

Membranes for CO₂ Capture

Liz Tennant and Ming-Ming Tran

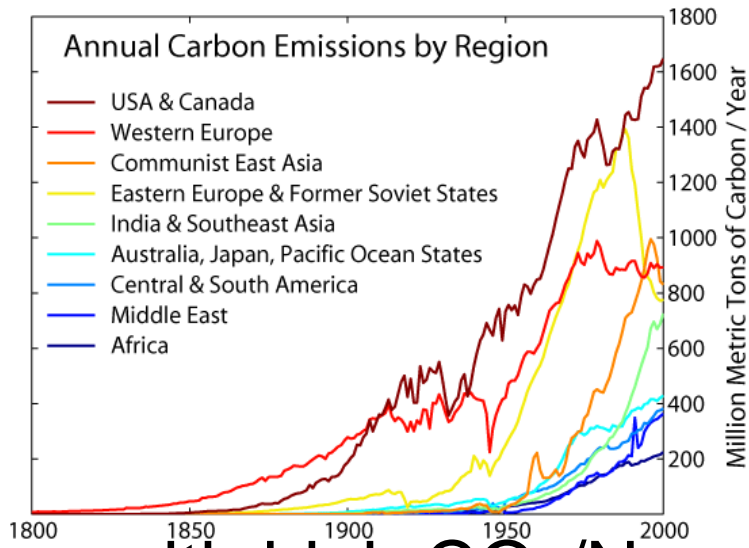
Department of Chemical and Biomolecular Engineering

Advisors: Dr. Scott Husson and Dr. Christopher Kitchens

Mentors: Jinxiang Zhou and Fiaz Mohammed



- Current solutions to carbon emissions are expensive and inefficient



<http://forums.accuweather.com/index.php?showtopic=7758&st=20>

- **Goal:** Create membranes with high CO₂/N₂ selectivity and permeance
- PAN (polyacrylonitrile) ultrafiltration membrane modified with:
 1. Addition of gutter layer + ionic liquids
 2. Addition of gutter layer + perfluorocyclobutyl

Supported Ionic Liquid Membranes (SILMs)

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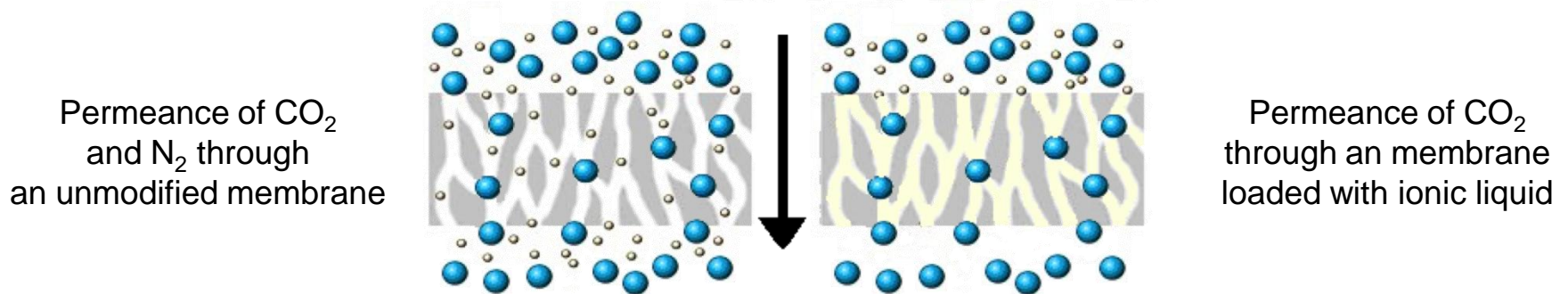
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- Testing Supported Ionic Liquid Membranes (SILMs) for CO₂/N₂ permeance and selectivity



- Addition of a CO₂ selective, ultrathin, non-porous barrier to the membrane to enable SILM operation:
 - at higher pressures
 - for longer periods of time

- Ionic liquids show high CO₂ solubility and diffusivity.
- CO₂ solubility = 0.103 mol L⁻¹ atm⁻¹

P = permeability of gas

S = gas solubility

D = gas diffusivity

a = ideal selectivity of a membrane

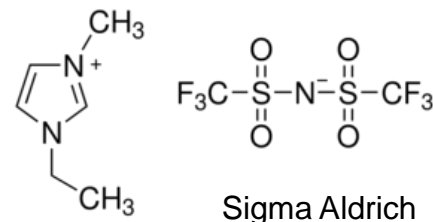
$$P_i = S_i D_i$$

$$a_{ij} = \frac{P_i}{P_j} = \frac{D_i S_i}{D_j S_j}$$

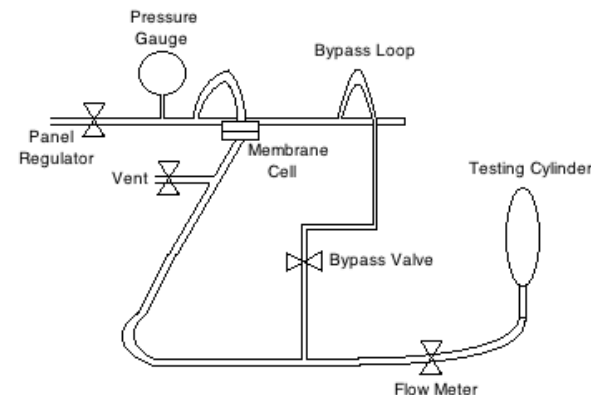
- Test ionic liquid loading methods to ensure an even load across the surface
 - Loading time
 - Desiccant
 - Vacuum + Desiccant
- Overcome a loss of ionic liquid
- Test ionic liquid loading into modified membrane
- Measure membrane performance



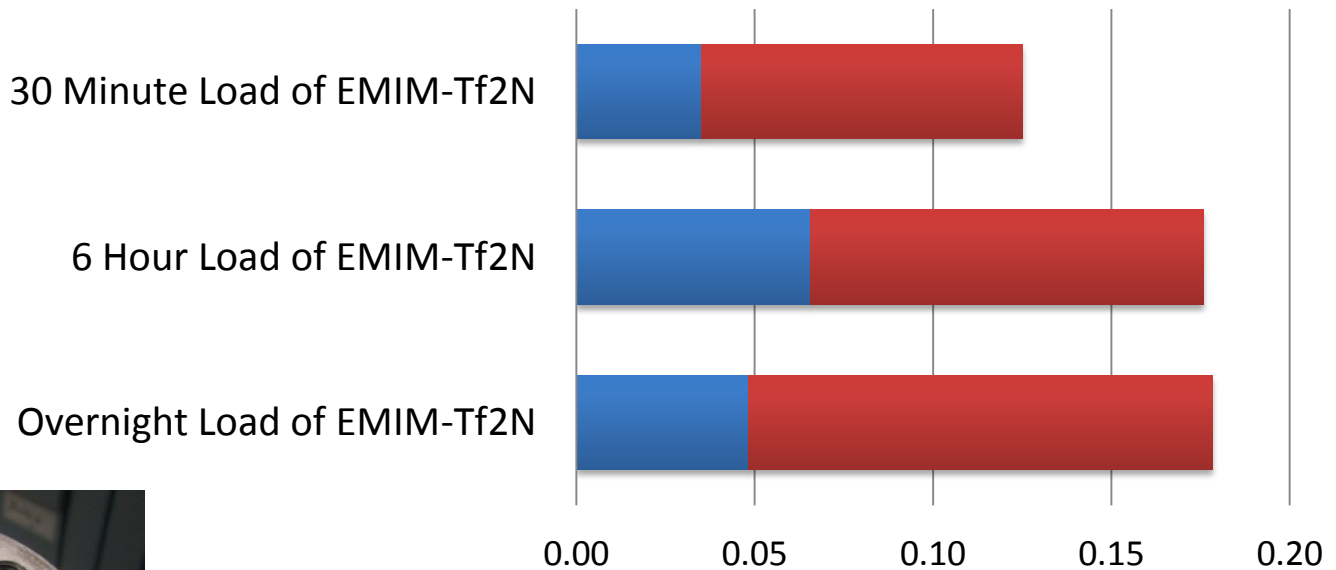
- Ionic liquid loading
 - 500 microliters EMIM-Tf₂N
 - Load for 30 minutes, 6 hours, and overnight
- Testing Apparatus
 - Test from 5 – 10 psi to 20-25 psi



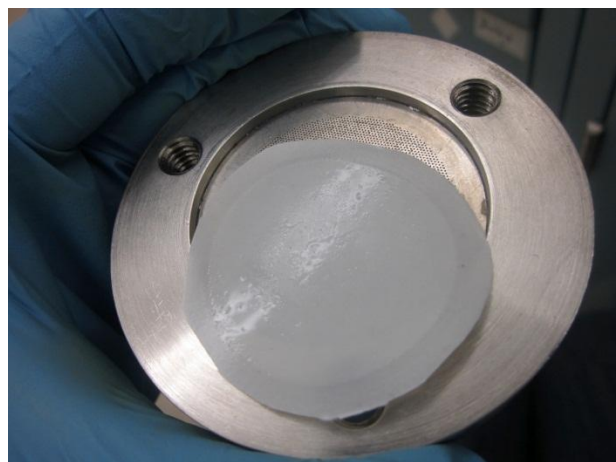
$$Permeance = \frac{P}{RTADP} \frac{dV}{dt}$$



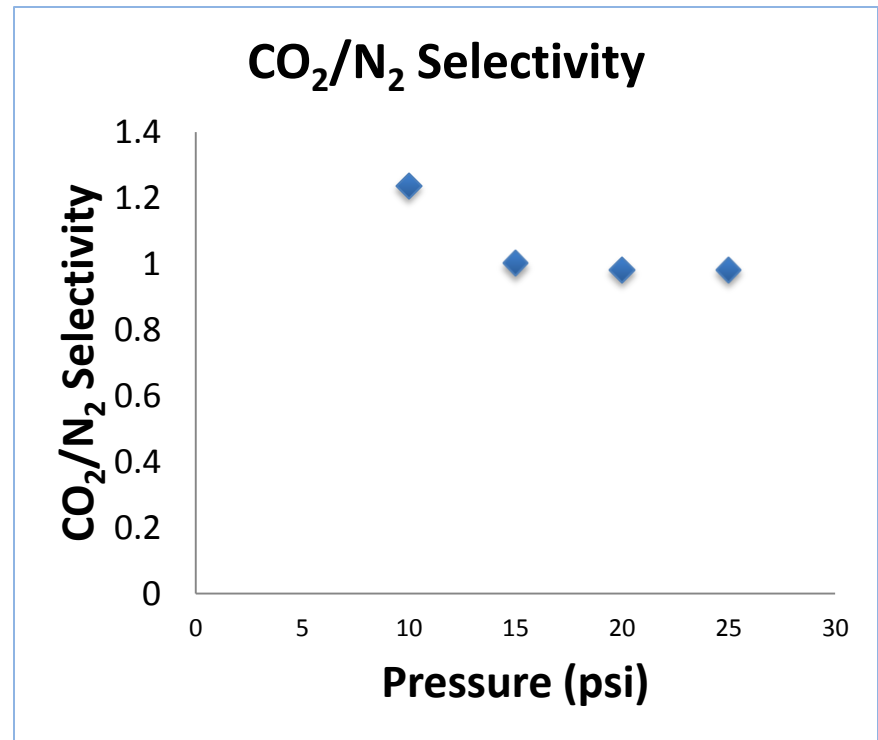
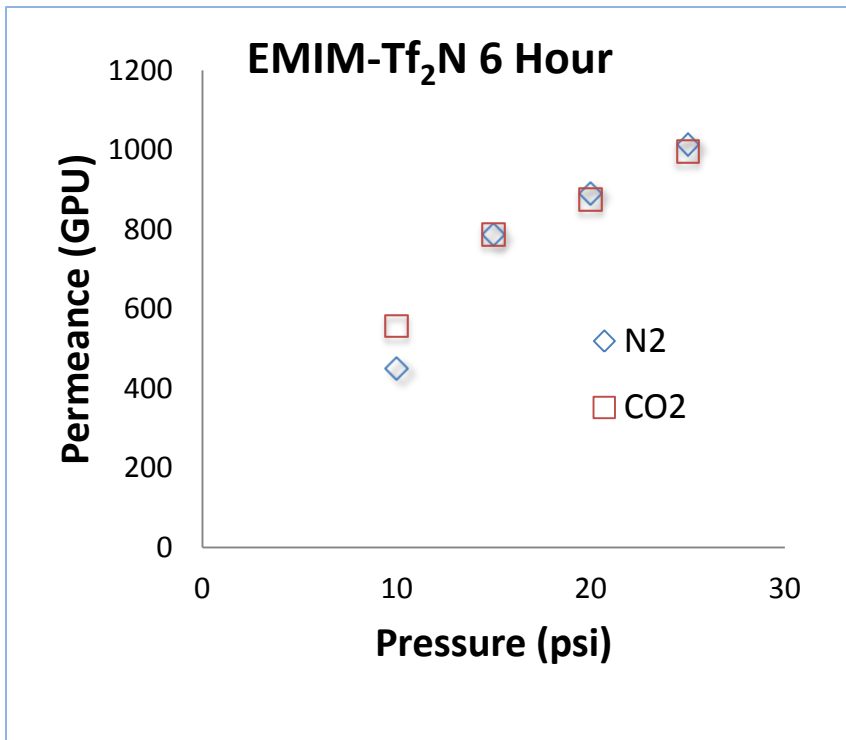
Percent Loss of EMIM Tf₂N During Testing



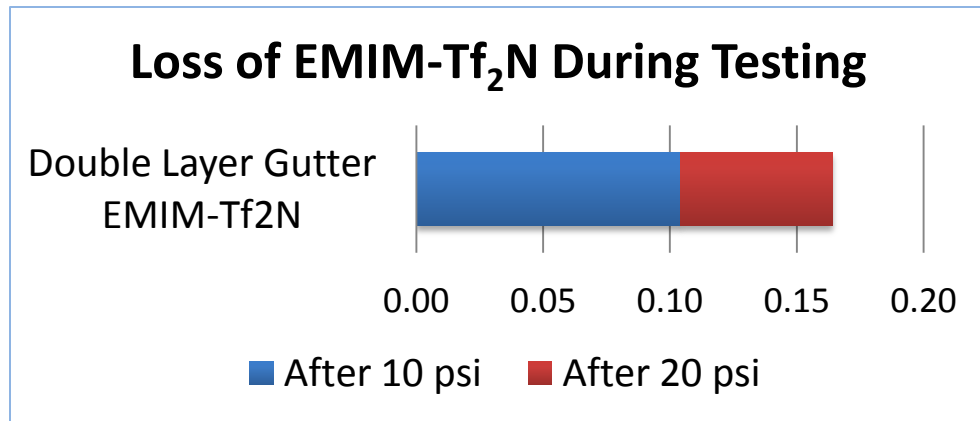
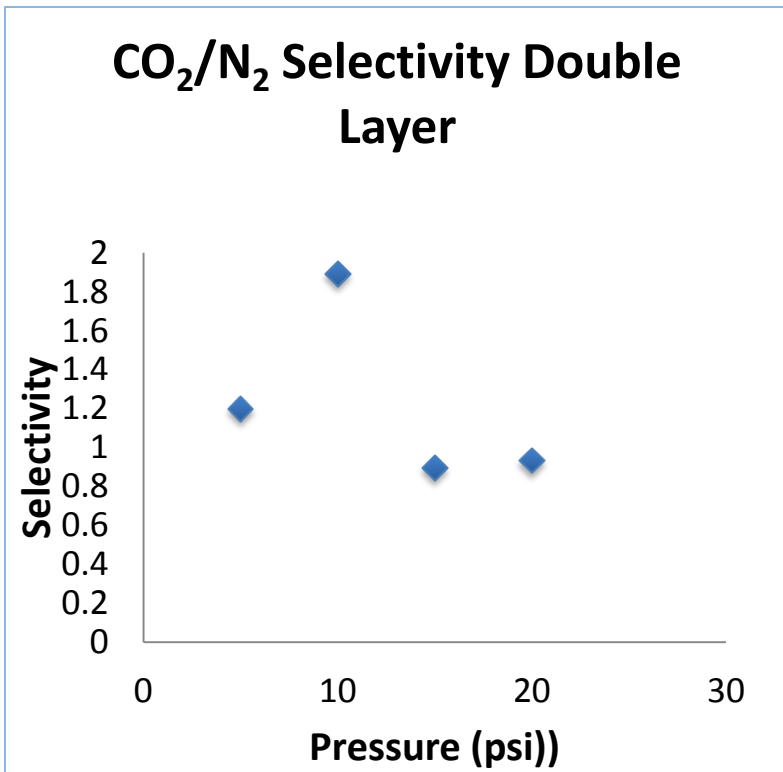
■ After Testing to 10 psi ■ After Testing to 25 psi



- Lack of selectivity
 - EMIM-Tf₂N is cited as having a CO₂/N₂ selectivity of 23.1.



- Application of Gutter Layer Over Both Sides of Ionic Liquid Loaded Membrane



- Support Membrane Coated with Barrier Layer Before Loading EMIM-Tf₂N

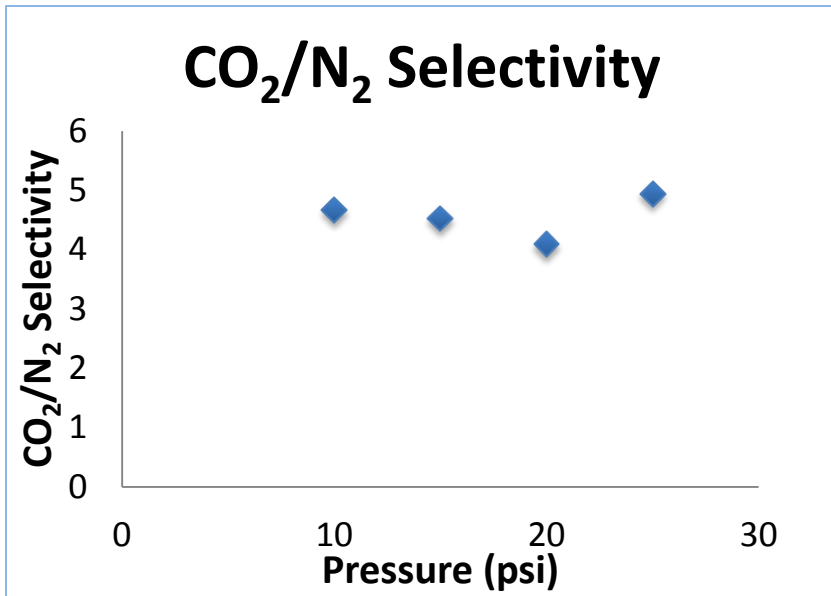


Figure 1: Selectivity of Gutter Layer Only

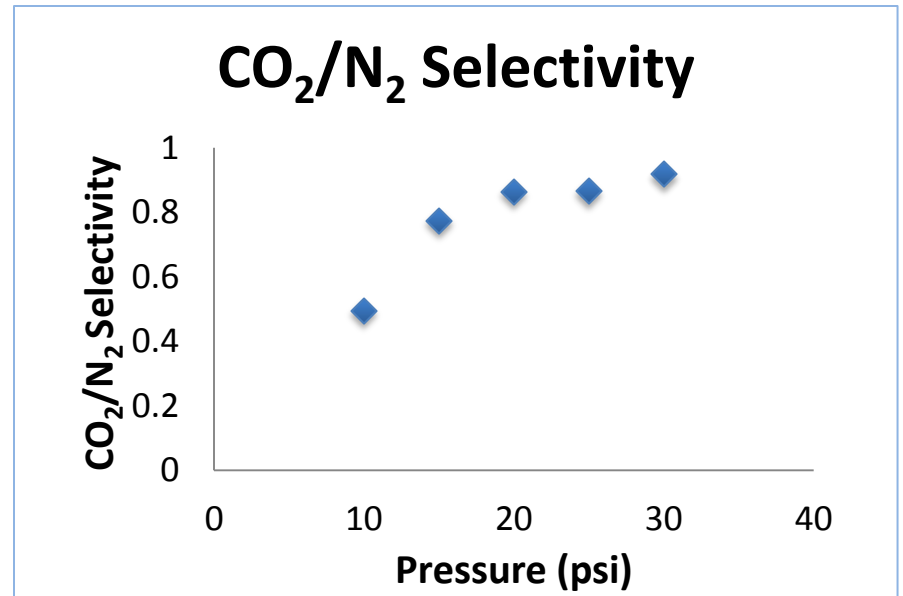
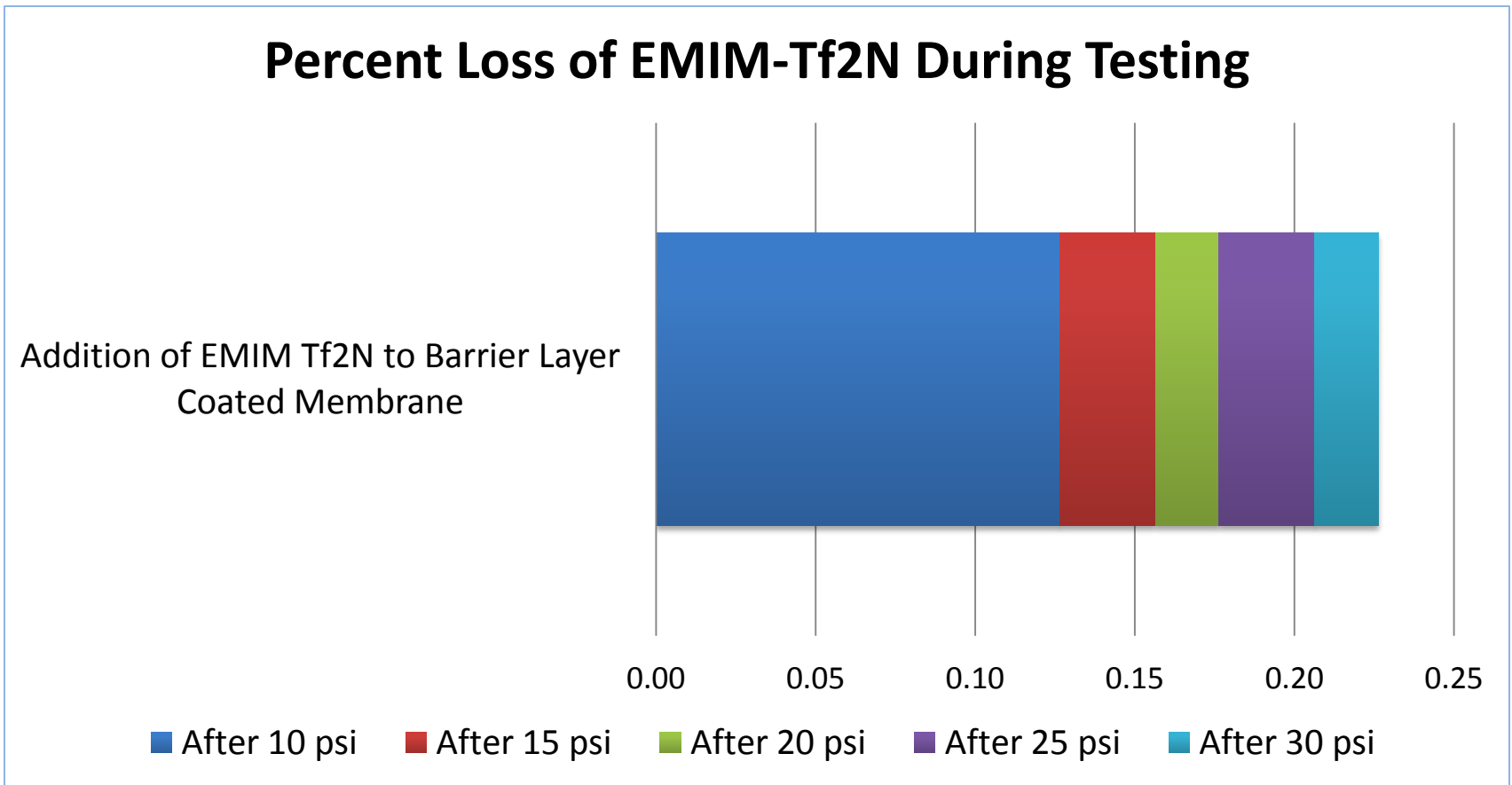


Figure 2: Selectivity of Gutter Layer with the Addition of EMIM-Tf₂N

- Support Membrane Coated with Barrier Layer Before Loading EMIM-Tf₂N



- The loss of ionic liquid may lead to a lower selectivity.
- The barrier layer does not perform as expected when placed over the SILM.
- The barrier layer may be compromised by the addition of ionic liquids.

- Use AFM imaging to determine if the ionic liquid is compromising the barrier layer.

Composite Perfluorocyclobutyl Membranes

Ming-Ming Tran

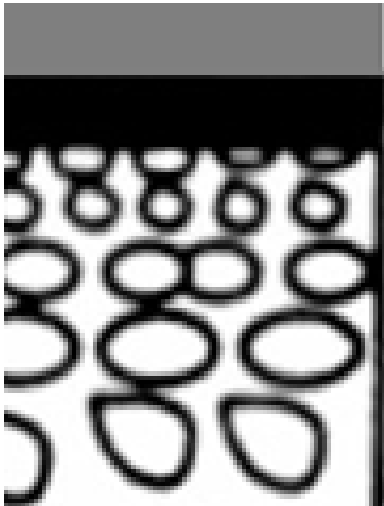
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- Glassy polymeric membranes have a good balance of permeability and selectivity
- However, they are also affected by issues such as aging and plasticization effects, especially in thin films



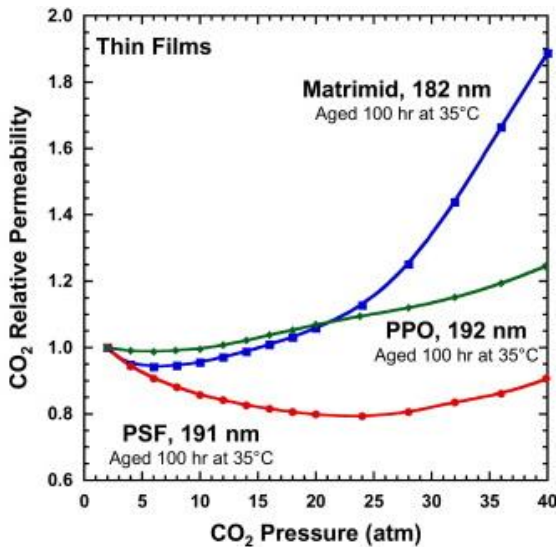
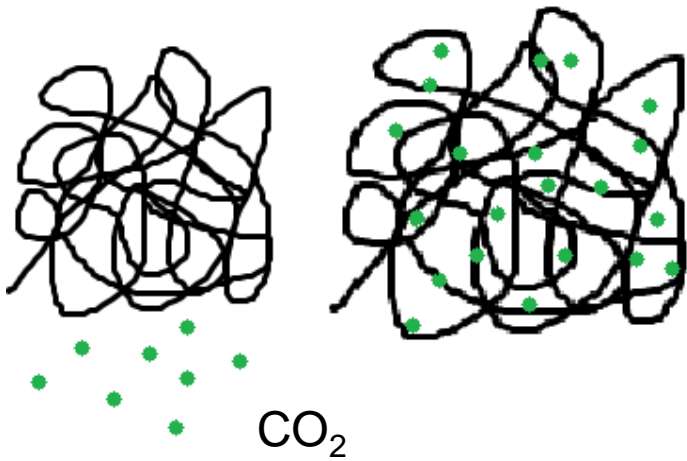
From bottom to top:

support layer: highly porous and permeable

gutter layer: selects for CO₂ but still very permeable

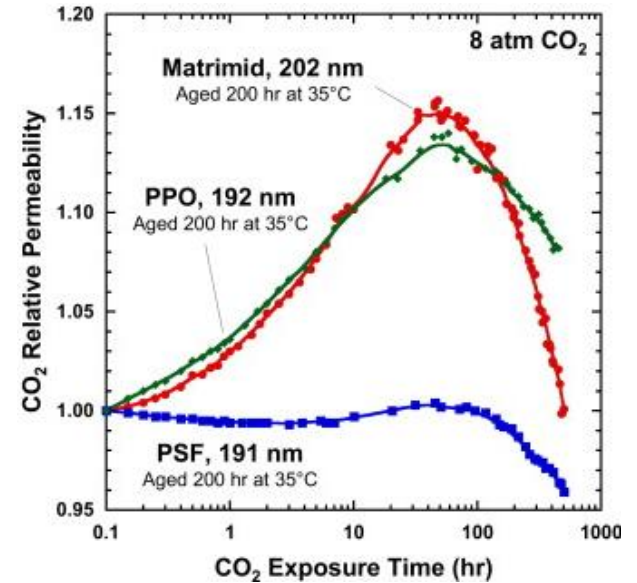
selective layer: selects strongly for CO₂

Plasticization



Increases permeability,
decreases selectivity

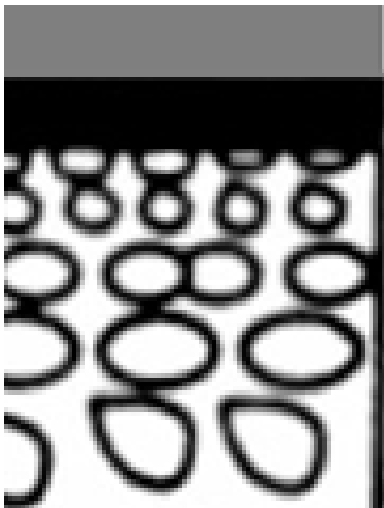
Aging



Decreases permeability

Eventually dominates
over plasticization

- Explore effects of selective layer thickness of PFCB polymer composite membranes on CO₂ plasticization
- Test membrane permeance for single gas (CO₂ and N₂) and CO₂/N₂ mixed-gas mixtures

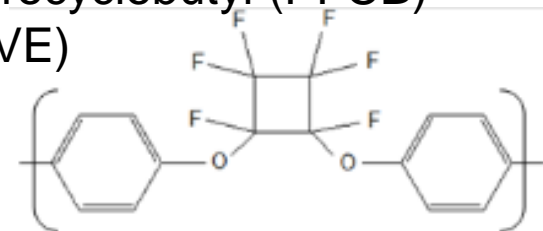


From bottom to top:

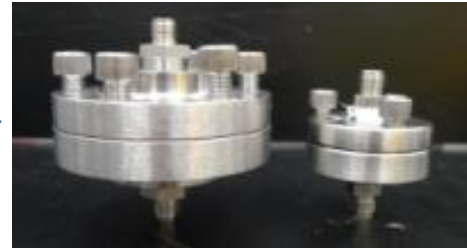
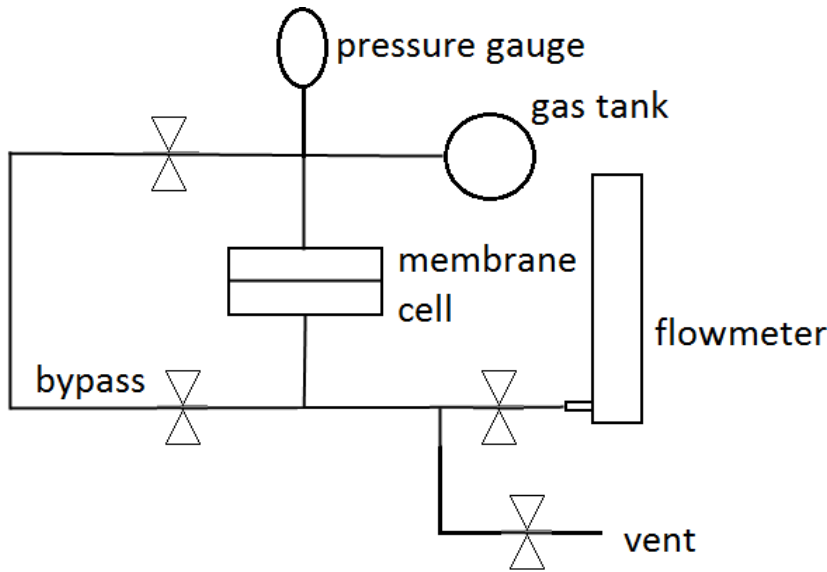
support layer: polyacrylonitrile (PAN50)

gutter layer: proprietary material

selective layer: perfluorocyclobutyl (PFCB)
biphenylvinyl ether (BPVE)



Experimental Apparatus

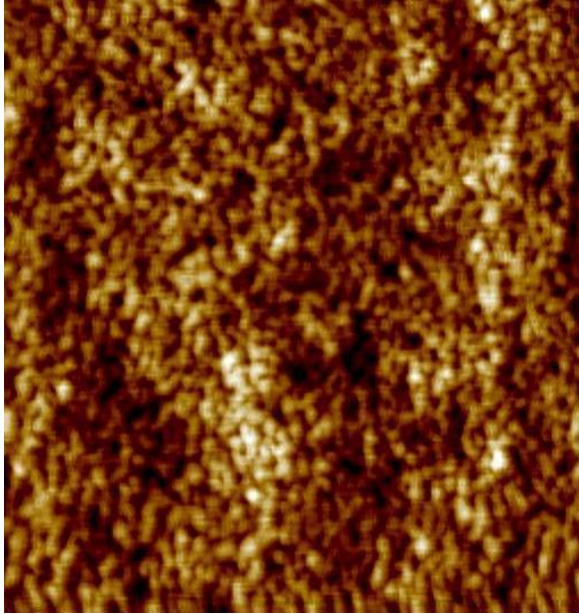


Large and small cells for gutter layer and PFCB testing, respectively.

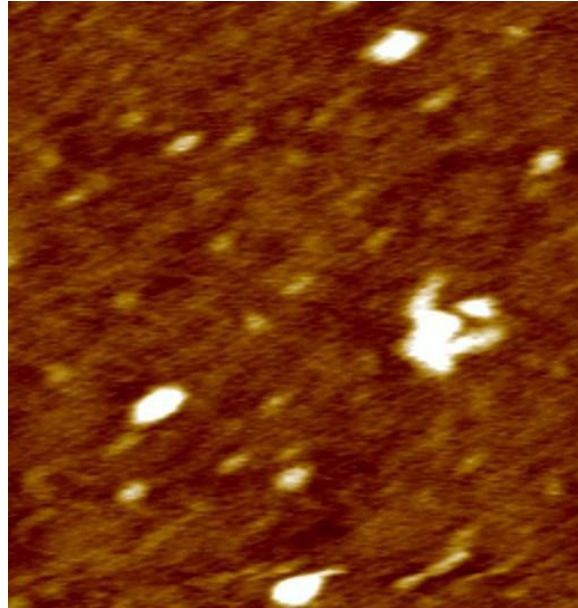
- 0.30wt% gutter layer solution
- 0.25-1.00wt% PFCB/chloroform solution, withdrawal speeds 100 mm/min or 211 mm/min
- Measure permeance of composite membranes at 20-500 psi
- Calculate permeance of PFCB layer using

$$Perm = \frac{flux}{\Delta p} = \frac{P}{\sigma} = \frac{1}{r} = \left(\frac{\sigma_a}{P_a} + \frac{\sigma_b}{P_b} \right)^{-1}$$

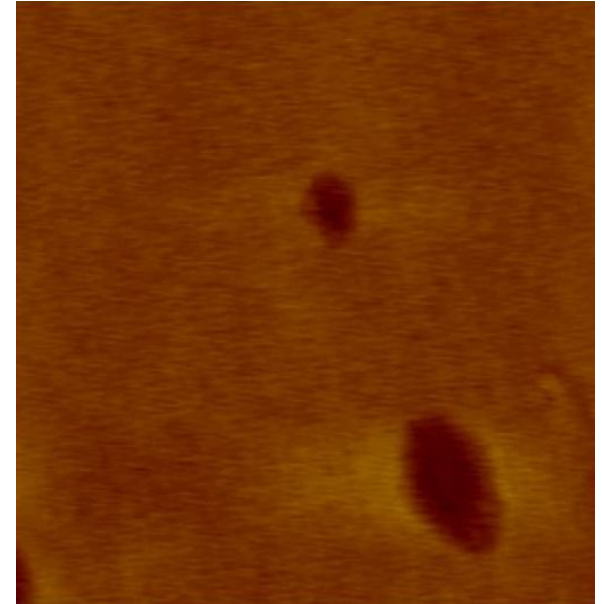
where Perm = permeance, p = pressure, P = permeability, σ = thickness, and r = resistance



PAN50 membrane
 1 x 1 μm . The porosity is approximately 50%, and RMS (roughness) = 2.5 nm.

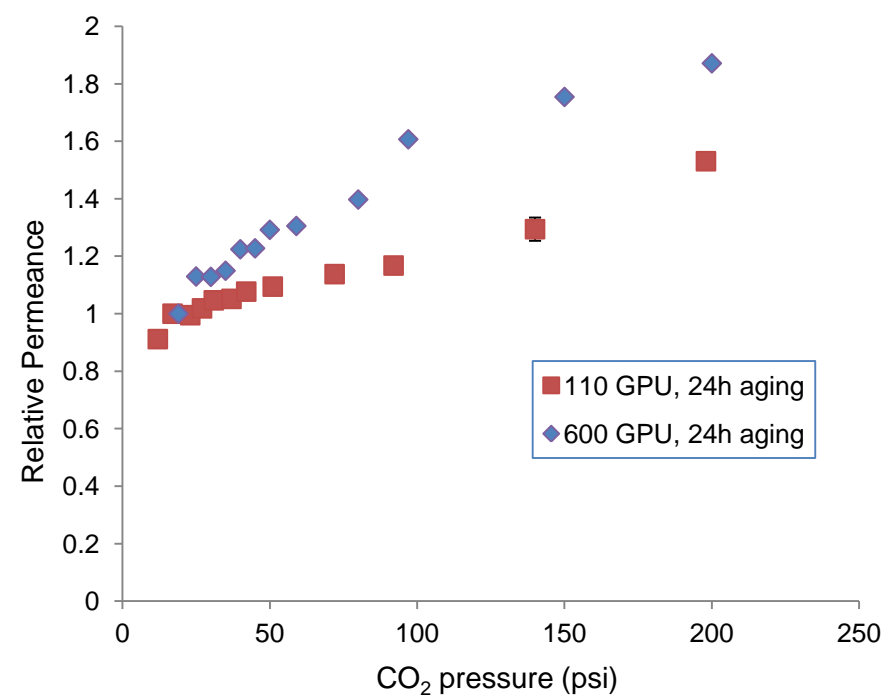
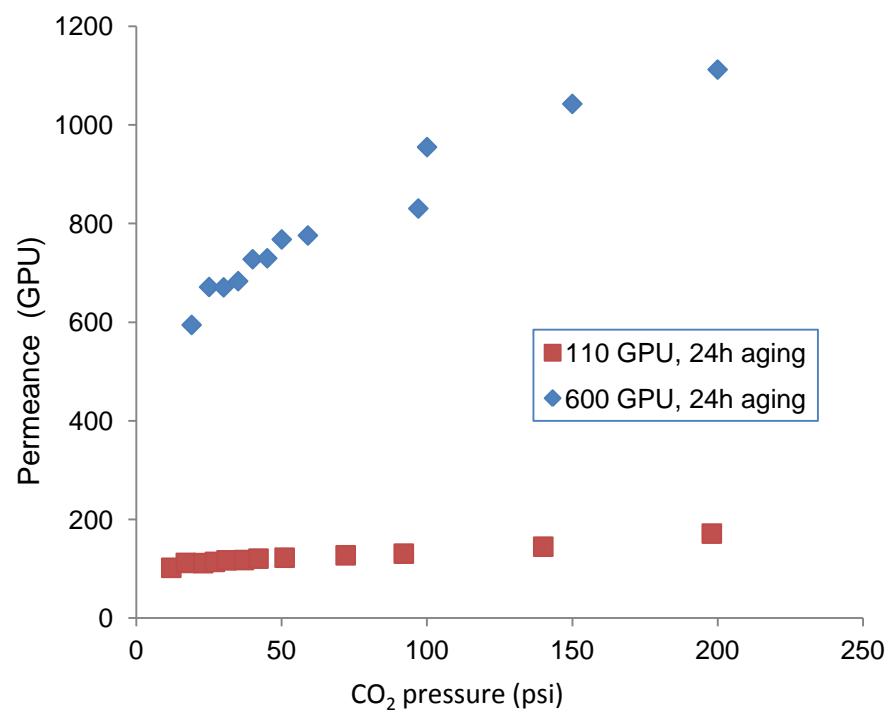


Plasma-treated gutter layer membrane
 1 x 1 μm . RMS = 1.5 nm.



PFCB coated membrane
 1 x 1 μm . 50 to 80 nm thick. RMS = 1.1 nm.

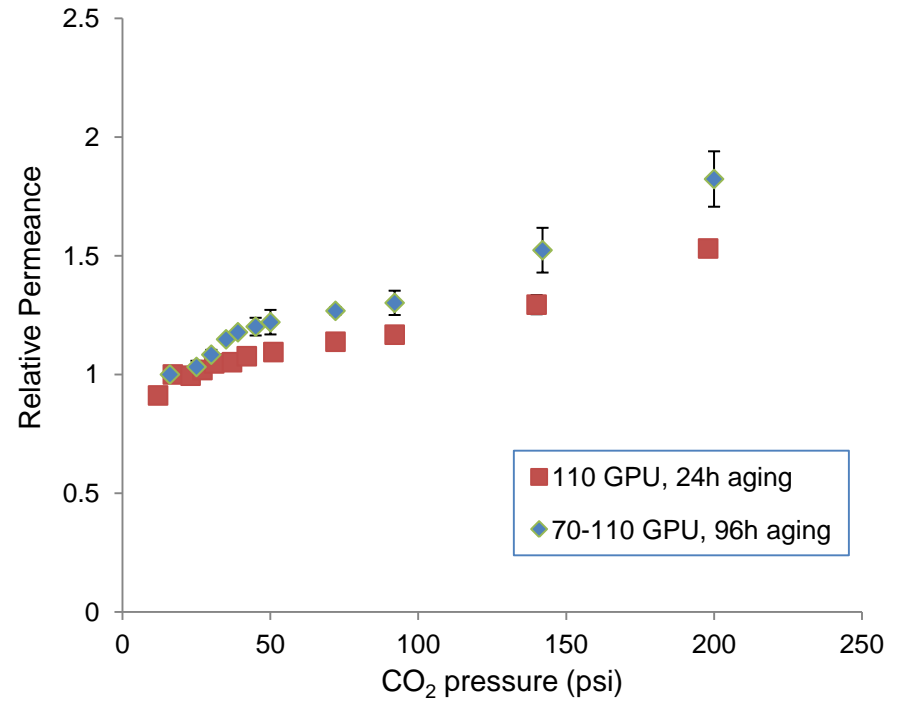
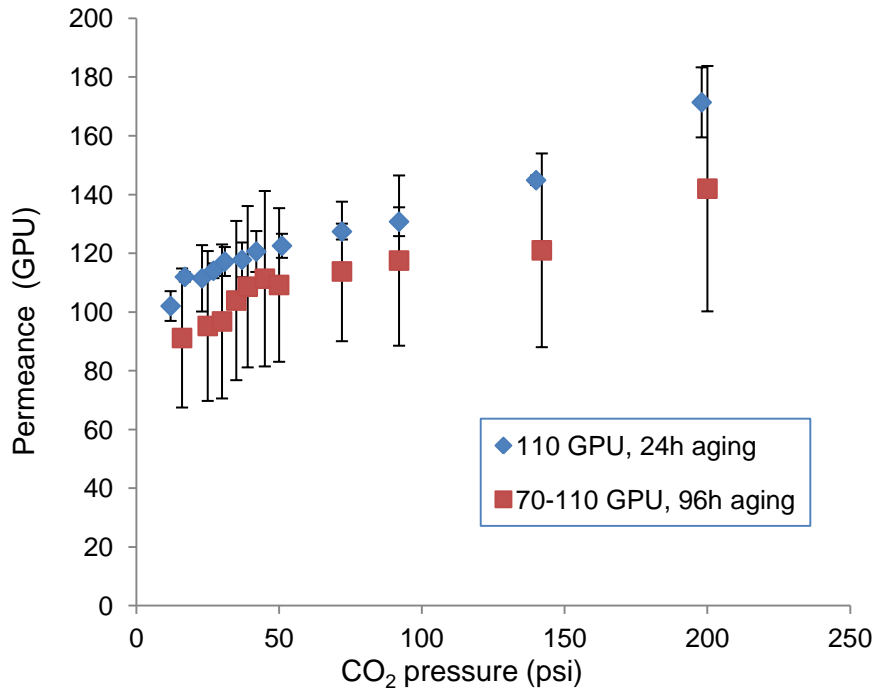
Thickness and Plasticization



On average, CO₂/N₂ selectivity decreased from 15.96 (standard deviation = 3.80) to 10.52 (standard deviation = 4.14)

Thickness has a clear effect – the thinner membranes (with higher permeance) experience more plasticization

Aging and Plasticization



- Aging does not appear to change much
- Further studies should be conducted with more repetition and longer aging times



Conclusions and Future Work



- Composite membranes with a thinner selective layer plasticize more
- Aging does not appear to affect plasticization
- Continue to study effect of thickness and aging on plasticization
- Use ellipsometry to study PFCB swelling in CO₂