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

Project Number: DE-FE0031968

Adrien Hosking, M.S. and Maksudul M. Alam, Ph.D.
InnoSense LLC, Torrance, CA

Professor Milind Deo, Ph.D.
University of Utah, Salt Lake City, UT
Outline

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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 (CO₂), 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 CO₂ capture from ambient air can cost $94–$232 per metric tonne.

- Current methods of DAC CO₂ 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
The overall objective of this project is to develop a disruptive DAC CO\textsubscript{2} separation system using a hybrid polymer membrane (HypoMem) from ambient air to reduce CO\textsubscript{2} separation costs and energy penalties.

**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\textsubscript{2} Separation from Ambient Air at a Reduced Cost.
Current project process of HypoMem based DAC CO₂ separation system

[1] Simulated Air Pre-Condition
   - Simulated Air
   - Humidity Control
   - Gas Mixer & Compressor
   - Heater (Temperature Control)

   - Active Layer Production
   - Support Layer Production
   - Membrane Characterization

[3] CO₂ Separation System
   - Gas Inlet
   - HypoMem
   - Gas Outlet
   - Permeation Cell

   - Expandable
   - 95% Purity
   - 90% Recovery
   - Permeate Gases
   - Analytical Instrument
   - Permeation (Vacuum) Tank
   - Vacuum Pump
Technical Approach/Project Scope

An overall process of HypoMem based DAC CO₂ separation system

1. Simulated Air Pre-Condition
   - Simulated Air
   - Humidity Control
   - Gas Mixer & Compressor
   - Heater (Temp. Control)

2. Membrane Fabrication
   - Active Layer Production
   - Support Layer Production
   - Membrane Characterization

3. CO₂ Separation System
   - Spiral Wound Membrane
   - Hollow Fiber Membrane

4. Post-Gas Evaluation
   - Permeate Gases
     - 95% Purity
     - 90% Recovery
   - Analytical Instrument
   - Reject Gases
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 CO₂
- 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 CO₂/N₂ 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.

**Active Layer Preparation**
1. Disperse GO/PBI in NMP to desired Wt. % concentration
2. Add PA Powder to desired Wt. % concentration
3. Formulated PA/GO/PBI solution

**Epoxy Resin Preparation**
4. Cast thin-film active polymer layer on glass substrate using a doctor blade
5. Add carbon veil (CV) layer for support layer
6. Drop-cast epoxy resin onto CV support layer & PA/GO/PBI active polymer layer

**HypoMem Preparation**
7. Tri-layered polymer membrane
8. Delaminate tri-layered polymer membrane from glass substrate
9. Dry in Air
10. HypoMem tri-layered polymer membrane

While the polymer is annealed:
- Generate PEG200 or PEG400, with MBCa solution (ratio 13:1)
- While the polymer is annealed
- Cast thin-film active polymer layer on glass substrate using a doctor blade

Prepare and clean glass substrate with IPA and Acetone
- Stir for 1 h until dissolved
- Stir for 1 h until dissolved
- Stir for 1 h until dissolved
- Stir for 1 h until dissolved
Preparation of 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 CO₂
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.

Consistently fabricated active polymer layer for HypoMem samples

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

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
Preparation of Epoxy Resin Support Layer

Fabrication of large flat HypoMem samples

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:** 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.

**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.
Gas permeation testing set up evaluates, permeability, permeance and CO₂ Selectivity
Gas permeation method and cell designed for HypoMem performance testing

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

\[
P = 10^{10} \times \frac{V_L}{P_{\text{Permeate}} A R T} \times \frac{dp(t)}{dt}
\]

(1)

where, \(P\) is the gas permeability across the membranes (in Barrers) \(1 \text{Barrer} = 10^{-10} \text{cm}^3 \text{ (STP)} \text{ cm/cm}^2 \text{ s cmHg)}\), \(P_{\text{Permeate}}\) 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 \(0.278 \text{ cm}^3 \text{ cmHg/cm}^3 \text{ (STP)} \text{ K}\).

Solving for permeance is a similar equation but does not factor in thickness of the sample \(L\). Permeance \(P_{\text{Permeance}}\) is calculated using Eq. 2:

\[
P_{\text{Permeance}} = 10^6 \times \frac{V}{P_{\text{Permeate}} A R T} \times \frac{dp(t)}{dt}
\]

(2)

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

\[
\alpha_{A/B} = \frac{P_A}{P_B} \times \frac{P_{\text{CO}_2}/P_{\text{N}_2}}
\]

(3)

where, \(P_A\) and \(P_B\) are the permeability coefficients of the pure gases \(\text{CO}_2\) and \(\text{N}_2\), 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: CO₂ 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 CO₂ and N₂ gases,
- Ambient temperature conditions and fixed upstream condition 75.9 cm Hg (101 kPa),

**Higher permeance value observed for CO₂ (6.83*10⁵) than N₂ (2.15*10⁵) 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\textsubscript{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\textsubscript{2} concentration is about the pre-industrial 300 ppm.
- Reaching a selectivity of 10 at permeance of 10,000, a permeate CO\textsubscript{2} concentration of 7560 ppm can be achieved.

**Base Case CO\textsubscript{2} Separation Parameters Used for Illustrative Calculations**

<table>
<thead>
<tr>
<th>CO\textsubscript{2} Separation Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upstream Pressure (kPa)</td>
<td>100</td>
</tr>
<tr>
<td>Downstream Pressure (kPa)</td>
<td>2</td>
</tr>
<tr>
<td>Initial CO\textsubscript{2} Concentration (mole fraction)</td>
<td>0.0004</td>
</tr>
<tr>
<td>Selectivity CO\textsubscript{2}/(Other)</td>
<td>30</td>
</tr>
<tr>
<td>Membrane Permeance (GPU)</td>
<td>10000</td>
</tr>
<tr>
<td>Membrane Area (cm\textsuperscript{2})</td>
<td>5</td>
</tr>
</tbody>
</table>

**Characteristics of All the Streams for Base Case CO\textsubscript{2} Separation**

<table>
<thead>
<tr>
<th>Streams</th>
<th>Feed</th>
<th>Permeate</th>
<th>Retentate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>Total</td>
<td>CO\textsubscript{2}</td>
<td>Other</td>
</tr>
<tr>
<td>Concentration (ppm)</td>
<td>1000000</td>
<td>400</td>
<td>999600</td>
</tr>
<tr>
<td>Flow Rates (ml/s)</td>
<td>10</td>
<td>4.00E-03</td>
<td>9.996</td>
</tr>
</tbody>
</table>
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 CO₂). CO₂ 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 CO₂ concentration
- In stage 2, increased selectivity has a moderate impact on the permeate CO₂ concentration
- By stage 3, increased selectivity has a strong impact on the permeate CO₂ 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: $6.83 \times 10^5$ GPU for CO$_2$ and $2.15 \times 10^5$ 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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