Doping and Redoping Effects on Hybrid Polymer Membranes for Direct Air Capture of CO_2

Project Number: DE-FE0031968

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U.S. Department of Energy

National Energy Technology Laboratory
Carbon Management Project Review Meeting
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Outline

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c. Technical Approach/Project Scope & Objectives
d. Team and Facilities
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Program Overview

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

b. Overall Project Performance Dates: 01/01/2021 – 03/31/2023

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 Scope and Objectives

The current project scope and objectives are to develop hybrid polymer membranes (HypoMem) and laboratory-scale testing and evaluation of their performance to demonstrate potential for DAC CO_2 separation from ambient air at a reduce costs and energy penalties.

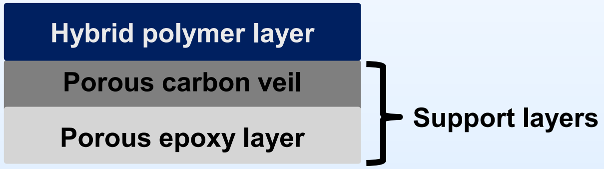
Project Technical Objectives

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

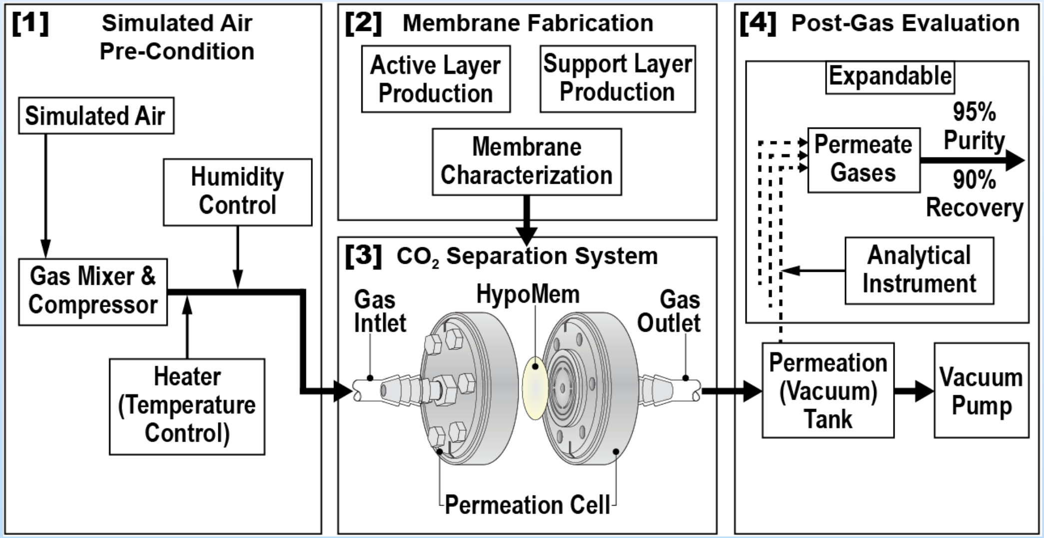
Objective 2. Development and Characterization of HypoMem Samples for Determining their Physical, Morphological and Mechanical Properties.

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.

HypoMem structure



Laboratory-scale testing of HypoMem samples



Team and Facilities

InnoSense LLC Team

Maksudul M. Alam, Ph.D.
Principal Investigator

Chamila Manankandayalage, Ph.D.
Formulation and Testing Scientist

Mohammad Mushfiq, B.S.
Senior Research Engineer

University of Utah Team

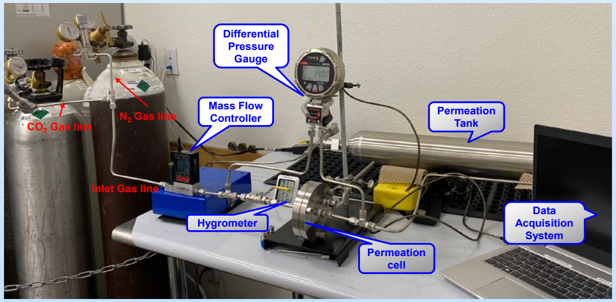
Professor Milind Deo, Ph.D.
Subaward Project Director

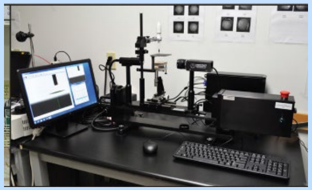
Palash Panja, Ph.D.
Subaward Co-Investigator

Cleanroom Certified ISO-7

Scanning Electron Microscope (SEM)

Gas Permeation Test Unit





Progress and Current Status of Project

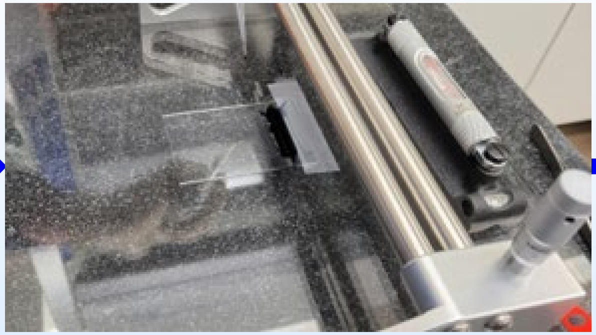
Project Team working strategically to meet project objectives

- Developed different hybrid polymer formulations,
- Fabricated large size HypoMem samples and prepared undoped, doped, dedoped and redoped samples
- Characterized HypoMem samples using Fourier-transform infrared spectroscopy (FTIR), UV-Vis spectroscopy, scanning electron microscope (SEM), and thermogravimetric (TGA) analysis
- Constructed an on-site gas permeation testing set-up
- Measured permeance, permeability, and CO_2/N_2 selectivity of HypoMem samples at room and elevated temperatures
- Performed computer simulation and modeling of HypoMem system

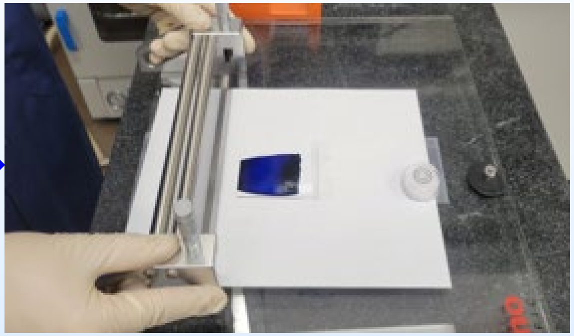
Casting Hybrid Polymer Layer

Cast thin-films of hybrid polymer layer on glass substrate using a doctor blade

Secured glass substrate to a level surface for deposition of polymer for the active layer



Deposited 200-400 μL of polymer onto secured glass substrate



Glided doctor blade over the polymer to produce a thin-film

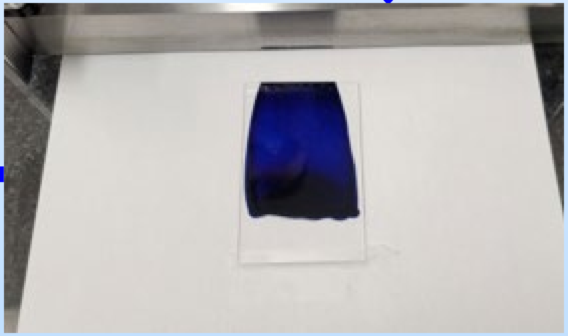
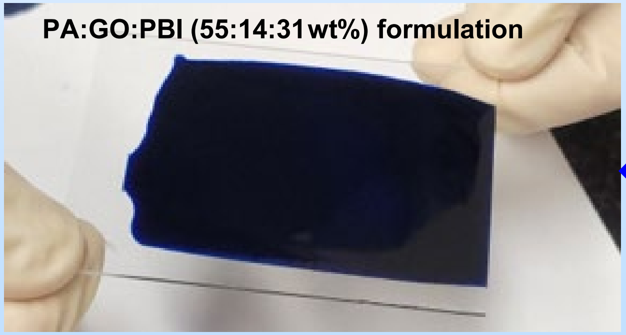
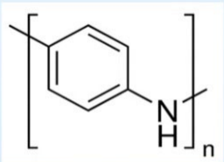


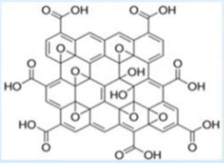
Image of thin-film polymer layer after doctor blading



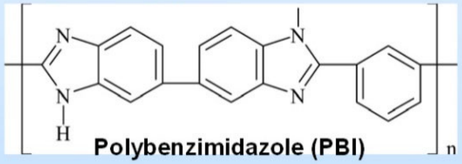
Dried in a vacuum oven at 80°C and annealed for 8 h, obtained dried film



Polyaniline (PA)



Graphene Oxide (GO)

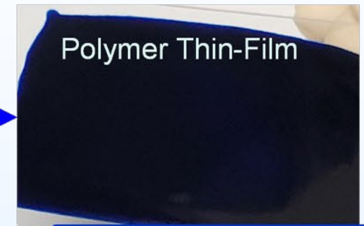


Polybenzimidazole (PBI)

Fabrication of HypoMem Samples

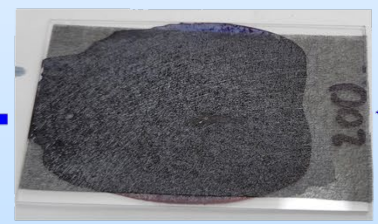
A
While the polymer is annealed, we generated an epoxy resin in two steps. 1st prepared a solution of PEG200, PEG400, and MBCa (ratio 5:5:1). Stirred for 2 h until dissolved

B
2nd Added Badge and stirred for 2 h until dissolved to formulate the completed epoxy resin (ratio of BADGE to MBCa 5:3)



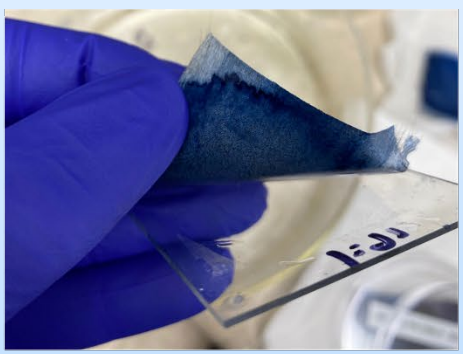
Layered 8 g/m^2 carbon veil (CV) on top of polymer thin-film

Drop-casted epoxy resin onto CV support layer & PA/GO active polymer layer



Epoxy resin dispersed onto CV support layer & PA/GO active polymer layer

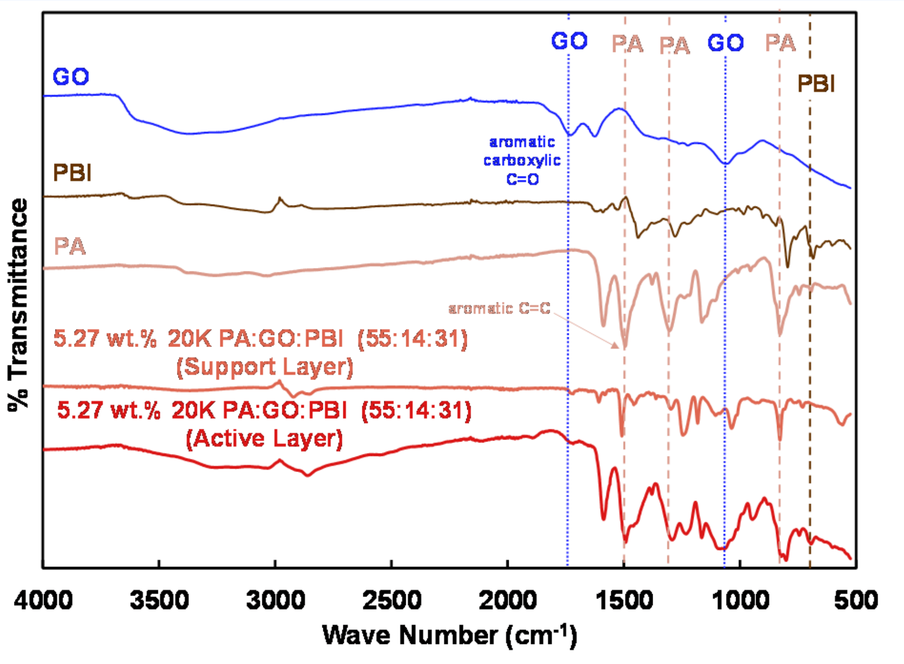
Annealed under vacuum at 80 °C for 8 h

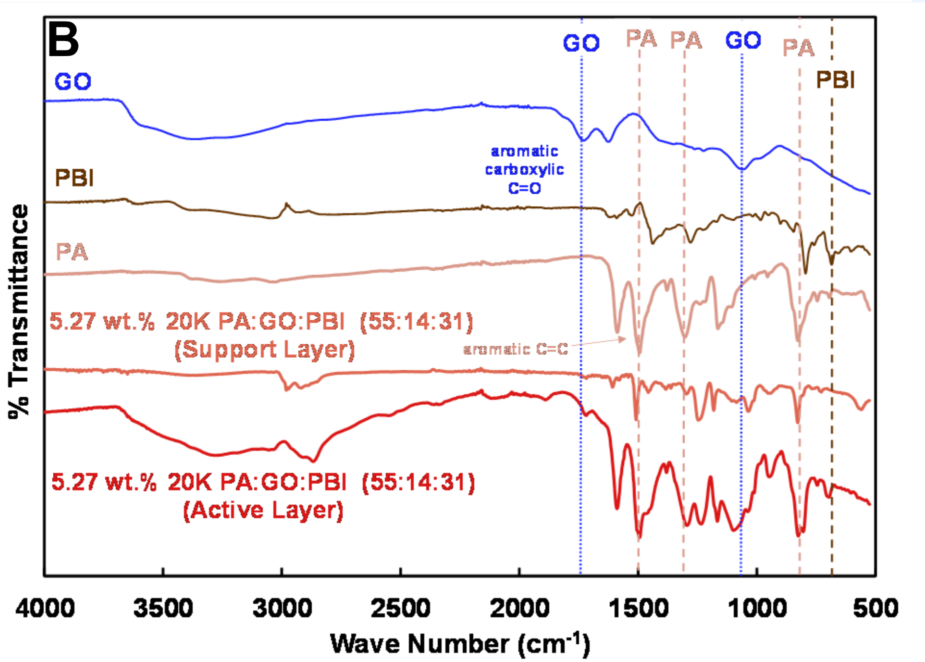


Submerged in water, and then thin-film lift off (T-FLO) of HypoMem sample

Characterization of HypoMem Samples: FTIR Analysis

1. After drying the epoxy resin solution, the tri-layered membrane was formed
2. Delaminated the tri-layered membrane from the glass substrate easily by submerging in water with the thin-film lift off method (T-FLO), and then stored them
3. Characterized by FTIR, UV-Vis, SEM and TGA analysis



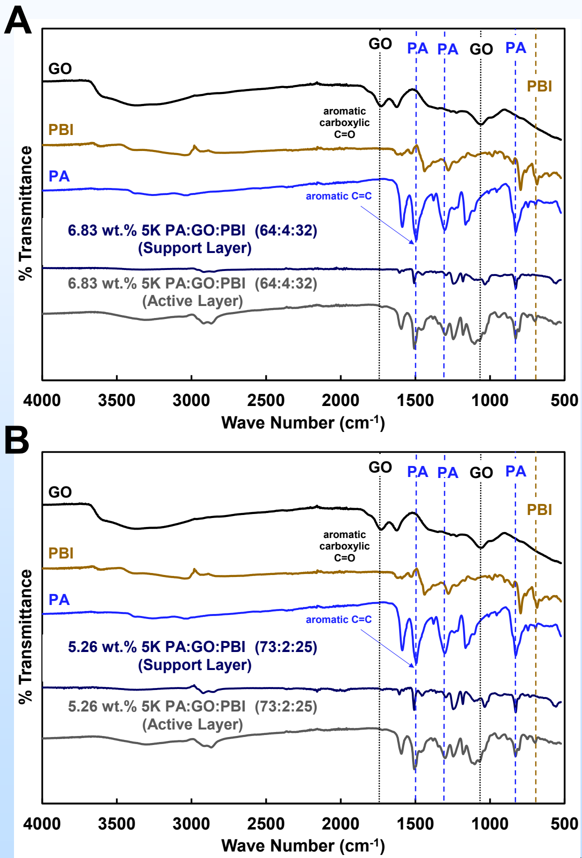


Observed characteristic FTIR peaks of PA, PBI, and GO in HypoMem samples

Characterization of HypoMem Samples: FTIR Analysis and Mechanical Flexibility

Prepared HypoMem samples with other PA:GO:PBI formulations:

60:10:30 wt%,
64:4:32 wt%,
68:2:30 wt%,
73:2:25 wt%
73:12:15 wt%



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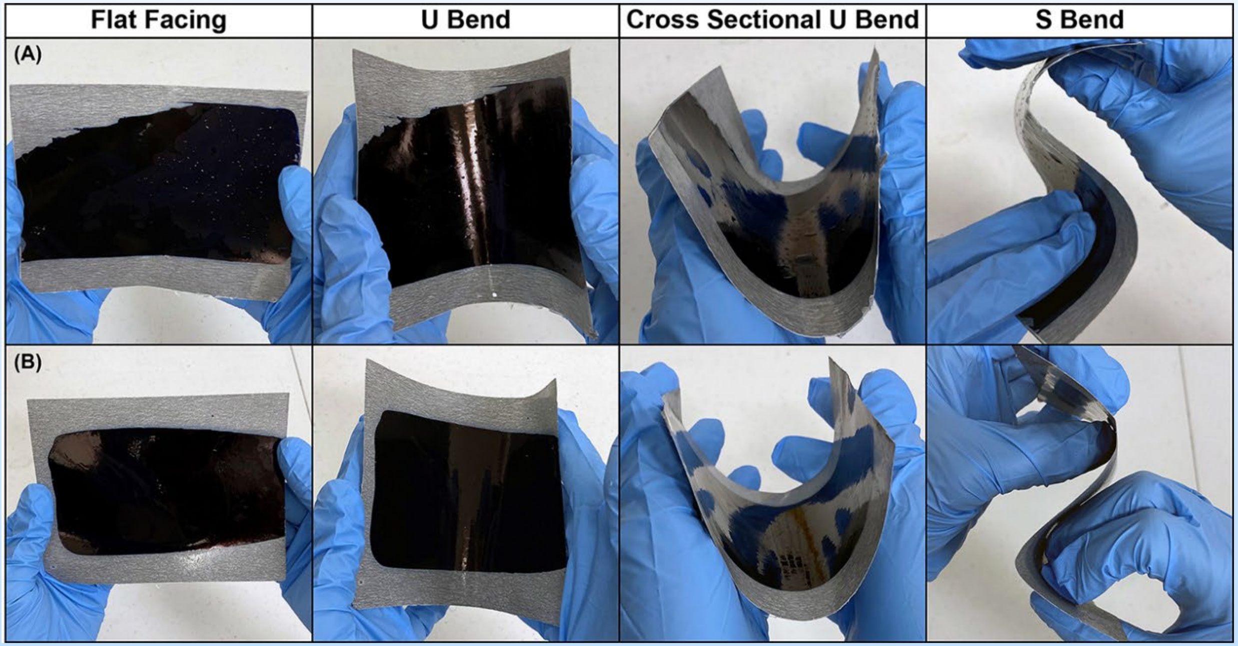
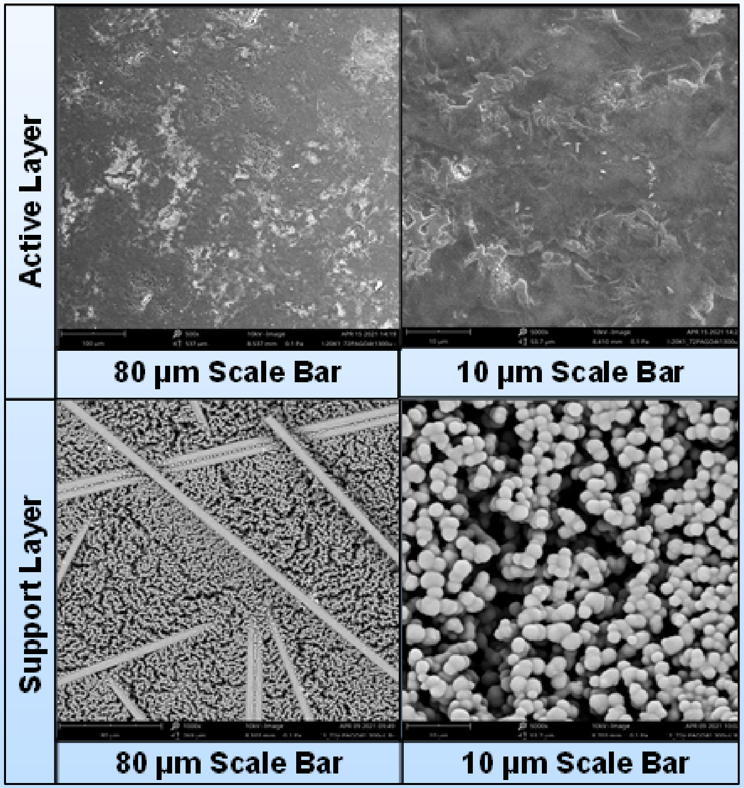


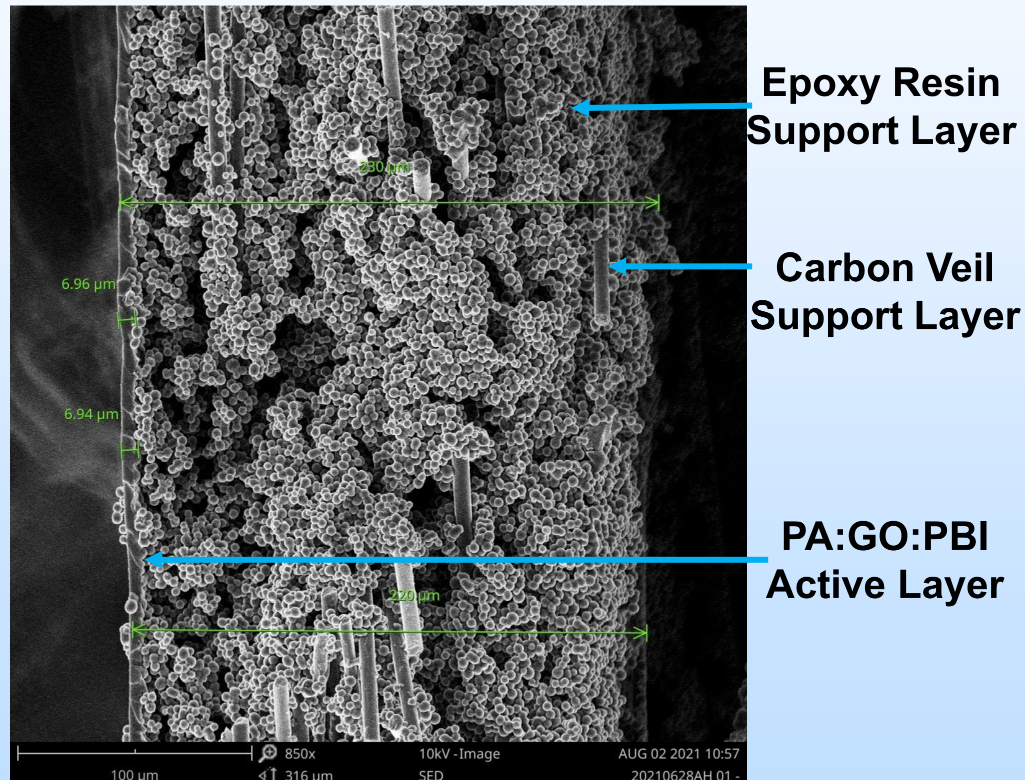
HypoMem samples are mechanically robust, flexible and workable

SEM Analysis of HypoMem Samples

HypoMem characterized with SEM analysis showing morphologies of both hybrid polymer and epoxy layer sides



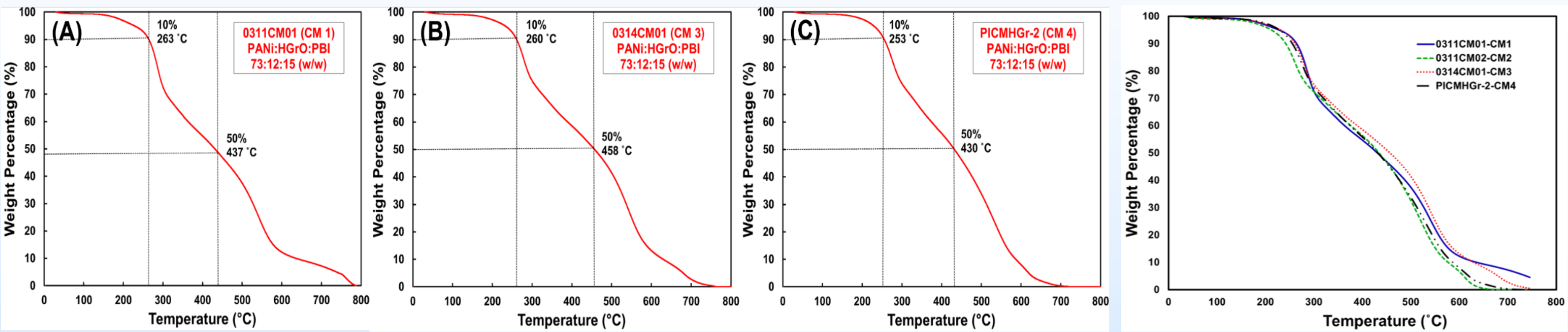
SEM analysis of a PA:GO:PBI (55:14:31 wt%) HypoMem sample



SEM image of a cross sectional PA:GO:PBI (55:14:31 wt%) HypoMem sample

Thermogravimetric Characterization of HypoMem Samples: Thermal Stability

TGA curves of four PA:HGrO:PBI (73:12:15 wt% and 60:10:30 wt%) HypoMem samples

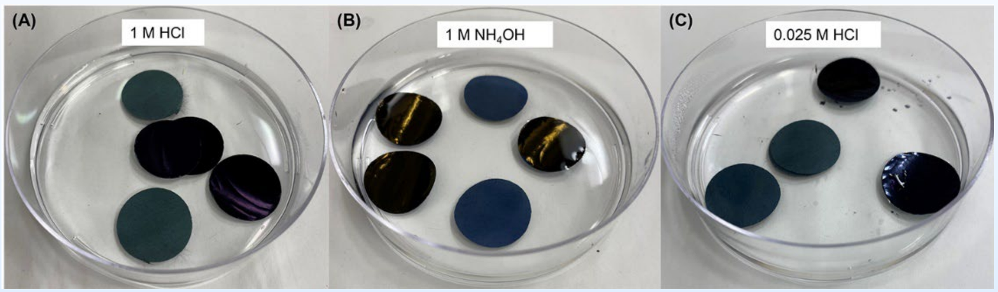


Sample ID	PANi:HGrO: PBI Composition (w/w)	Decomposition Onset Temperature (˚C)	Temperature (˚C) of 10% Weight Loss	Temperature (˚C) of 50% Weight Loss	Residual Weight (%) at 600 ˚C
0311CM01-CM1	73:12:15	263.21	263	437	12.07
0311CM02-CM2	60:10:30	227.71	240	437	6.20
0311CM02-CM3	73:12:15	251.11	262	458	12.71
PICMHGr-2-CM4	73:12:15	241.80	253	430	7.64

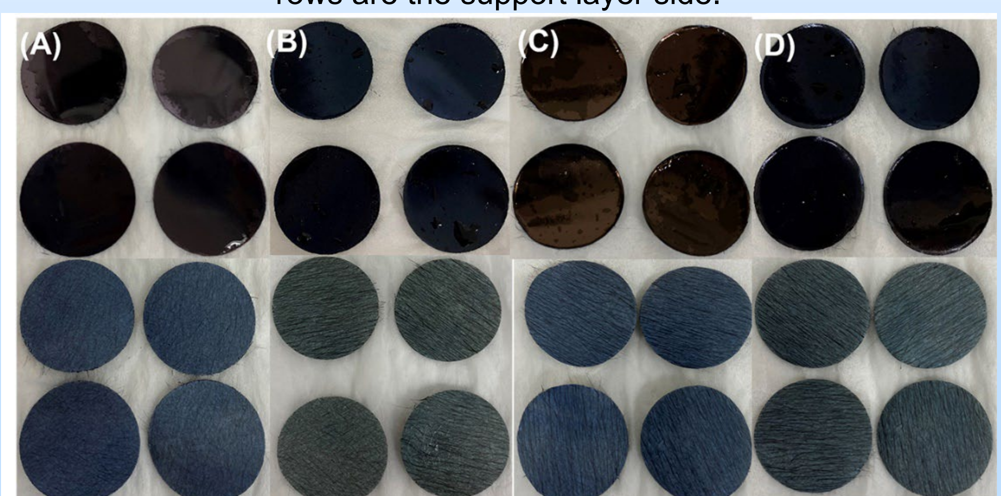
HypoMem samples show good thermal stability up to 250 °C

Doping, Dedoping and Redoping of HypoMem Samples

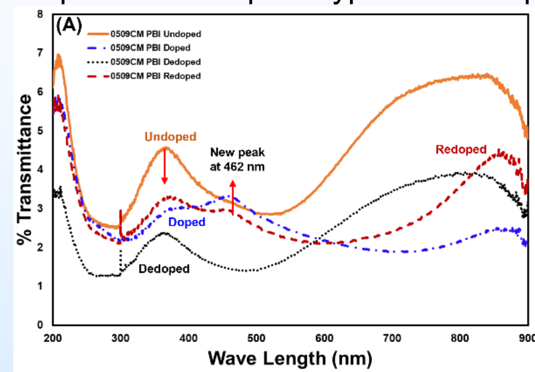
(**A**) Doping: 1 M HCl acid treatment for 4 h, (**B**) Dedoping: 1 M NH_4OH base treatment for 24 h, and (**C**) Redoping: 0.025 M HCl treatment for 16 h.

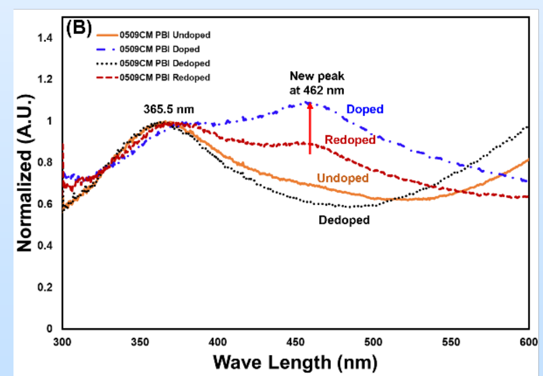


Photographs of **(A)** undoped, **(B)** doped, **(C)** dedoped, and **(D)** redoped. Top two rows are the active layer side, and bottom two rows are the support layer side.

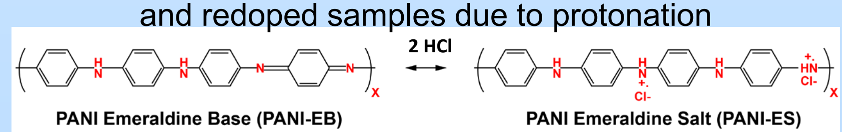


Spectroscopic characterization of undoped, doped, dedoped and redoped HypoMem samples



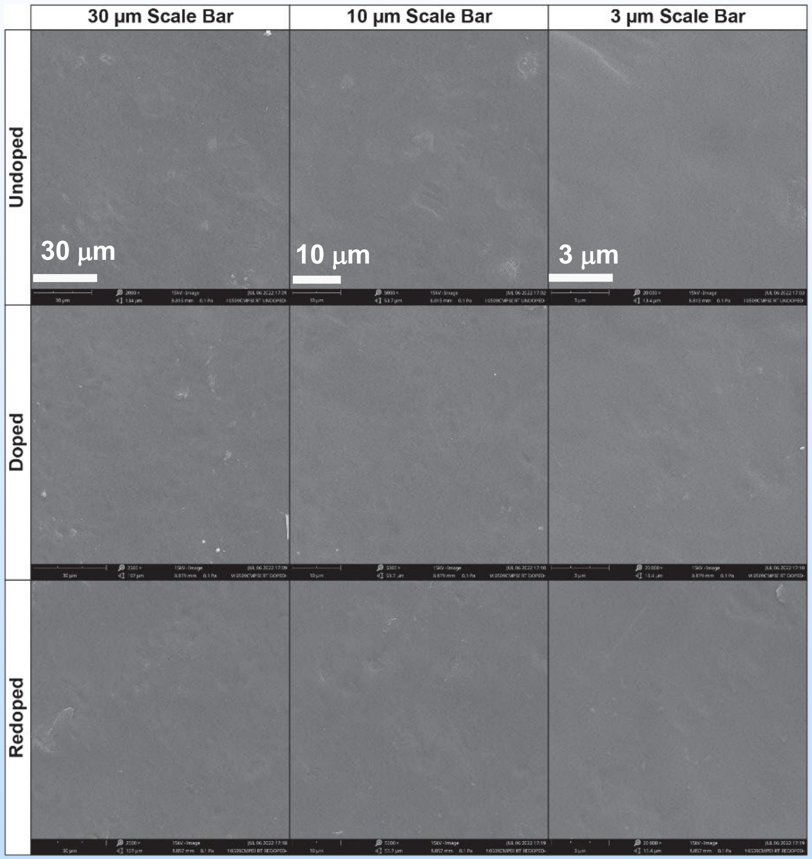


New peak appeared at 462 nm for doped and redoped samples due to protonation



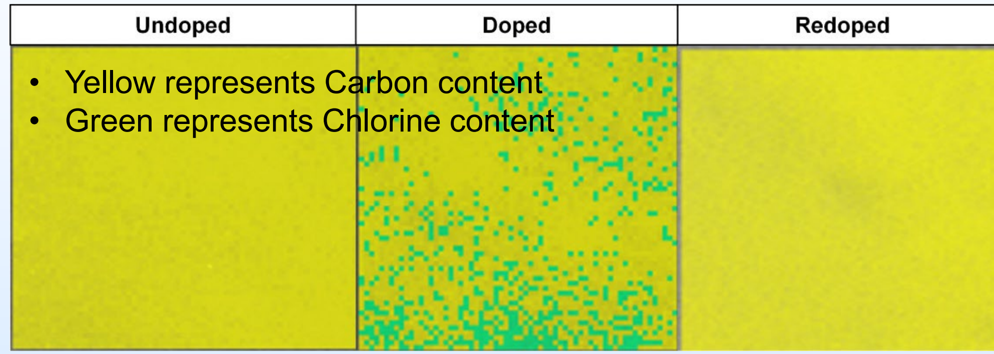
SEM Characterization of undoped, doped and redoped HypoMem Samples

SEM images of undoped, doped and redoped samples



Observed no significant difference in morphologies (within the recorded magnifications) of the undoped, doped and redoped samples

Elemental mapping by EDS analysis of undoped, doped, dedoped and redoped HypoMem samples



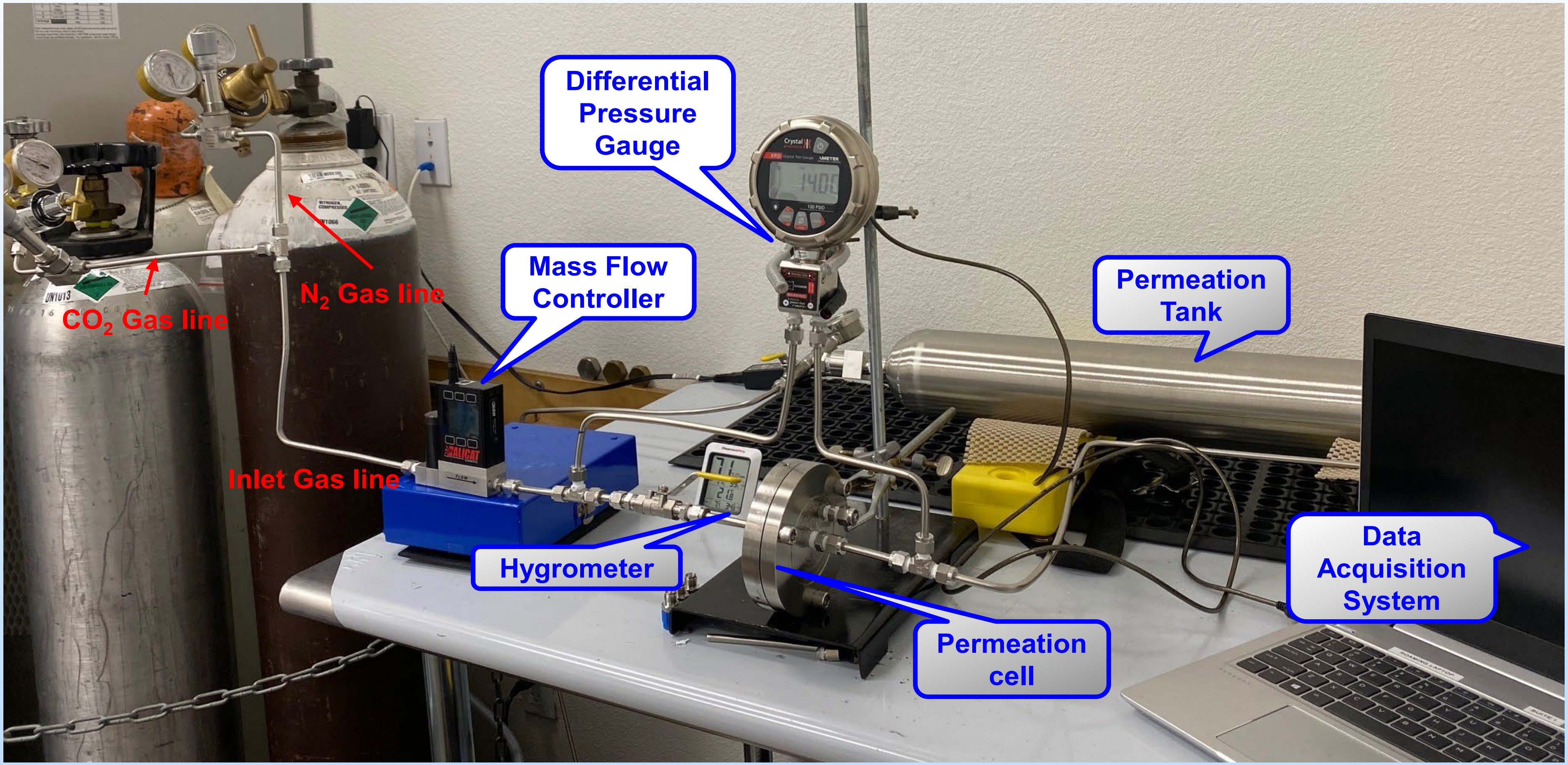
Elemental distribution data for the undoped, doped and redoped samples

Element Name	Element Symbol	Weight Conc.		
		Undoped	Doped	Redoped
Au	Gold	70.10	77.98	73.82
C	Carbon	27.25	16.63	22.65
N	Nitrogen	1.80	1.65	1.83
O	Oxygen	0.84	0.66	0.72
Cl	Chlorine	-	3.07	0.98

Doped and redoped samples contain chlorine which came from HCl treatment

Constructed On-Site Gas Permeation Testing Setup

Gas permeation testing set up for evaluating 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:

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

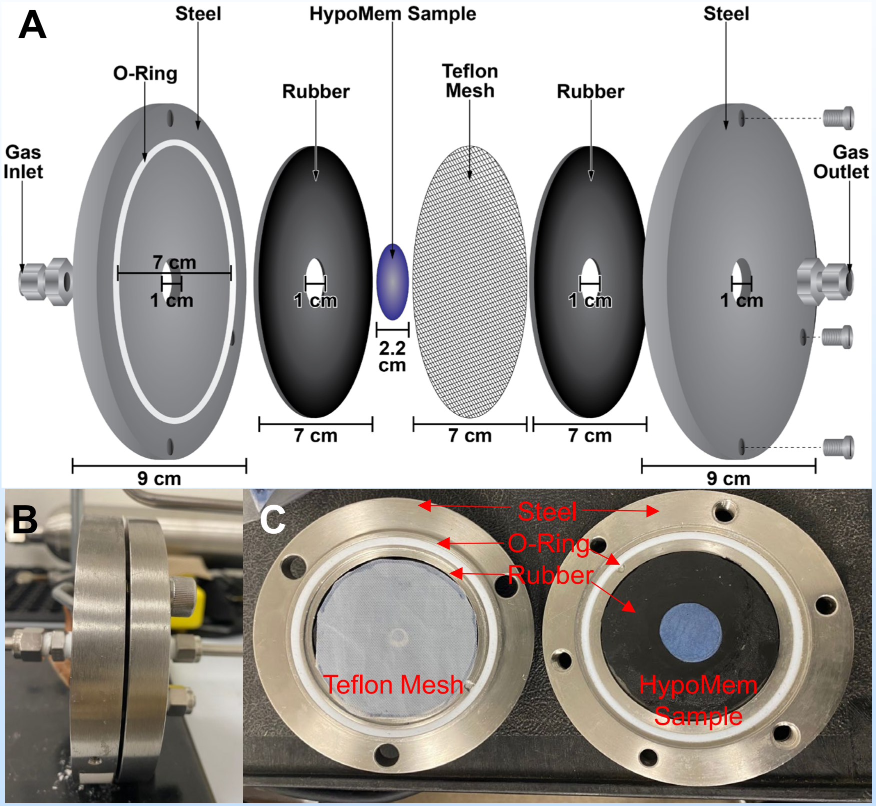
where, P is the gas permeability across the membranes (in Barrers) [1Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg], $P_{Permeate}$ is the permeate pressure (in cmHg), *dp/dt* is the rate of the steady-state permeate side pressure increase (in cmHg/s), V is the standardized permeate volume (in cm^3), L 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:

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

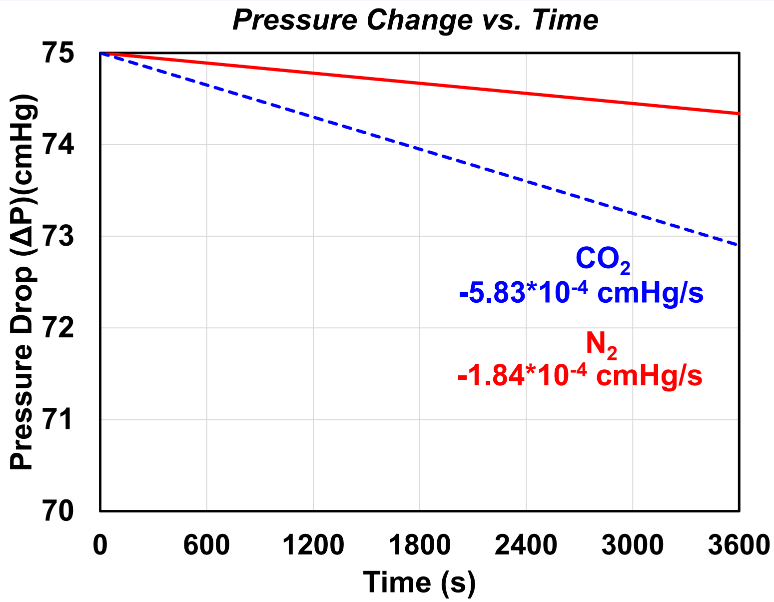
where, P_A and P_B are the permeability coefficients of the pure gases CO_2 and N_2, respectively.

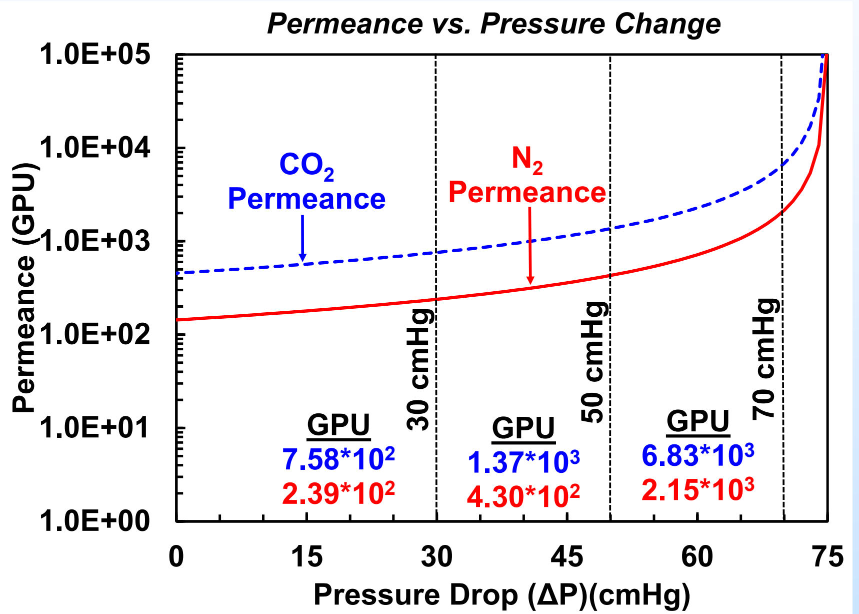


(**A**) Exploded view of the permeation cell
(**B**) Closed permeation cell
(**C**) Open permeation cell showing components

HypoMem's Membrane Performance: CO_2 Permeance and Selectivity

Gas permeation test profiles of a HypoMem sample #20210628AH01





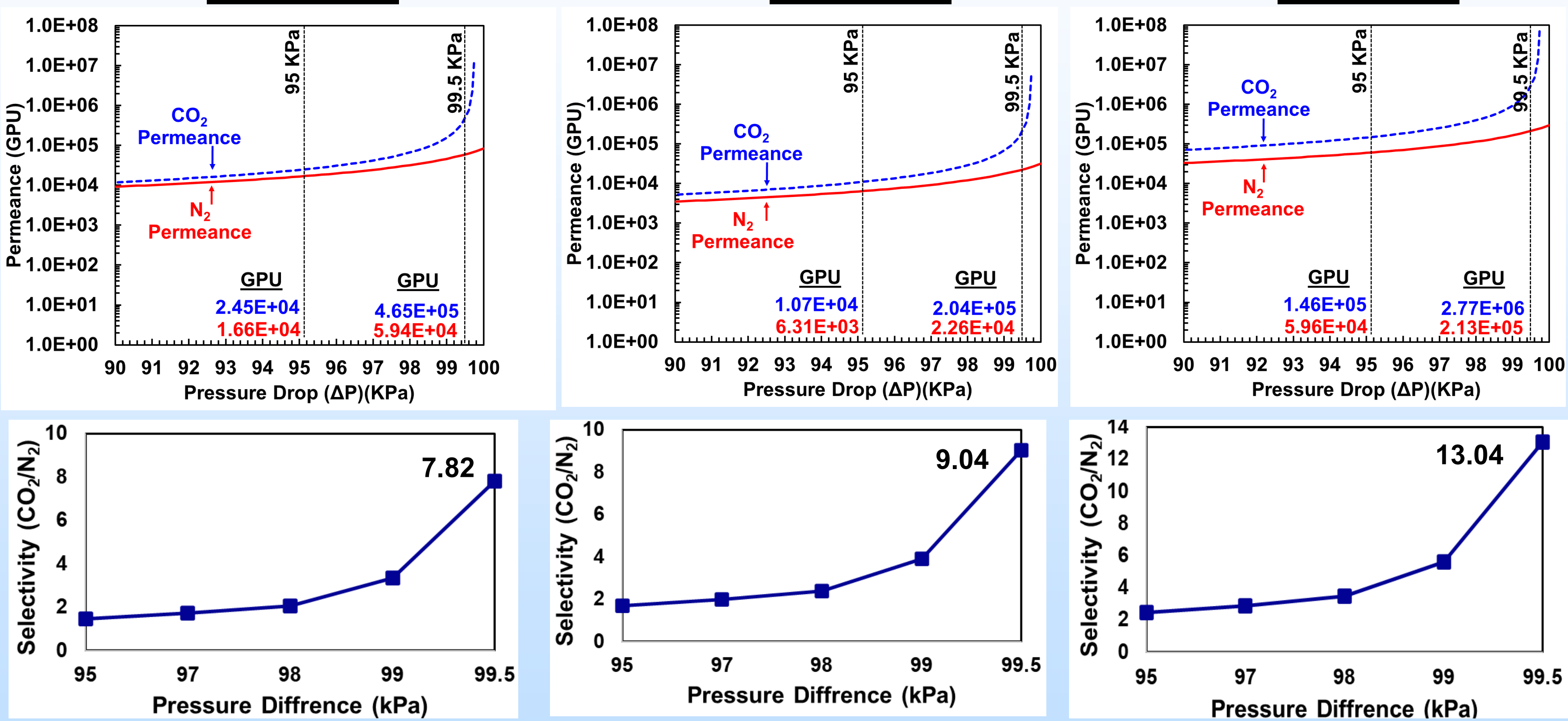
Test Conditions:

- *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 difference across the membrane of 70 cm Hg (~95 kPa)

PANI:GrO:PBI (60:10:30 wt%) HypoMem Performance: CO_2 Permeance and Selectivity

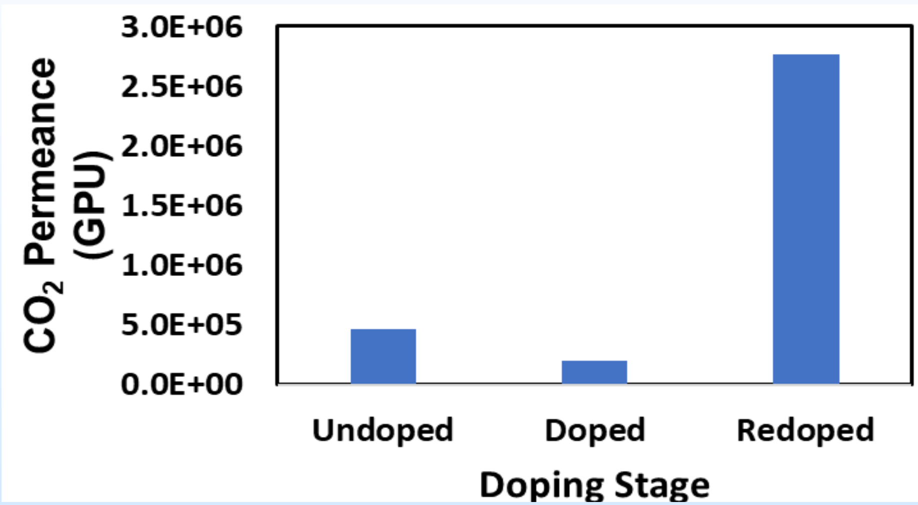
Undoped **Doped** **Redoped**



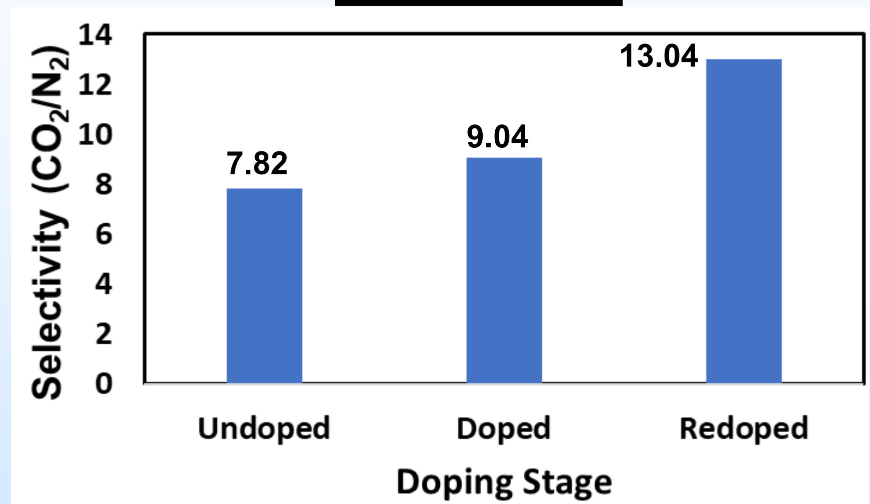
CO_2/N_2 selectivity increased with doping and redoping stages

CO_2 Permeance and Selectivity of PANI:GrO:PBI (60:10:30 wt%) HypoMem

Permeance



Selectivity

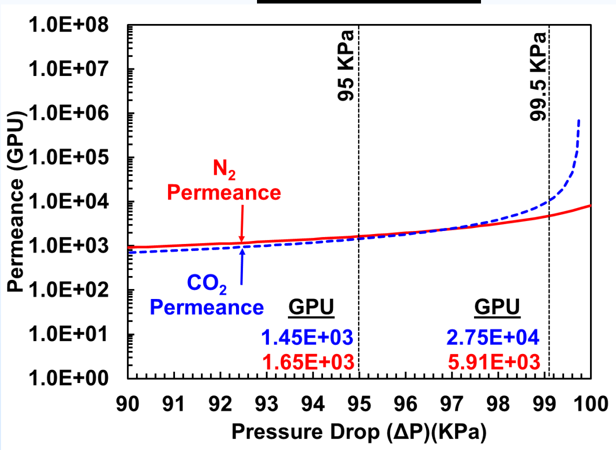


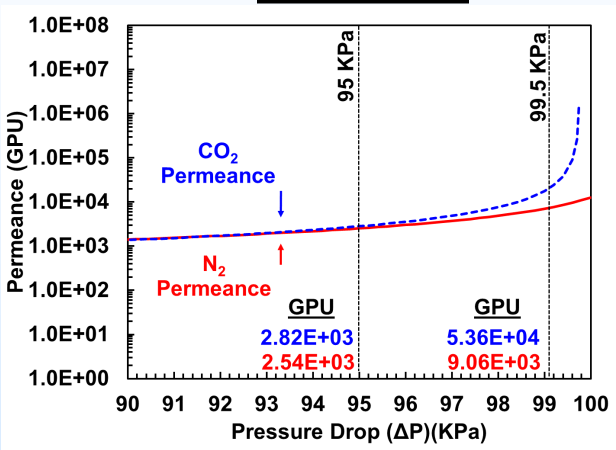
0311CM02 PA:HGr:PBI (60:10:30)	Selectivity (CO_2/N_2) at Different Pressure differences (KPa)					CO_2 Permeation (GPU)
	95	97	98	99	99.5	99.5 kPa
Undoped films	1.47	1.73	2.08	3.35	**7.82**	465000
Doped films	1.70	1.99	2.40	3.87	**9.04**	204000
Redoped films	2.45	2.88	3.46	5.59	**13.04**	2770000

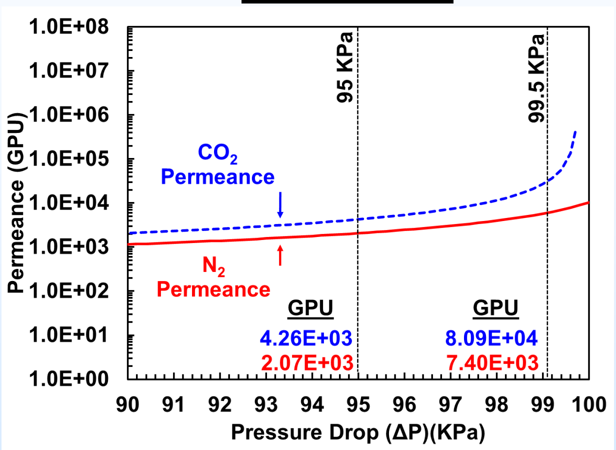
CO_2 Permeance and selectivity increased with doping and redoping stages

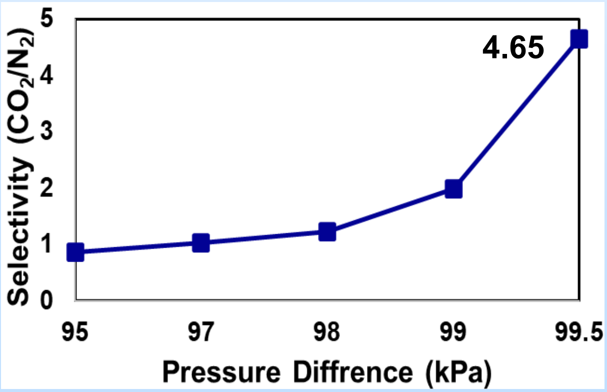
73:12:15 wt% PANI:GrO:PBI HypoMem Performance: CO_2 Permeance and Selectivity

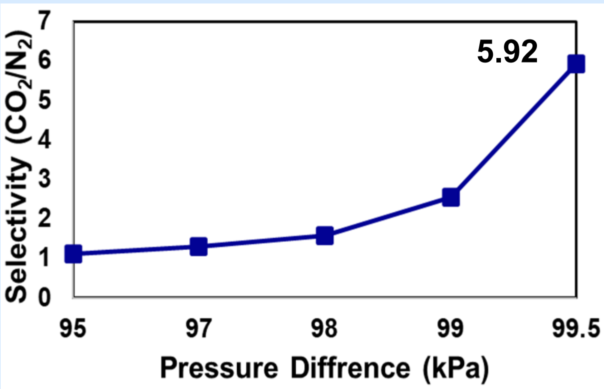
Undoped | **Doped** | **Redoped**

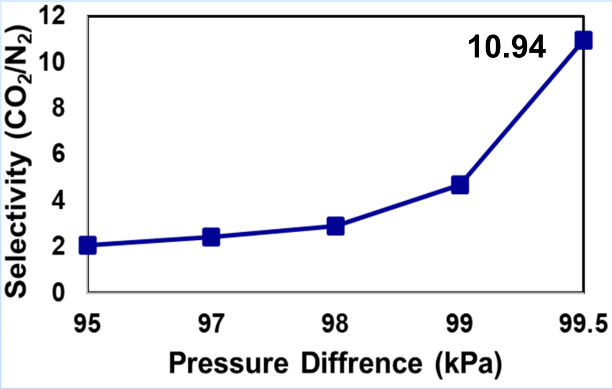






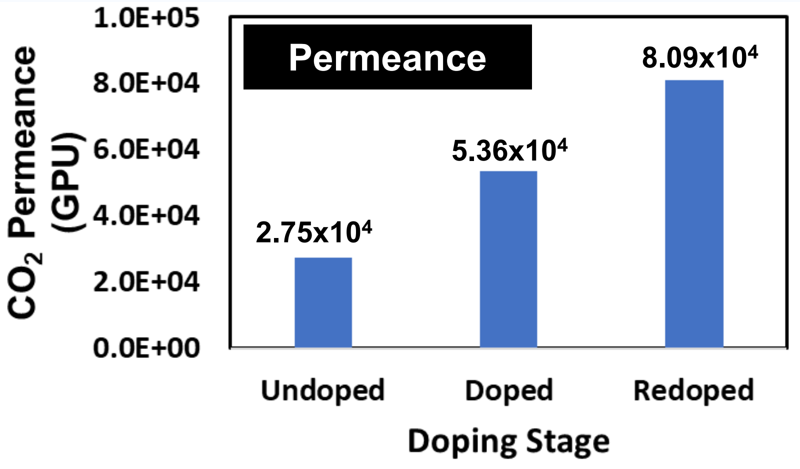


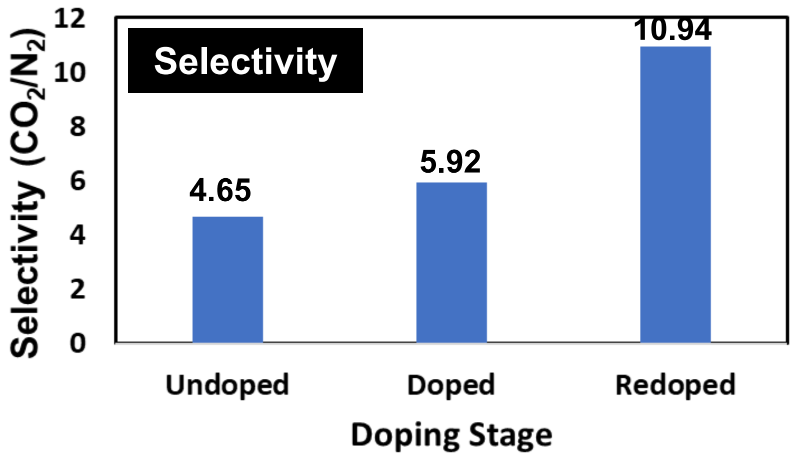




Observed CO_2/N_2 selectivity 10.94 for redoping sample

CO_2 Permeance and Selectivity of PANI:GrO:PBI (73:12:15 wt%) HypoMem





CO_2 Permeance and selectivity increased with doping and redoping stages

0311CM01 PA:HGr:PBI (73:12:15)	Selectivity (CO_2/N_2) at Different Pressure differences (KPa)	CO_2 Permeation (GPU)
	99.5	99.5 kPa
Undoped films	**4.65**	27500
Doped films	**5.92**	53600
Redoped films	**10.94**	80900

Different redoped 73:12:15 PANI:GrO:PBI membranes: Repeatability of membranes' performance

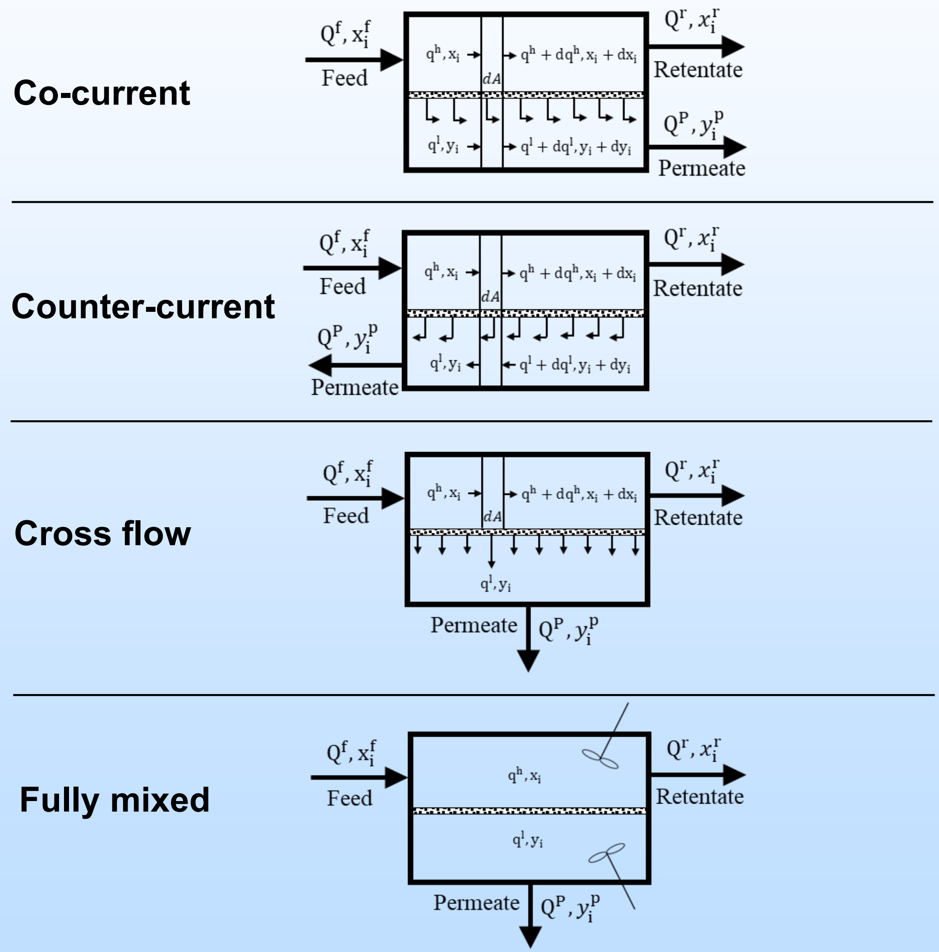
PA:HGr:PBI (73:12:15) Redoped Sample ID	Selectivity (CO_2/N_2) at Different Pressure differences (KPa)				CO_2 Permeation (GPU)
	97	98	99	99.5	99.5 kPa
0311CM01	2.42	2.90	4.69	**10.94**	80900
PICMHGr-2	2.12	2.55	5.07	**9.62**	175000
0314CM01	2.66	3.20	5.16	**12.05**	1700000

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 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

Various flow patterns in a single module of membrane separation



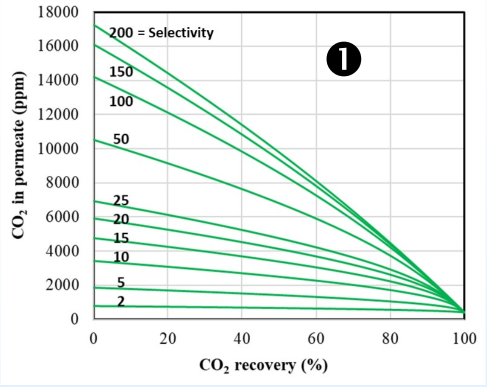
Computer Simulation and Modeling : Co-current flow and single stage

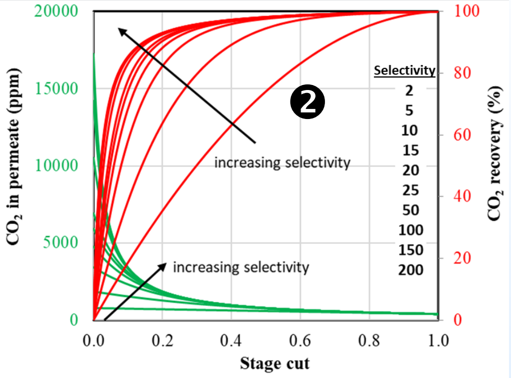
$$Selectivity = \frac{Permeability\ of\ CO_2}{Permeability\ of\ N_2}$$

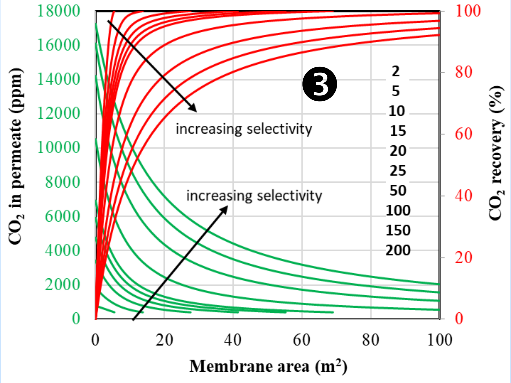
$$Stage\ cut, \theta = \frac{Permeate\ flowrate}{Feed\ flowrate}$$

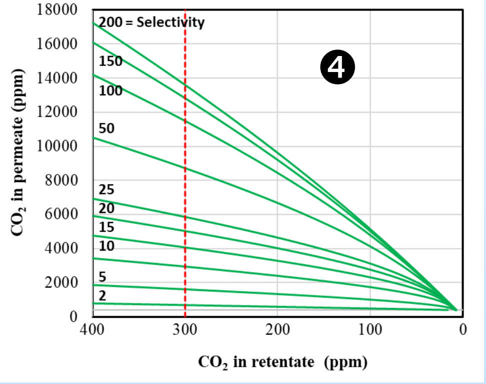
$$CO_2\ Recovery = \frac{CO_2\ mole\ in\ permeate}{CO_2\ mole\ in\ feed}$$

- Flux model : **Constant permeability**
- Flow pattern : **Co-Current**
- CO_2 con. in feed : **400 ppm**
- Upstream pressure, p' (kPa) : **110**
- Downstream pressure, p'' (kPa): **2**
- Permeability of CO2 (Barrer) : **10000**
- Selectivity: **2 to 200**





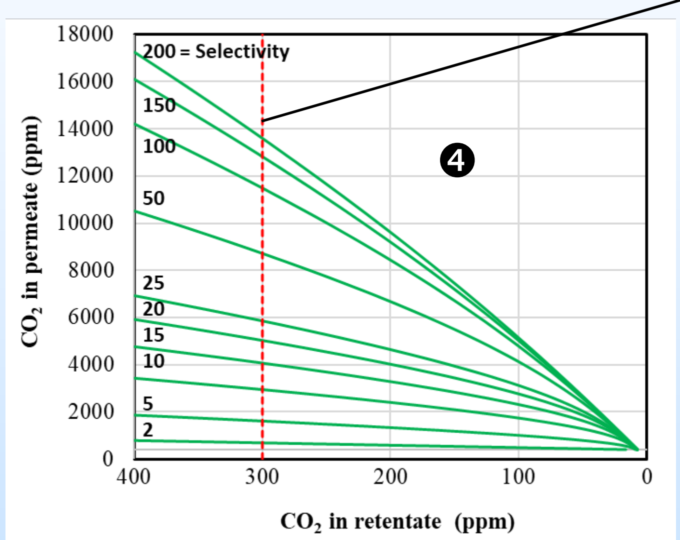


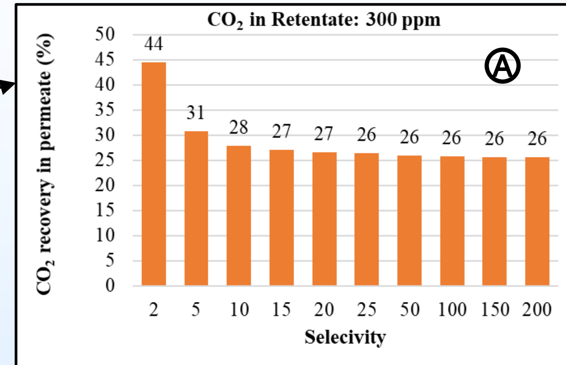


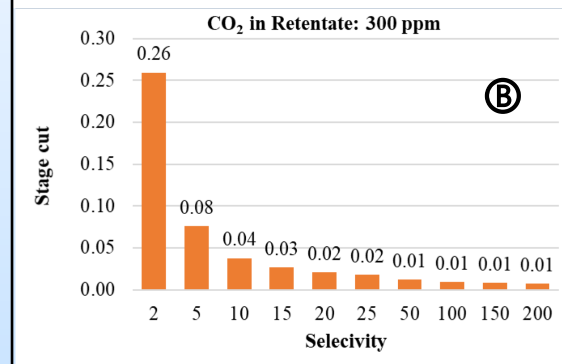
- **Figure 1**: CO_2 purity (i.e., ppm in permeate) is inversely proportional to its recovery.
- **Figures 2 and 3**: CO_2 purity increases with selectivity for a fixed stage cut or membrane area.
- **Figure 4**: CO_2 purity is inversely proportional to CO_2 concentration in permeate due to equilibrium.

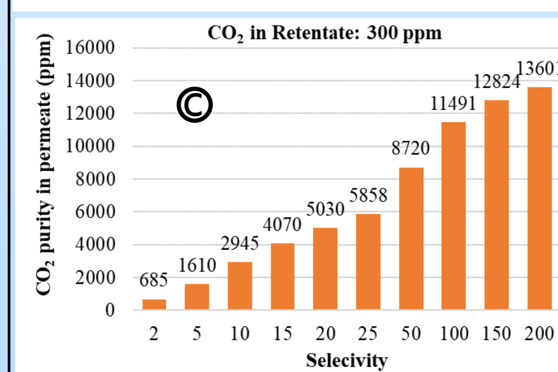
Computer Simulation and Modeling : Co-current flow and single stage

- CO_2 concentration in feed : **400 ppm**
- CO_2 concentration in retentate : **300 ppm**









For fixed CO_2 concentration in retentate

- **Figures A and B**: CO_2 recovery and stage cut are high at lower selectivity.
- **Figure C**: However, CO_2 purity is low at lower selectivity.
- Higher CO_2 purity and recovery can be achieved with higher selectivity and multiple-stage in combinations.

Computer Simulation and Modeling : Co-current flow and multi-stage

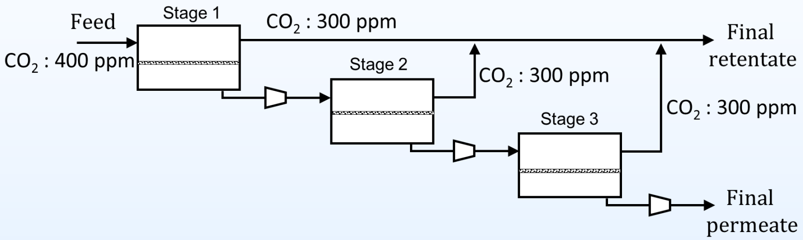
Some Basic Considerations for HypoMem Simulation

- 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

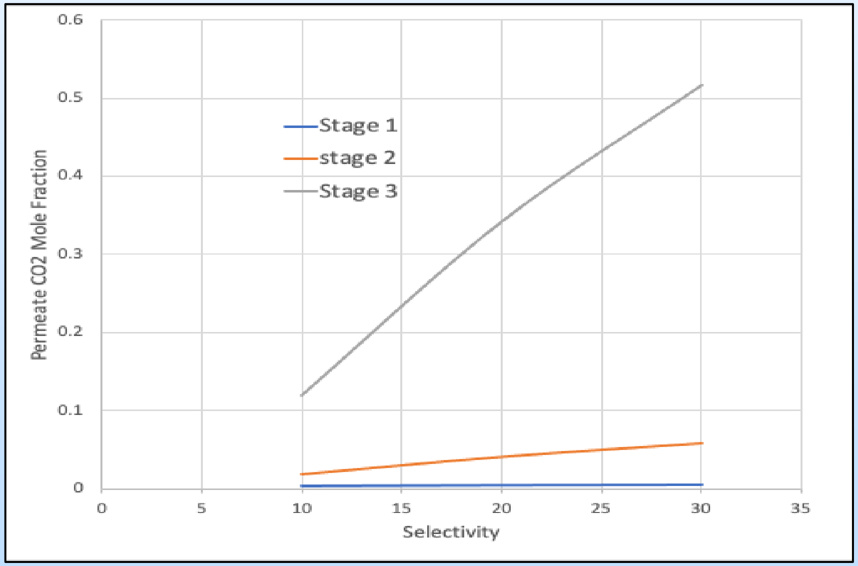
- Permeate concentration dependence
  - Pressure ratio (upstream to downstream for each stage)
  - Selectivity
- Throughput
  - Combination of flowrate, GPU and membrane area

- ***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***

Schematic of three stage DAC CO_2 separation



Simulated effect of selectivity throughout three stages



Plans for Future Development

- In this project
  - Conduct gas permeation testing on HypoMem samples at different weathering conditions such as elevated temperatures and icy condition.
  - Optimize permeance, permeability, and CO_2 selectivity performance.
  - Continue performing computer simulation and modeling based on HypoMem experimental data/results, and process economics.
- 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

- Developed hybrid polymer formulations and fabricated HypoMem samples with different compositions.
- Characterized HypoMem samples by FTIR analysis and their morphologies (both active polymer and support epoxy sides) and thickness by scanning electron microscope (SEM) analysis.
- Performed doping, dedoping and redoping of HypoMem samples and characterized them by microscopy and spectroscopy.
- Observed CO_2 selectivity of ≥10 with permeance ≥8×10^4 GPU for redoped samples at a pressure difference of 99.5 kPa across the membrane.
- Observed a trend of an increase in CO_2 permeance and selectivity with doping stage
- Computer simulation and modeling suggested that multi-stage process is required to achieve the desired CO_2 permeate concentration for successful DAC CO_2 separation

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