Membranes for CO_2 Capture

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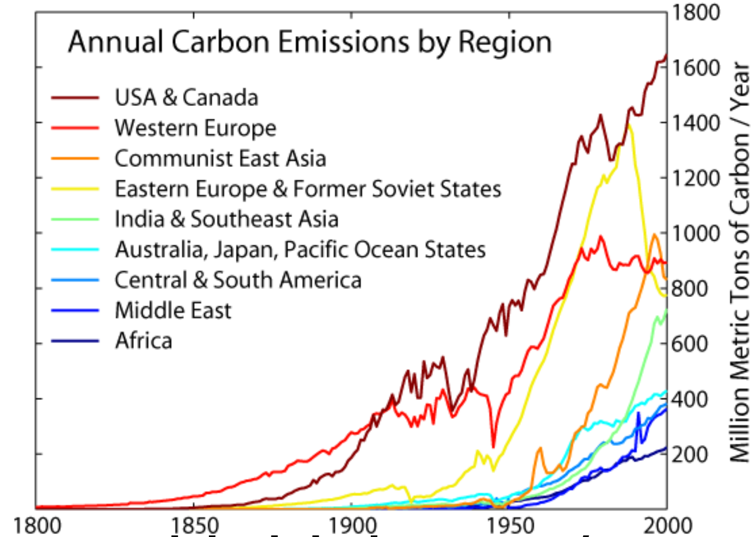
This work was part of the National Science Foundation REU Site: Advanced Functional Membranes at Clemson University. Support was provided by NSF under award EEC 1061524.

Introduction

- Current solutions to carbon emissions are expensive and inefficient



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

- **Goal**: Create membranes with high CO_2/N_2 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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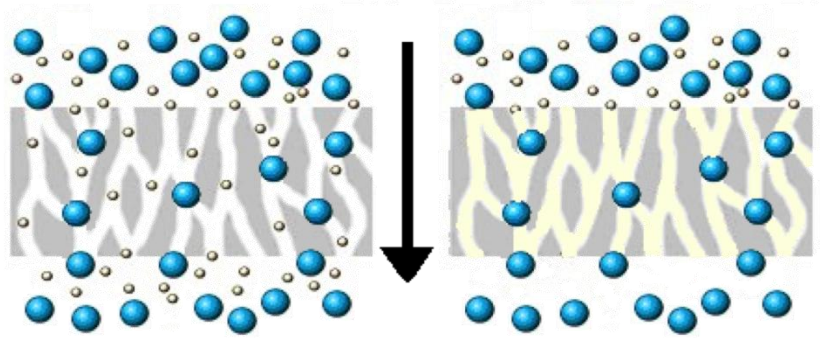
Overview

- Testing Supported Ionic Liquid Membranes (SILMs) for CO_2/N_2 permeance and selectivity

Permeance of CO_2 and N_2 through an unmodified membrane



Permeance of CO_2 through an membrane loaded with ionic liquid

- Addition of a CO_2 selective, ultrathin, non-porous barrier to the membrane to enable SILM operation:
    - at higher pressures
    - for longer periods of time

Overview

- Ionic liquids show high CO_2 solubility and diffusivity.
  - CO_2 solubility = 0.103 mol L^{-1} atm $^{-1}$

$$P_i = S_i D_i$$

$$P = permeability\ of\ gas$$

$$S = gas\ solubility$$

$$D = gas\ diffusivity$$

$$a = ideal\ selectivity\ of\ a\ membrane$$

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

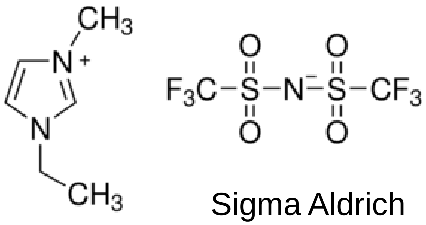
Objectives

- 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

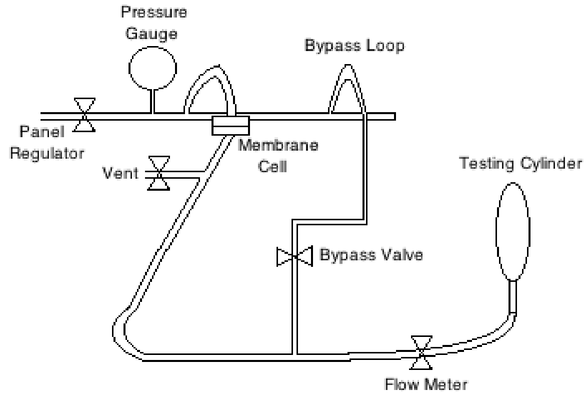
Procedure and Apparatus

- Ionic liquid loading
  - 500 microliters EMIM-Tf_2N
  - Load for 30 minutes, 6 hours, and overnight
- Testing Apparatus
  - Test from 5 – 10 psi to 20-25 psi



Sigma Aldrich

$$Permeance = \frac{P}{RT\Delta P}\frac{dV}{dt}$$



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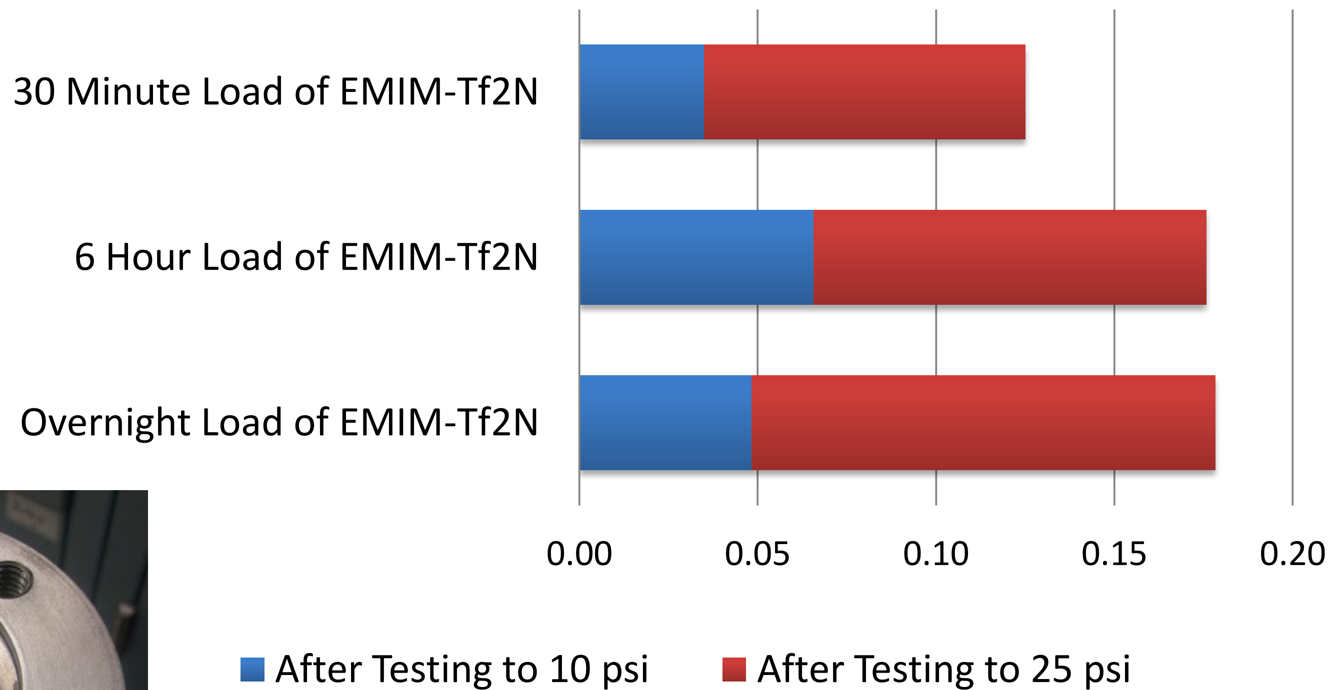
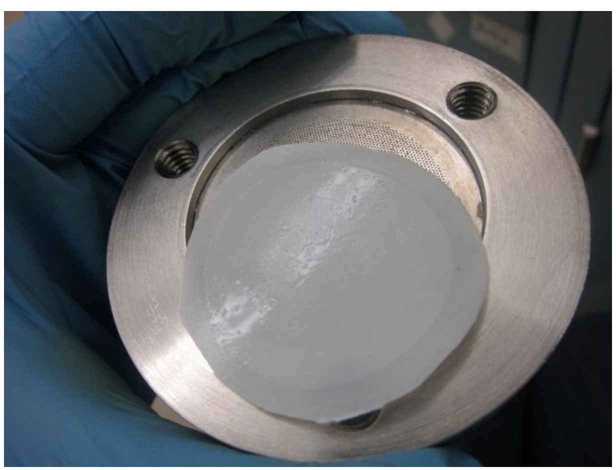
Results

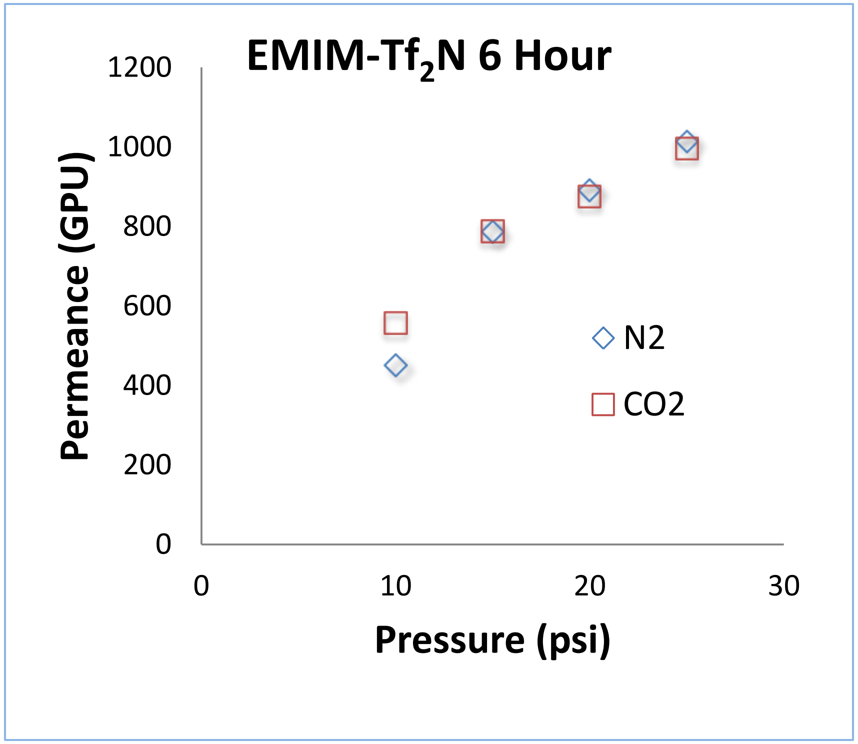
Percent Loss of EMIM Tf_2N During Testing

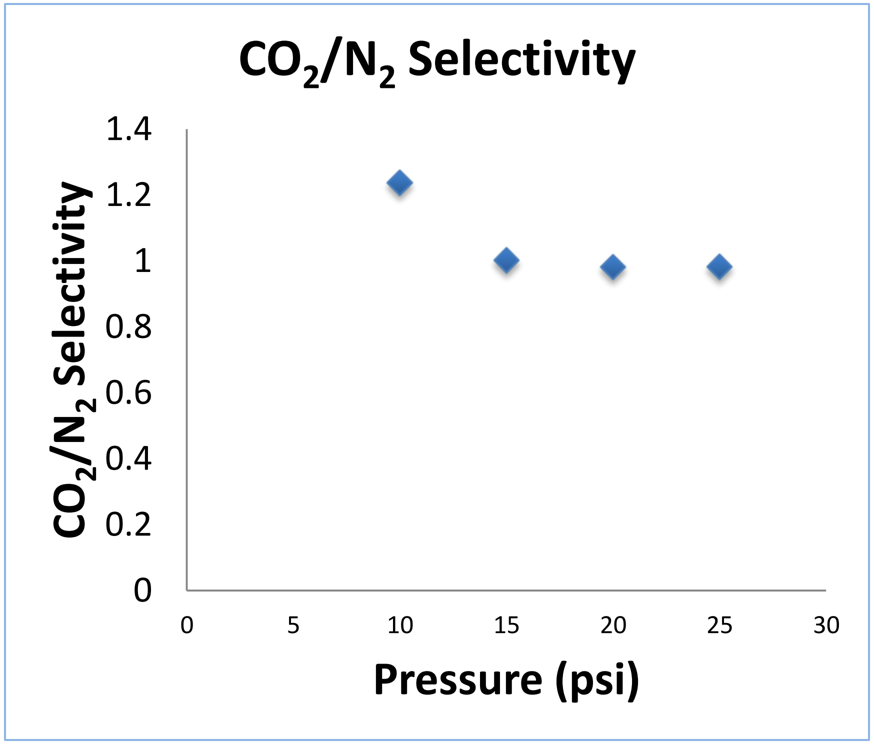




Results

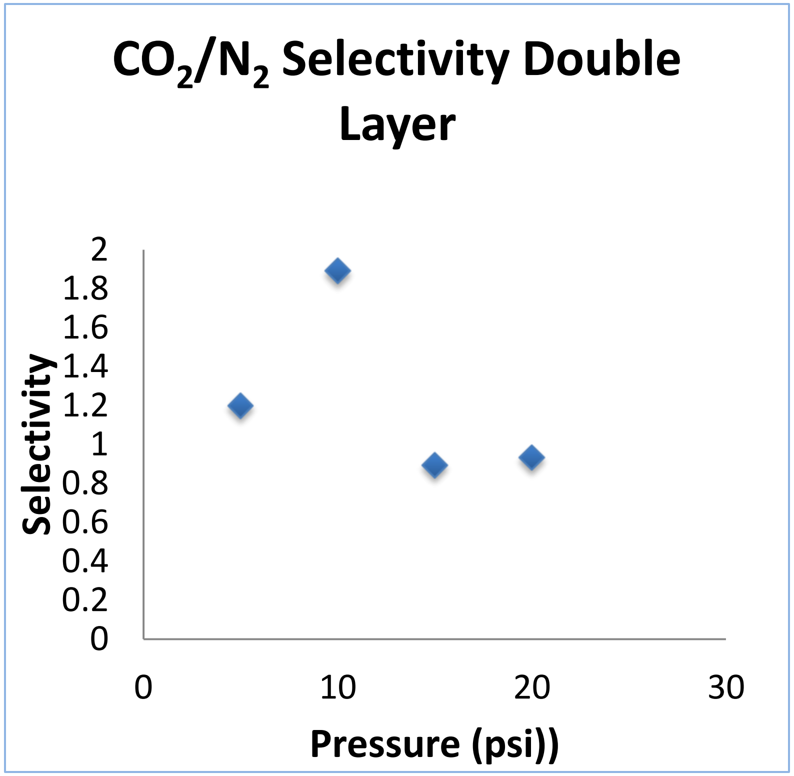
- Lack of selectivity
  - EMIM-Tf_2N is cited as having a CO_2/N_2 selectivity of 23.1.

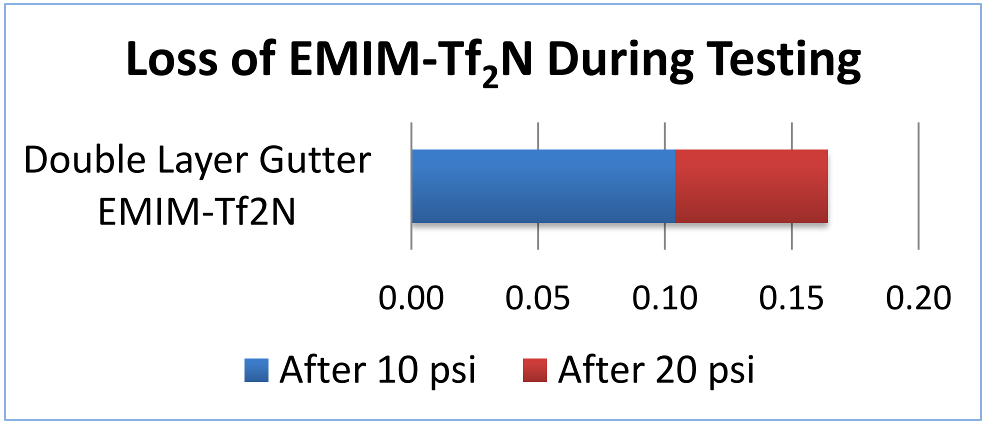




Results

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





Results

- Support Membrane Coated with Barrier Layer Before Loading EMIM-Tf_2N

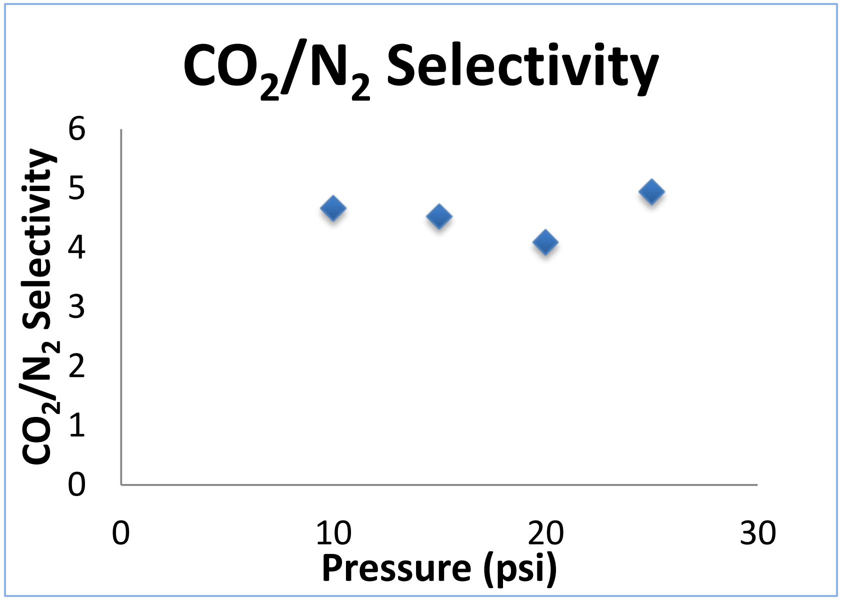


Figure 1: Selectivity of Gutter Layer Only

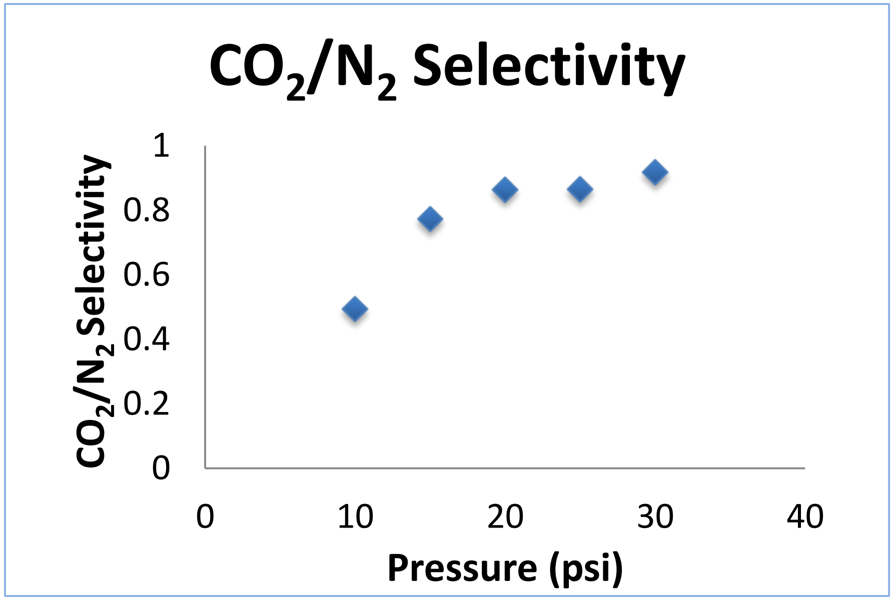
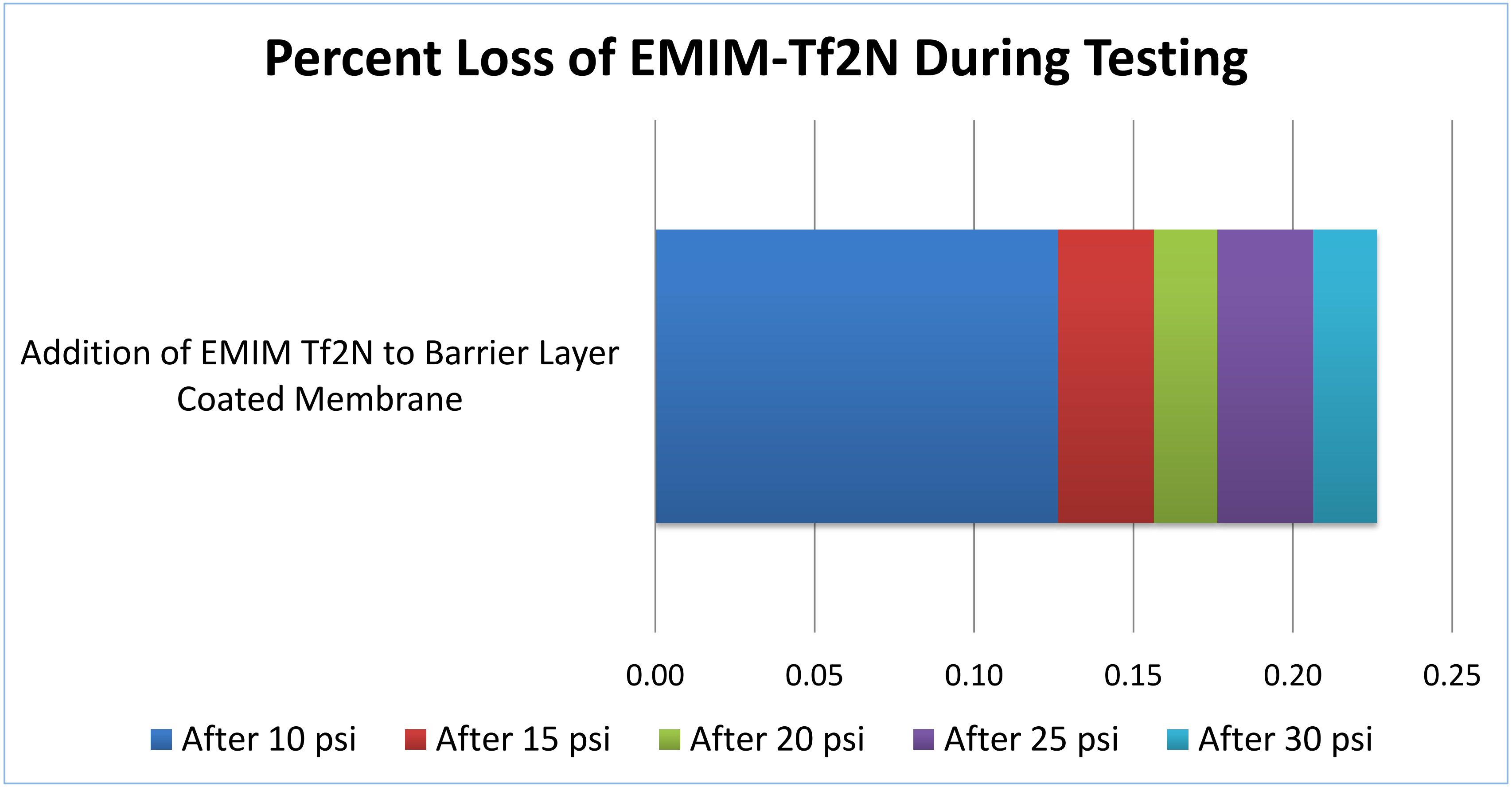


Figure 2: Selectivity of Gutter Layer with the Addition of EMIM-Tf_2N

Results

- Support Membrane Coated with Barrier Layer Before Loading EMIM-Tf_2N



Conclusions and Future Work

- 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

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Advisor: Dr. Scott Husson
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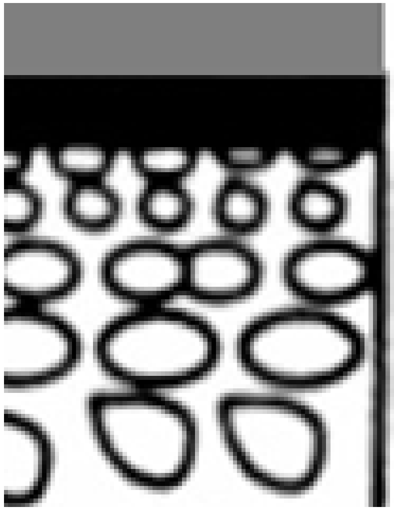
Overview

- 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 CO_2 but still very permeable
selective layer: selects strongly for CO_2

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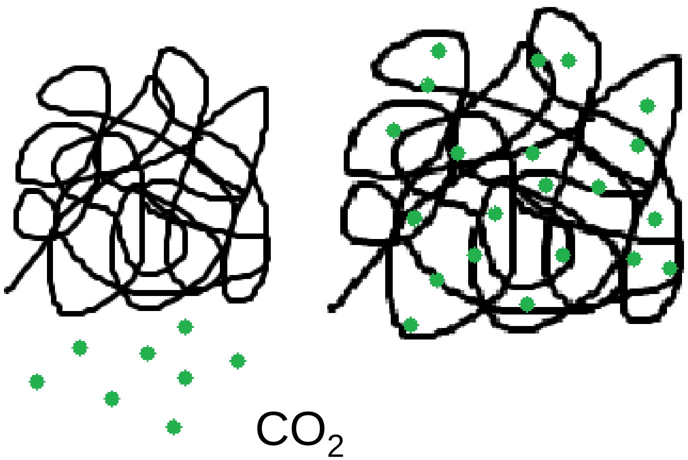
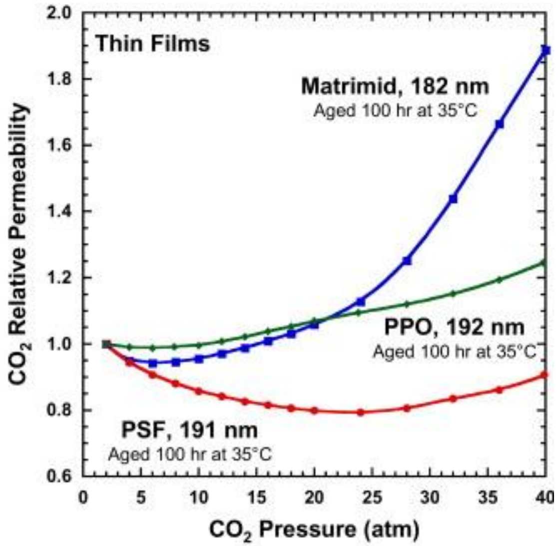
Overview

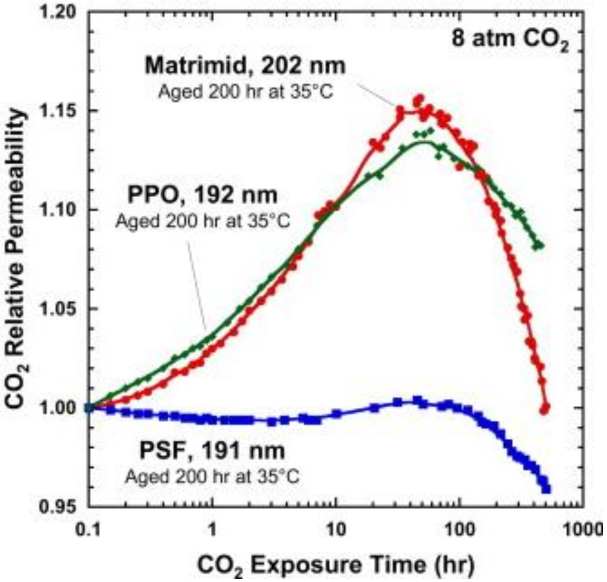
Plasticization





Increases permeability, decreases selectivity

Aging



Decreases permeability

Eventually dominates over plasticization

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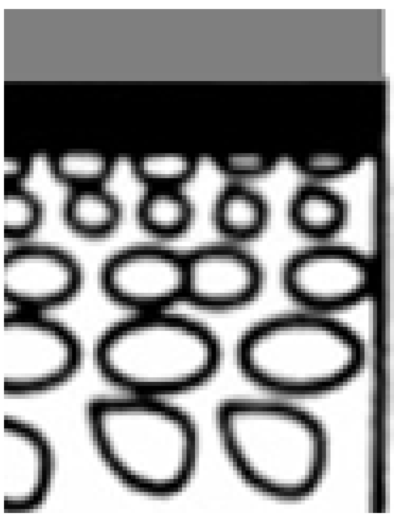
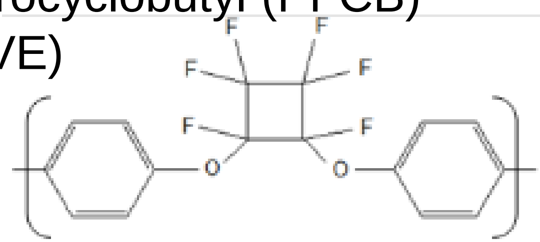
Goals

- Explore effects of selective layer thickness of PFCB polymer composite membranes on CO_2 plasticization
- Test membrane permeance for single gas (CO_2 and N_2) and CO_2/N_2 mixed-gas mixtures



From bottom to top:
support layer: polyacrylonitrile (PAN50)
gutter layer: proprietary material
selective layer: perfluorocyclobutyl (PFCB) biphenylvinyl ether (BPVE)



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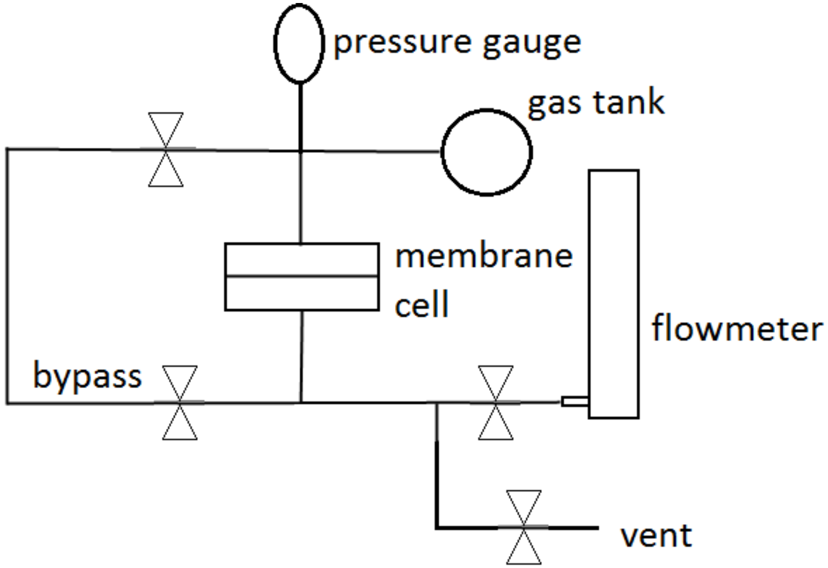
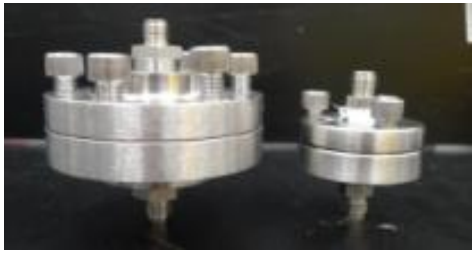
Experimental Apparatus





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

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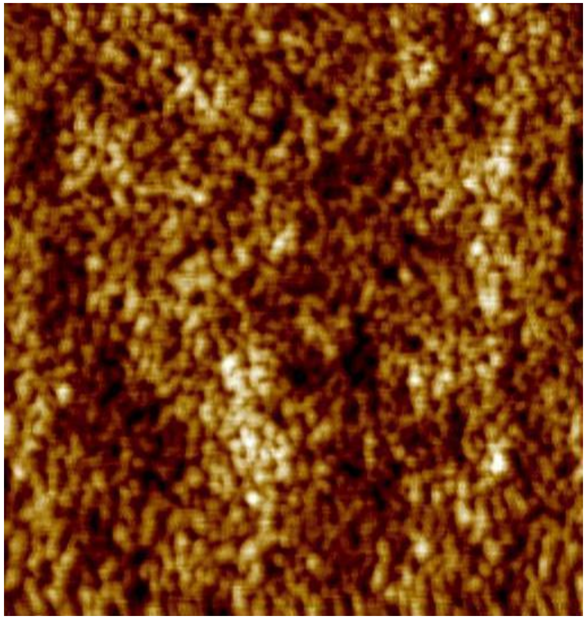
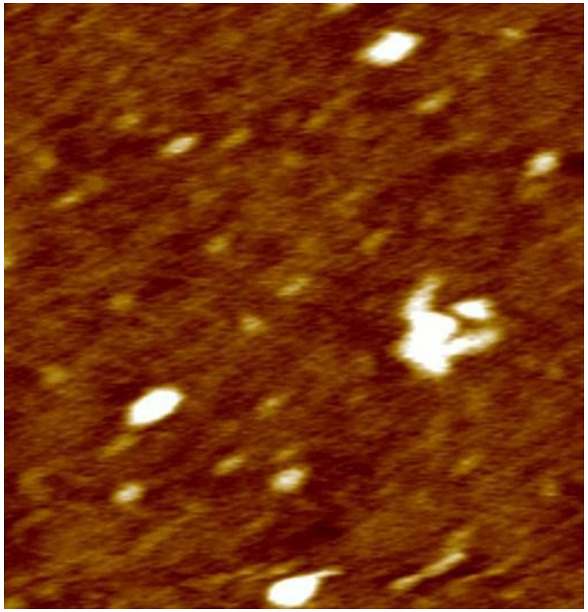
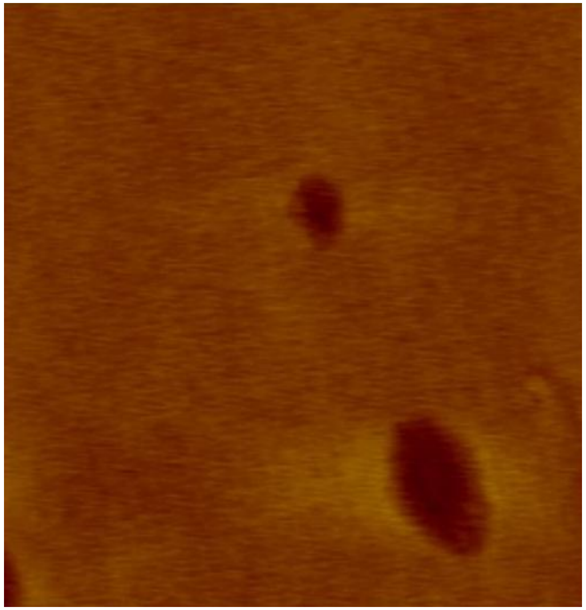
Membrane AFM Images



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



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



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

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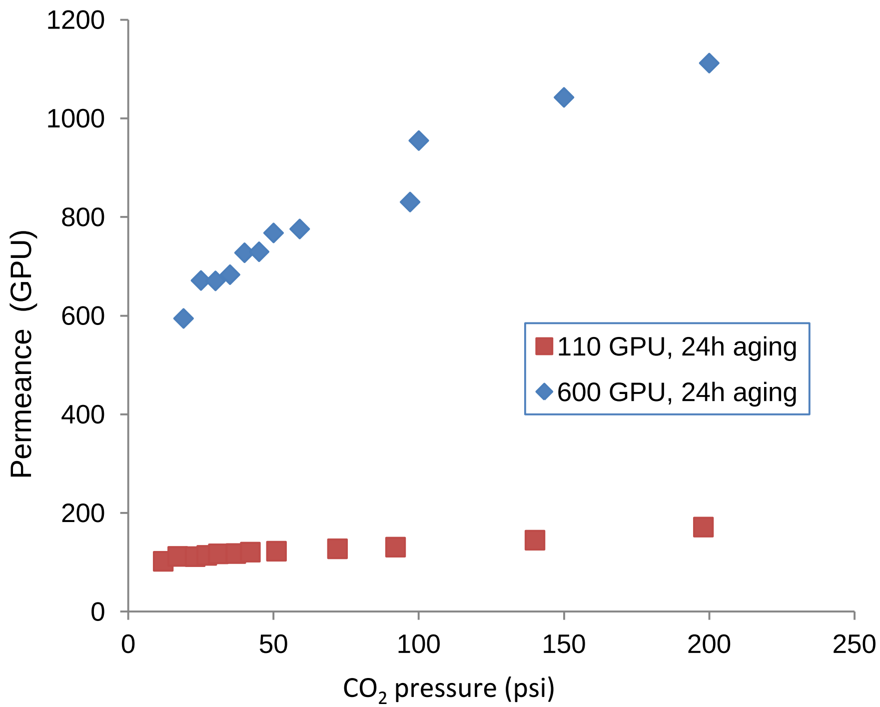
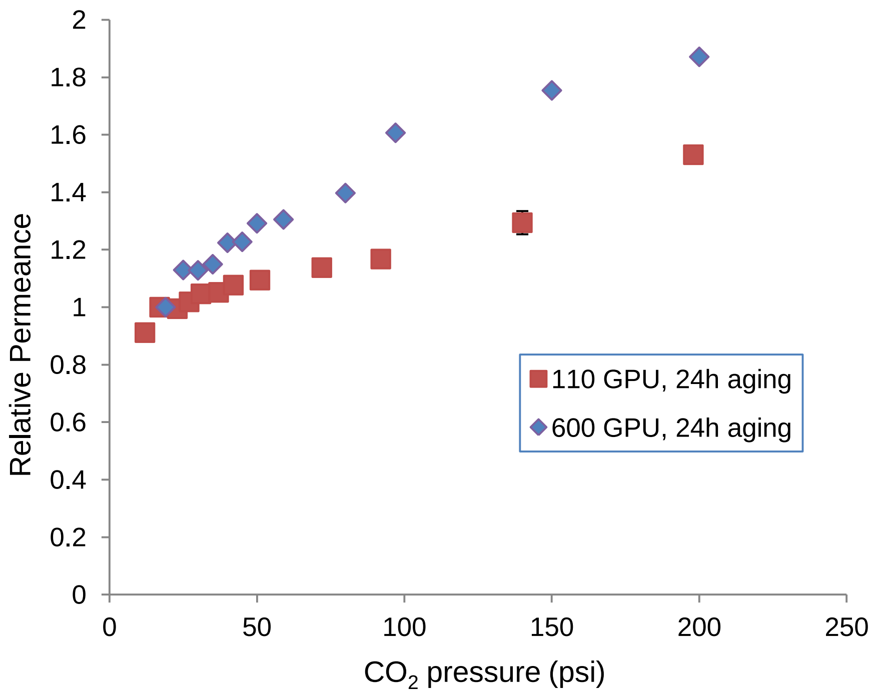
Thickness and Plasticization





On average, CO_2/N_2 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

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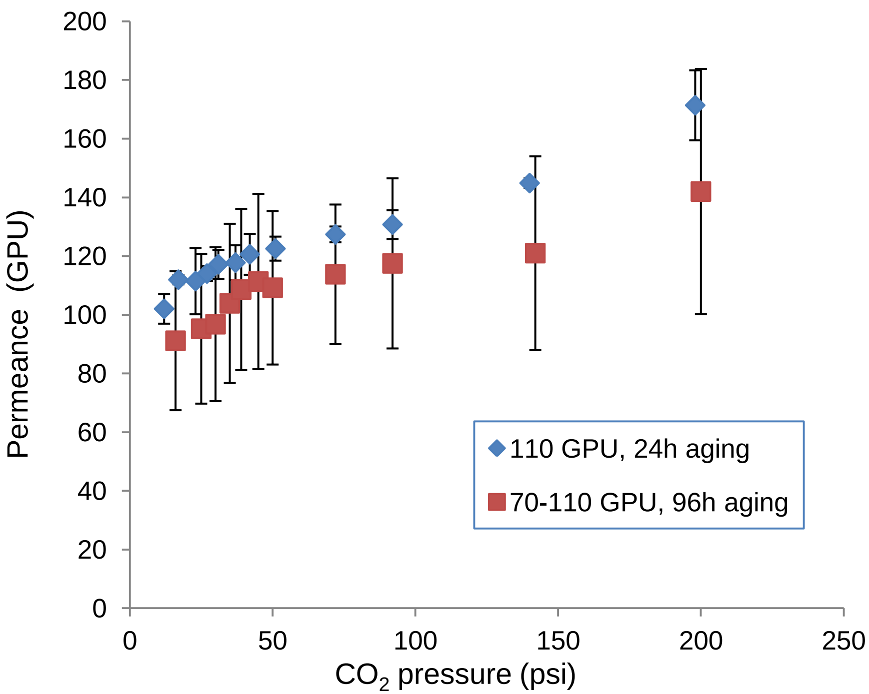
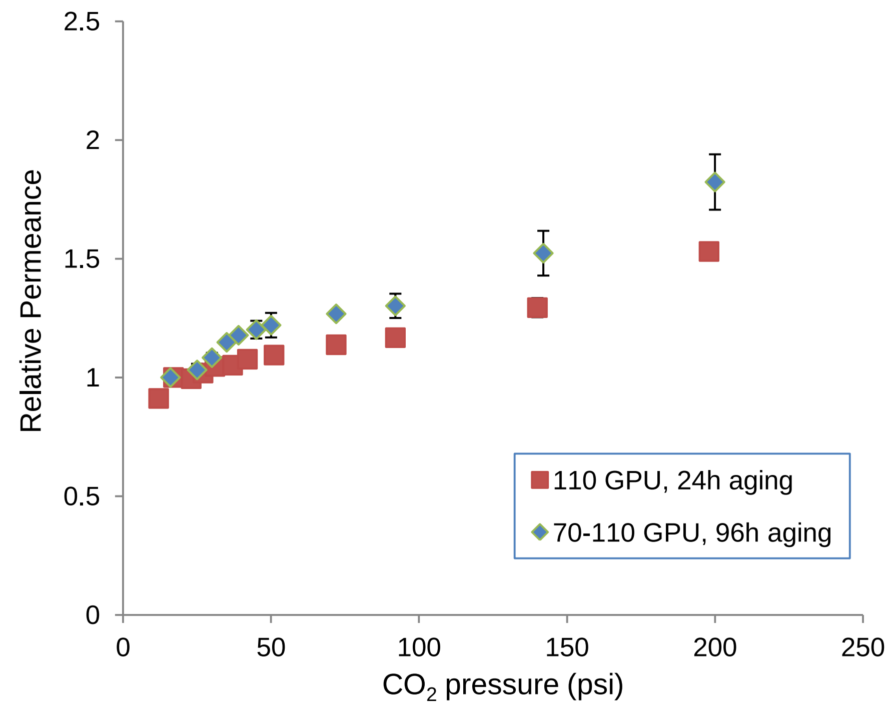
Aging and Plasticization





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

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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 CO_2