Advanced Air Separations Using Novel Mixed Matrix Membranes

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Project Description and Objectives

- The objective of this project is develop an air separation technology to be utilized in advanced fossil energy based modular energy systems that will make substantial progress toward enabling cost-competitive, coal-based power generation and small scale modular gasification plant with near-zero emissions.
- The **Advanced Energy Systems (AES) program** focuses on improving the efficiency of coal-based power systems, increasing plant availability, and maintaining the highest environmental standards.
- **This project supports the Gasification Systems Program** element of AES that is developing advanced technologies to reduce the cost and increase the efficiency of modular systems.

Strategic Alignment with Fossil Energy Objectives

This project supports the US Clean Coal Program by focusing on developing advancements in technology that increase the performance, efficiency and availability of existing and new coal-fueled power generation to provide the United States with the best opportunity to maximize the full potential of its abundant fossil energy resources in an environmentally sound and secure manner.

Technical Goal: Deliver a stream of oxygen enriched air (O_2 90-95%) suitable for use in a 1-5 MWe coal fired small modular power plant

Project Objectives and Status

- **Overall Project Goal**: **<u>Develop membrane materials and processes that have the ability to generate a 90-95% O2 stream from air</u>**
  - **TECHNICAL BARRIER: Low selectivities or poor permeabilities limit membrane utility**
  - *Develop the knowledge needed to form lab scale hollow fiber (HF) membranes with predictable performance translatable to larger scale manufacturing*
  - *Membranes will be suitable for manufacturing: commercially applicable hollow fiber format*
  - *Membranes need to be durable and fouling resistant*
  - *Project scope includes materials optimization and characterization, scale up, and techno-economic assessment based on performance and predicted CAPEX, OPEX, and COE.*
  - *Overall scope addresses 3 budget periods*
- **Advantages of the INL/ANL Mixed Matrix Membrane approach**
  - *Lower energy consumption – no need to heat the gas stream or use heat/power to condense or desorb O2*
  - *<u>Engineering to develop and deploy large surface area membrane modules is mature</u>*
  - *Potentially lower capital cost (CAPEX)*
  - *Modular, ease of deployment*
  - *Flexible – designed to interface well with variable load demands.*

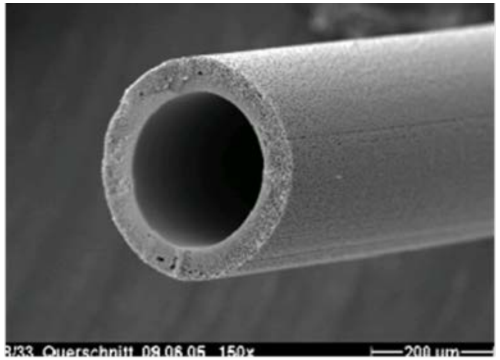
Status at Beginning of the Project

***Driving question** – how can membrane performance be improved to provide a viable and less energy intensive alternative to cryogenics, pressure swing absorption, or high temperature membrane processes for providing **90-95% O2** to support oxycombustion in small modular coal fired power plants or gasification systems?*

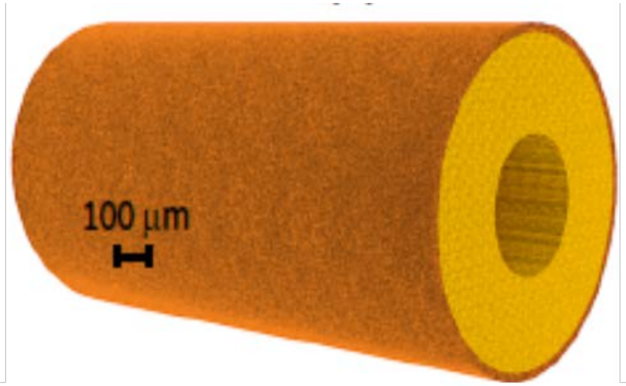
Technical questions that must be addressed to reach the project goal:

1. Hypothesis: Nanodiamonds (NDs) in a MMM material can increase membrane permeability and selectivity. Can this be shown?
2. Do NDs impact or influence membrane formation behaviors?
3. Can we characterize the materials to yield structure-function relationships and can these be translated to the HF format?
4. How do polymer/membrane formation and behaviors influence cost of oxygen?

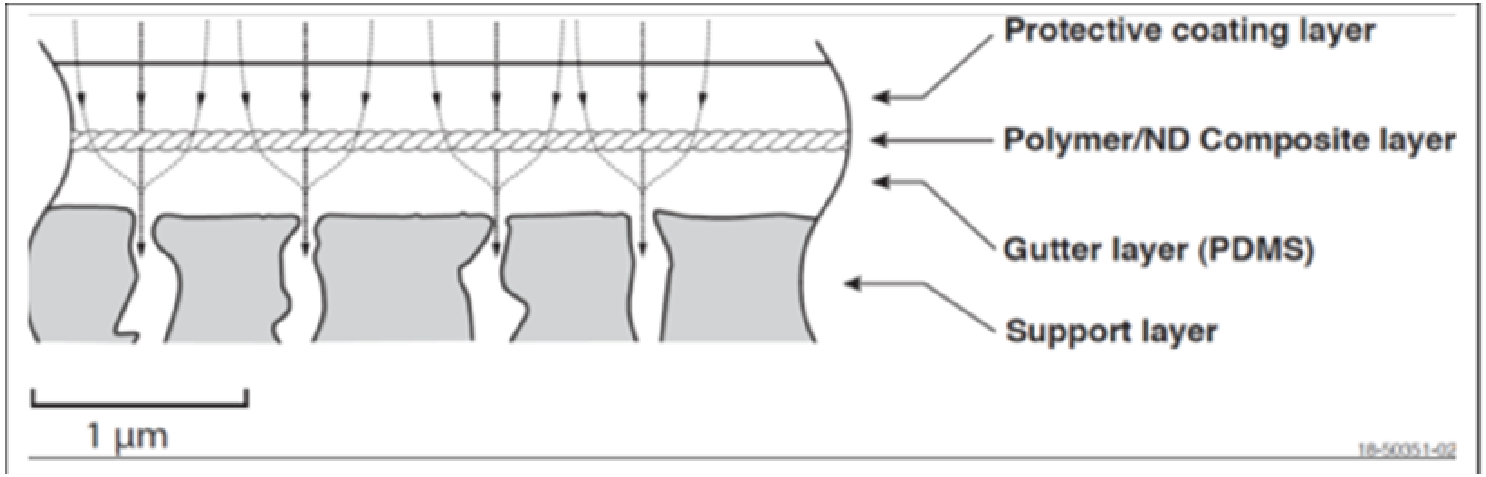
Functional Hollow Fibers (HF) are the End Goal (HF Anatomy)



Hollow Fiber Cross-Section



Hollow fiber support material

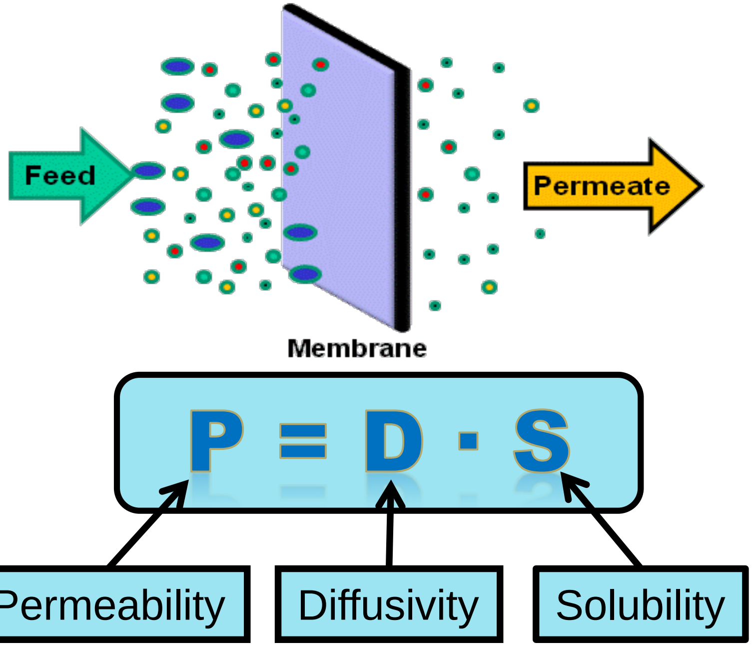


Multi-layer asymmetric membrane cross-section.

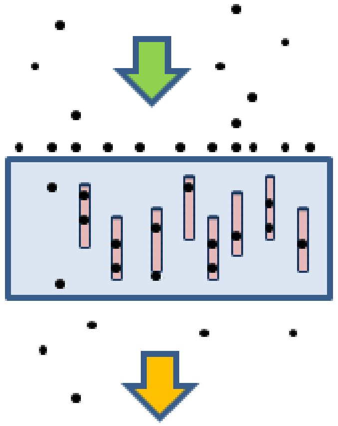
BP1 Technical tasks:

1) Develop optimized PSF supports through ND screening/inclusion and membrane characterization
2) Optimize/improve gutter layer performance

Gas Transport Mechanisms

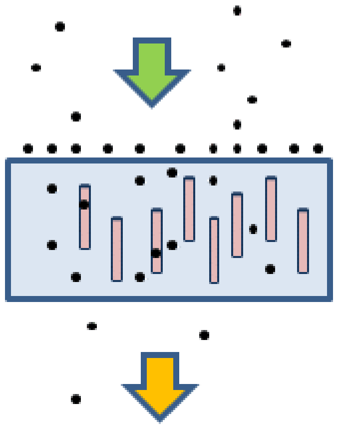


- **Permeability (P) - product of overall gas transport.**
- **Diffusivity (D) - pressure-induced transport of gases through the polymer matrix (molecular sieving).**
- **Solubility (S) - interactions between the gases and polymer matrix (sorption).**



Diffusivity (D)

Gas particles find the path of least resistance; channels & void space (molecular sieving)



Solubility (S)

Gas particles interact with the polymer structure (solution-diffusion)

Both mechanisms can be manipulated in our approach to achieve the goals of this project

$$\text{Selectivity} = P_A/P_B$$

Nanodiamond Purification

Detonation soot **Nano-diamond**

Control of the dispersal critical to being able to load these symmetrically into the polymer host

Purification from sp^2 carbon:
- up to 40% of cost of DND
- 35L of acids are needed for 1 kg of DND
- purification using Ozone\air mixture
  (U.S.Patent 8,389,584; Shenderova et al. J.Phys Chem C, 2011)

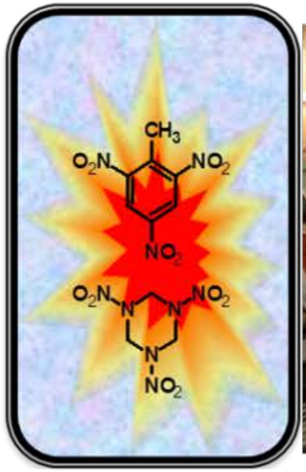
Annual world production of detonation soot: ~4-5 tons
Cost of detonation soot: $500-$900/kg
Cost of ND: $1500-$40,000/kg

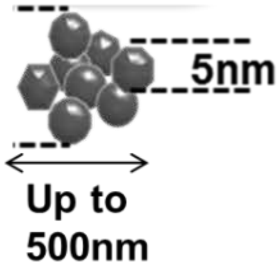
Nanodiamond Formation and Properties

- Can be as small as 3-5nm (large surface area 250-450 m^2/g)
- Chemically inert and mechanically stable crystalline diamond core
- Non-toxic & biocompatible
- Reactive surface: can be customized for specific applications
- Possess functional defects in the lattice
- Produced in large quantities (tons/ year)

ND of Dynamic Synthesis

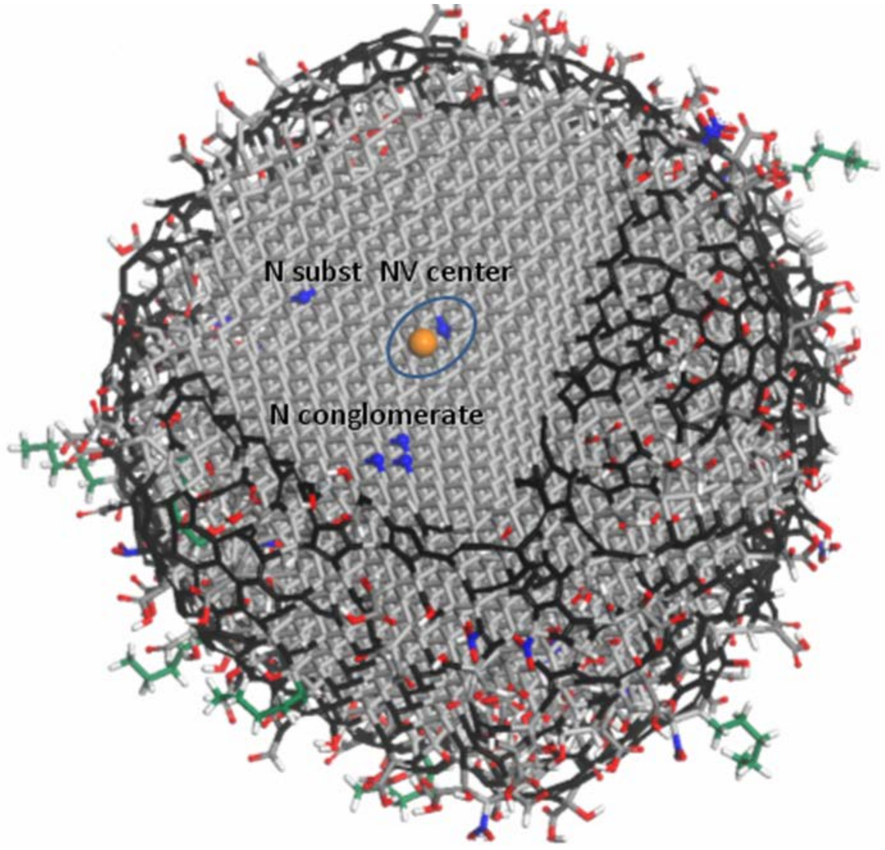
Detonation Nanodiamond (DND)

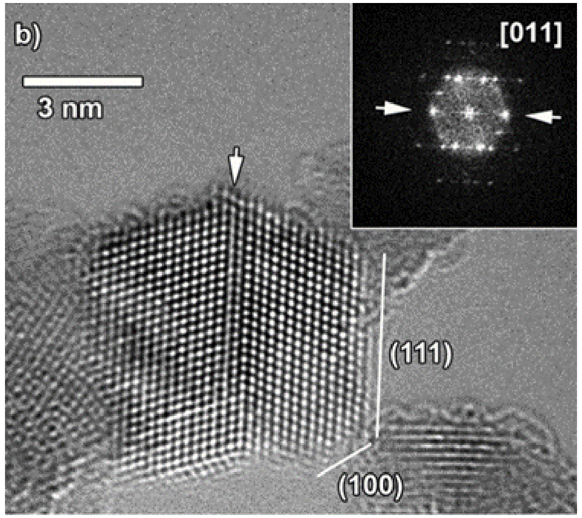




NDs can be:
1) completely deagglomerated into individual particles, or 2) clustered into porous structures

ND functionalization – Influencing Diffusivity and Solubility





V.Mochalin, O.Shenderova, D.Ho, Y.Gogotsi, *Nature Nanotech*, 2012
Book *Ultrananocrystalline Diamond* (Eds Shenderova, Gruen), 2012

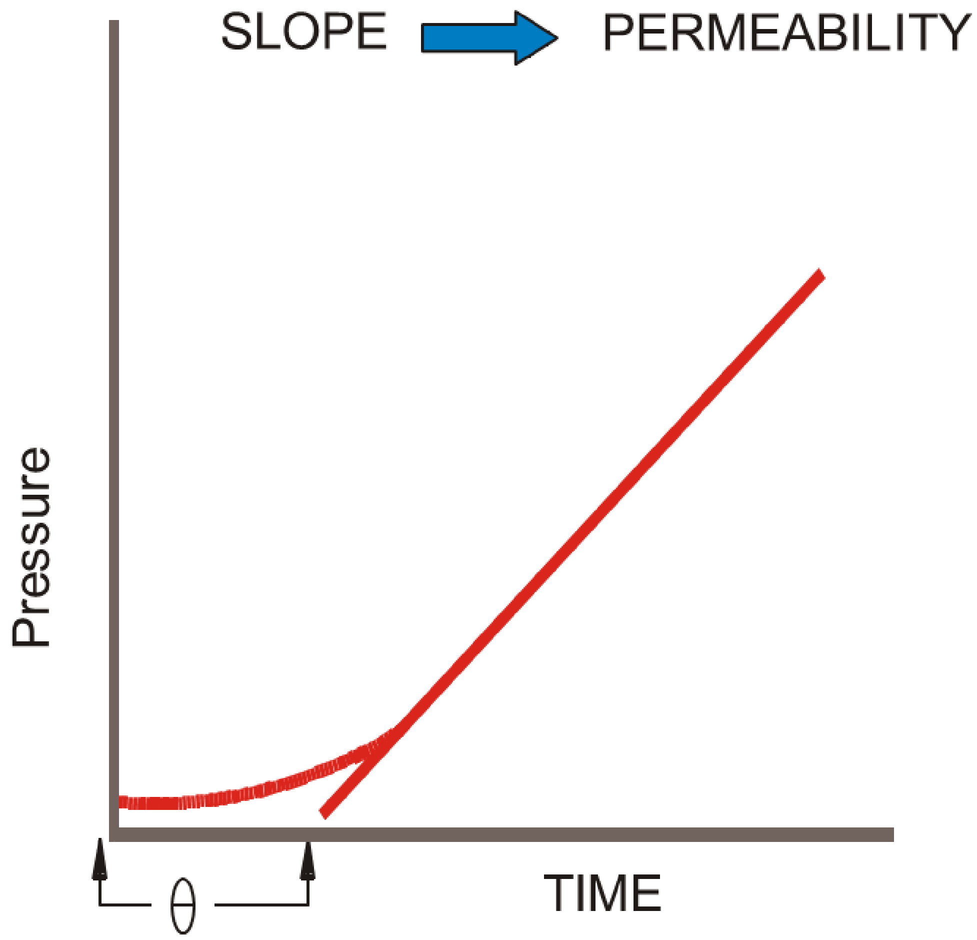
Surface functionalization to influence particle zeta potential, hydrophobic/hydrophilic balance

Also expected to influence dispersal in solvent

Agglomeration influences **gas diffusion** through induced porosity

Surface chemistry may influence **gas solubility**

Experimental Methods – Pure gas measurements



Barometric Technique

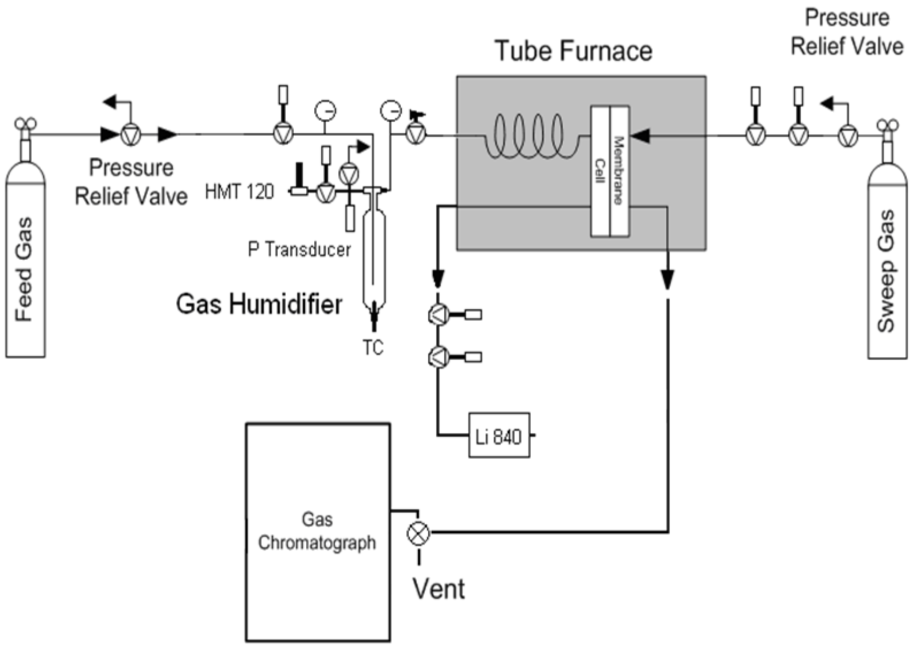
- Feed pressure: 30 psi
- Low temperature: <100 C

Mixed Gas Analysis

Analytical Technique

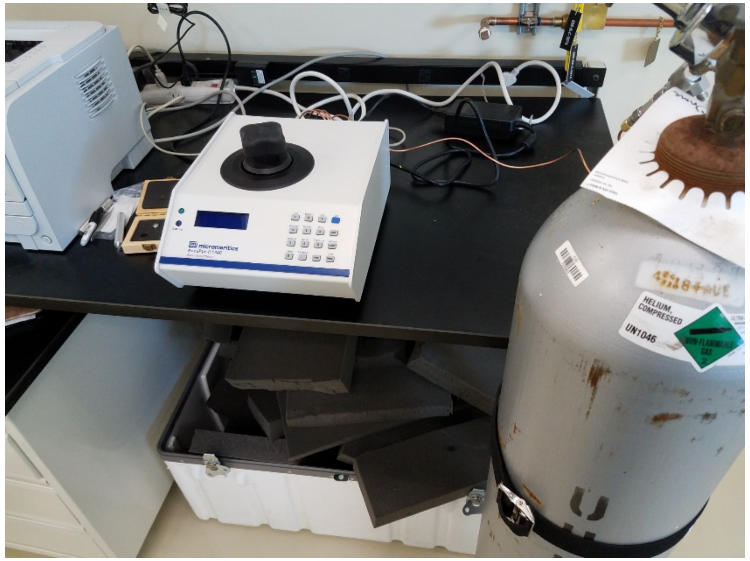
Two systems that differ by Temperature control

- Low temperature: <100 C
- Higher Temperature: <500 C



Current Status of the Project

- **Results compared to benchmark** – New start, establishing benchmarks for permeability, selectivity
  - Early results match well with benchmark literature values
  - Collection of other data such as density, thermomechanical behavior (initiated), and positron annihilation lifetime spectroscopy (PALS).
- **Describe how/if objectives have changed** – Nothing has changed



Helium pycnometry for "hyper-accurate" densities

Thermal analysis suite for measuring physical properties

Project Update/Accomplishments

- **Administrative tasks to support project initiation**
  - Technical and administrative tasks begun early January, 2019.
  - Project kickoff meeting completed January 22, 2019
  - MPO to Argonne National Laboratory completed in February ($250K)
  - Travel to Adamas Nanotechnologies (Raleigh, NC) February 11, 2019
    - Selection and acquisition of nanodiamonds
  - Acquired polysulfone (PSF) polymer, membranes, and other materials necessary to begin work
- **First steps moving forward**:
  - Performance Benchmarking
    1. Techniques for performance measurements
    2. Pure polysulfone (PSF) and polydimethylsiloxane (PDMS)
    3. Identify nanodiamonds – porosity, agglomeration, surface functionalization
  - Membrane Formation – NDs appear to aid in defect free membrane formation

- **Technical and/or collaborative challenges** – choosing the correct materials for the permeability testing – examples: PDMS vs Viton or-ring seals and sealing cells.

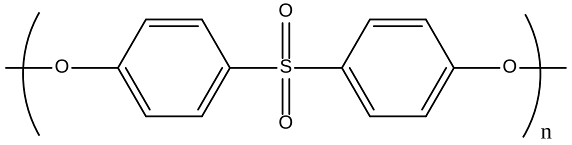
Industry/input or validation - Benchmarking PSF

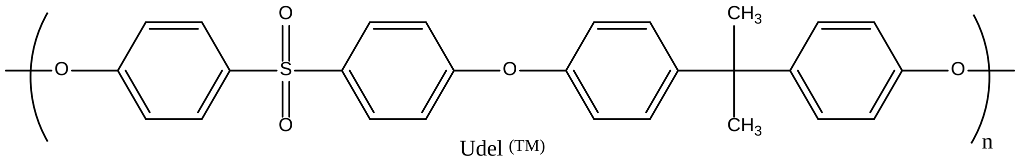
Membrane Material	O2 Permeability (Barrer)	O2/N2 Selectivity	Additive	Reference
PSF/CNF mixed matrix	2.2	3.86	Carbon Nanofiber	1
PSF with 20% silica nanoparticles	5.0	4.50	Silica	2
PSF with 5% µCX	15.3	7.03	Zeolite	3
PSF with 5% CX	17.8	5.95	Pyrolytic Carbon	4
Pure PSF	1.2	6	None	5

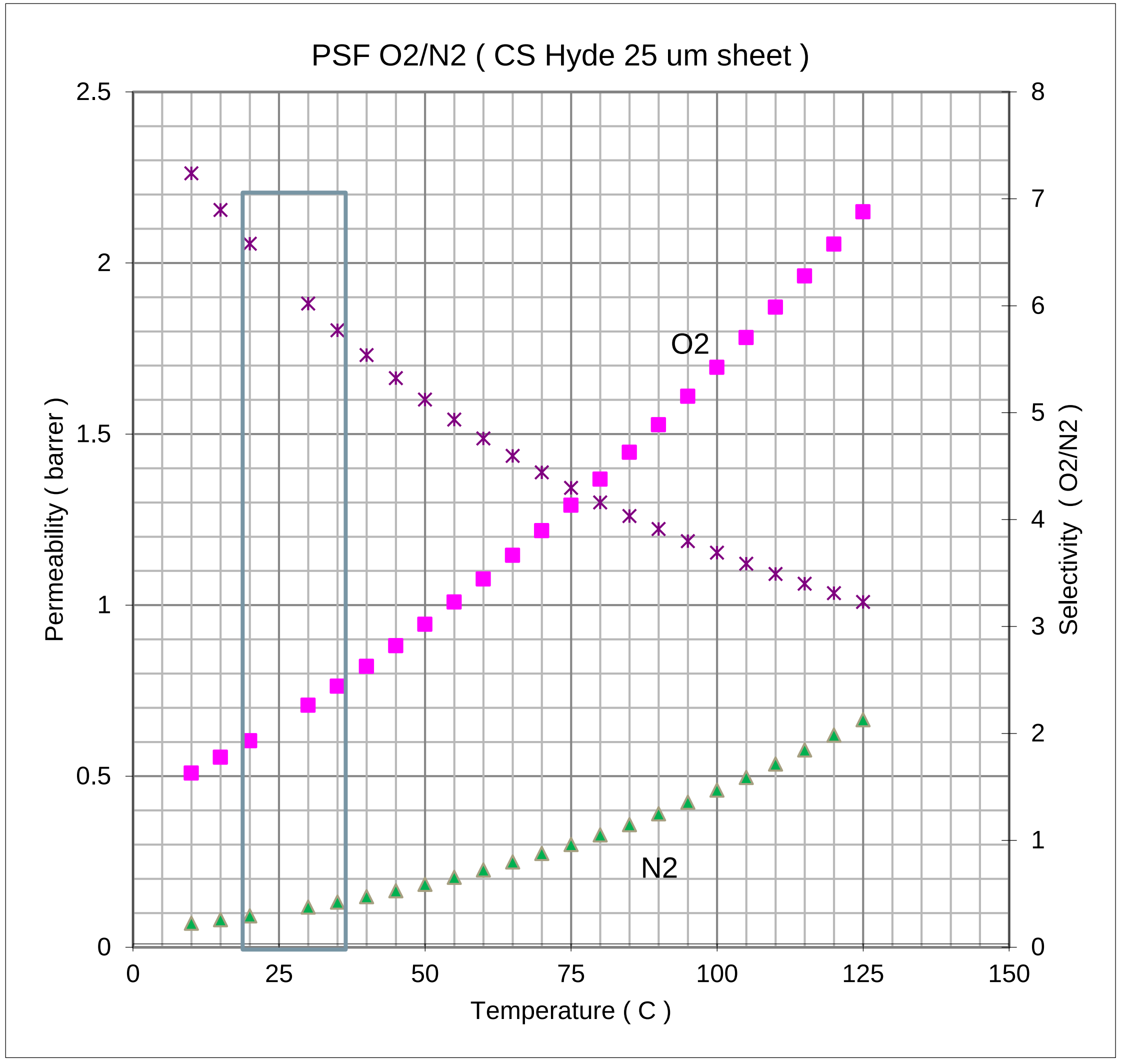
1. Kiadehi, A.D.; Rahimpour, A.; Jahanshahi, M.; and Ghoreyshi, A.A. (2015). "Novel carbon nano-fibers (CNF)/polysulfone (PSf) mixed matrix membranes for gas separation", *Journal of Industrial and Engineering Chemistry,* 22, 199-207.
2. Golzar, K.; Amjad-Iranagh, S.; Amani, M.; and Modarress, H. (2014). "Molecular simulation study of penetrant gas transport properties into the pure and nanosized silica particles filled polysulfone membranes", *Journal of Membrane Science,* 451, 117-134.
3. Weng, T.-H.; Wey, M.-Y.; and Tseng, H.-H. (2010). "Enhanced O_2/N_2 separation performance of poly(phenylene oxide)/SBA-15/carbon molecular sieve multilayer mixed matrix membrane using SBA-15 zeolite particles", *Proceedings from the 2010 International Conference on Chemistry and Chemical Engineering*, Kyoto, Japan, 245-248.
4. Magueijo, V.M.; Anderson, L.G.; Fletcher, A.J.; and Shilton, S.J. (2013). "Polysulfone mixed matrix gas separation hollow fibre membranes filled with polymer and carbon xerogels", *Chemical Engineering Science,* 92, 13-20.
5. Robeson, L.M. (1999). "Polymer Membranes for Gas Separation", *Current Opinions in Solid State and Materials Science,* 4, 549.

Project Results: Technology Benchmarking – Pure PSF

- Analysis based on pure gas determinations of O2 and N2 permeability taken at 3 temperatures (20, 30, and 40 °C)
  - Data calculated from an Arrhenius relationship
  - Ideal selectivity = α = P_{O2}/P_{N2}
- PSF chosen for several reasons:
  - Predictable performance
  - Commercially available
  - Readily formed into flat sheet membranes and hollow fibers





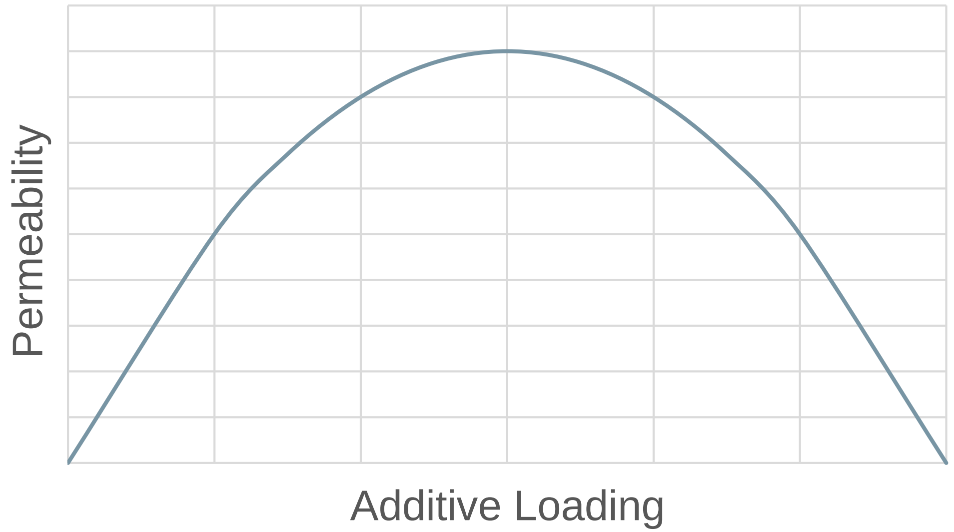


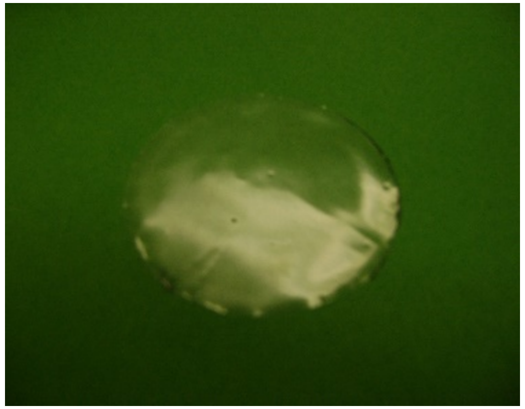
Understanding MMM formation

Loading of materials into polymers

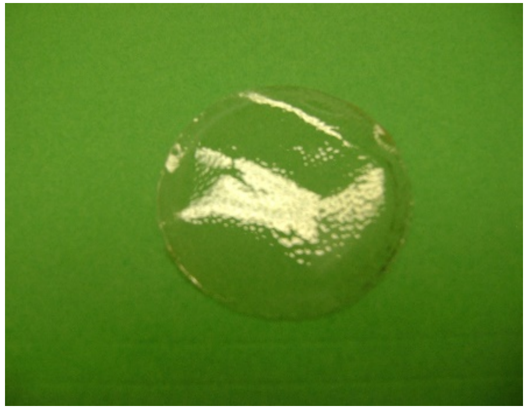
- Experiments begun with:

1. Zeolites: to probe the effect of porous additives (3, 4, and 5 Å pores)
   - Expected: 3Å enhances α but water sensitive
   - 5 Å exhibits little selectivity
2. Functionalized NDs
   - Initial result: The expected relationship between P and loading %

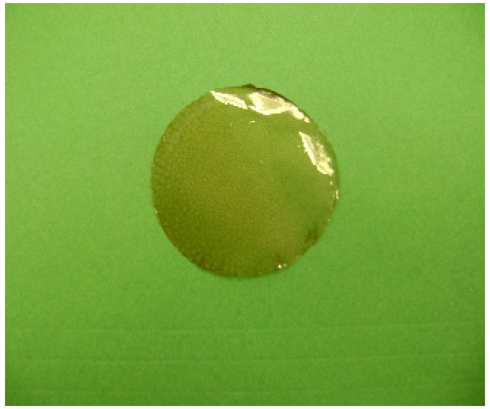




25 µm Udel PSF membrane



Udel PSF with 5% ND



Udel PSF with 10% ND Aggregate

Summary: Progress on Technical Questions

- Do NDs in a MMM material increase or decrease permeability and selectivity?
  - Status: We do not know. We have just started to collect gas permeability data – need more replicates before data can be published.
- Do NDs impact or influence membrane formation behaviors?
  - YES. NDs tend to add viscosity to membrane casting solutions that assists in forming defect free films. This is an important observation and will enable HF formation
- Can we characterize the materials to yield structure-function relationships and can these be translated to the HF format?
  - YES. ANL will be conducting permeability tests to support INL's work. Also, at INL we have a post-doc who will perform SEM and are hiring an intern for thermal analysis.
  - Film forming improvement may be due to chemistry between the polymer and ND – should be reflected in the glass transition temperature (Tg) – experiments on-going
- How do polymer/membrane formation and behaviors influence cost of oxygen?
  - Status: We do not know at this time; however we have a new INL staff member (former post-doc) who has begun to develop an ASPEN Plus flowsheet to allow us to computationally compare approaches

Preparing Project for Next Steps: Technical

- **Continue to investigate Permeability and Selectivity as a function of**:
  - Focus on flat sheet geometry – quick and easy to screen a variety of formulations
  - ND loading
  - Choice of ND (functionalization)
  - Temperature
  - Polymer – both substrate and gutter layers (PSF and PDMS)
- **Characterize membranes**
  - DMA – Mechanical behaviors as a function of temperature
  - TGA - Thermal stability
  - DSC – Glass transitions, molecular interactions between polymer host and NDs
  - Microscopy – Defect structure
  - Porosimetry
  - Density – quick and easy proxy for fractional free volume
  - Positron Annihilation Lifetime Spectroscopy – Fractional free volume and its link to gas permeation.
- **Set up for successful HF formation – ensure that critical attributes will translate from film to fiber**

Preparing Project for Next Steps

- **Market Benefits/Assessment**
  - Market is mature for membrane systems giving 99.5% N_2 or 30-50% O_2
  - Membrane systems yielding 90-95% O_2 not mature
  - Growing market - $1.3 billion by 2025, Predicted Compound Annual Growth Rate (CAGR) of 8.4% (2015-2025).*
  - Complete Techno- Economic Assessment of this work planned for BP3
  - Applications for low-cost oxygen enrichment: medical (45%), enhanced combustion (20%), water treatment (25%)
- **Technology to Market Path**
  - Protection of Intellectual Property (INL Invention Disclosure Record expected by 7/1/2019)
  - Engage INL Technology Deployment and Industrial Engagement staff to support agreements management and licensing, market research, etc.
  - Bridging from this project to industry
    - ARPA-E
    - SBIR
    - SPP, CRADA, others

* Creedence Research, 2018 (www.credenceresearch.com/press/global-oxygen-enriched-membrane-market)

Concluding Remarks

- **Overall Project Objectives:** Enable small modular coal fired gasification while minimizing environmental impact
- **Applicability of the Technology to FE objectives:** *Air separation technology to be utilized in advanced fossil energy based modular energy systems that will make substantial progress toward enabling cost-competitive, coal-based power generation with near-zero emissions*
- **Project Status – new start 12/1/2018.**
- **Budget Period 1 Technical Milestones: On-schedule**
  - Complete initial flat sheet membrane formation study to demonstrate defect-free films can be made, optimize the ND loading (10/30/2019)
  - Complete study of flat sheet membrane suitable for publication (11/30/2019)

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