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Advanced Oxygen Separation from Air Using a Novel Mixed Matrix Membrane

2021 DOE/FE Spring Research Meeting - Gasification Systems Project Review, Virtual from Idaho Falls, ID

Project # FWP-B000-18-061

NETL

Argonne NATIONAL LABORATORY

INL Idaho National Laboratory

Project description and program alignment

Purpose: Develop a novel hollow fiber membrane-based approach to 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

Aligned with NETL program goals:

Advanced Energy Systems (AES) program: 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.*

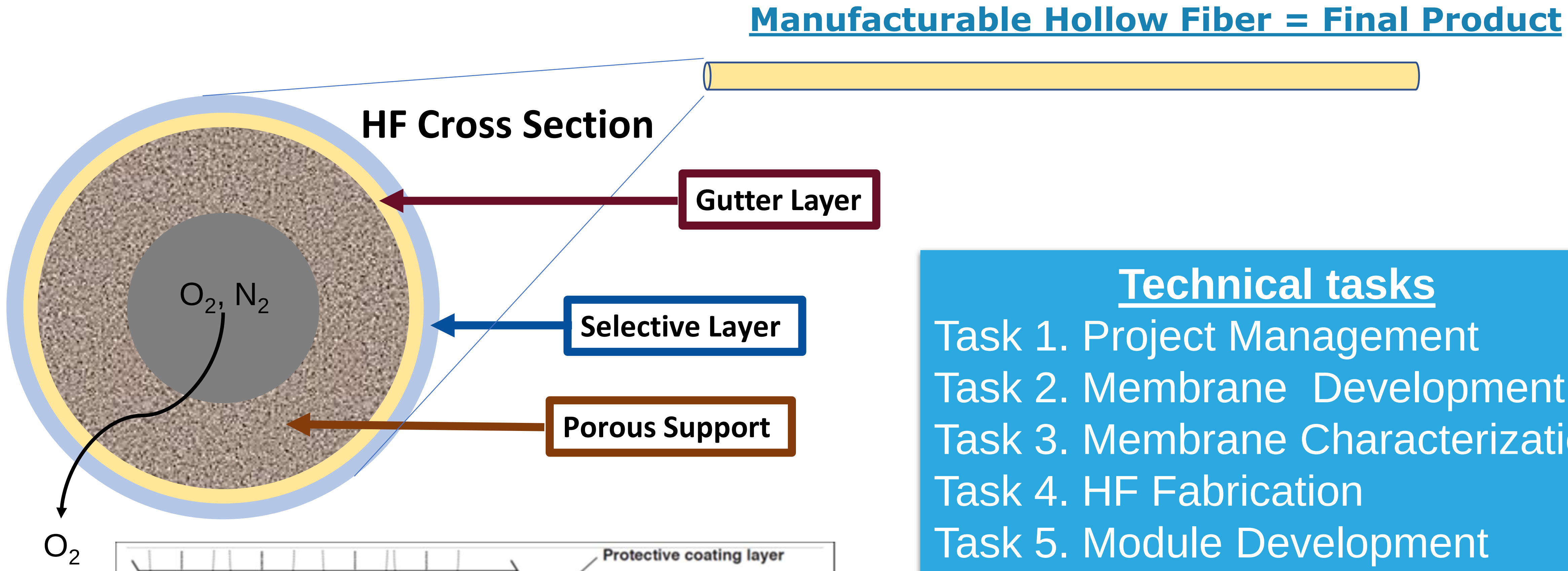
Project objectives

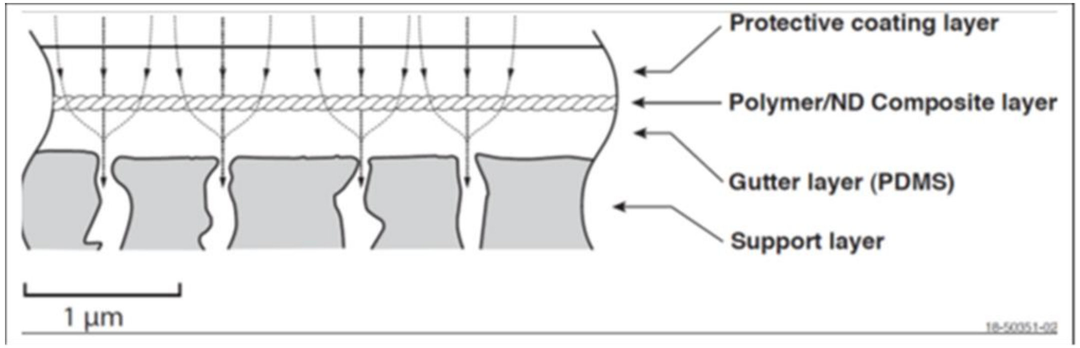
***Driving question** – how can membrane performance be improved to provide a viable and less energy intensive alternative to cryogenics, pressure swing absorption, or high temperature membrane processes for providing **90-95% O_2** to support oxycombustion in small modular coal fired power plants or gasification systems?*

Barriers and Challenges

- Poor permeance and selectivity of polymeric membranes
- How to convert knowledge gleaned from flat sheets to HFs
- How to best use nanodiamond (NDs) to enhance performance
- Balance the need for minimum layer thickness against defect formation
- Formation of single and multi-fiber cells

Project task overview





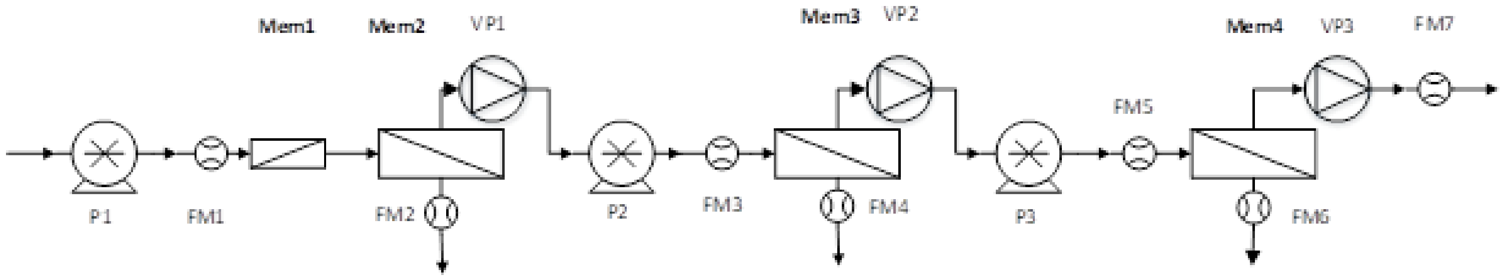
Multi-layer asymmetric membrane cross-section.

Technical tasks

Task 1. Project Management
Task 2. Membrane Development
Task 3. Membrane Characterization
Task 4. HF Fabrication
Task 5. Module Development
Task 6. TEA

TEA as a method to define benchmarks

- Technoeconomic Analysis (TEA)
  - User defined parameters
  - Included labor, materials, energy, financing
  - Sensitivity Analysis
  - System Design



Process flow diagram of gas separation system

- **Manuscript published: *Separation and Purification Technology 2021, 268, 118703.***

Parameter	Input values
Number of Membrane Modules	1,2 or 3
Material of the membrane module	stainless steel, carbon steel, polypropylene or polyethylene
O_2/N_2 selectivity of the membrane	2-10
O_2 permeance, GPU	100-10000
Inlet volume of air, L/h	100,000 – 16,000,0000
Pressure of inlet air, psi	25-75
Temperature of inlet gas, ˚C	22
Relative Humidity of input air, %	40
Particles in air, ppm	3000
Hours of operation per year	8000
Permeation factor for O_2	0.9
Permeate pressure, psi	14.7
Rejectate pressure, psi	14.7
Permeate temperature, ˚C	22
Rejectate temperature, ˚C	22
Membrane effective thickness, µm	0.1
Temperature of pump, ˚C	22
Material of the pump	stainless steel, carbon steel, polypropylene or polyethylene
Pump efficiency	user chooses
Delivery pressure of a compression pump, psi	25
Vacuum pump pressure, psi	5
Membrane cost, $\$/m^2$	5-50
Membrane installation factor	0.5
Electricity cost, $/kWh	0.04-0.24
Air cost, $/kg	0.0001

Best-case scenarios for 90%+ O_2 and comparison to other methods

Product Gas Cost as a Function of # of Stages for **100 tonne/day** production (1-5 MWe scale)

Number of Stages	Gas Product Cost	Permeance (GPU)	Selectivity
Two	$58/tonne	**500-1000**	**5.5**
Three	$68/tonne	**500-1000**	**3.2**

Literature Data for Competing Technologies (large scale optimum installations)

Method	Gas Product Cost	O_2 Concentration	Scale
Cryogenic Distillation	$45/tonne	95%+	3000-4000 tonnes/day
Pressure Swing Absorption	$65/tonne	90%	1000 tonnes/day

Initial studies were not encouraging

Initial data collected at 30 ^{O}C

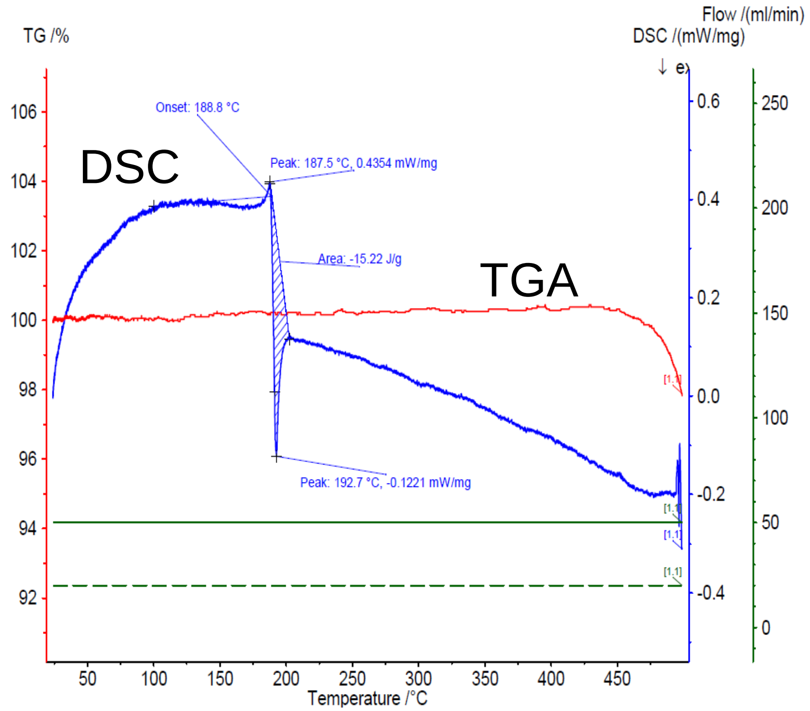
Composition (PSF cast from NMP)	O_2 Perm (Barrers)	O_2/N_2	Notes
No NDs	0.73	6.1	
2% ND	0.72	6.5	Durability increased
5% ND	0.41	2.6	Possible defects
10 % ND	NA	NA	Membrane Fractured

- Limited literature data suggested inclusion of ND reduced O_2 permeability
- Initial experiments in our lab supported this conclusion

Polymer	Permeability (Barrer)	Selectivity	Additive	Reference
P84 co-polyimide	H_2 = 8.0	H_2/CO_2 = 3.6	None	1
	H_2 = 6.7	$H2/CO_2$ = 4.1	1% ND	
Poly(phenylene oxide) (PPO)	O_2 = 33.2	O_2/N_2 = 3.25	None	2
	31.8	3.61	1% ND	
	29.7	3.81	3% ND	
	28.4	4.06	5% ND	
Poly (phenylene-isophtalamide)	O_2 = 0.032	O_2/N_2 = 5.9	None	3
	0.029	6.3	1% ND	
	0.029	10.0	3% ND	
	0.017	1.2	5% ND	

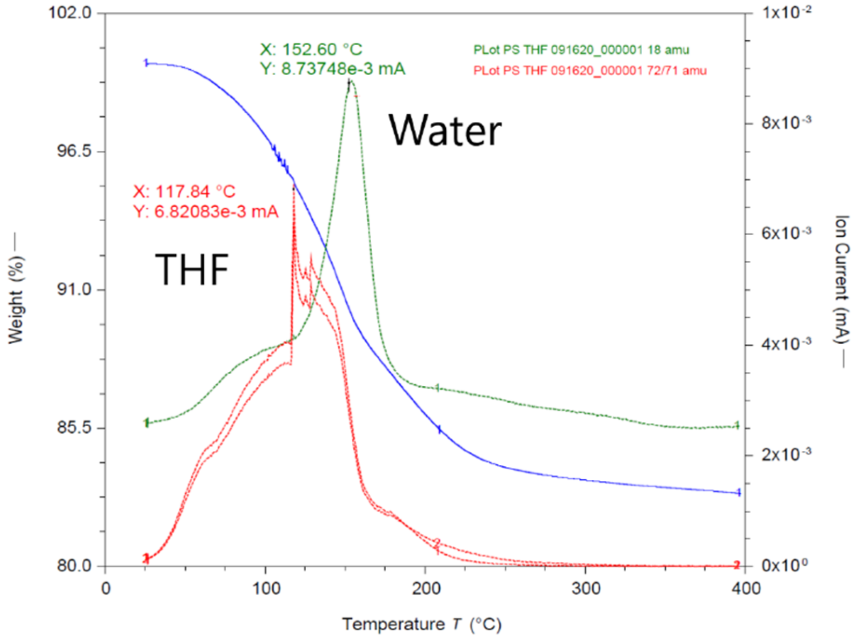
1. Pulyalina, A.; Polotskaya, G.; Rostovtseva, V.; Pientka, Z. and Toikka, A. (2018), *Polymers,* 10, 828-841.
2. Polotskaya, G.A.; Avagimova, N.V..; Toikka, A.M.; Tsvetkov, N.V.; Lezov, A.A.; Strelina, I.A.; Gofman, I.V.; and Pientka, Z. (2018), *Polymer Composites,* DOI 10.1002/pc24437.
3. Avagimova, N.; Pototskaya, G.; Toikka, A.; Pulyalina, A., Moravkova, Z., Trchova, M.; and Pienka, Z. (2018), *Journal of Applied Polymer Science,* 135,46320.

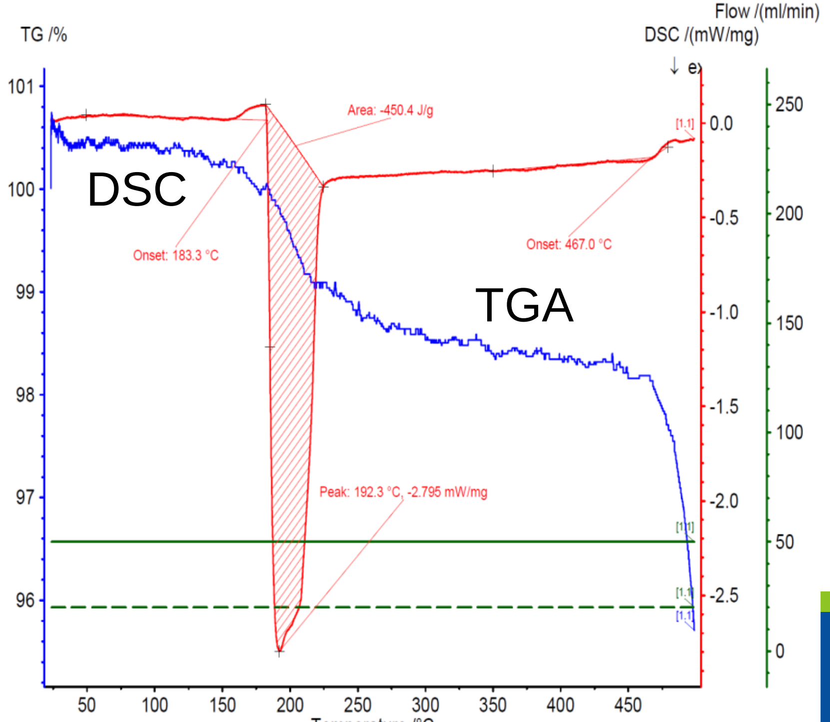
Thermal analysis of PSF-ND Composites



Pristine PSF

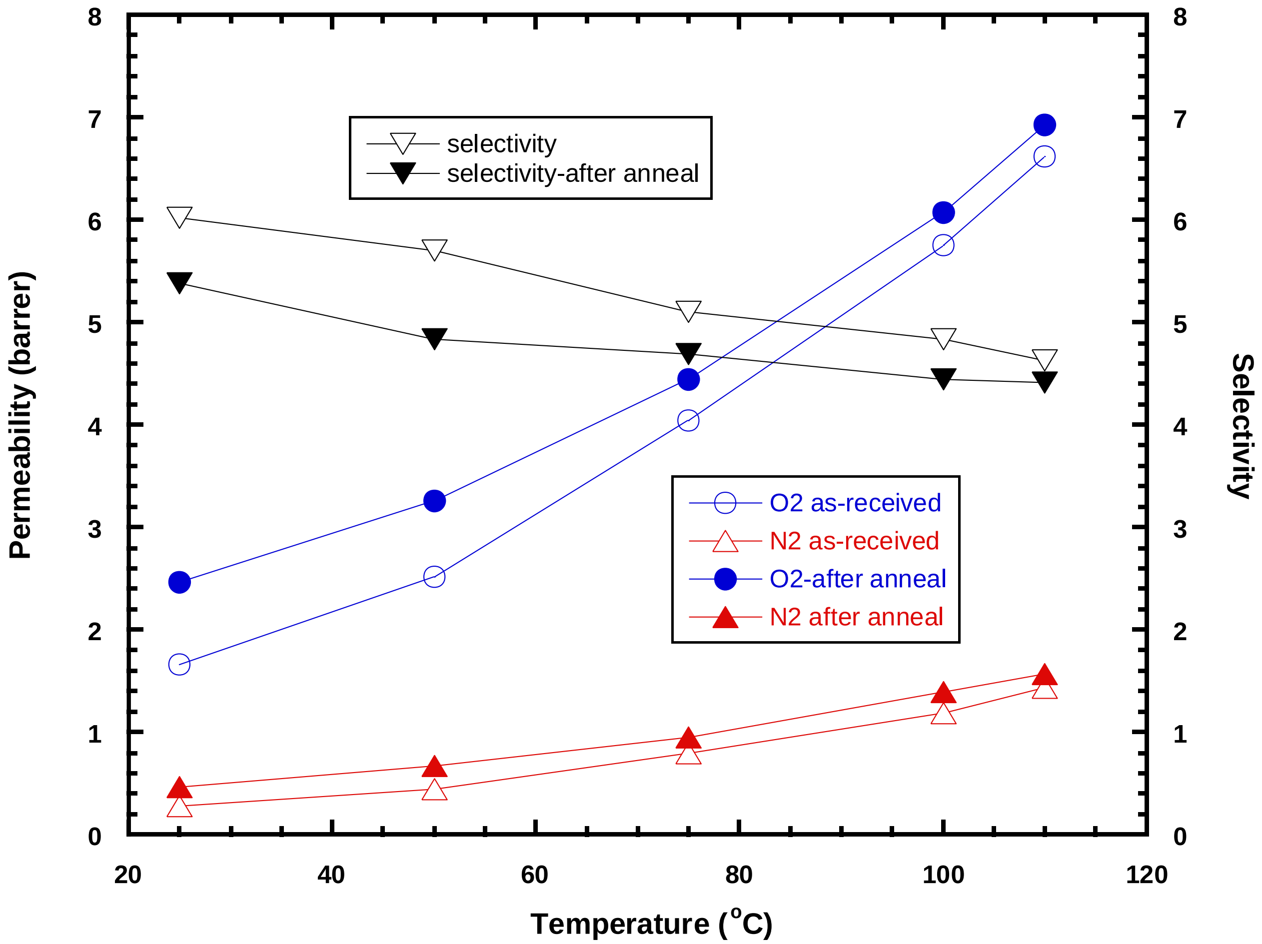
Entrained solvent is found even after “reasonable” drying processes





PSF with 1 % ND

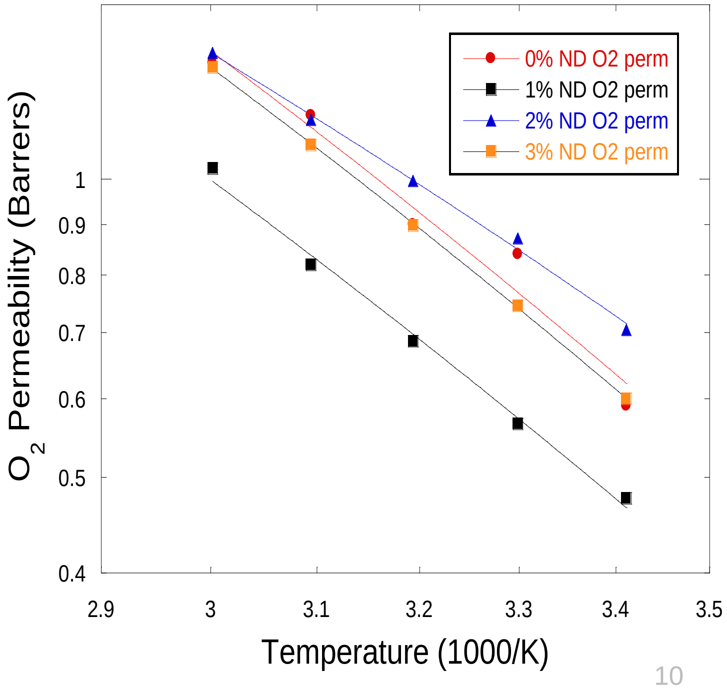
Comparative study of residual solvent

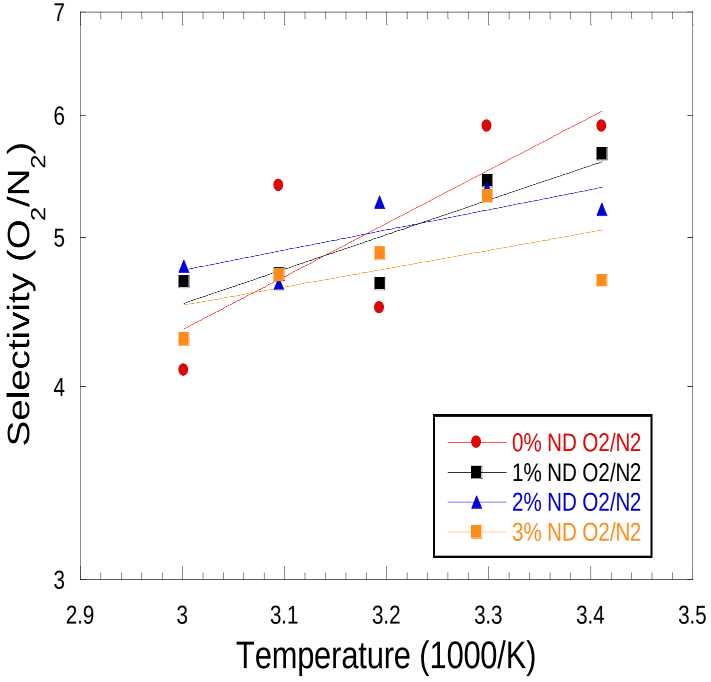


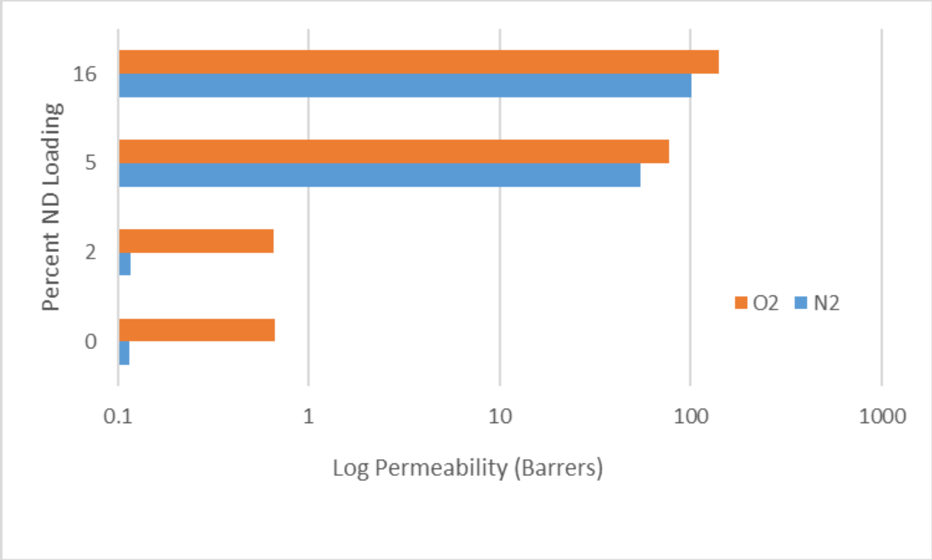
- Impact of film annealing with the goal of releasing entrained solvent
  - UDEL 1700 PSF with 1 % ND
- Annealing Procedure
  - 185 ^{O}C for 45 minutes
  - *In-situ* with N_2 on the feed side and He as a sweep
- Removal of solvent results in increased performance
- Solvent may reside in spaces within the membrane and block gas permeation

Varying ND loading up to 3% had little impact on P_{O2}

- Thin films are formed from 0 to 3 % ND loading
- Above 3%, microporosity is formed
- Microporous regions tend to increase permeance at the cost of selectivity





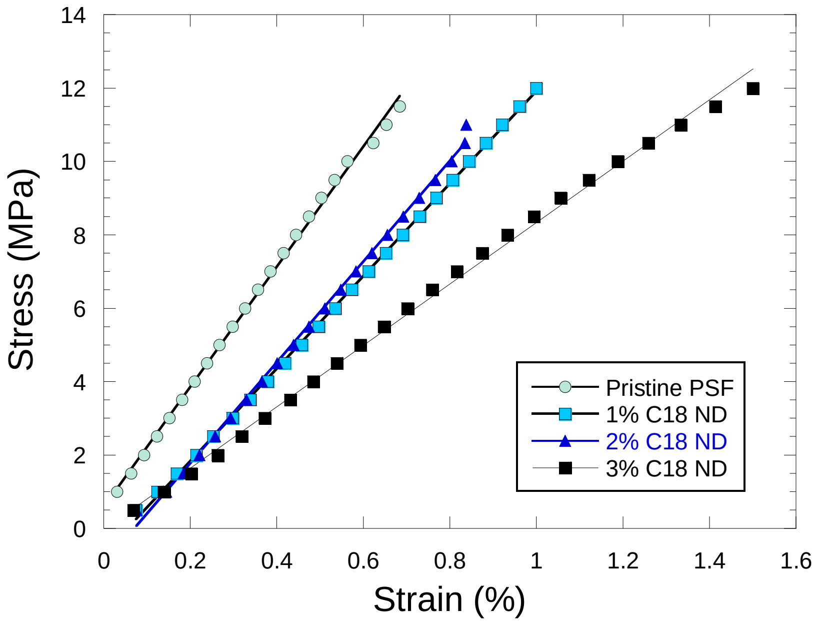


Significant increase in O_2 permeability with > 5% ND content

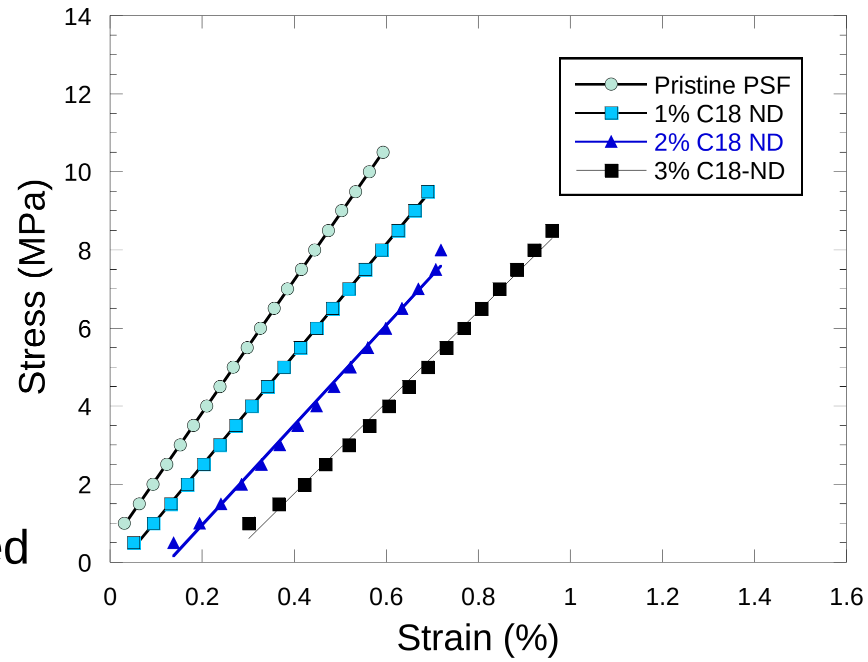
Selectivity falls from 6 to 1.4

Young's modulus studies elucidate impacts of NDs and solvent

Material	200 °C Processed	100 °C Processed
Pristine PSF	17.02 MPa	16.41 MPa
1% C18 ND	14.15 MPa	12.61 MPa
2% C18 ND	12.79 MPa	13.74 MPa
3% C18 ND	11.66 MPa	8.37 MPa



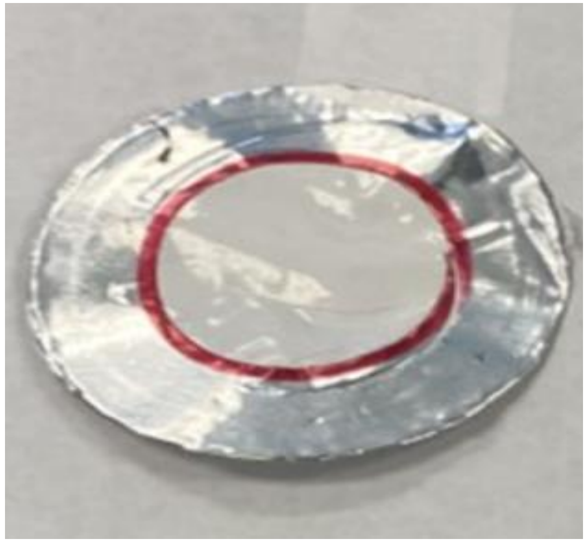
100 °C processed membrane



200 °C processed membrane

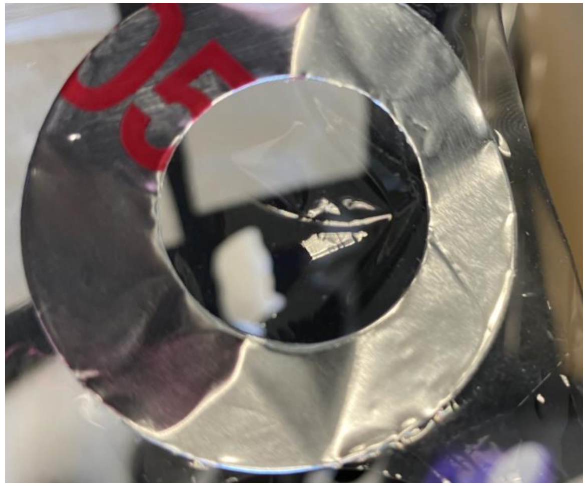
Decreasing Young's modulus suggests less embrittlement with an increasing ND content

Porous PSF-ND supports gives high O_2 permeance



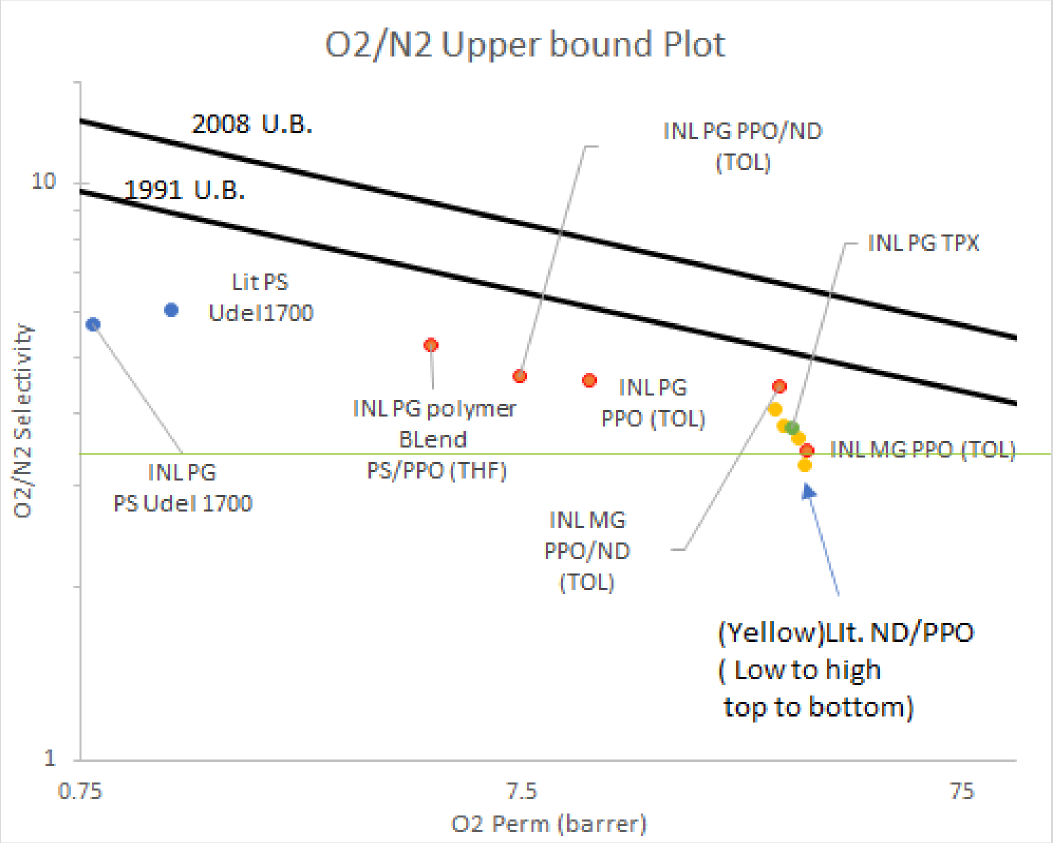
Phase inversion yields an opaque film

Initial Phase Inverted Membranes (PSF Cast From NMP)	O_2 Permeance (GPU)	O_2/N_2 Selectivity
No ND's	52054	0.91
2% 5nm-COOH ND (No Heat)	48802	0.91
2% 5nm-COOH ND (Heated to 100 C/10 min)	57007	1.09



Dense films typically are transparent

Selective layer performance improvements – PPO and Blends

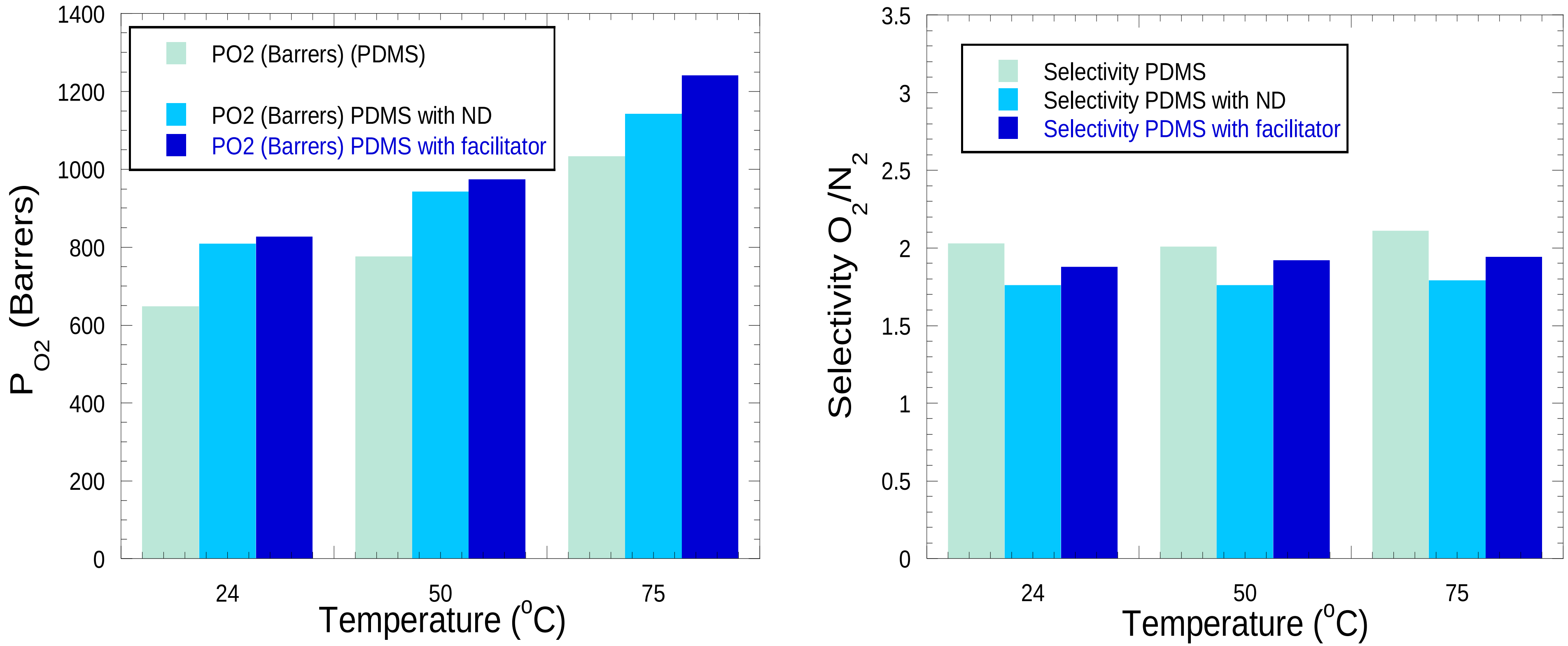


Polymer	ND wt. %	O_2 Perm (Barrers)	N_2 Perm (Barrers)	O_2/N_2	Processing Temp (^oC)
PPO	0	10.5	2.7	3.9	70
	1	11.3	2.3	4.9	70
	2	7.1	1.4	4.9	70
	2	37.3	8.5	4.4	150

Solvent removal also important for other polymers such as PPO

Legend:
- U.B. = Robeson theoretical upper bound in permeability/selectivity correlation published in 1991 and 2008; tol = toluene casting solvent;
- THF = tetrahydrofuran casting solvent;
- PS = polysulfone;
- Udel 1700 = commercial brand of PSF; PG = pure gas testing method;
- MG = mixed gas analysis method
- Green line indicates minimum selectivity need to reach the TEA performance goals

Gutter Layer: NDs give 25 % improvement in P_{O2}



O_2 permeability (left) and O_2/N_2 selectivity (right) of PDMS membranes neat, and with NDs and a facilitator as a function of temperature.

Translation of PSF-ND composites to hollow fibers

Dope Feed Rate (~3 to 5 ml/min)

$$\left(4.5 \cdot \frac{ml}{min}\right) = 270\ \frac{ml}{hr}$$

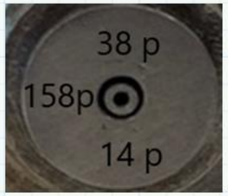
Dope Solution Composition:

~22% Udel-1700 (PS)
~2% wt ND
~31% THF
~31% NMP
~14% ETOH

Bore Fluid: DI water
Bore Fluid Flow Rate (1 to 2 ml/min)
(internal coagulation rate 1:3 with the polymer dope feed rate)

$$\left(\frac{1}{3}\right) \cdot \left(4.5 \cdot \frac{ml}{min}\right) = 1.5\ \frac{ml}{min} \qquad \left(\frac{1}{3}\right) \cdot \left(4.5 \cdot \frac{ml}{min}\right) = 90\ \frac{ml}{hr}$$

DI water temperture conditions : 23 C

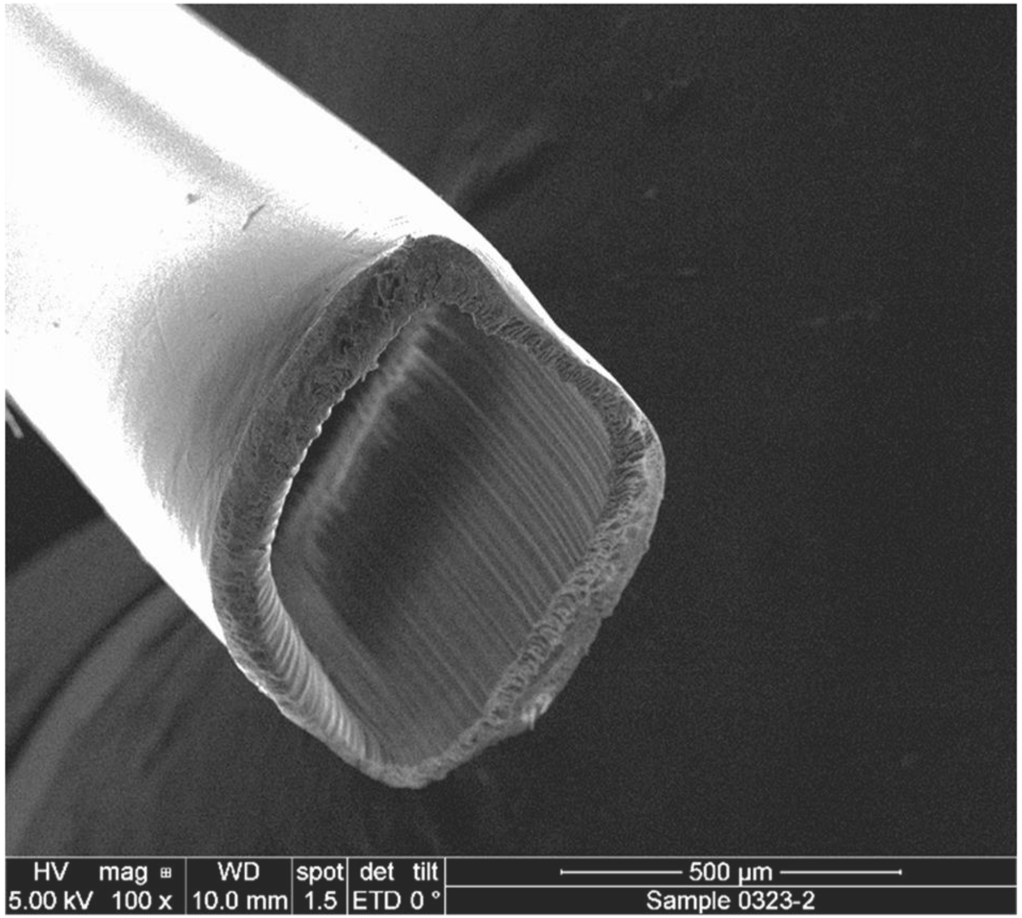


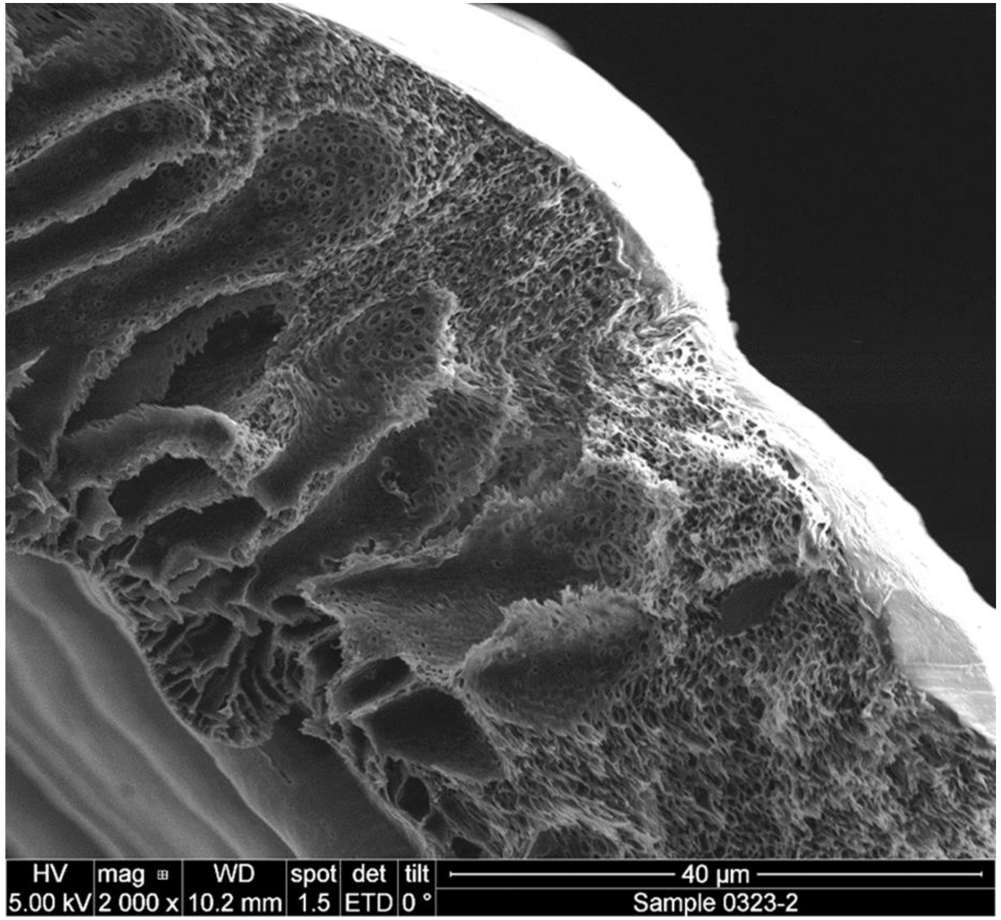
$$P := 0.04 \cdot mm$$

~OD : 1.5 mm ~ID : 0.5 mm

Identified polymer dope, bore fluid, and coagulation bath compositions to form prototype hollow fibers

Hollow fiber characterization





Preparing project for next steps

- **Accomplishment Summary**
  - The **TEA is published** and is guiding research
  - Created porous high permeance ND-containing Hollow Fiber supports
  - PPO is a promising selective layer – exceeds minimum selectivity
  - 25 % improvement is PDMS gutter layer permeance
- **Continue to investigate HF formation:**
  - HF coating with optimized PDMS-ND (gutter) and PPO-ND (selective layer) composites
  - HF bundling
  - HF module characterization
- **Technology to Market Path**
  - Protection of Intellectual Property (**US Patent filed in February 2021**)
  - 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, TCF
  - SPP, CRADA, others
  - Expansion to other gas separations – CO_2

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