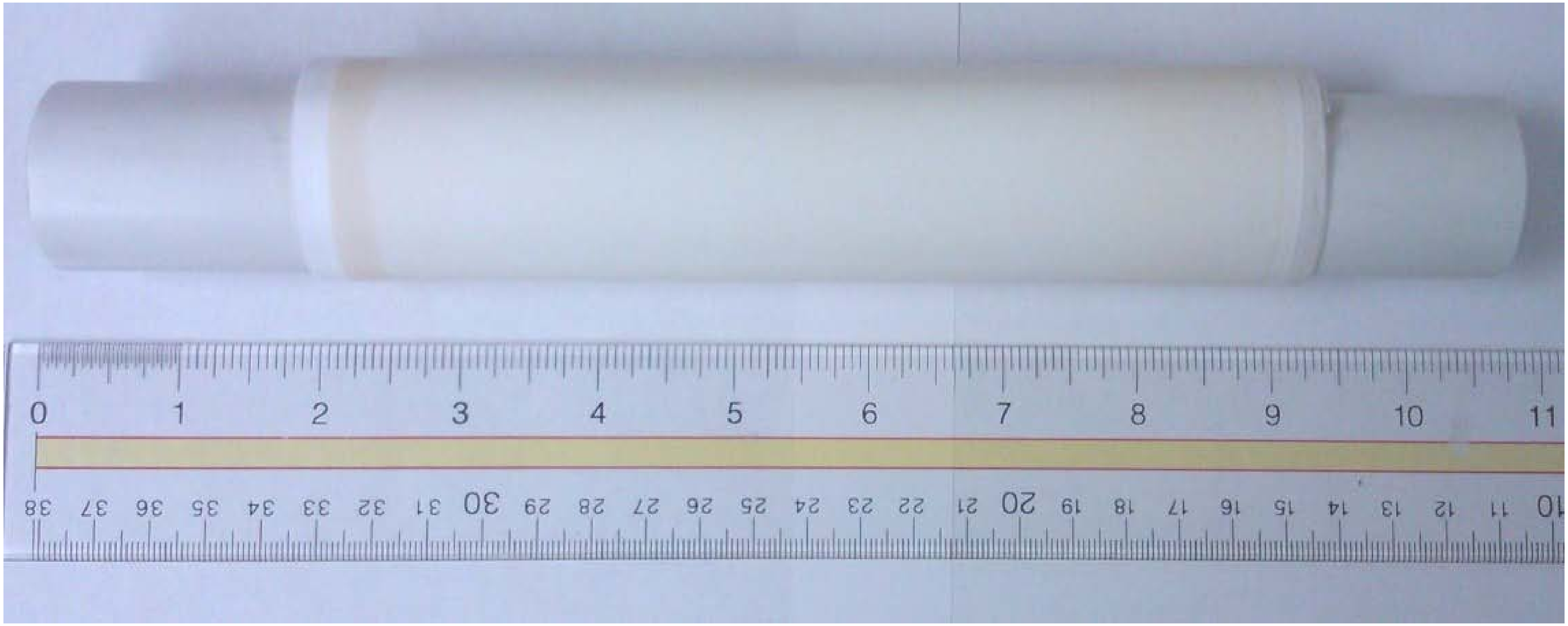
Zeolite-Y 40 nm seed layer < 1 µm

PES support

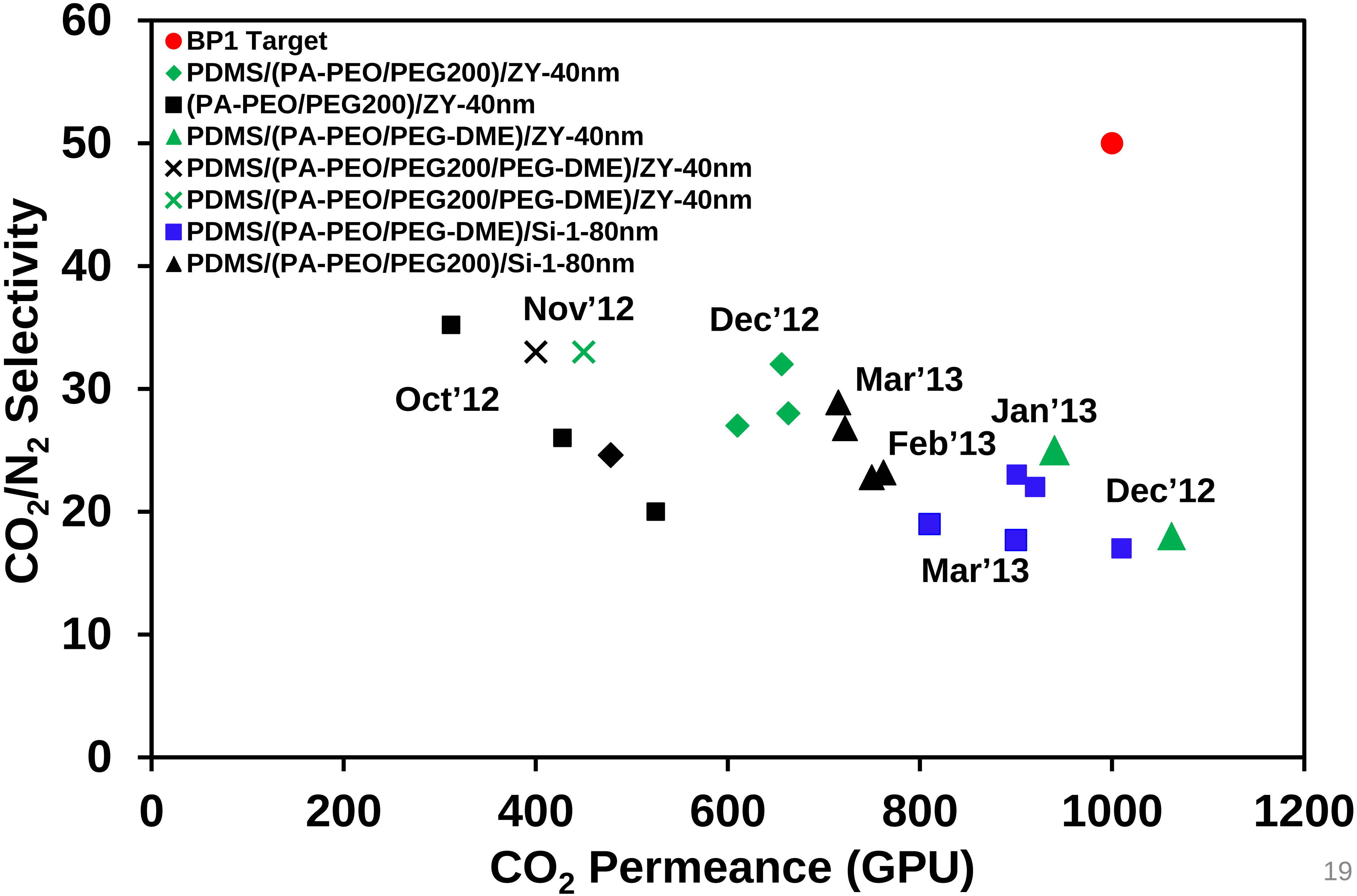
Zeolite-Polymer Composite Membranes Containing Amine Cover Layer at ~102ºC



Zeolite/Polymer Spiral-Wound Membrane Element Rolled Successfully



Zeolite-Polymer Composite Membranes with SO_2-Insensitive Cover Layer at 57°C

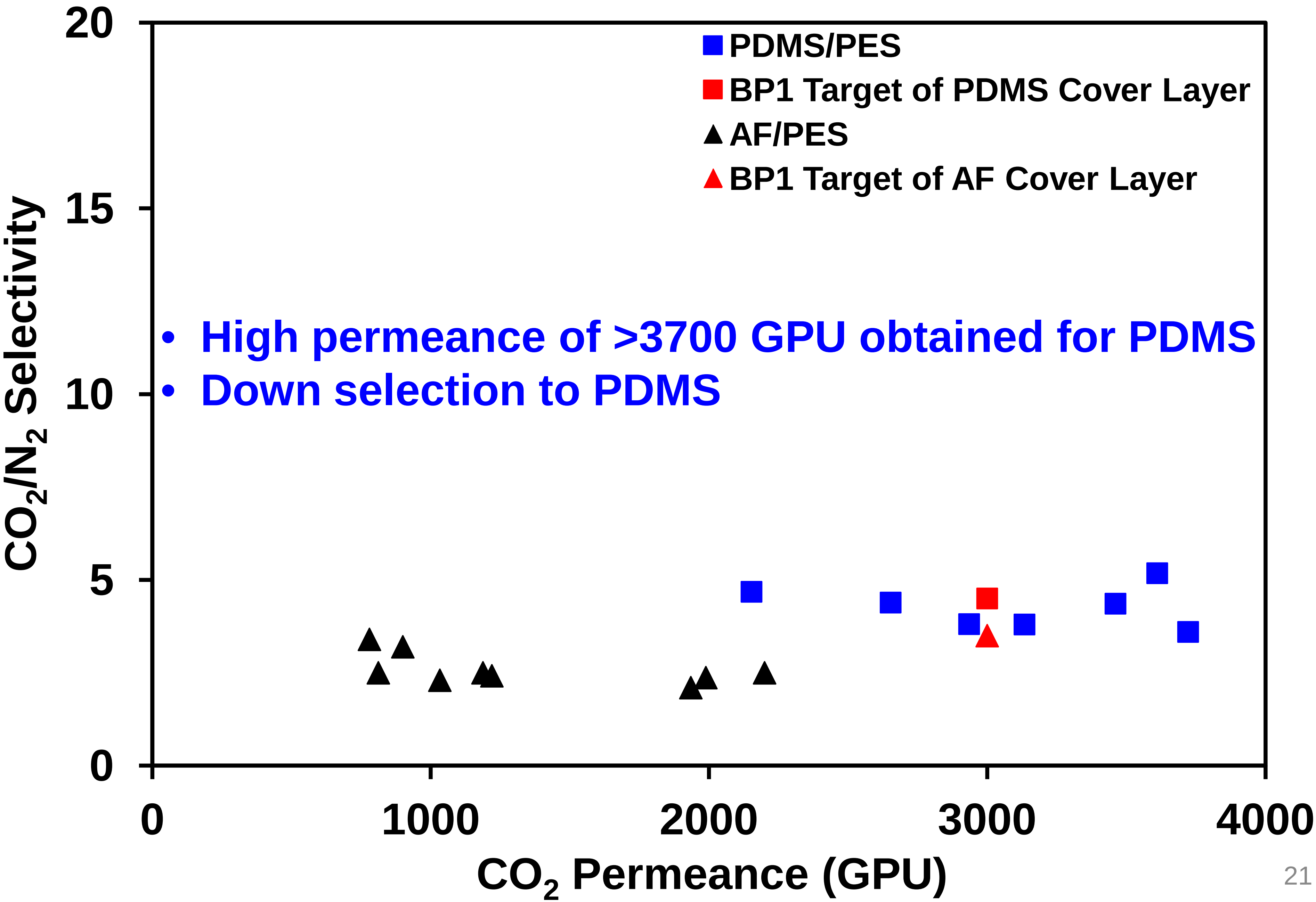


Additional Polymer Cover Layer Approaches for Defect Abatement

- **PDMS (polydimethylsiloxane) cover layer**

- **AF (amorphous fluorinated) polymer cover layer**

Polymer Cover Layers for Defect Abatement



- High permeance of >3700 GPU obtained for PDMS
- Down selection to PDMS

Cost Calculations

Assumptions

- **CO_2 Permeance: 1100 GPU, CO_2/N_2 Selectivity >200**
  - **Based on present membrane lab data with amine membrane**
- **Operating Feed Pressure of 1.5 atm at ~100ºC**
  - **Permeate pressure of 0.2 atm for Stage 1 and 1 atm for Stage 2 (air sweep)**
  - **Selectivity of >200 under these conditions has negligible effect on costs**
  - **Pressure recovery using turboexpander**

Results

- **Increase on Cost of Electricity (COE) = 46.0% with 1100 GPU Capture Cost = $27.7/tonne CO_2**
- **If CO_2 Permeance = 3000 GPU**
  - **COE increase is 38.2% with a capture cost of $23.7/tonne CO_2**

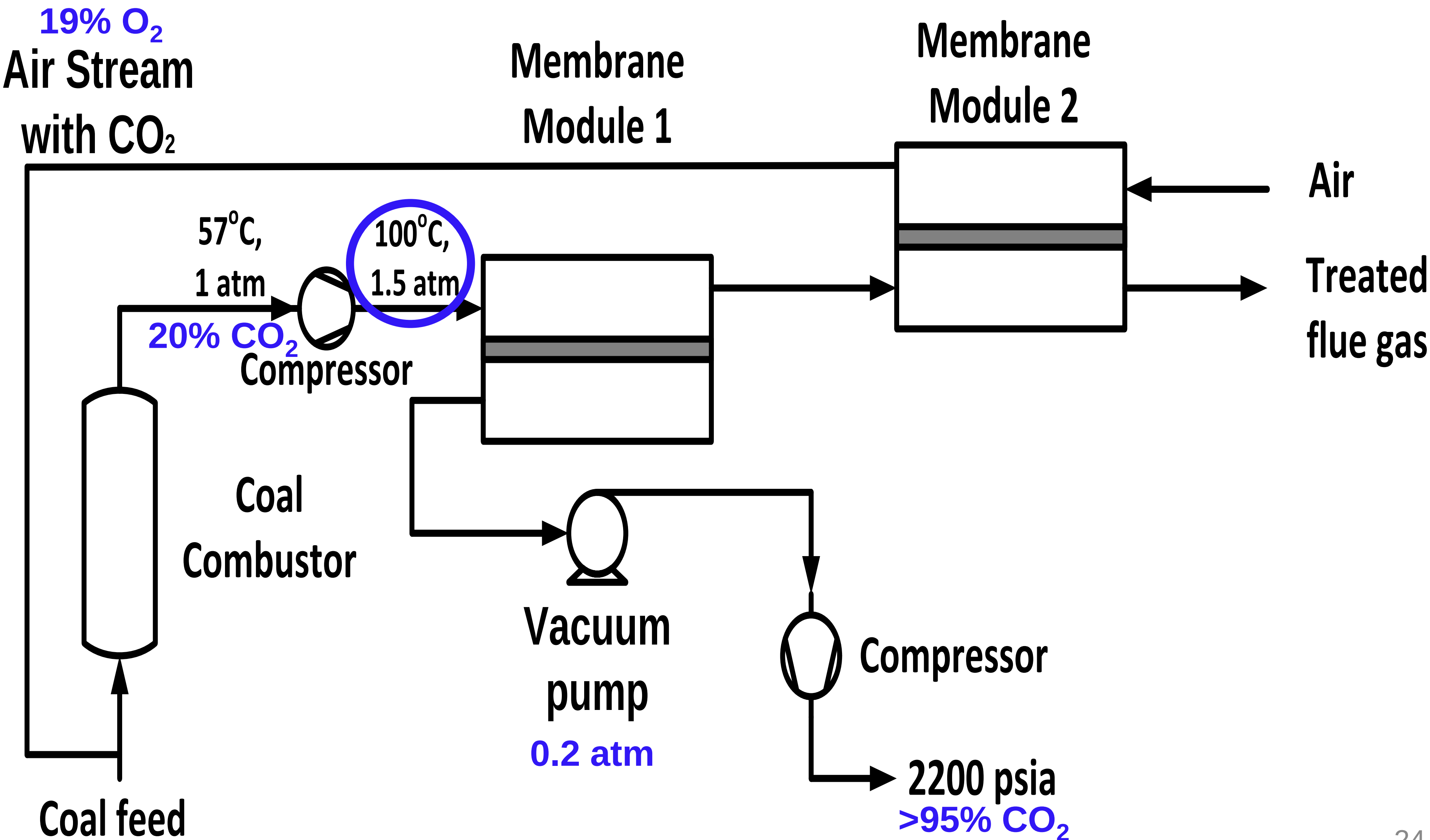
State-of-the-Art Amine Scrubbing

- **86% Increase on COE and Capture Cost of $71/ton CO_2**

BP1 Technical Research Needs

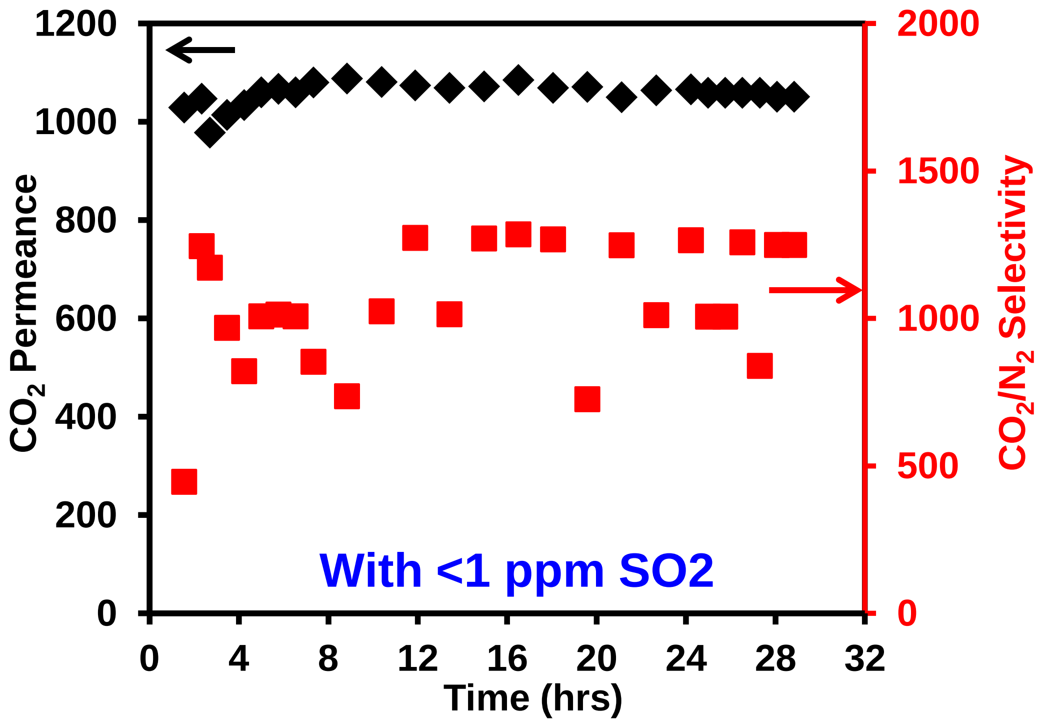
- **Temperature Effect**
  - **Amine Membrane operational at 102^{o}C**
  - **Compression from 1 atm to 1.5 atm needed for cost optimization**
    - **Temperature increases from 57^{o}C to 100^{o}C**
- **SO_2 Effects and Solutions**
  - **Approach 1: SO_2-Sensitive Amine Polymer Cover Layer meets BP1 Goals**
    - **SO_2 Polishing Step required**
  - **Approach 2: SO_2-Insensitive Polymer Cover Layer meets BP1 Permeance Goal**
    - **But selectivity (30) needs to be improved**

Temperature Mitigation for CO_2 Capture from Flue Gas in Coal-Fired Power Plants



SO_2 Effects on Amine-containing Membranes

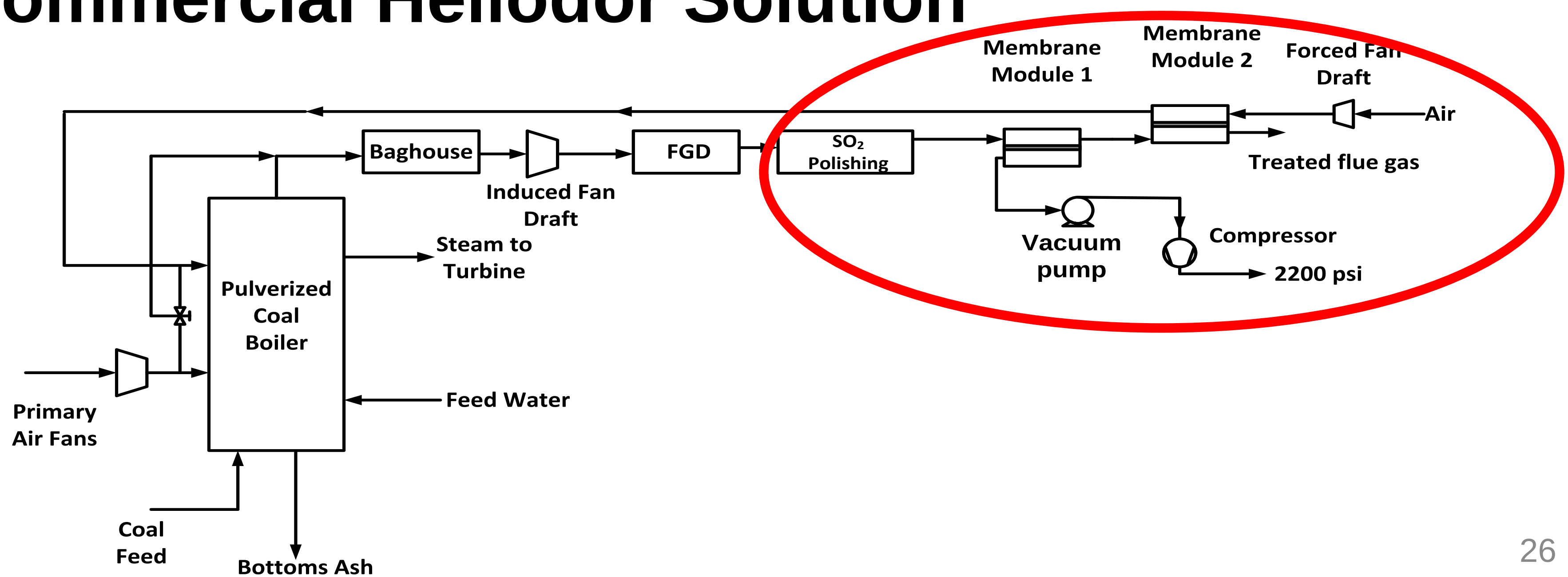
- **SO_2 Effects**
  - **SO_2 at ≥10 ppm appeared to affect stability of membrane containing amine cover layer**
  - **SO_2 at ≤1 ppm appeared not to affect stability of membrane with amine cover layer**
  - **More study required between 1 – 10 ppm SO_2**



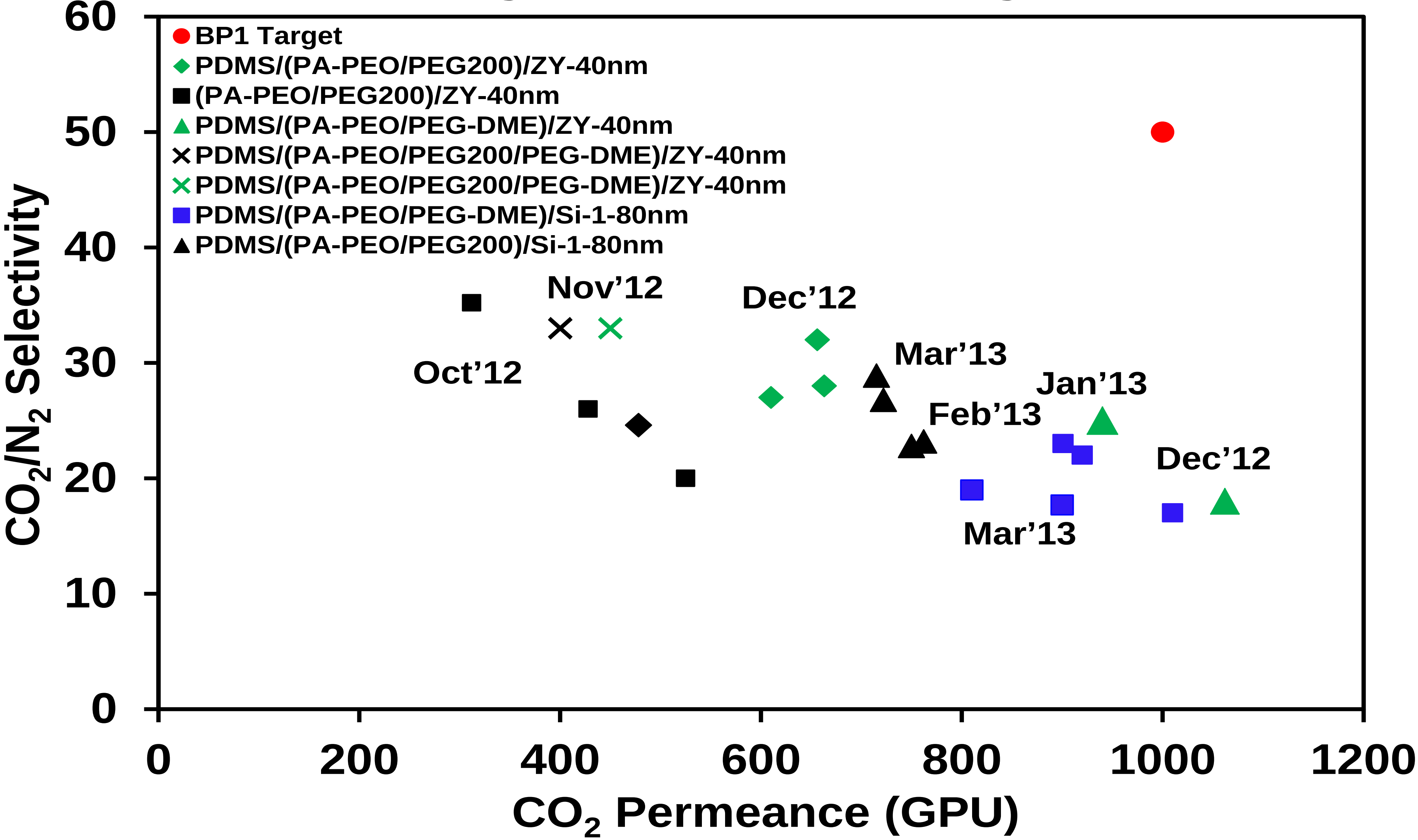
- **Propose SO_2 Polishing Step before membrane**

Approach 1: SO_2 Membrane Mitigation raised in BP 1

- **Absorption into 20 wt% NaOH Solution**
  - + Polishing step based on NETL baseline document
    - ++ Estimated to be about <1.5% increase on COE
  - + Non-plugging, low-differential-pressure, spray baffle scrubber
  - + Efficiencies can reach >95%
  - + SO_2 can be reduced from 44 ppm to <2 ppm
- **Commercial ZnO for SO_2 Clean-up to <0.1 ppm**
- **Commercial Heliodor Solution**



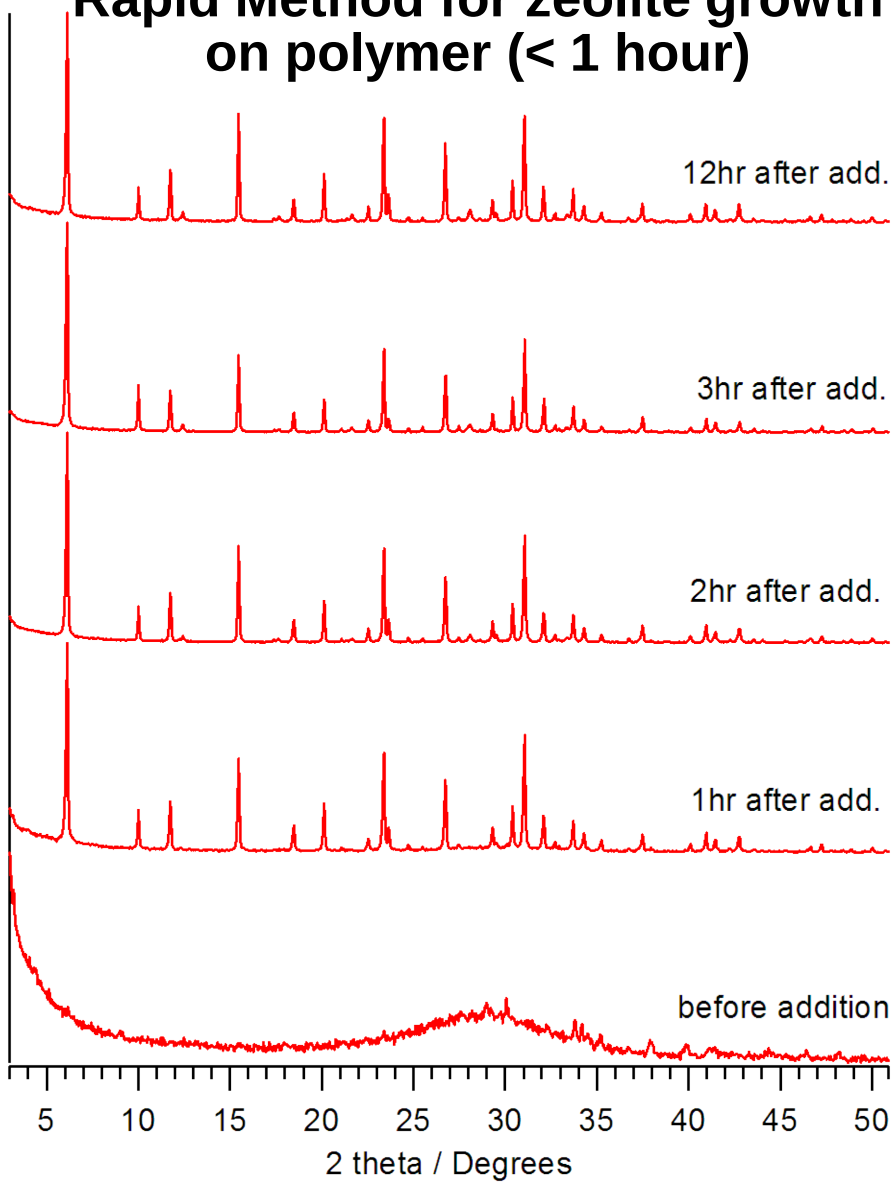
Approach 2: Develop SO_2-Insensitive Polymer Cover Layer



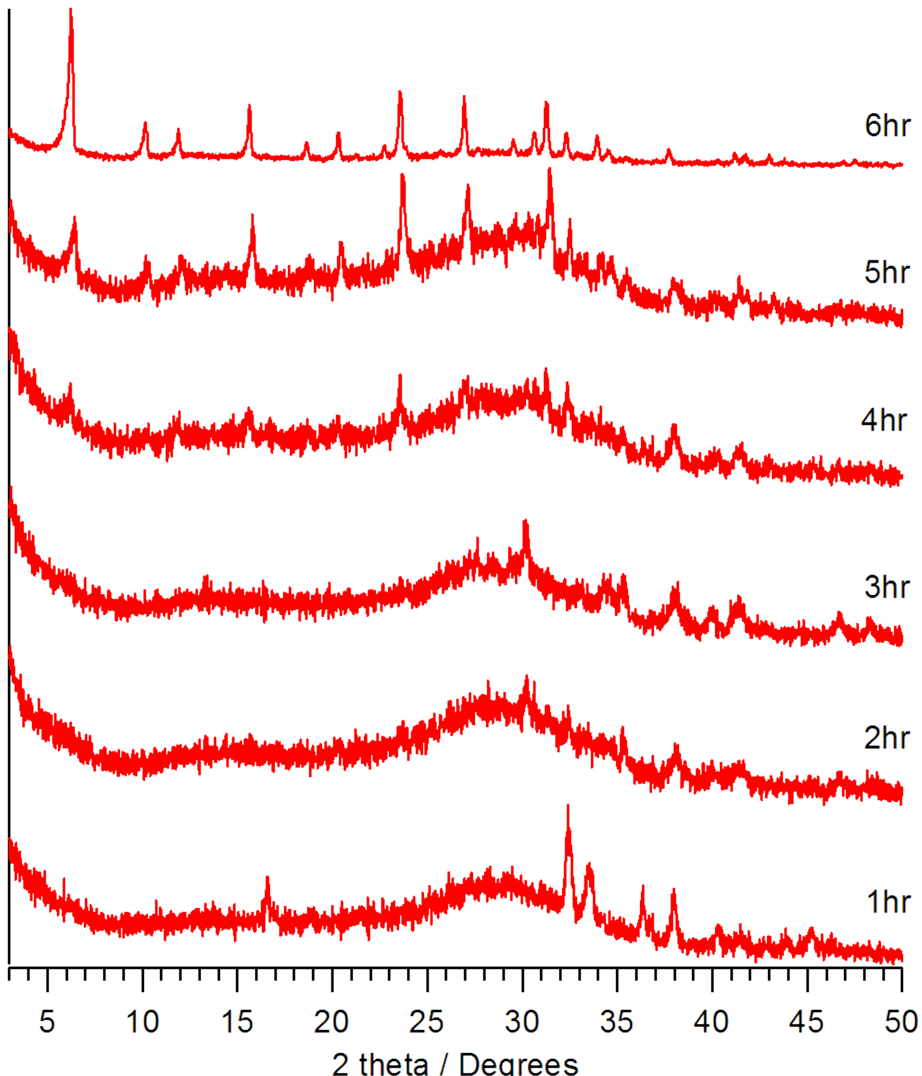
Improve Selectivity Further by Manipulation of Zeolite Layer

X-ray Diffraction Patterns indicative of Zeolite Formation

Rapid Method for zeolite growth on polymer (< 1 hour)



Conventional Method requiring 6 hour minimum



Membrane Scale-up

Continuous Membrane Fabrication Machine at OSU

Plans for Future Testing/Development

- **BP2**
  - Bench scale membrane synthesis and characterization continue
    - + Membrane performance and stability (with SO_2)
  - Continuous membrane fabrication
  - Update techno-economic analysis

- **BP3**
  - 3 prototype modules for testing with simulated flue gas
  - Update and finalize techno-economic analysis
  - EH&S evaluation with Gradient Technology and AEP