September 2, 2020

Frederick F. Stewart, Ph.D.

Balu Balachandran, Ph.D., ANL

Christopher J. Orme, INL

Tae H. Lee, Ph.D., ANL

John R. Klaehn, Ph.D., INL

Birendra Adhikari, Ph.D., INL

Advanced Air Separations Using Novel Mixed Matrix Membranes

2020 Annual Project Review Meeting for Crosscutting, Rare Earth Elements, Gasification and Transformative Power Generation, September 2, 2020, 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

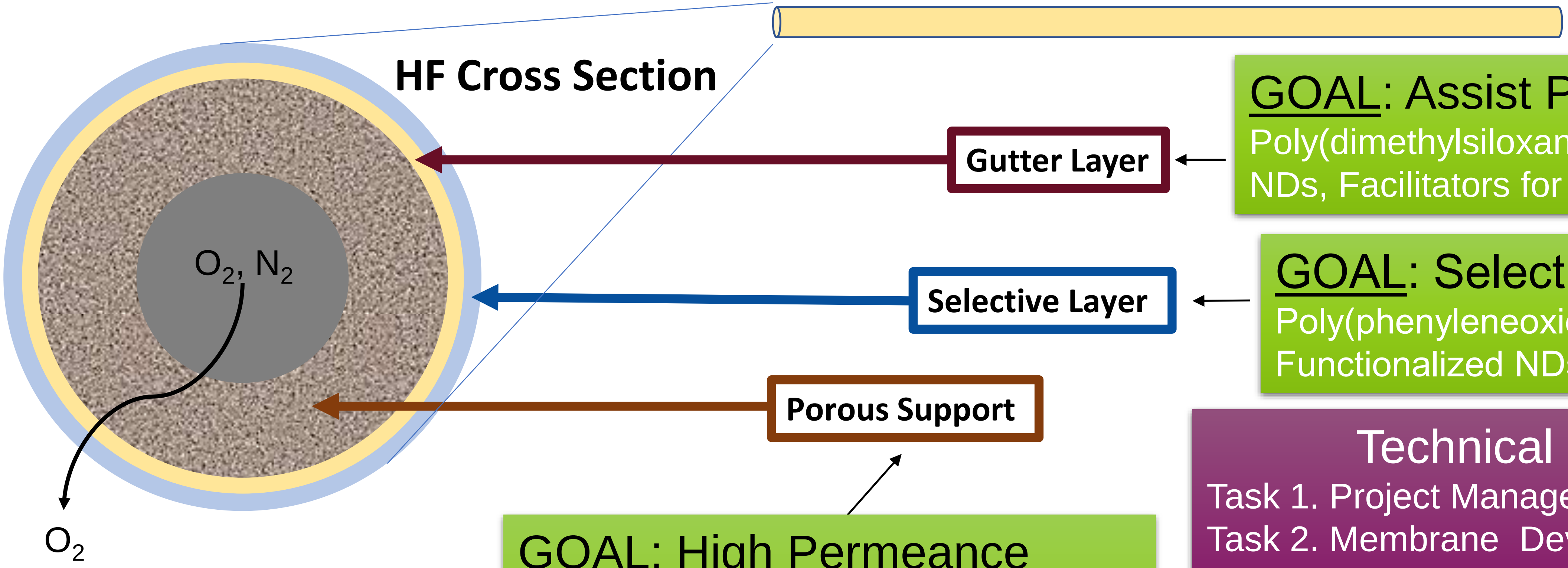
- **Aligned with NETL program goals:**
  - **Advanced Energy Systems (AES) program:** improving the efficiency of coal-based power systems, increasing plant availability, and maintaining the highest environmental standards.
  - **This project supports the Gasification Systems Program** element of AES that is developing advanced technologies to reduce the cost and *increase the efficiency of modular systems.*

Project Objectives

- Barrers and Challenges
  - Poor permeance and selectivity of polymeric membranes
  - How to convert from flat sheet to hollow fiber formats that enable scale-up
  - How to best use nanodiamonds as additive to improve properties
  - Balance the need for minimum layer thicknesses against defect formation
  - The need to understand material durability

Project Task Overview

Manufacturable and Durable Hollow Fiber = Final Product



GOAL: Assist Performance
Poly(dimethylsiloxane) (PDMS)
NDs, Facilitators for oxygen

GOAL: Selectivity 3-5
Poly(phenyleneoxide) (PPO)
Functionalized NDs

GOAL: High Permeance Supports
Polysulfone (PSF) thin-dense films
Phase inversion
Functionalized NDs (F-NDs)
Characterization of MMMs

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

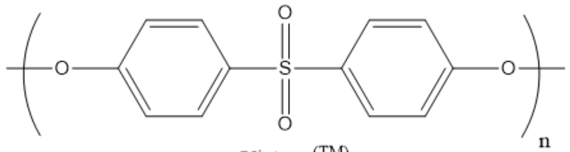
Technoeconomic analysis: to guide the research, set performance targets, and quantify final costs

Technology Benchmarking – Polysulfone (PSF) Mixed Matrix Membranes (MMMs)

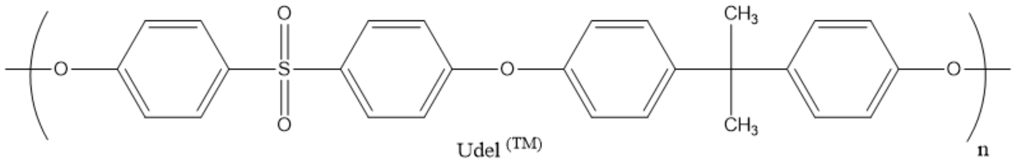
Membrane Material	O_2 Permeability (Barrer)	O_2/N_2 Selectivity	Additive	Reference
PSF/CNF mixed matrix	2.2	3.86	Carbon Nanofiber	1
PSF with 20% silica nanoparticles	5.0	4.50	Silica	2
PSF with 5% CX Fiber	1.78	5.95	Pyrolytic Carbon Xerogel (PDMS gutter layer)	3
PSF with 5% CX Fiber	17.5	1.13	Pyrolytic Carbon Xerogel (no gutter layer)	3
Pure PSF	1.2	6	None	4

From the limited selection of literature data, the trade-off between permeability and selectivity is evident.

None are produced commercially as modules



Victrex (TM)



Udel (TM)

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.
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3. 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.
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Technology Benchmark: Polymer-ND MMMs for Gas Separations

Membrane 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 (COOH)	
Poly(phenyleneoxide) (PPO)	O_2 = 33.2	O_2/N_2 = 3.25	None	2
	31.8	3.61	1% ND (COOH)	
	29.7	3.81	3% ND (COOH)	
	28.4	4.06	5% ND (COOH)	
Poly(phenylene-isophtalamide)	O_2 = 0.032	O_2/N_2 = 5.9	None	3
	0.029	6.3	1% ND (COOH)	
	0.029	10.0	3% ND (COOH)	
	0.017	1.2	5% ND (COOH)	

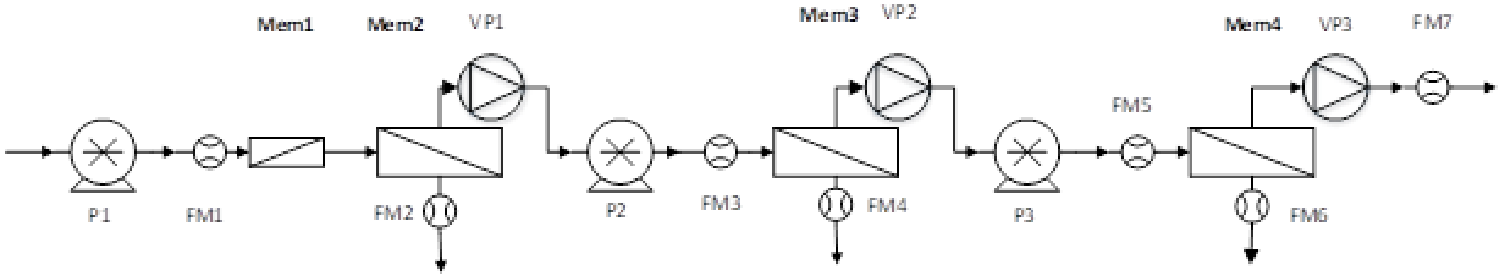
1. Pulyalina, A.; Polotskaya, G.; Rostovtseva, V.; Pientka, Z. and Toikka, A. (2018), *Polymers,* 10, 828-841.
2. Polotskaya, G.A.; Avagimova, N.V..; Toikka, A.M.; Tsvetkov, N.V.; Lezov, A.A.; Strelina, I.A.; Gofman, I.V.; and Pientka, Z. (2018), *Polymer Composites,* DOI 10.1002/pc24437.
3. Avagimova,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

In three differing reports, all experiments showed that NDs tended to decrease permeability and selectivity

TEA as a Method to Define Benchmarks

- Question: What is the best goal for membrane performance?
- Technoeconomic Analysis (TEA)
  - User defined parameters
  - Included labor, materials, energy, financing
  - Sensitivity Analysis
  - System Design

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



Process flow diagram of gas separation system

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	**1000**	**5.5**
Three	$68/tonne	**1000**	**3.2**

Literature Data for Competing Technologies (large scale optimum installations)

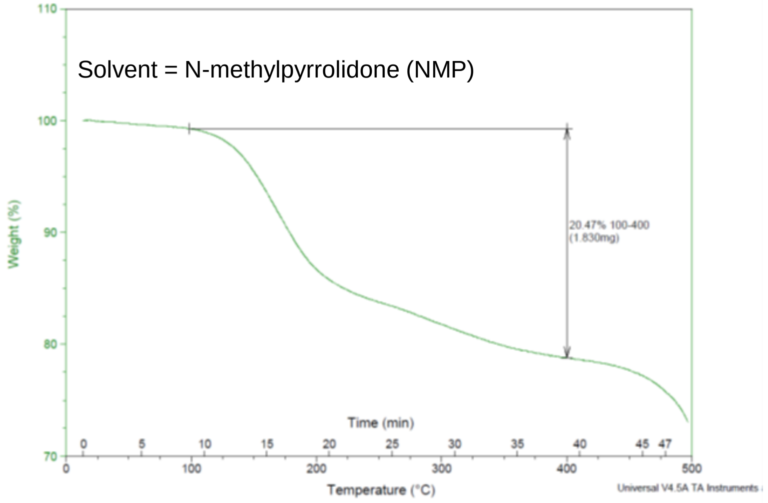
Method	Gas Product Cost	O_2 Concentration	Scale
Cryogenic Distillation	$45/tonne	95%+	3000-4000 tonnes/day
Pressure Swing Absorption	$65/tonne	90%	1000 tonnes/day

Initially, Nanodiamonds in Thin Film PSF Yielded Little Value

Initial Experiments with COOH-NDs

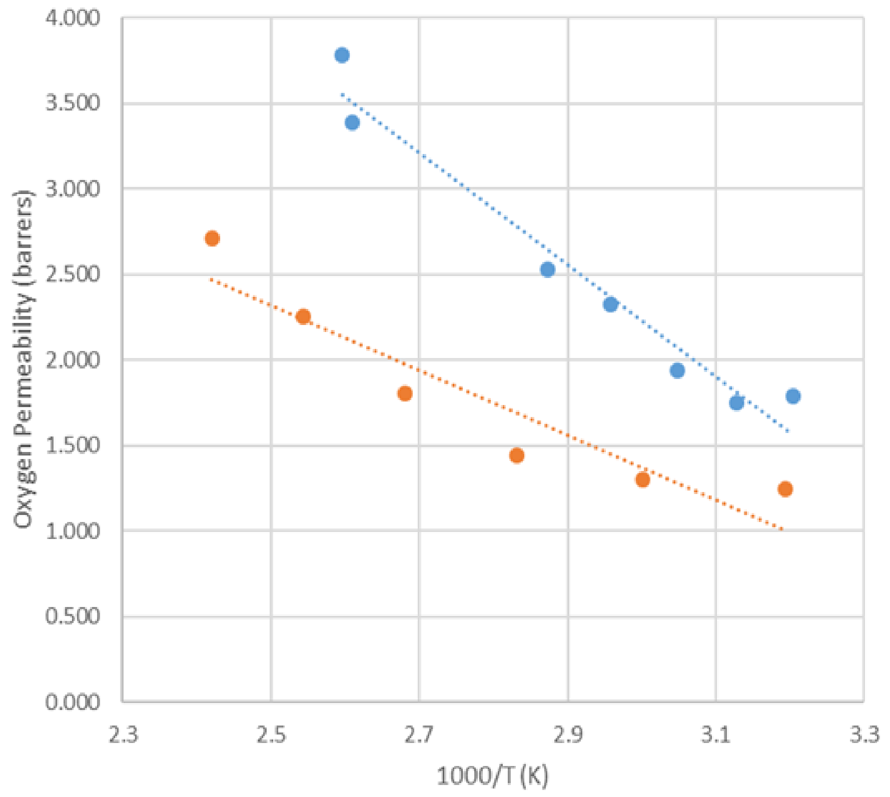
Membrane composition (UDEL PSF Cast from NMP)	O_2 Permeability (Barrers)	O_2/N_2 Selectivity	Notes
No NDs	0.73	6.1	
2% 5nm-COOH ND	0.72	6.5	
5% 5 nm-COOH ND	0.41	2.6	
10% 5 nm-COOH ND	NA	NA	Membrane shattered Testing not possible

Solvent removal from thin-films was a challenge

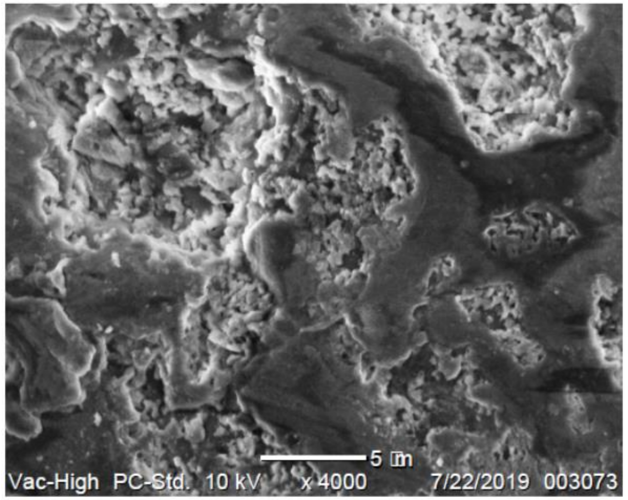


At 5% loading, both permeability and selectivity dropped, and at 10%, the membrane failed. Also, at these loadings, cloudy areas in the films suggested self-assembly of NDs

PSF-F-NDs did yield small improvement in O_2 permeability with solvent removed to <2 %

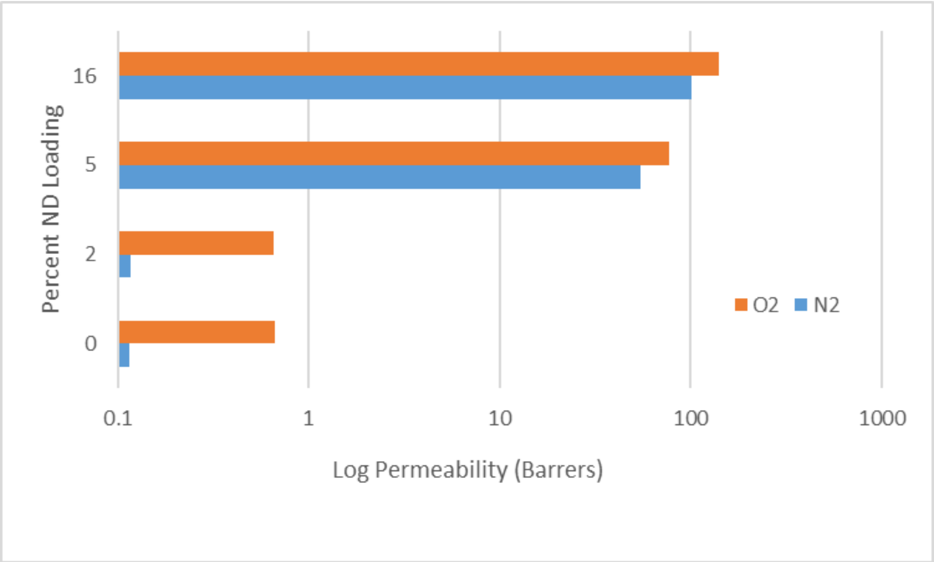


F-NDs have better compatibility with PSF



SEM showing ND induced pores and polymer regions

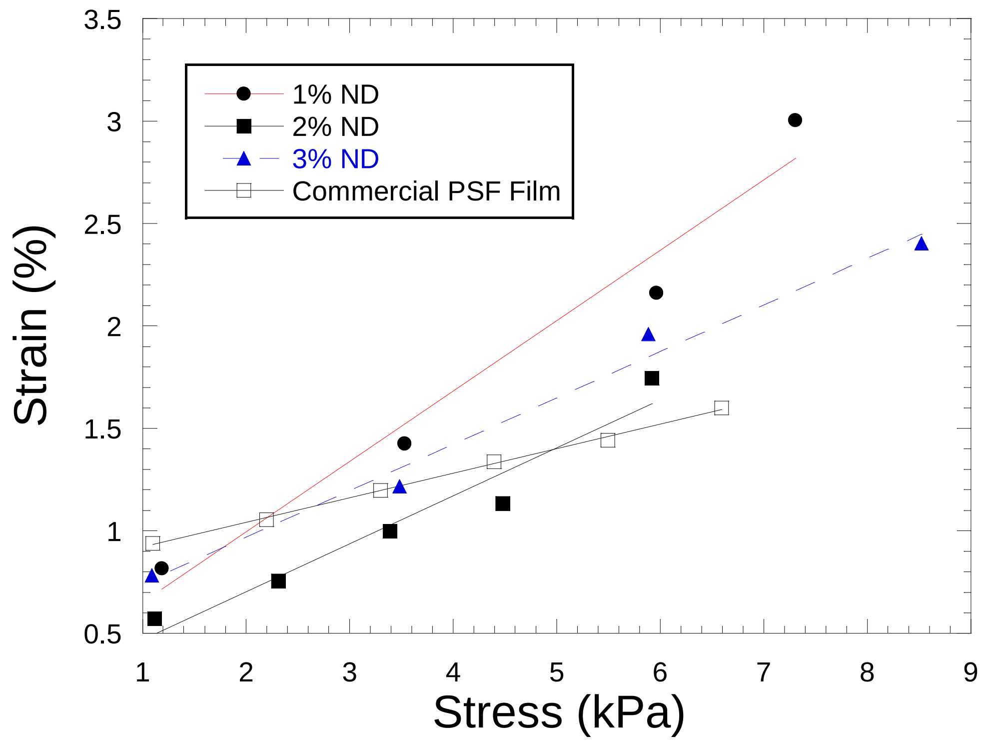
- Thin films are formed to 2% ND loading
- At 3% and above, microporosity is formed
- Microporous regions tend to increase permeance at the cost of selectivity

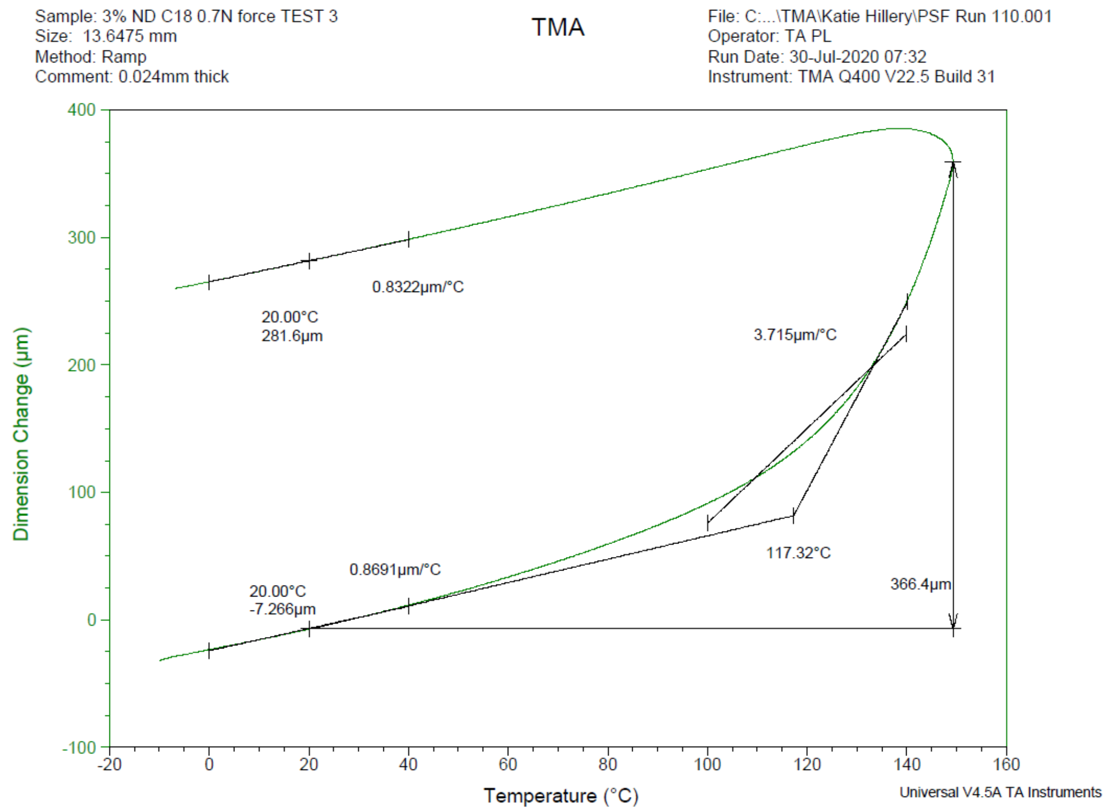


Significant increase in O_2 permeability with > 5% ND content

Selectivity falls from 6 to 1.4

Polymer-ND affinity: F-NDs alter thermally induced creep





C-18 ND Content	Strain/Stress (%/ kPa)
Commercial Film (no NDs)	0.120
1 % (wt %) F-ND	0.344
2 % (wt. %) F-ND	0.234
3 % (wt. %) F-ND	0.227

Samples were exposed to a constant force and temperature was ramped from -10 °C to 150 °C, and then back to room temperature

Plasticization is seen with 1 % of F-NDs; however, > 1 % appears to make the material more brittle

NDs do not homogenously distribute in thin films

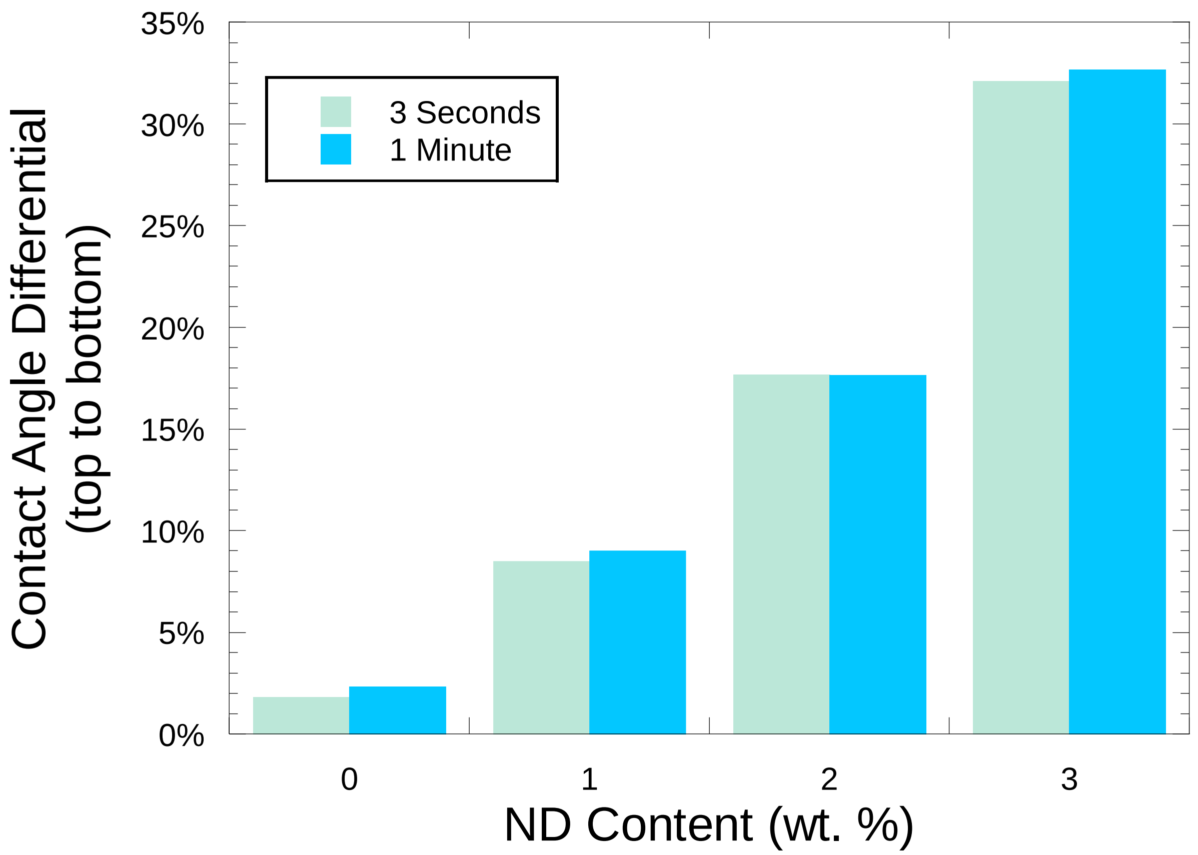
The small difference in the 0 % F-ND membranes (blank) reflect surface morphology differences between the top and bottom surfaces

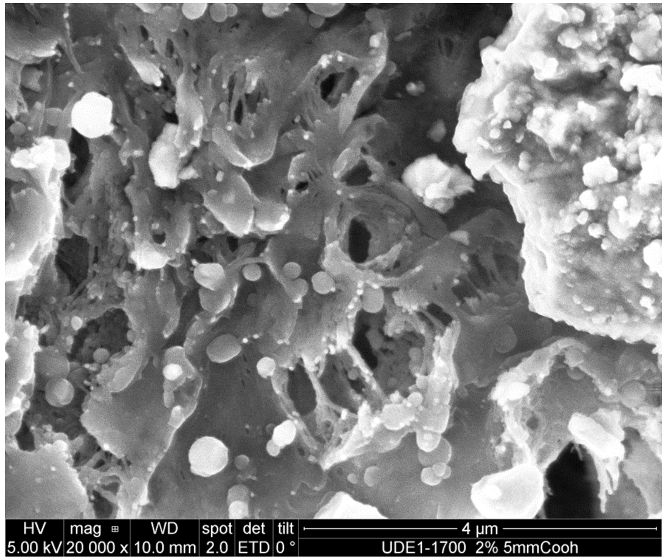
The differential increases with higher F-ND loadings where the bottom surfaces change little compared to the blank

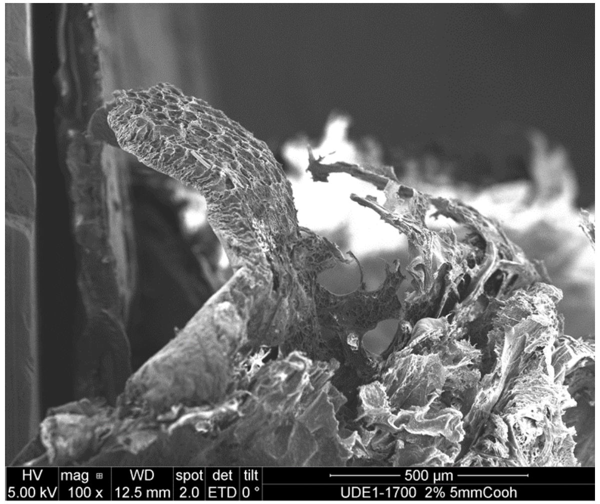
Hydrophilicity may increase with increased ND content

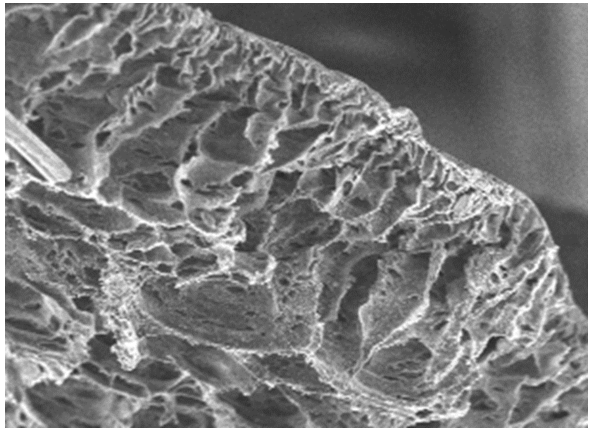
Phase inversion should result in a more even distribution of particles

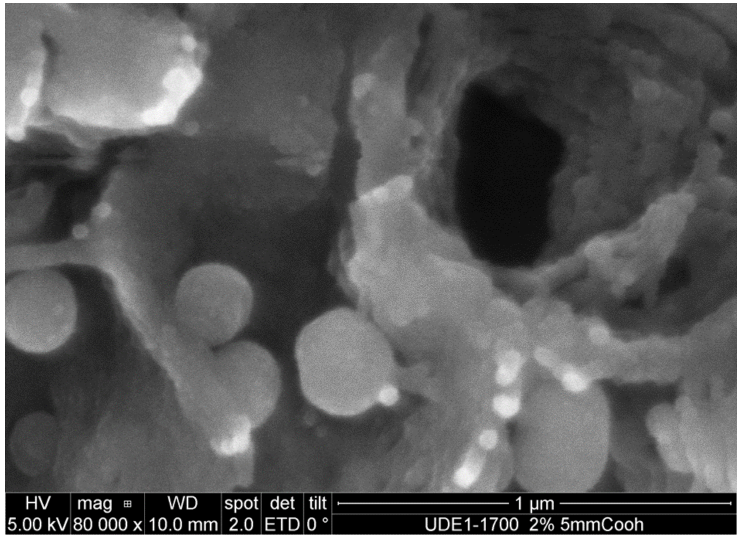
SEM studies pending





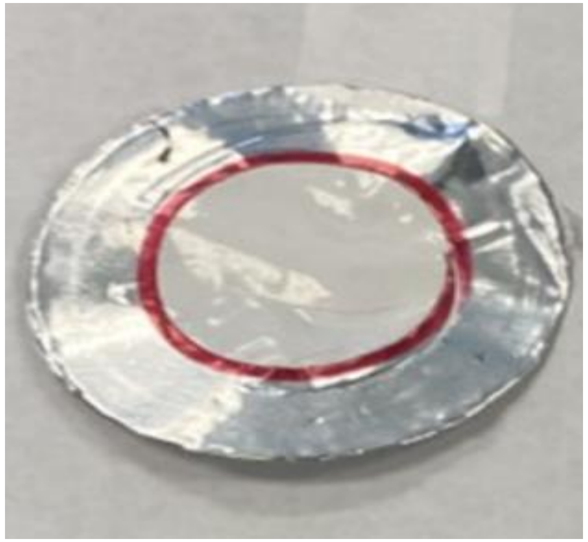






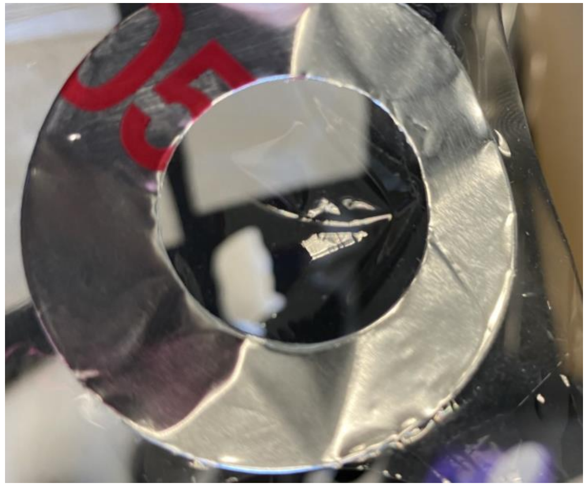
Successful Phase Inversion of 2% ND/PSF

Phase Inverted PSF-ND 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% F-ND (No Heat)	48802	0.91
2% F-ND (Heated to 100 C/10 min)	57007	1.09



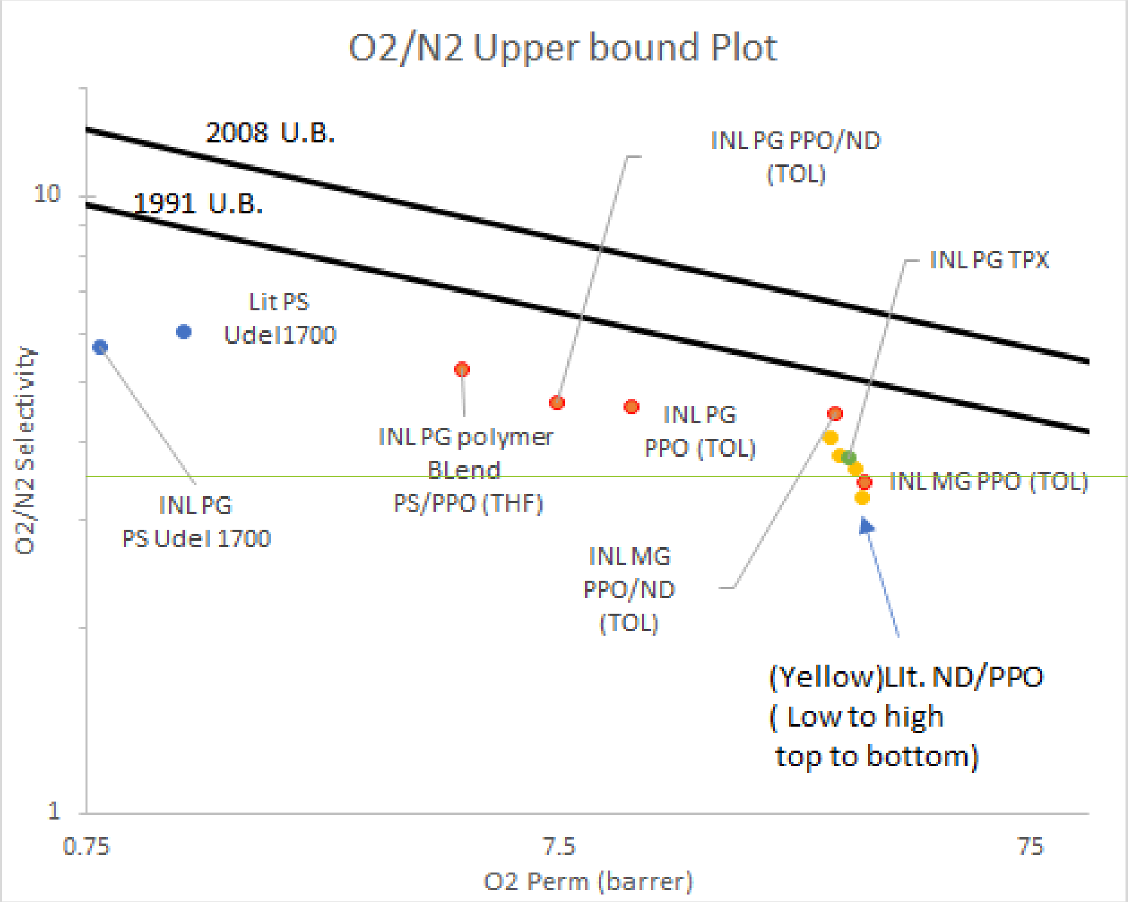
Dense films typically are transparent

Selective Layer Performance Improvements – PPO and Blends

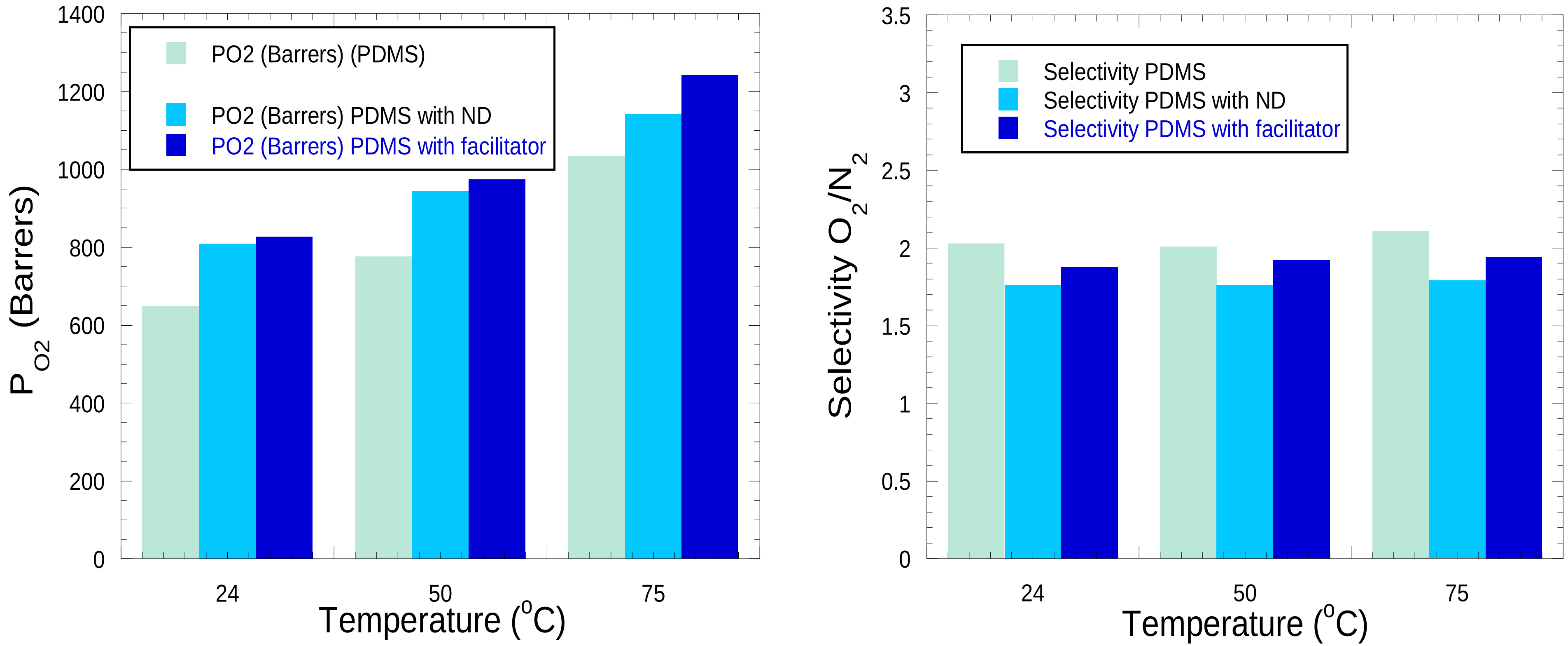
Summary of PPO performance (selectivity vs O2 permeability).

Legend:

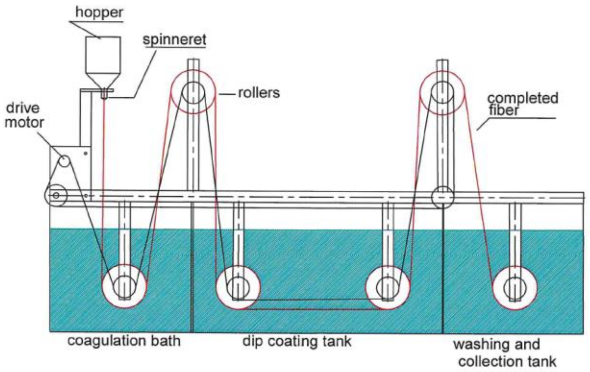
- U.B. = Robeson theoretical upper bound in permeability/selectivity correlation published in 1991 and 2008; tol = toluene casting solvent;
- THF = tetrahydrofuran casting solvent;
- PS = polysulfone;
- Udel 1700 = commercial brand of PSF; PG = pure gas testing method;
- MG = mixed gas analysis method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



Gutter Layer: NDs give 25 % improvement in O_2 perm



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.



Preparing Project for Next Steps

- **Accomplishment Summary**
  - TEA is complete and is guiding research
  - Created high permeance ND-containing supports
  - PPO is a promising selective layer – exceeds minimum selectivity
  - 25 % improvement is gutter layer permeance
- **Continue to investigate Permeability and Selectivity as a function of**:
  - Phase inversion and coating
  - ND loading
  - ND selection – F-ND
  - Polymer – substrate gutter, and selective layers
- **Design HF formation process (at left)**
  - Lab-scale HFs
  - Spinneret Design
  - Process design

Preparing Project for Next Steps

- **Market Benefits/Assessment – Value not just limited to gasification**
  - 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).*
  - Applications for low-cost oxygen enrichment: medical (45%), enhanced combustion (20%), water treatment (25%)
- **Technology to Market Path**
  - Protection of Intellectual Property (Provisional Patent filed in February 2020)
  - 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

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

Concluding Remarks

- **Overall Project Objectives:** Successfully demonstrated improvements in all three parts of the HF membranes, complete TEA guides the work.
- **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 – Project began 12/1/2018. Currently in BP2.**
- **Budget Period 1 Technical Milestones: Completed 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)
- **Budget Period 2 –** Three-plus month delay due to COVID-19 related shut down of lab work

Acknowledgements

- DOE – National Energy Technology Laboratory
  - PM: K. David Lyons
  - FPM: Venkat Venkataraman
- Argonne National Laboratory
  - Dr. Balu Balachandran
  - Dr. Tae H. Lee
- Idaho National Laboratory
  - Christopher J. Orme, INL
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  - Birendra Adhikari, Ph.D., INL
  - James P. Pittman, INL
  - Andrew Han, summer 2020 intern, Penn State, PA
  - Kaitlyn Hillery, summer 2020 intern, Fort Hays State, KS