High-Performance, Hybrid Polymer Membrane for Carbon Dioxide Separation from Ambient Air

primary project goal

InnoSense LLC is developing a direct air capture (DAC) system for carbon dioxide (CO_2) separation from ambient air using a hybrid polymer membrane to reduce CO_2 separation costs and energy penalties. Highly CO_2-selective, ultra-thin, functionalized hybrid polymer membranes (HypoMem), integrated with carbon materials such as graphene oxide (GO), are being designed to improve CO_2 capture performance from ambient or near-ambient conditions, thermal and chemical stability, and ease of processability for scale-up.

technical goals

- Fabricate ultra-thin (<100 nm) robust HypoMem and evaluate its properties and performance to establish selection/acceptance criteria for use in a novel CO_2 separation system.
- Conduct lab-scale CO_2 capture experiments to understand the effects of membrane performance (thickness, permeability, selectivity, etc.) and processing conditions (temperature, pressure, humidity, gas compositions, flow rate, etc.) for process optimization on CO_2 capture capacity.
- Integrate the optimized bench-scale CO_2 capture system in the recipient's lab at InnoSense.

technical content

In current DAC processes, sorbents and solvents are commonly used as CO_2 capture media. The disadvantages of sorbents and solvent systems include the need to build a very large structure, the cost and complexity of regenerative systems, and the loss of moisture in dry environments.

Carbon dioxide separation using membrane technology offers energy efficiency, lower cost and simple operation, and is an environmentally friendly process. Deficiencies of polymer membranes still remain, which include low gas permeability and selectivity, high temperature instability, and low flexibility and robustness. In this project, HypoMem is being utilized to overcome these deficiencies. Improvements to polymer membrane separation properties have been achieved by adding GO into the polymer matrix. Improving CO_2 separation performance using mixed matrix membranes has been demonstrated in prior studies where different levels and concentrations of inexpensive GOs were used to improve CO_2 selectivity of membranes. A variety of HypoMems have been created, embedding GO in polymer matrices, such as polyaniline (PANi), Polybenzimidazole (PBI), and Pebax® MH 1657, to improve CO_2 selectivity.

Figure 1 shows the thin-film liftoff (T-FLO) technique for HypoMem fabrication. Here, the active layer, which determines the membrane properties, is cast separately from the support layer. The support layer determines active layer perm-selectivity and morphology. The physical and chemical properties of the active

program area:
Carbon Dioxide Removal

ending scale:
Laboratory Scale

application:
Direct Air Capture

key technology:
Membranes

project focus:
Hybrid Polymer Membrane for DAC

participant:
InnoSense LLC

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predecessor projects:
N/A

NETL project manager:
Dustin Brown
dustin.brown@netl.doe.gov

principal investigator:
Maksudul M. Alam
InnoSense LLC
maksudul.alam-1@innosense.us

partners:
University of Utah

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67%

layer can be investigated independently from the entire membrane composite. The T-FLO technique shows potential for scaling the HypoMem for real-world applications.

Carbon Dioxide Permeability and Selectivity of HypoMem: HypoMem has demonstrated potential for high CO_2 permeability (up to 1,279 Barrers with pure CO_2) by controlling polymer and GO content. The addition of GO increased not only the free volume between the polymer chains, but also the stability of the membranes.

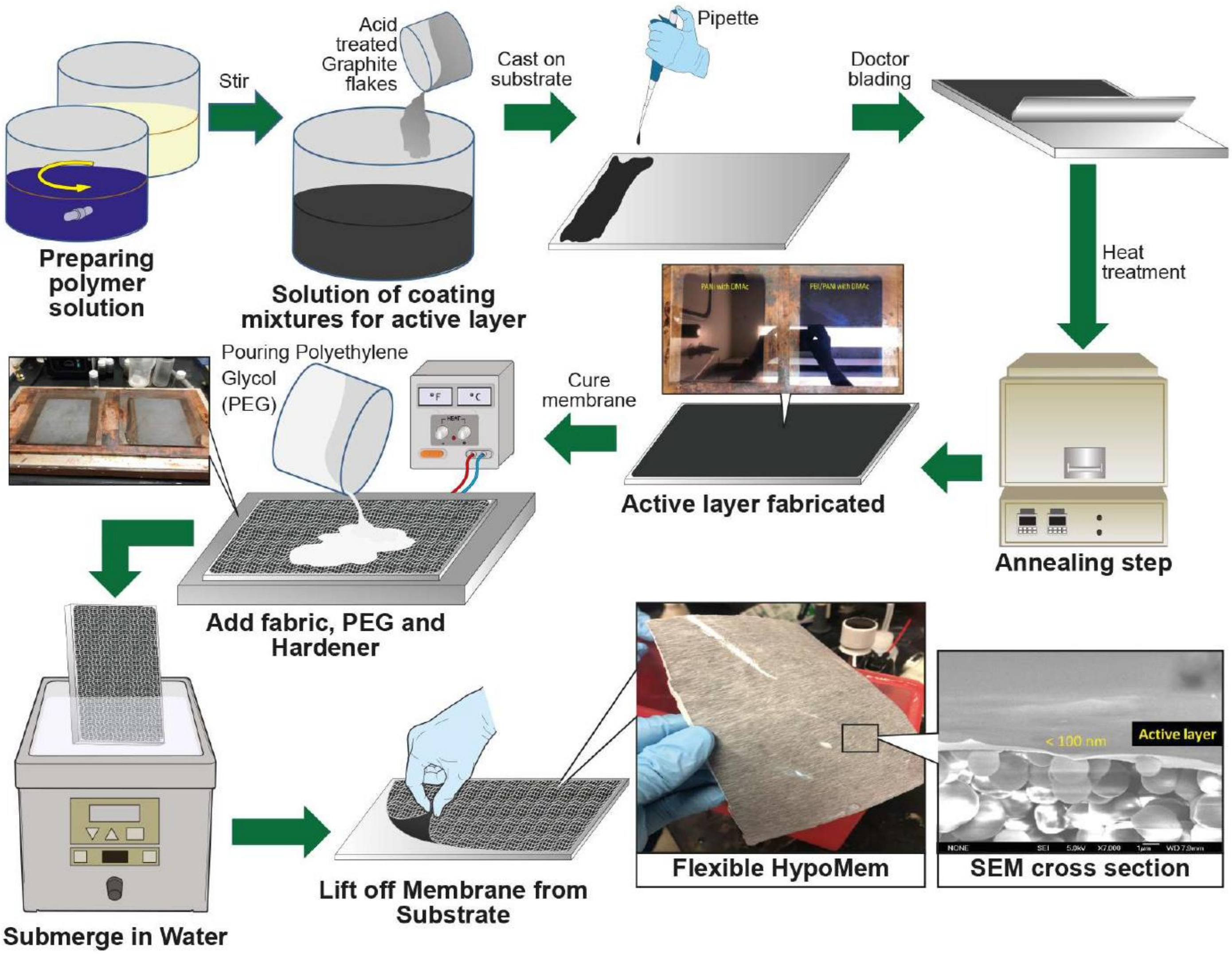

Figure 1: Schematic (follow the arrow from upper left corner) for fabricating HypoMem with functionalized additives.

These morphological changes primarily influence the permeant diffusivity and gas selectivity. The CO_2 permeability and selectivity of HypoMem samples made using the T-FLO technique were demonstrated using pure CO_2 and nitrogen (N_2) gases along with mixtures (15% CO_2, 5% oxygen [O_2], balance N_2) for CO_2 separation tests and compared with other membranes in Figure 2 (A). In earlier work performed, the selectivity and permeability were tuned by employing various polymers and different oxidation levels of carbon materials. Further, HypoMem CO_2 permeability and selectivity were tuned by doping, de-doping, and re-doping with selected acids (e.g., hydrochloric acid [HCl]) and bases (e.g., ammonium hydroxide [NH_4OH]) as reported in literature. HypoMem exhbitis excellent CO_2 separation performance, and is also flexible and mechanically robust. In this project, HypoMem is being formed into spiral-wound configurations for an alpha demonstration. The transport and separation in membranes involves molecular-scale interactions of the permeating gas component with the active layer. More importantly, the extremely thin and defect-free active layer requires a highly porous non-selective support layer. Also, permeability is a pressure- and thickness-normalized flux of a desired gas component. Figure 2 (B) presents the effect of active layer thickness on CO_2 permeability and selectivity in earlier studies. Since the pore size of both the fabric and epoxy layers can be controlled with the T-FLO technique, the molecular transport mechanism can be optimized to further develop HypoMems.

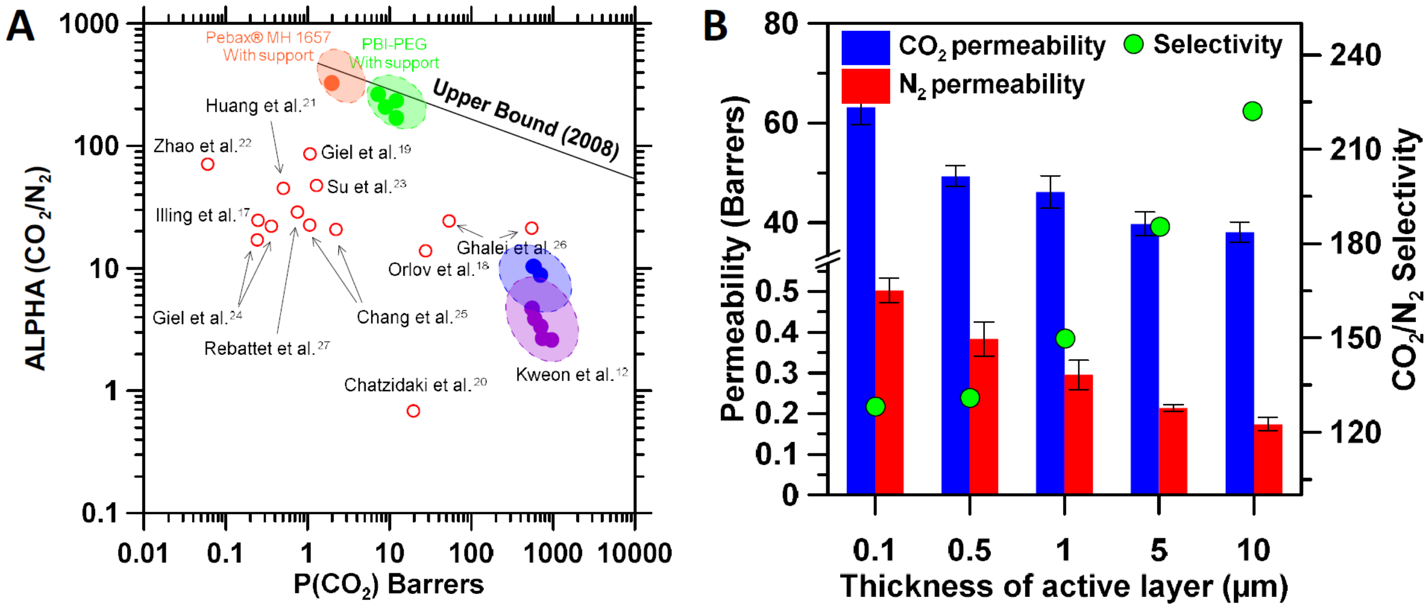

Figure 2: (A) A Robeson plot comparing the performance of the developed HypoMem against other polymer composite membranes for CO_2/N_2 gas separations. (B) Permeability and ideal selectivity data for different thicknesses of active layers with pure CO_2 and N_2.

For gas molecules (e.g., CO_2, N_2, and O_2) smaller than 4 Å, HypoMem combined with functionalized GOs improves gas transport properties with thermal and chemical stability since the gaps of individual GO sheets are slightly bigger than feed gas molecules. Functional groups such as amine and ethylene oxide attached on the active layers have a strong affinity to CO_2 molecules in the presence of N_2 and O_2. However, freestanding polymer membranes tend to crystallize, swell, and break, especially at high water content. To overcome this limitation, different molecular weights of polyethylene glycol (PEG), diglycidyl resin, and diamine hardener have been used in the T-FLO technique. Therefore, in the current scenario, by adding support layer separately, more stable membranes can be generated without changing properties of the active layer. Different molecular weight PEGs are now being employed to control the permeability of crosslinked networks in the support layer. These membranes rely on reversible chemical reactions between the target CO_2 gas and specific functional groups attached to the polymer matrix. Therefore, only the reacting species (CO_2) are transported across the membrane by this mechanism, theoretically increasing both permeability and selectivity. Amines are able to bind CO_2 selectively through different possible chemical mechanisms, such as those shown in Figure 3. The membranes contain amine groups that are considered a convenient medium to selectively transport CO_2 in the presence of humidity. Another important parameter to consider is pH, as it influences amine protonation equilibrium, which in turn affects CO_2 interaction with the active layers. Thus, to exploit the facilitated transport mechanism presented, a neutral amine form is needed to maintain high pH values during material purification and membrane preparation.

<u>Cycle and Operating Conditions</u>: Figure 4 is an overall process schematic of the HypoMem system. First, an ultra-thin active layer is fabricated individually, and then support layers are added to form mechanically robust HypoMem (Figure 4 [2]). Next, HypoMem is formed and packed into the spiral-wound membrane module. If necessary, use of a hollow-fiber module will be examined (Figure 4 [3]). Then, the CO_2 separation system is sealed, and simulated air is injected, passing first through a gas pre-conditioning unit to control humidity and temperature (Figure 4 [1]). Following CO_2 separation, the permeate gas (high-purity CO_2) and rejected gases (N_2, O_2, sulfur dioxide [SO_X], nitrogen dioxide [NO_X], etc.) are collected and exhausted safely (Figure 4 [4]), and, if necessary, additional post treatments can be added. Following a sufficient duration of simulated air injection (one day ≤ t ≤ 30 days), the membrane modules are characterized for any performance degradation.

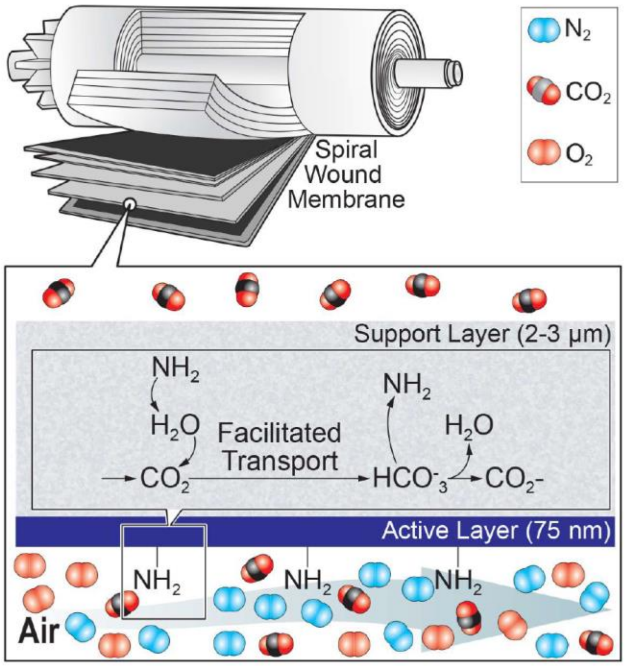

Figure 3: Schematic of facilitated transport mechanism for CO_2 separation from ambient air.

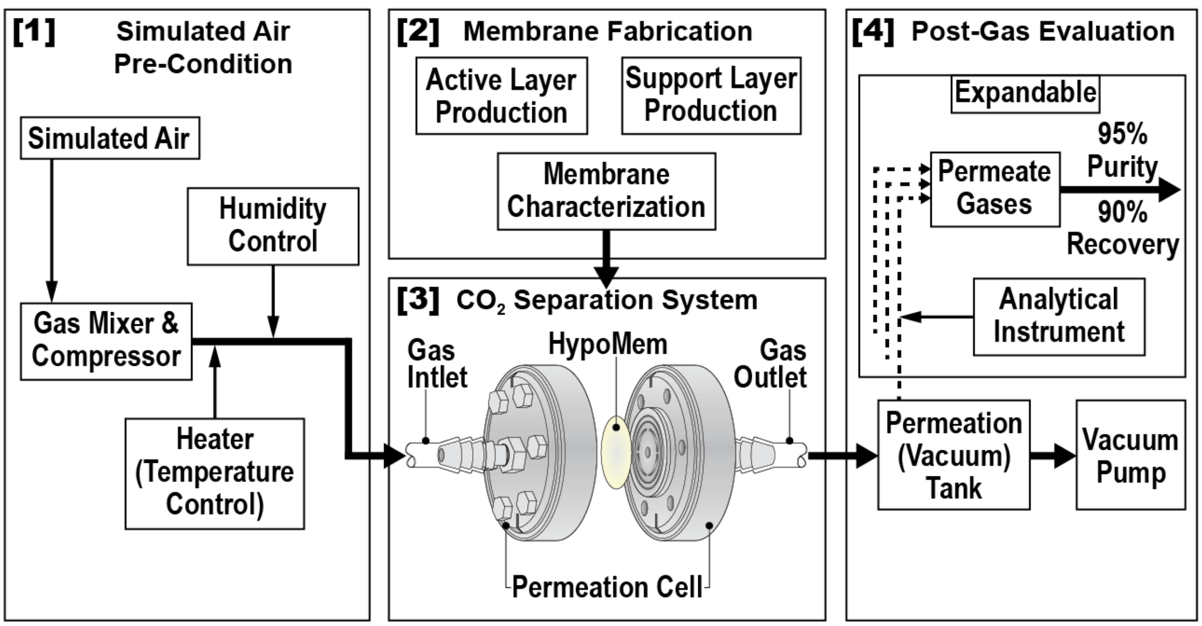

Figure 4: An illustration of the HypoMem CO_2 separation system.

Also, in an earlier study, a multi-stage membrane separation process was considered to improve CO_2 purity and energy efficiency. Final CO_2 purity obtained was 82.1% with 90.7% overall recovery with the use of three stages.

Different compositions of ultra-thin robust HypoMem are a pioneering approach to a cost-effective process for CO_2 separation from a low concentration of CO_2. Through active and support layer modification and chemical treatments, (doping, de-doping, and re-doping), the CO_2 permeability and selectivity can be tuned as needed. The CO_2 separation system's robustness has been demonstrated in terms of CO_2 permeability and selectivity with CO_2 and N_2 mixed gases, and the impact of active layer modification and thickness control on mass transfer resistance has been revealed. Because membrane gas separation is pressure-driven, the thickness of the active layer is the key to maximizing the permeation rate. Using the T-FLO technique, a high-permeance membrane is being fabricated with processability that enables scale-up for commercial applications.

technology advantages

- Material formulations featuring ultra-thin and chemically stable membranes for CO_2 separation.
- T-FLO technique enables controllable pore size fabrication and thickness, enabling improved performance of the active membrane layer.
- Efficient and scalable CO_2 separation system.
- High-permeance membrane that is scalable for commercial applications.
- Mechanically, chemically, and thermally stable membranes reduce costs since the feed streams would not require pretreatment.
- Development of spiral-wound modules and parallel membranes allows for maximum packing density with lower pressure tolerances, enabling maximum CO_2 separation and minimum energy use.

R&D challenges

- Optimizing permeance, permeability, and CO_2 selectivity performance.

status

InnoSense LLC has formulated and fabricated hybrid polymer HypoMem samples with reasonably large size (~8x12 cm) and have verified consistent thicknesses and morphologies of both active polymer layer and epoxy support layers. Researchers have also constructed an onsite gas permeation testing apparatus and observed higher permeance values: 6.83×10^5 gas permeation unit (GPU) for CO_2 and 2.15×10^5 GPU for N_2 at a pressure drop across the membrane of 70 cm of mercury (~95 kPa). The CO_2 selectivity was observed to be 3.17 at permeance of 6,830 GPU. The trend of an increase in CO_2 selectivity corresponded to a decrease in permeability. Computer simulations suggest a multi-stage process is needed to achieve the desired CO_2 permeate concentration for successful DAC CO_2 separation.

available reports/technical papers/presentations

Maksudul M. Alam, "High-Performance, Hybrid Polymer Membrane for Carbon Dioxide Separation from Ambient Air," Direct Air Capture Kickoff Meeting Presentation, Pittsburgh, PA, February 2021. *http://www.netl.doe.gov/projects/plp-download.aspx?id=11095&filename=High-Performance%2c+Hybrid+Polymer+Membrane+for+Carbon+Dioxide+Separation+from+Ambient+Air.pdf*.

Maksudul M. Alam, Adrien Hosking, Milind Deo, "Development of Hybrid Polymer Membranes for Direct Air Capture of Carbon Dioxide," NETL Carbon Management Research Project Review Meeting, Pittsburgh, PA, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_CDRR_Alam.pdf*