Development of Hybrid Polymer Membranes for Direct Air Capture of Carbon Dioxide

Project Number: DE-FE0031968

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National Energy Technology Laboratory
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Outline

Program Overview

a. Funding: DOE $799,985 and Cost Share $200,001

b. Overall Project Performance Dates: 01/01/2021 – 06/30/2022

c. Project Participants: InnoSense LLC (Torrance, CA) and University of Utah (Salt Lake City, UT)

d. Overall Project Objectives: Develop hybrid polymer membrane capable of direct air capture (DAC) CO_2 separating from ambient air at a low cost (low hundreds in $) per metric tonne by 2030

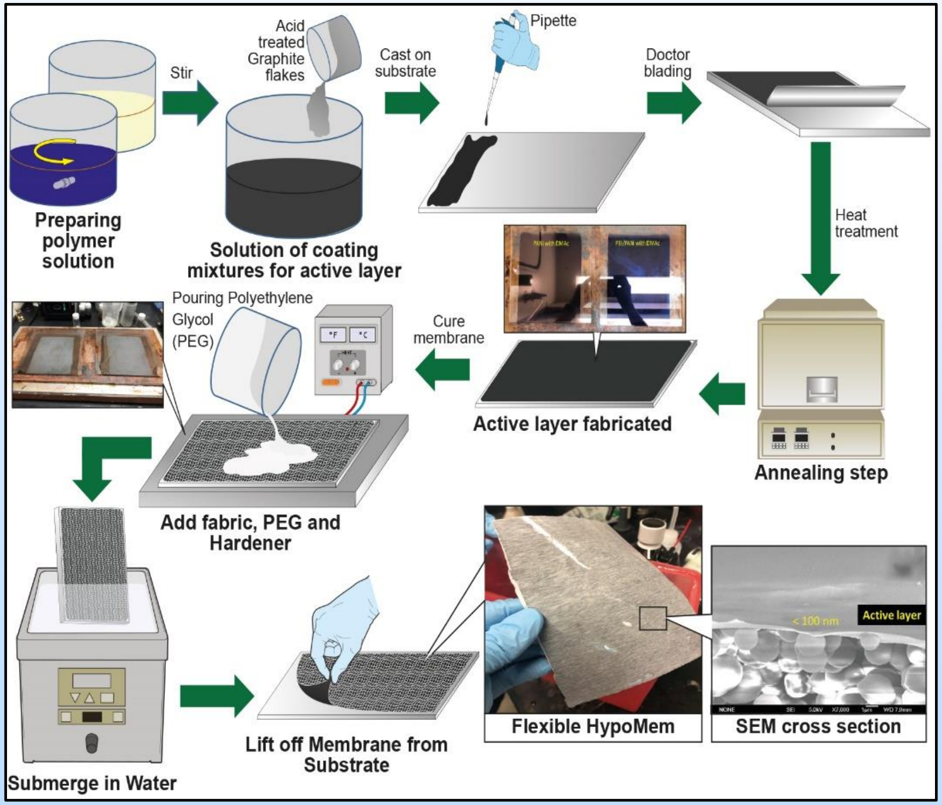
Technology Background

- Carbon dioxide (CO_2), captured directly from ambient air, is a leading method for carbon management and reducing greenhouse gas emissions
- A recent study estimates that primary processes envisioned for large-scale CO_2 capture from ambient air can cost $94–$232 per metric tonne
- Current methods of DAC CO_2 separation from ambient air (~0.04%) are intrinsically inefficient due to:
  - Thermal energy losses
  - Large footprint
  - Degradation of sorbent materials
- Sorbents and solvents used in the DAC process have many disadvantages:
  - Need to build a very large structure
  - High cost and complexity of regenerative systems
  - Loss of moisture in dry environments

Technical Approach / Project Objectives

The overall objective of this project is to develop a disruptive DAC CO_2 separation system using a hybrid polymer membrane (HypoMem) from ambient air to reduce CO_2 separation costs and energy penalties.

Step-by-step processes for developing HypoMem



Project Technical Objectives

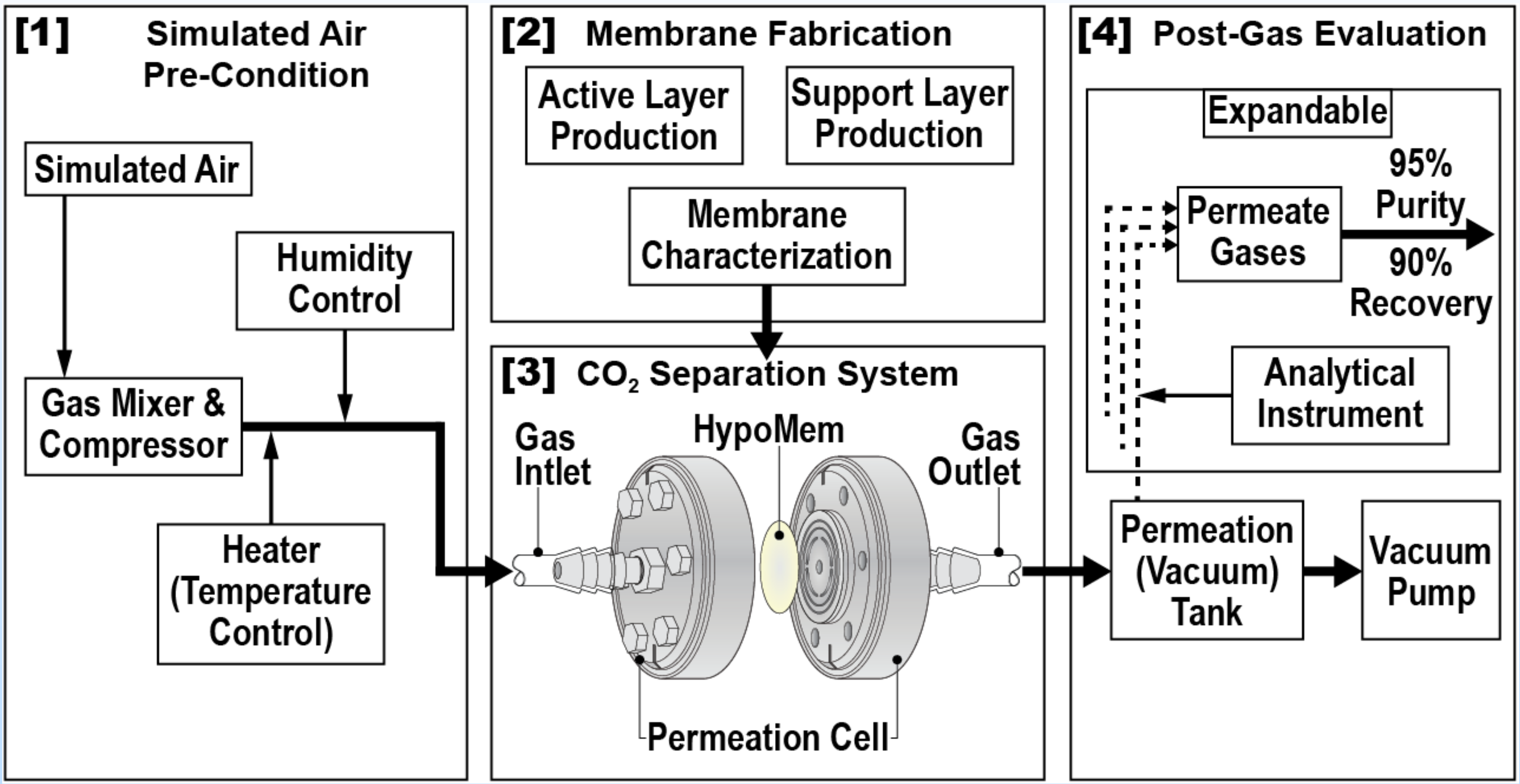
Objective 1. Formulation and Processing of Functional Polymer Materials for the Development of Hybrid Polymer Membrane (HypoMem).

Objective 2. Development and Characterization of HypoMem Samples for Determining their Physical, Morphological and Mechanical Properties.

Objective 3. Laboratory-Scale Testing and Evaluation of Flat and Stack HypoMem Sample Performance Under Simulated Air to Demonstrate Potential for DAC CO_2 Separation from Ambient Air at a Reduced Cost.

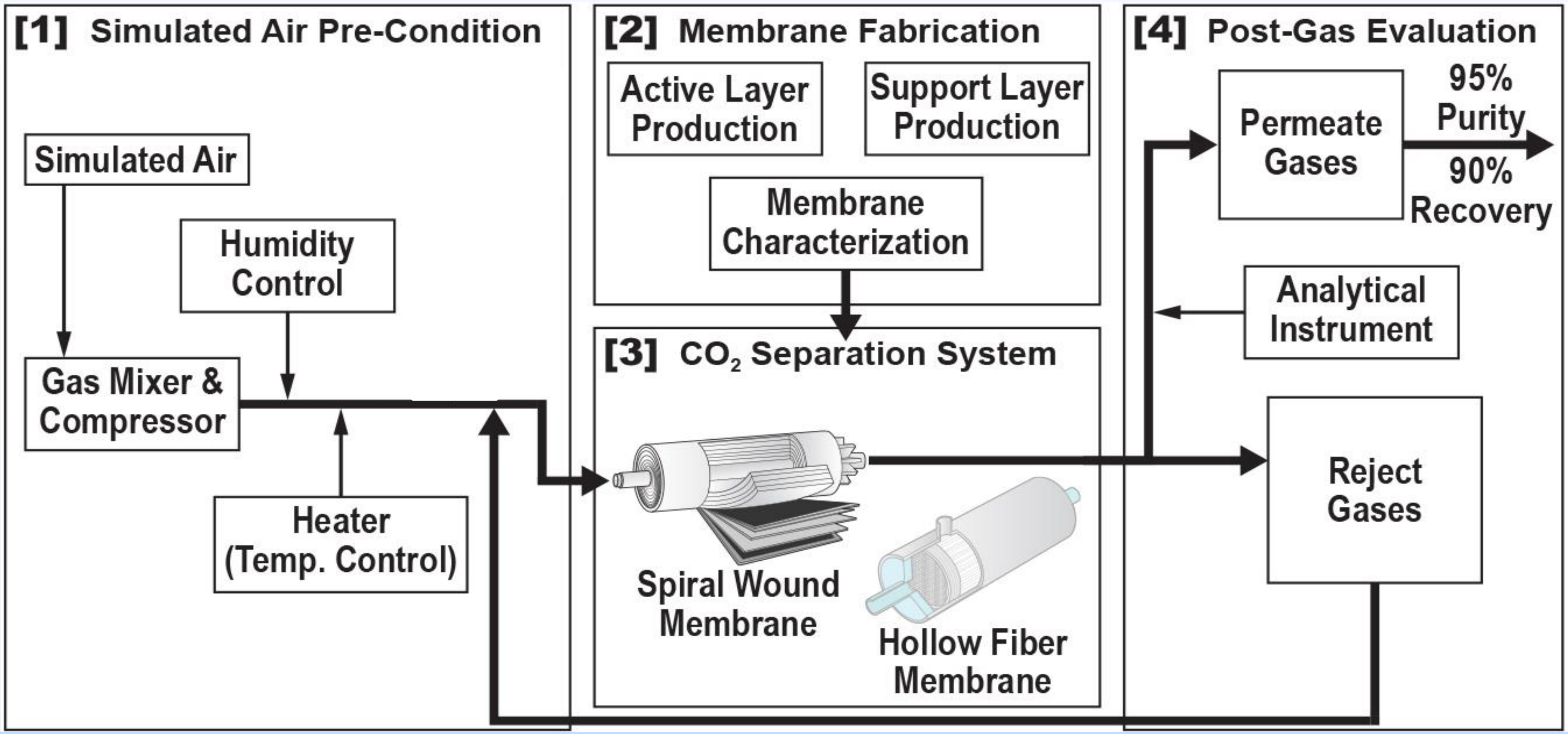
Technical Approach/Project Scope

Current project process of HypoMem based DAC CO_2 separation system



Technical Approach/Project Scope

An overall process of HypoMem based DAC CO_2 separation system



Team and Facilities

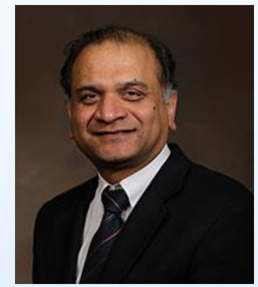
InnoSense LLC Team


Maksudul M. Alam, PhD
Principal Investigator


Adrien Hosking, MS
Design & Formulation Scientist

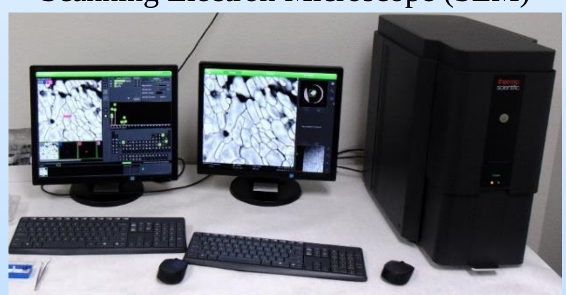

Thomas Saremi, BS
Research Engineer

University of Utah Team

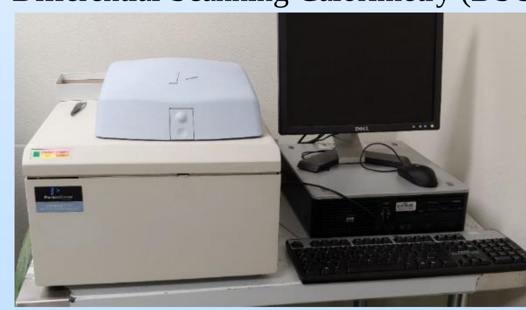

Professor Milind Deo, PhD
Subaward Project Director

Cleanroom Certified ISO-7

Scanning Electron Microscope (SEM)



Differential Scanning Calorimetry (DSC)



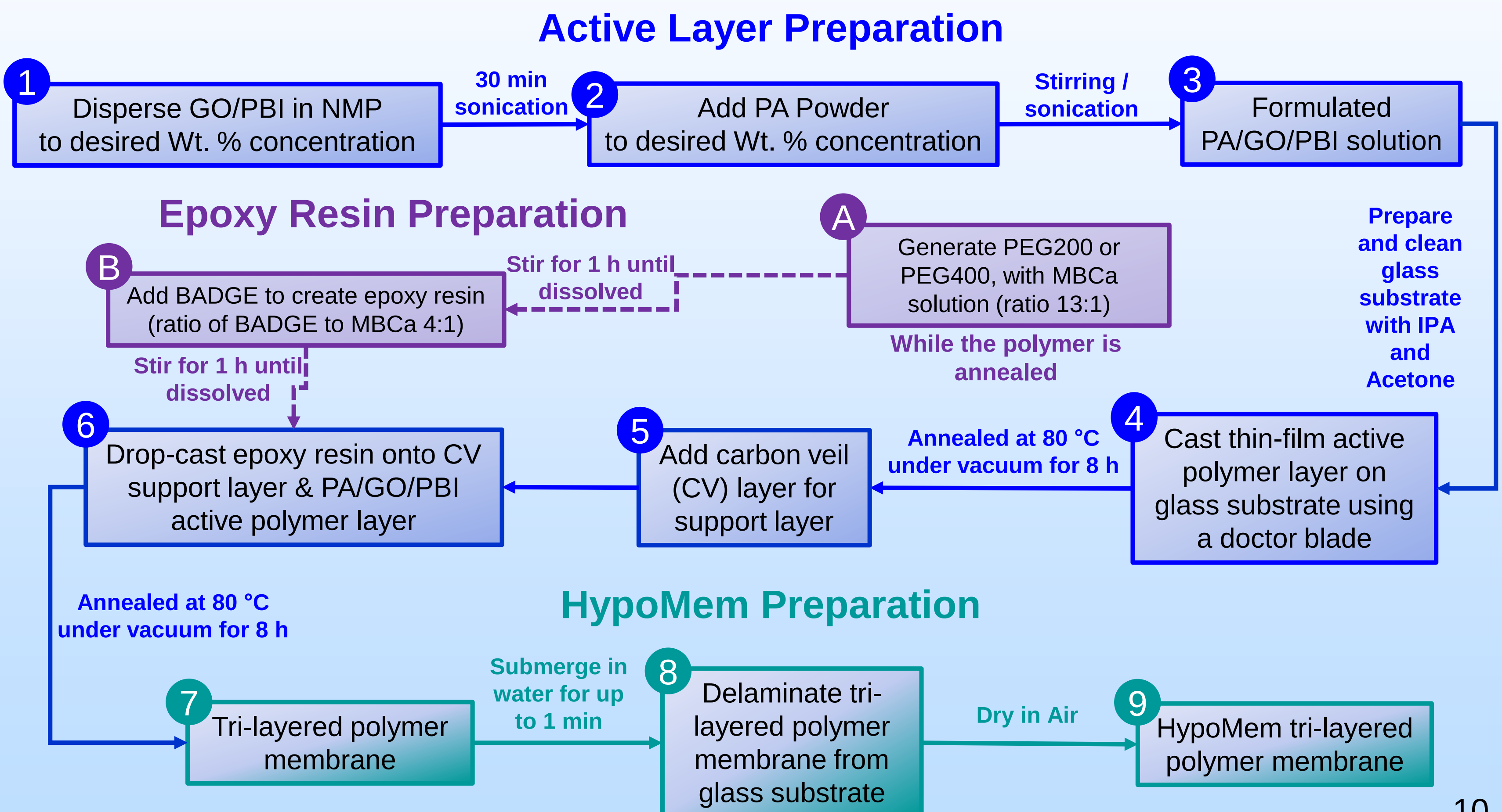
Progress and Current Status of Project

Project Team working strategically towards Project Objectives

- Selected desired functional polymers that are selective toward CO_2
- Fabricated large flat and stacked HypoMem samples
- Characterized HypoMems through FT-IR and SEM analysis
- Constructed an on-site gas permeation testing set-up
- Measured the permeance, permeability, and CO_2/N_2 selectivity of HypoMem samples
- Began process simulation to model the HypoMem in application

Flow Diagram for Fabricating Flat and Stacked HypoMem Samples

Flow diagram shows the fabrication steps for large flat HypoMem samples



Preparation of Active Polymer Layer

Consistently fabricated active polymer layer for HypoMem samples

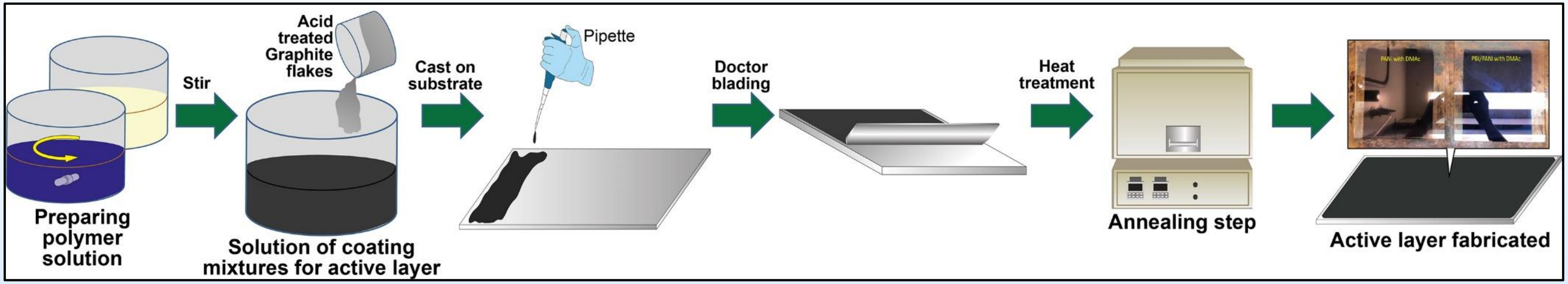
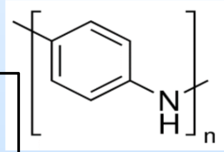
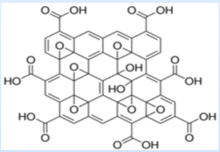


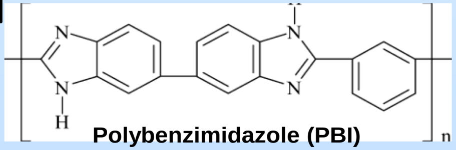
Figure: *Chemical structures of polymers and additives used in the formulations*



Polyaniline (PA)



Graphene Oxide (GO)



Polybenzimidazole (PBI)

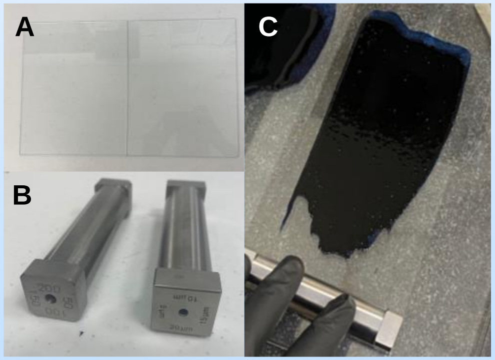
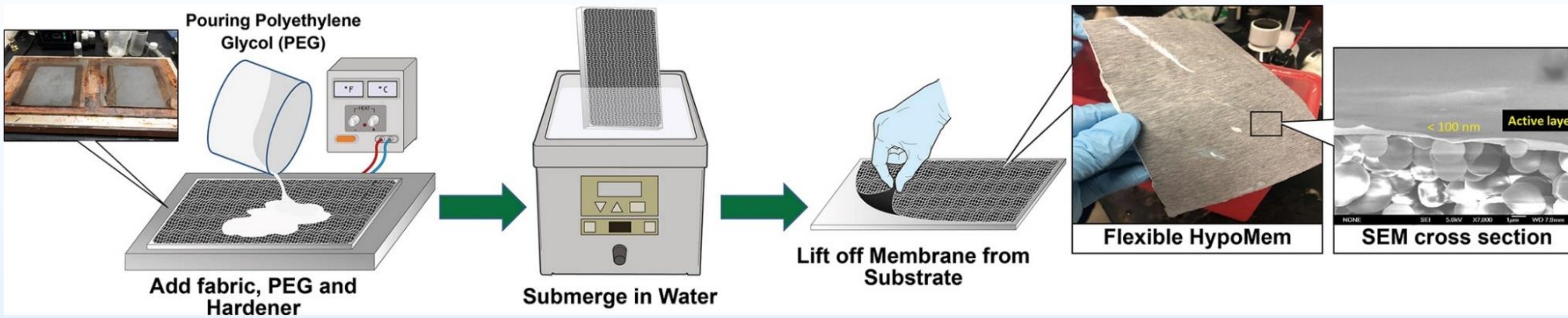


Figure: *Methods and materials for active polymer layer casting: (**A**) large 8" by 10" glass substrates, (**B**) doctor blades, and (**C**) freshly cast active polymer layer*

1. Disperse and dissolve PA and PBI polymers in *N*-methylpyrrolidone (NMP)
2. Add functionalized nanomaterials such as GO to increase permeability and selectivity of CO_2
3. Filter with syringe and cast onto large glass substrate. Generate polymer membrane layer with doctor blade. Dry and anneal under heat (~70 °C) to remove solvent.

Preparation of Epoxy Resin Support Layer



Fabrication of large flat HypoMem samples

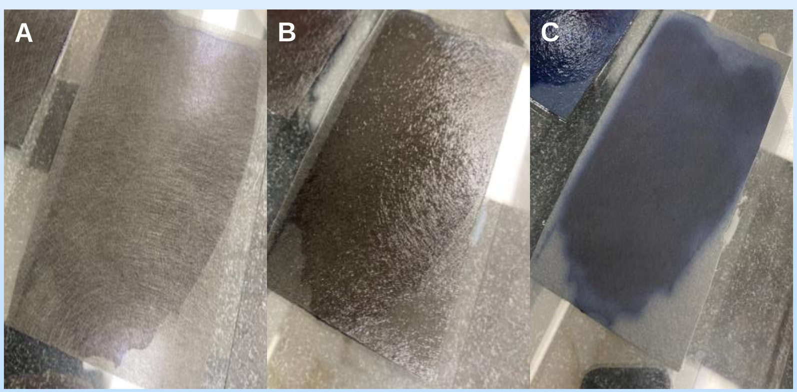


Figure: *Preparation of HypoMem films applying epoxy resin on large glass substrate: (**A**) Carbon veil placed on annealed active polymer membrane; (**B**) Epoxy resin formulation drop cast and diffused on the carbon veil; and (**C**) Fully annealed tri-layered polymer membrane showing support layer side.*

1. Create epoxy resin support layer solution standardized based on carbon veil area with a targeted ratio of polyethylene glycol (PEG)200 to bisphenol A diglycidyl ether (BADGE) to methylene-bis(cyclohexylamine) (MBCa).
2. Place carbon veil onto dried active polymer layer and then drop cast epoxy resin layer onto carbon veil.
3. Dry under vacuum (~70°C)

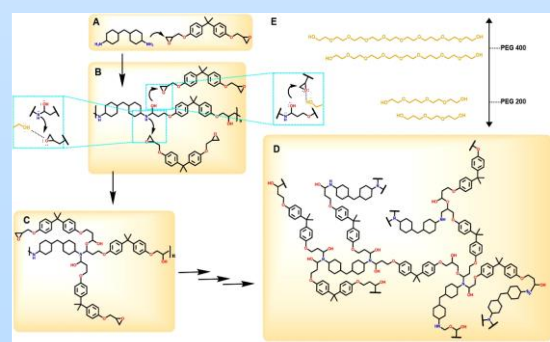


Figure: *Schematic of support materials*

HypoMem Preparation & Characterization

Fabricated Large Flat HypoMems characterized by distinct peaks in FT-IR Analysis

1. After drying the epoxy resin solution, the tri-layered membrane is fabricated.
2. Delaminate the tri-layered membrane from the glass substrate easily by submerging in water with the thin-film lift off method (T-FLO). Store in wet conditions.
3. Characterized by FT-IR and SEM Analysis

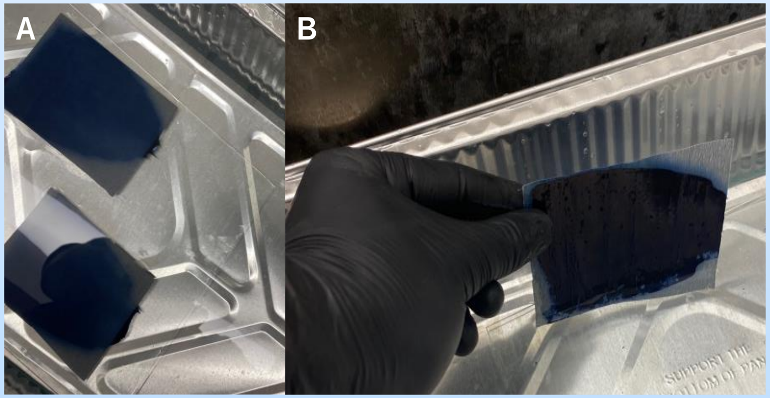
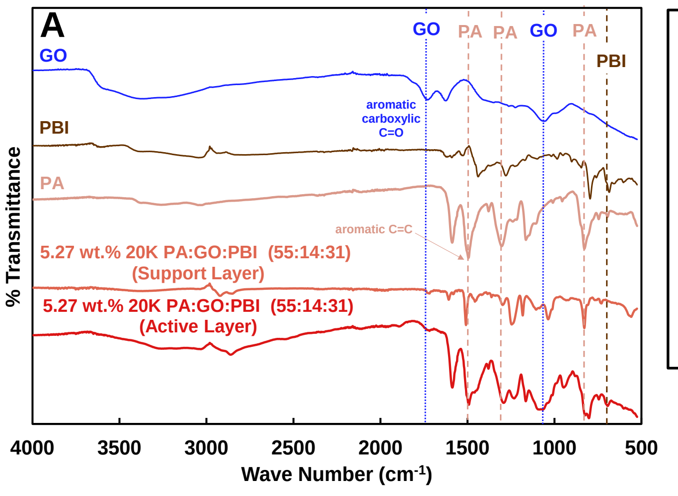


Figure: *Thin-film lift off method (T-FLO) with HypoMem samples: (**A**) Submerged in water; and (**B**) Lifted off the large glass substrate.*



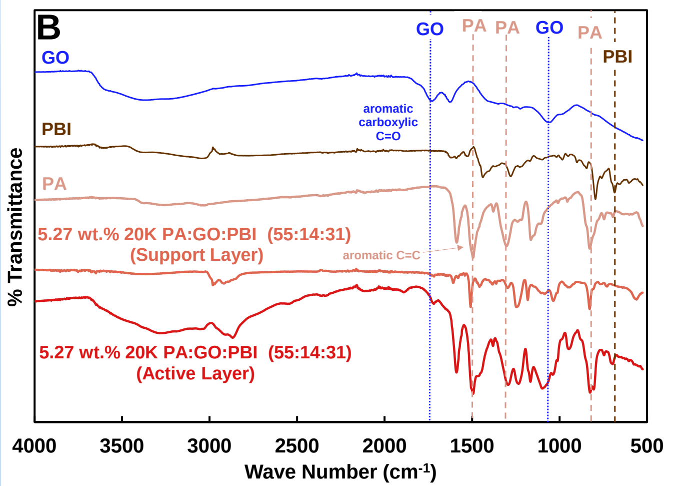


Figure: *Observed characteristic FTIR peaks of PA, PBI, and GO in a HypoMem sample*

SEM Analysis of HypoMem Samples

HypoMem characterized with SEM analysis showing uniform and consistent morphology

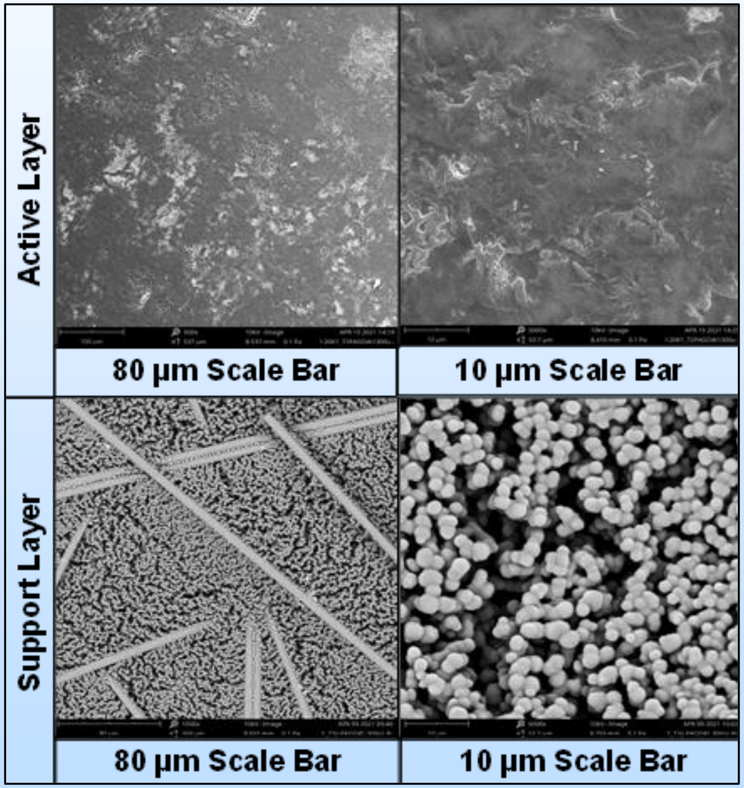


Figure: *SEM analysis of a PA:GO:PBI HypoMem sample.*

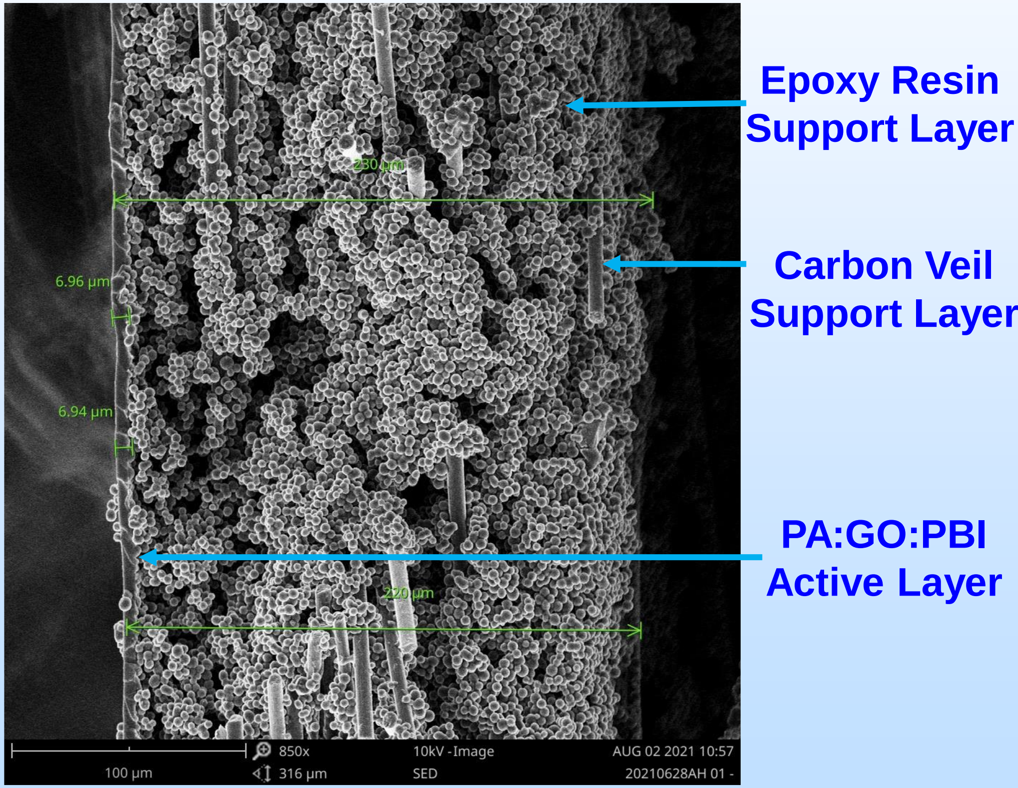
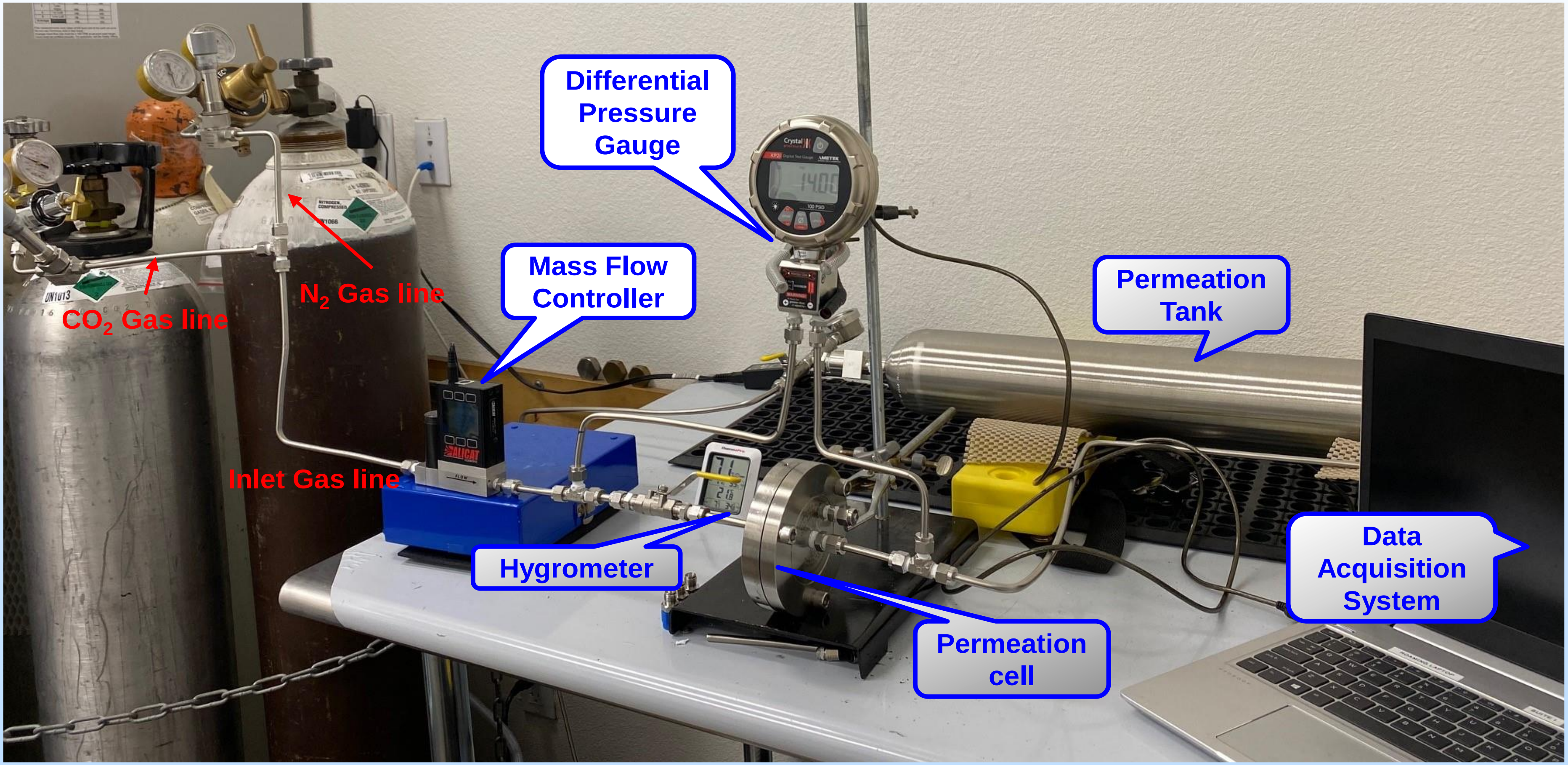


Figure: *SEM image of a cross sectional PA:GO:PBI HypoMem sample.*

Constructed On-Site Gas Permeation Testing Setup

Gas permeation testing set up evaluates, permeability, permeance and CO_2 Selectivity



Components of Gas Permeation Cell and Method for Testing

Gas permeation method and cell designed for HypoMem performance testing

With this type of setup installed, the gas permeability was calculated using Eq. 1:

$$P = 10^{10} \times \frac{VL}{P_{Permeate}ART} \times \frac{dp(t)}{dt} \quad (1)$$

where, P is the gas permeability across the membranes (in Barrers) [1Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg], $P_{Permeate}$ is the permeate pressure (in cmHg), dp/dt is the rate of the steady-state permeate side pressure increase (in cmHg/s), V is the standardized permeate volume (in cm^3), L is the active layer thickness (in cm), A is the effective surface area of the membrane (in cm^2), T is the experimental temperature (K), and R is the gas constant [0.278 cm^3 cmHg/cm^3 (STP) K]. Solving for permeance is a similar equation but does not factor in thickness of the sample L. Permeance $P_{Permeance}$ is calculated using Eq. 2:

$$P_{Permeance} = 10^{6} \times \frac{V}{P_{Permeate}ART} \times \frac{dp(t)}{dt} \quad (2)$$

The ideal selectivity (α) was obtained from the ratio of permeability coefficients using Eq. 3:

$$\alpha_{A/B} = \frac{P_A}{P_B} \times \frac{P_{CO2}}{P_{N2}} \quad (3)$$

where, P_A and P_B are the permeability coefficients of the pure gases CO_2 and N_2, respectively.

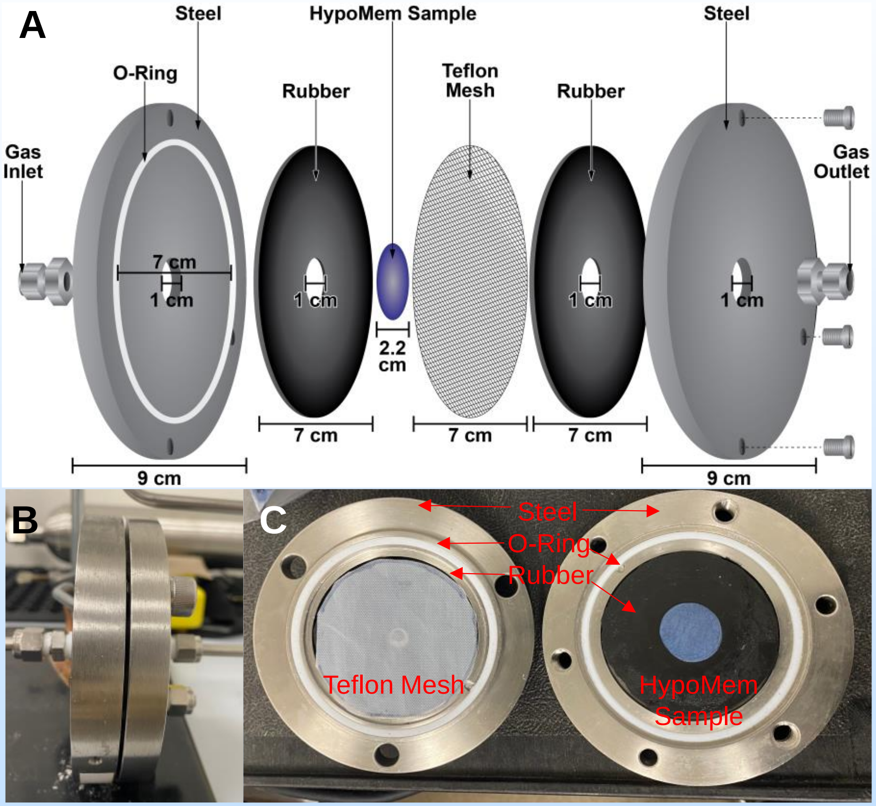
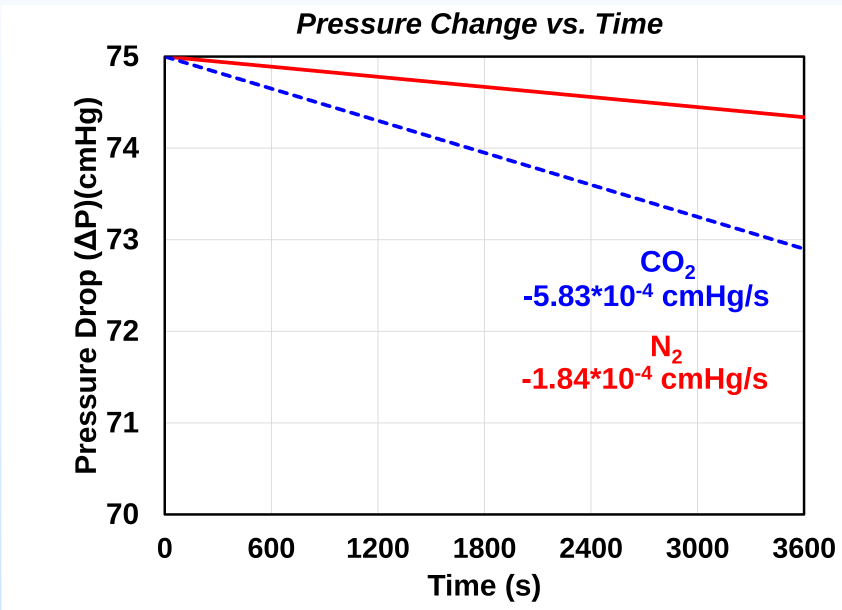
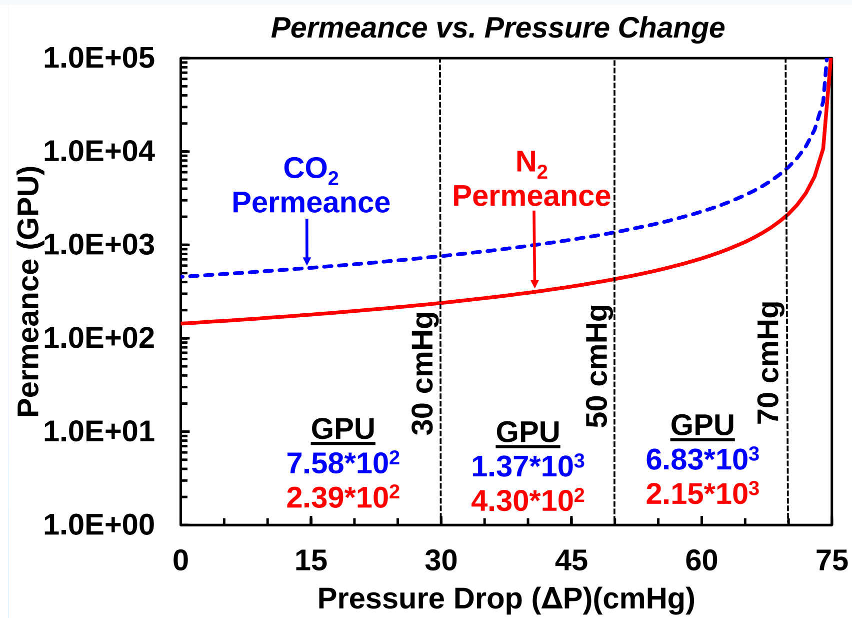


***Figure:** The component parts of the permeation cell at ISL: (**A**) Exploded view of the permeation cell; (**B**) Closed permeation cell; and (**C**) Open permeation cell showing components.*

HypoMem's Membrane Performance: CO_2 Permeance

Gas permeation test profiles of a HypoMem sample #20210628AH01





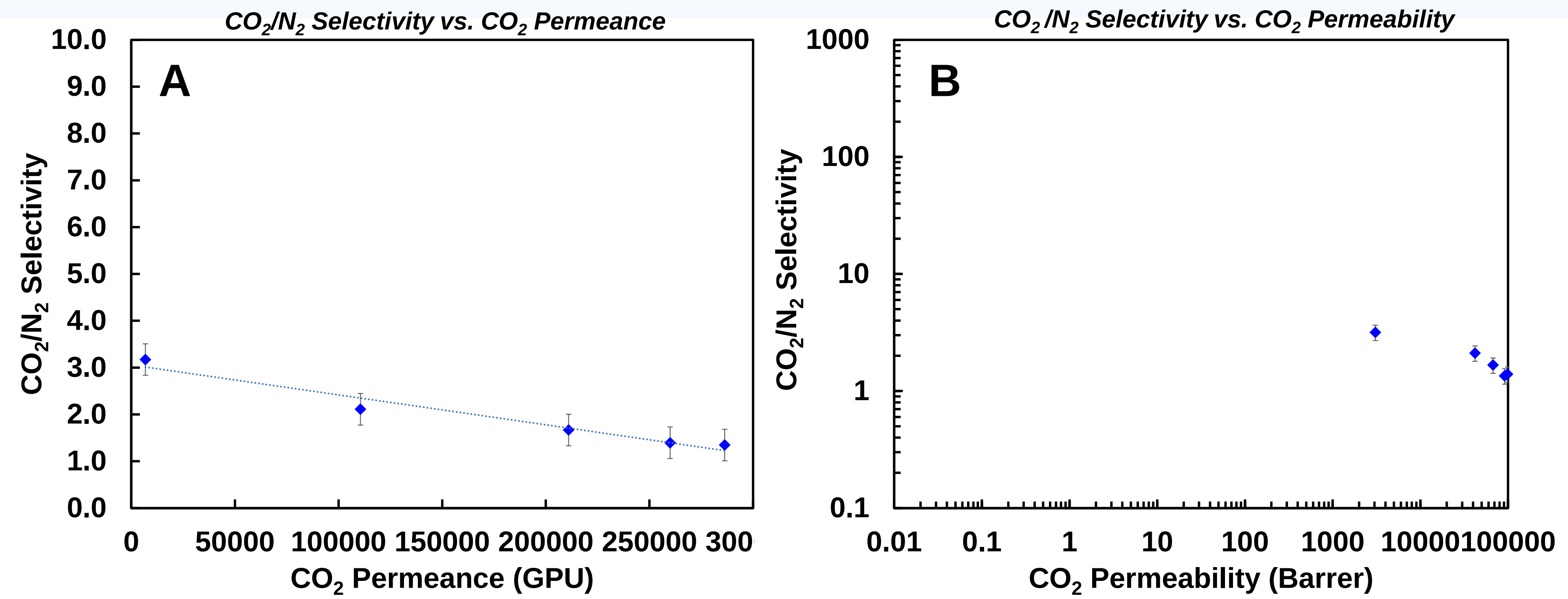
Test Conditions:

- *Membrane diameter of 1 cm, active layer thickness of 9.0 μm, and epoxy layer thickness ~ 225 μm,*
- *Feed flow rate of 0.172 ml/s for both CO_2 and N_2 gases,*
- *Ambient temperature conditions and fixed upstream condition 75.9 cm Hg (101kPa),*

Higher permeance value observed for CO_2 ($6.83*10^5$) than N_2 ($2.15*10^5$) for a pressure drop across the membrane of 70 cm Hg (~95 kPa)

HypoMem's Membrane Performance: CO_2 Selectivity

Selectivity vs permeation profiles of a HypoMem sample #20210628AH01



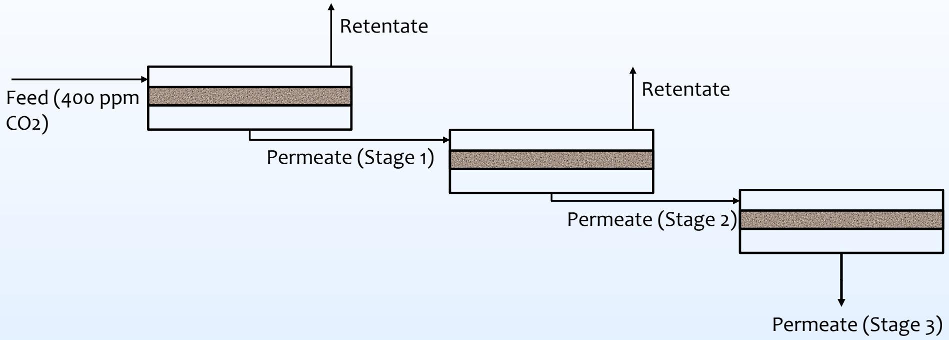
- *Observed CO_2 selectivity value of 3.17 at permeance of 6,830 GPU for a pressure drop across the membrane of 70 cm Hg (~95 kPa)*
- *Determined CO_2 selectivity values by varying the permeance via different feed flow rates and active layer thicknesses*
- *Observed a trend of an increase in selectivity with a decrease permeance or permeability*

Computer Simulation and Modeling on Direct Air Capture Membranes

Simulation of HypoMem membrane performance model will guide future work

- Material balances on species and permeance calculations were performed to establish the membrane outlet characteristics
- Given certain operational parameters, the permeate and the retentate compositions are fixed
- flow rates (volumetric and molar) for the species are dictated by their partial pressure differences between the outlet and the inlet
- The outlet concentration of CO_2 in the permeate is a function of the inlet concentration, the inlet and the outlet pressures, and the membrane selectivity
- The total throughput through the membrane is governed by its GPU and area.
- The parameters are adjusted so that the retentate CO_2 concentration is about the pre-industrial 300 ppm
- Reaching a selectivity of 10 at permeance of 10,000, a permeate CO_2 concentration of 7560 ppm can be achieved

Schematic of three stage DAC CO_2 separation



Base Case CO_2 Separation Parameters Used for Illustrative Calculations

CO_2 Separation Parameters	Value
Upstream Pressure (kPa)	100
Downstream Pressure (kPa)	2
Initial CO_2 Concentration (mole fraction)	0.0004
Selectivty CO_2/(Other)	30
Membrane Permeance (GPU)	10000
Membrane Area (cm^2)	5

Characteristics of All the Streams for Base Case CO_2 Separation

Streams	Feed			Permeate			Retentate		
Species	Total	CO_2	Other	Total	CO_2	Other	Total	CO_2	Other
Concentration (ppm)	1000000	400	999600	1000000	7560	992440	1000000	309	999691
Flow Rates (ml/s)	10	4.000E-03	9.996	0.125	9.480E-04	0.124	9.878	3.052E-03	9.875

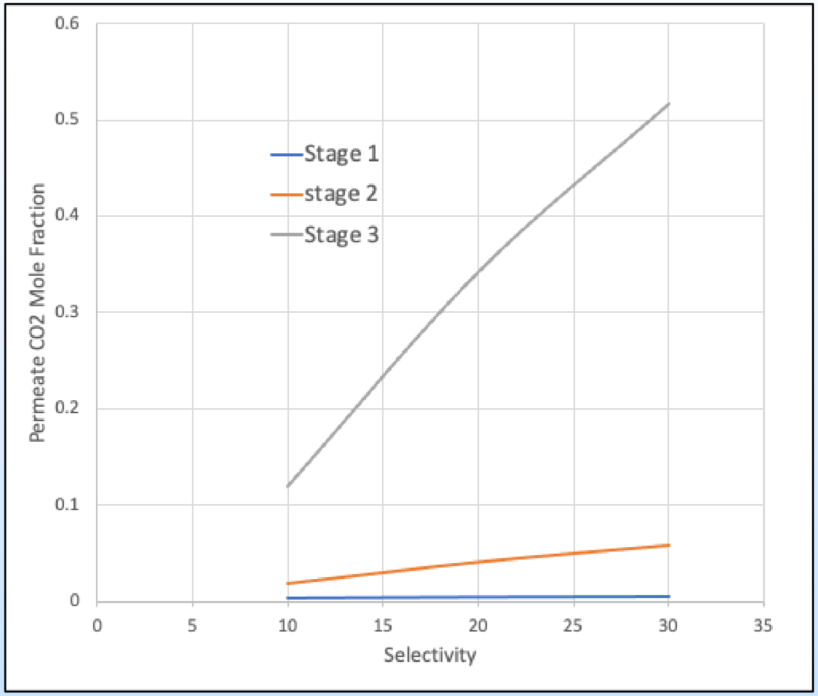
Computer Simulation and Modeling on Direct Air Capture Membranes

Some Basic Considerations for HypoMem Simulation

- Since the starting concentration is low (~400 ppm), multistage separation is essential
- Each stage is operated under vacuum
- The process is usually designed to maintain a concentration of 300 ppm in the retentate (pre-industrial concentration of CO_2)
- CO_2 purity of about 50% possible after three stages

- Permeate concentration dependence
  - Pressure ratio (upstream to downstream for each stage)
  - Selectivity
- Throughput
  - Combination of flowrate, GPU and membrane area

Simulated effect of selectivity throughout three stages



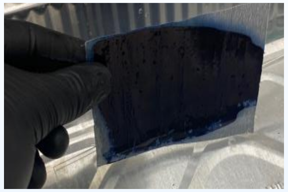
- ***In stage 1, increased selectivity has minimal impact on the permeate CO_2 concentration***
- ***In stage 2, increased selectivity has a moderate impact on the permeate CO_2 concentration***
- ***By stage 3, increased selectivity has a strong impact on the permeate CO_2 concentration***

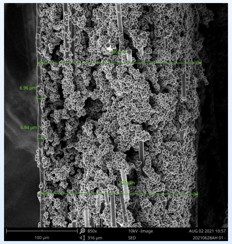
Plans for Future Development

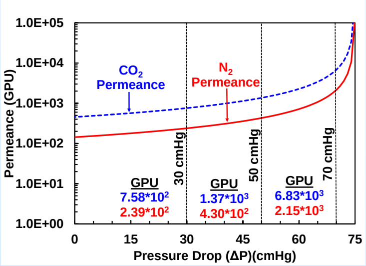
- In this project
  - Continue developing HypoMem samples modifying composition, active layer thickness, and fabrication processes such as thin-film lift off (T-FLO).
  - Continue conducting gas permeation testing on HypoMem samples.
  - Optimize permeance, permeability, and CO_2 selectivity performance.
  - Perform basic level Techno-Economic Analysis (TEA), Technology Gap Analysis, and Environmental Health and Safety Risk (EH&S) Assessment.
- After this project
  - Optimize fabrication processes for large size membrane and scale-up production.
  - Prototype development and field level testing for DAC CO_2 separation from ambient air.

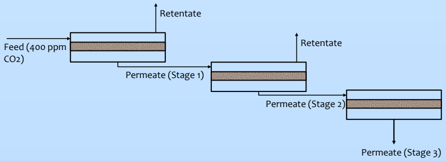
Summary

- Formulated and fabricated hybrid polymer HypoMem samples with reasonably large size (~8 by 12 cm).
- Verified consistent thicknesses and morphologies of both active polymer layer and epoxy support layer by SEM.
- Constructed an on-site gas permeation testing set-up utilizing a standard constant-volume/variable-pressure test method.
- Observed higher permeance values: $6.83*10^5$ GPU for CO_2 and $2.15*10^5$ GPU for N_2 at a pressure drop across the membrane of 70 cm Hg (~95 kPa).
- Observed CO_2 selectivity value of 3.17 at permeance of 6,830 GPU at a pressure drop across the membrane of 70 cm Hg (~95 kPa)
- Observed a trend of an increase in selectivity with a decrease permeance or permeability
- Computer simulation suggested that multi-stage process is required to achieve the desired CO_2 permeate concentration for successful DAC CO_2 separation









Acknowledgements

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NATIONAL ENERGY TECHNOLOGY LABORATORY

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