Gelled Ionic Liquid-Based Membranes

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Colorado
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3M

EPRI ELECTRIC POWER RESEARCH INSTITUTE

TOTAL

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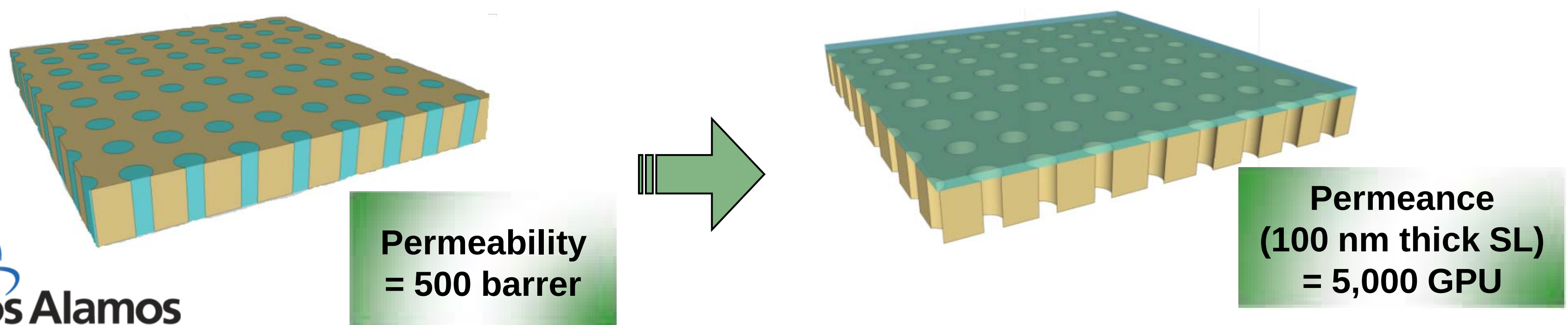
Project Objectives and Goals

- A carbon-capture membrane with CO_2 permeance approaching 5,000 GPU and moderate CO_2/N_2 selectivity could significantly reduce cost of post-combustion carbon capture from flue gas
- Room-temperature ionic liquids (RTILs) are attractive materials due to high permeability (>1000 barrer) and good CO_2/N_2 permselectivity (20–50)
- To meet performance target, RTILs must be ***immobilized as a continuous, defect-free thin film,*** ***ca.*** **100 nm thick** (permeability dependent), on a porous support - achievable via industrially relevant coating/fabrication techniques



Project Overview

- **Project Start Date: Feb. 1, 2011**
- **End Date: Jan. 31, 2014**
- **Total funding: $3,927,591**
  - **DOE ARPA-E: $3,142,071**
  - **DOE cost share numbers: $785,520 (of which $600,000 is provided by TOTAL, S.A.)**
- **This work is a result of a collaboration between the**
  - **University of Colorado (CU), Boulder**
  - **Los Alamos National Laboratory (LANL)**
  - **Electric Power Research Institute (EPRI)**
  - **3M**
  - **TOTAL, S.A.**

Project Team

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Key Milestones

BP01	**Title:** Assessment of Ability of Proposed Technology to Meet Project Permeance & Selectivity Targets **Criteria:** • Demonstration of ability to increase permeance by ≥ an factor of 2 over benchmark data using material modifications and membrane fabrication optimization • Demonstrate membrane CO_2/ N_2selectivity ≥ 20 • Demonstrate membrane adhesion at predicted process temperatures (>50 °C)	Completed
BP02	Down-select and rank selective layer materials with highest potential to achieve project goals and DOE Program targets	Completed
BP02	Down-select and rank selective layer materials and material/coating methodology combinations with highest potential to achieve project goals and DOE Program targets	Completed
BP02	Report results of preliminary membrane process design based on initial membrane performance data	In-progress
BP03	**Title:** Assessment of Ability of Proposed Technology to Meet ARPA-E, DOE-FE NETL Program Targets (cost and carbon emissions reduction) as Defined via Systems & Economic Analysis **Criteria:** Demonstration of ability to meet project's permeance and selectivity targets (5000 GPU, CO_2/ N_2selectivity ≥ 20).	In-progress

Project Tasks

- **Selective Layer Design Synthesis & Evaluation**
  - Tailored gel-RTILs, RTIL/poly(RTIL) composites, incorporation of task-specific CO_2 complexation chemistries
  - Optimize *permeability/selectivity* and *material properties* of Selective Layer Materials
- **Ultra-Thin Membrane Fabrication, Optimization, & Testing**
  - Commercially viable fabrication techniques development for new RTIL-based materials - to enable controlled ultra-thin SL deposition on commercially attractive support platforms
    - Ultrasonic spray coating technique (USCT)
    - Roll to roll casting
- **Membrane, Systems, and Economic Analyses**

Project Overview

University of Colorado Boulder

Selective Layer Material Design and Synthesis

Los Alamos National Laboratory / 3M

Ultra-Thin Membrane Fabrication

CO_2 Permeance ≥ 5,000 GPU

CO_2/N_2 selectivity ≥ 20

Systems Process Modeling

EPRI – Electric Power Research Institute

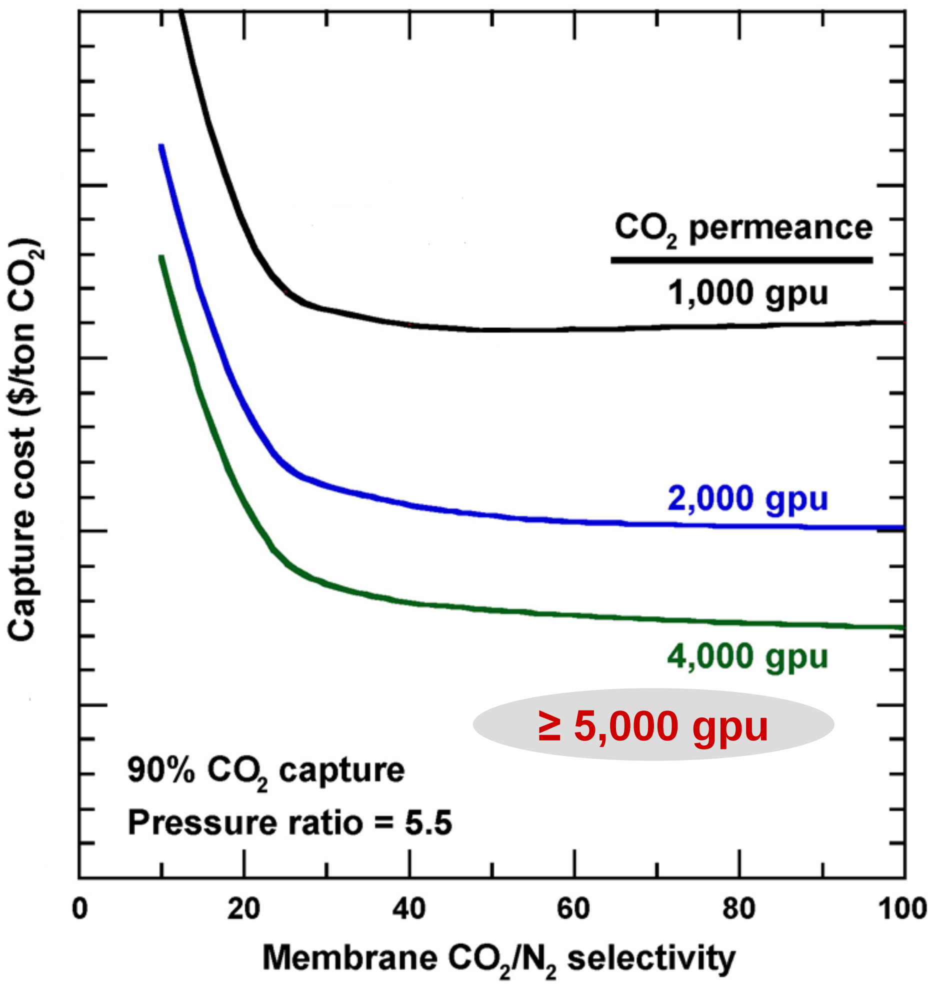
Membrane Terminology

- **Permeability** is a ***material*** **property: describes rate of permeation of a solute through a material, normalized by its thickness and the pressure driving force**

  $$Permeance = \frac{Permeability}{Thickness} = \frac{Flux}{\Delta p}$$

- **Permeance** is a ***membrane*** **property: calculated as solute flux through the membrane normalized by the pressure driving force (but not thickness)**
- **Ideal selectivity describes separation factor: the ratio of permeability (or permeance) of two different components in a membrane, and is a** ***material*** **property**
- **High membrane permeance is achieved by both material selection (high permeability) and membrane design (low thickness)**

High Permeance – Economic Advantages



- Membrane separation systems with high CO_2 permeance and moderate CO_2/N_2 selectivity are desirable
- Estimated capture cost is proportional to CO_2 permeance for CO_2/N_2 selectivities greater than 30

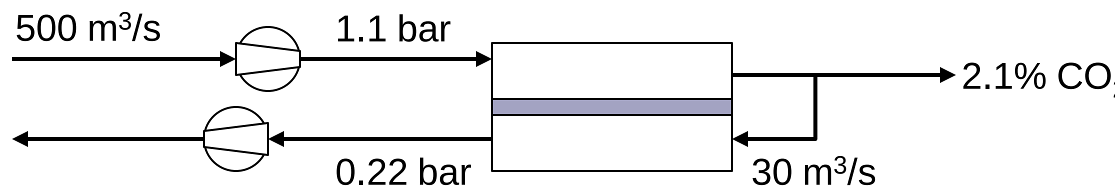
"Higher CO_2 permeance will lead to reduction in capture cost"

Adapted from: T. C. Merkel et al., *J. Memb. Sci.*, *359*, **2010**, 126-139.

Preliminary Economic Evaluation

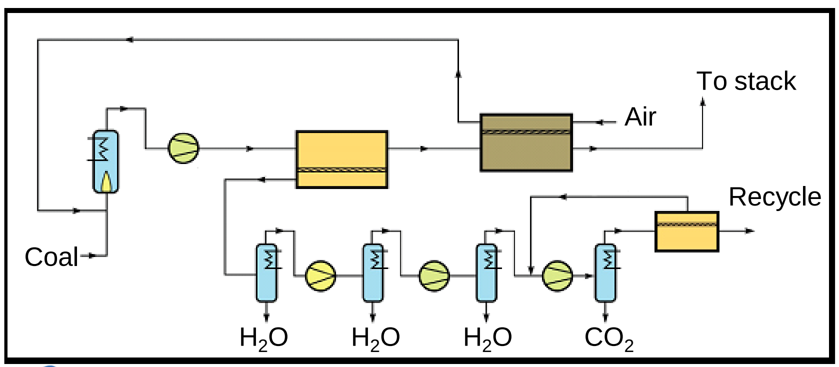
➢ ***Task 1*: Benchmarking with MTR results**

Single counter current sweep stage



Case	Membrane area (MM m²)	Total power MTR* (MW)	Total power This work (MW)
Dry feed	4.3	46.4	44.6
Wet feed	3.9	47.2	53.1

The MTR process



Total Area	1.3 MM m²	**Blower pressure**	2 bar
Capture Rate	90%	**Vacuum pressure**	0.2 bar

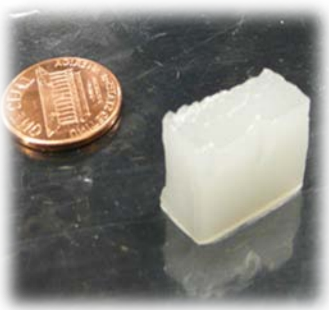
Total power required (MW)

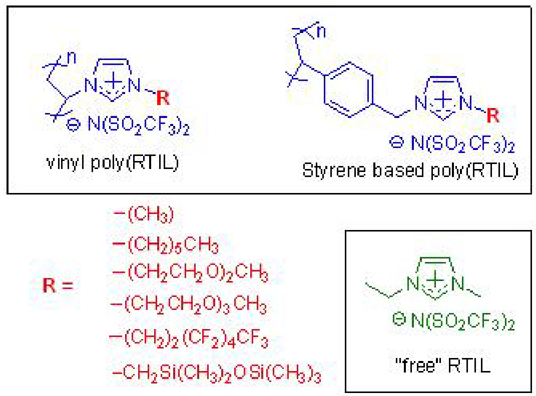
MTR	This work
97	102

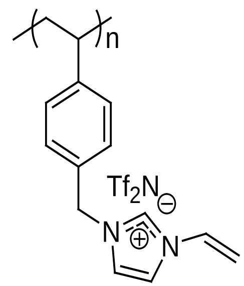
*T. C. Merkel et al., *JMS*, *359*, **2010**, 126-139.

Bulk RTIL Membrane Materials Overview

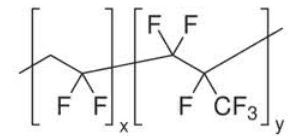
Gelled RTIL	Linear Poly(RTIL)/RTIL Composites	Photo-curable Poly(RTIL)s and Composites	PVDF-*co*-HFP/RTIL Composites







\+ "free" RTIL



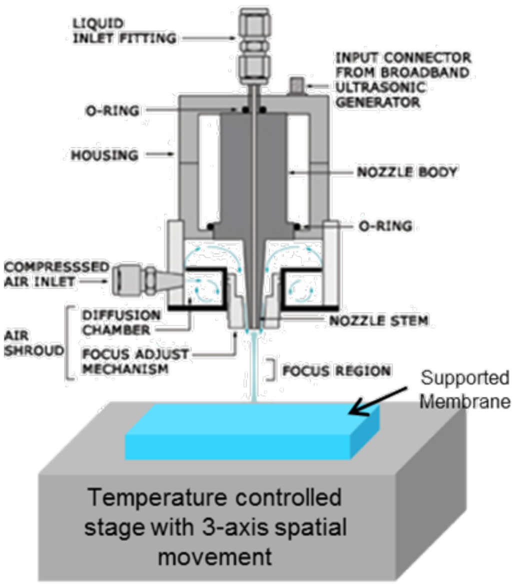
\+ "free" RTIL

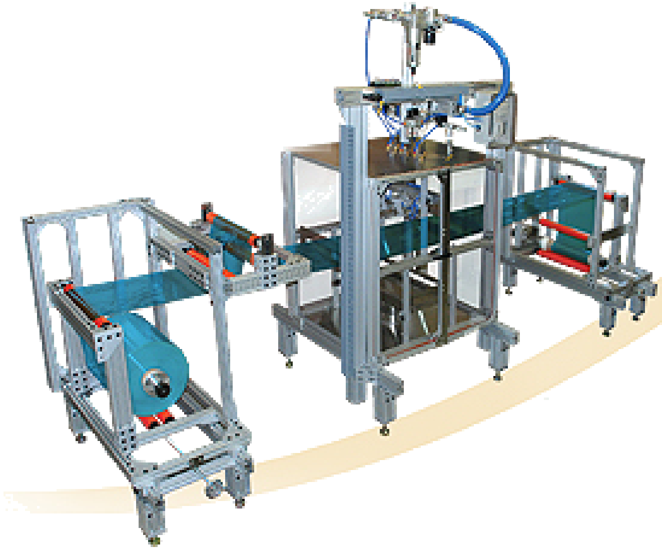
Evolution of Materials →

Bulk Material:	Gelled RTIL	Linear Poly(RTIL)/RTIL	Photo-curable Poly(RTIL)/RTIL	PVDF-*co*-HFP/RTIL
RTIL Loading (wt%):	98	40	80	80
CO_2 Permeability (barrers):	950	105	650	650
CO_2/N_2 Selectivity:	21	21	35	35
Physical Properties:	Mechanically weak	Brittle	Good	Good

Fabrication Approach 1: Ultrasonic Spray Coating

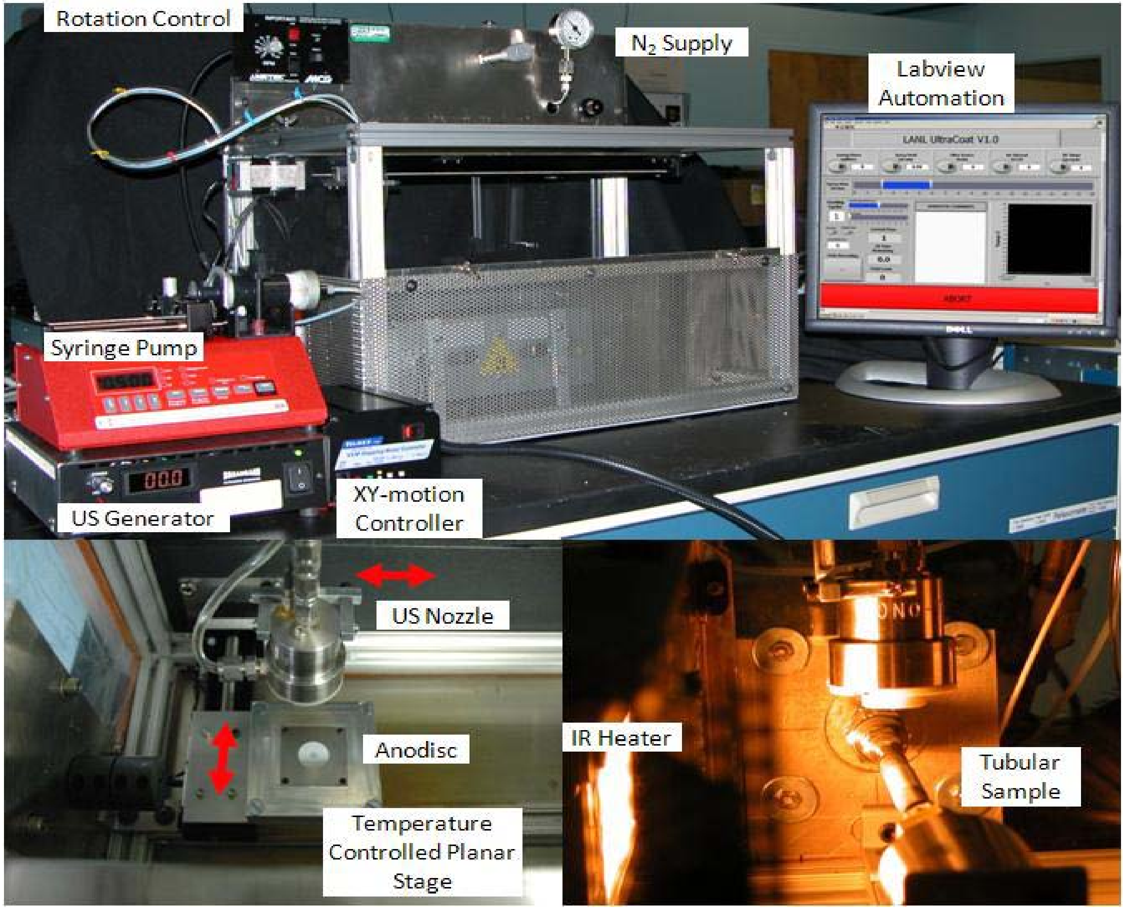
- **Ultra-Thin Membrane Fabrication, Optimization, & Testing**
  - **Commercially viable fabrication technique development using ultrasonic spray-coating technology (USCT) -- enables controlled ultra-thin SL deposition on commercially attractive support platforms**
  - **Maximize *Permeance* Attainable with *Selectivity Retention* -- defect mitigation with cohesive coating achieved**





USCT-based Deposition

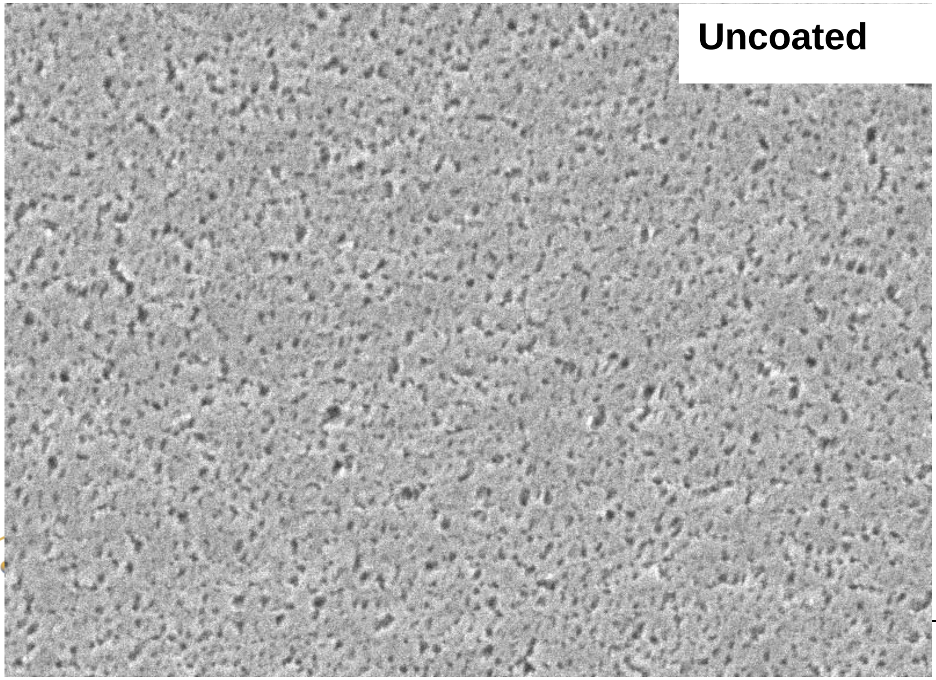
- Semi-automated small scale ultrasonic spray coating system for ultra-thin film deposition on tubular and planar substrates with *in-situ* processing
- System control parameters include:
  - Liquid flow rate
  - Spray geometry/profile
  - Coating profile / Raster speed
  - Substrate temperature
  - In-situ IR and UV irradiation
  - LabView® automation
  - Self-contained enclosure

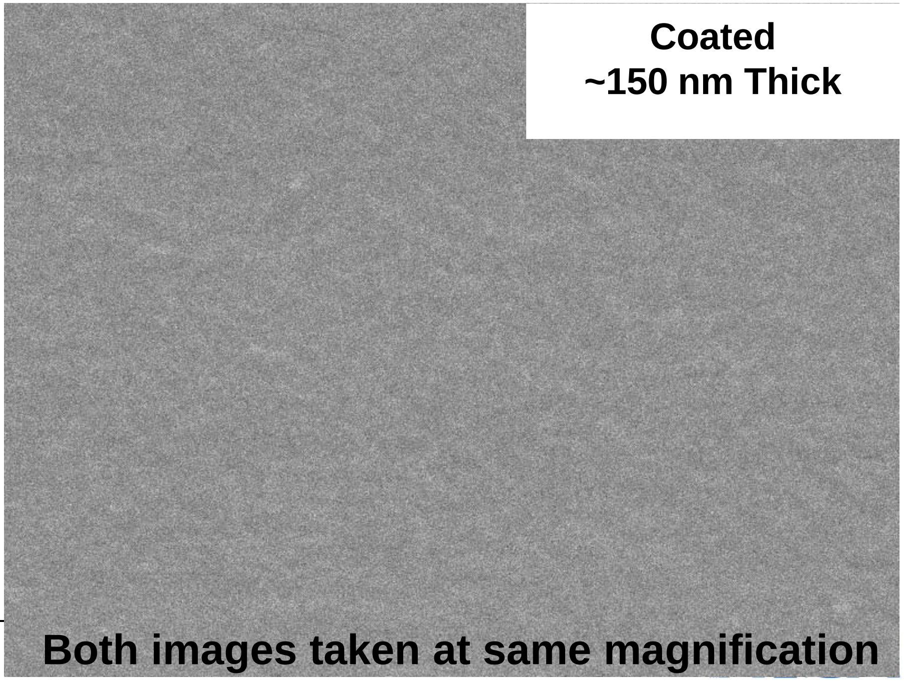


RTIL based Ultra-thin Coating Development

- **Developed methods to fabricate RTIL based selective layers on commercially attractive porous polymer supports**
  - **Numerous membranes fabricated to understand the effects of various coating parameters on selective layer deposition and its gas permeation characteristics**

- **Coating process optimization lead to 100-150 nm defect free coatings**



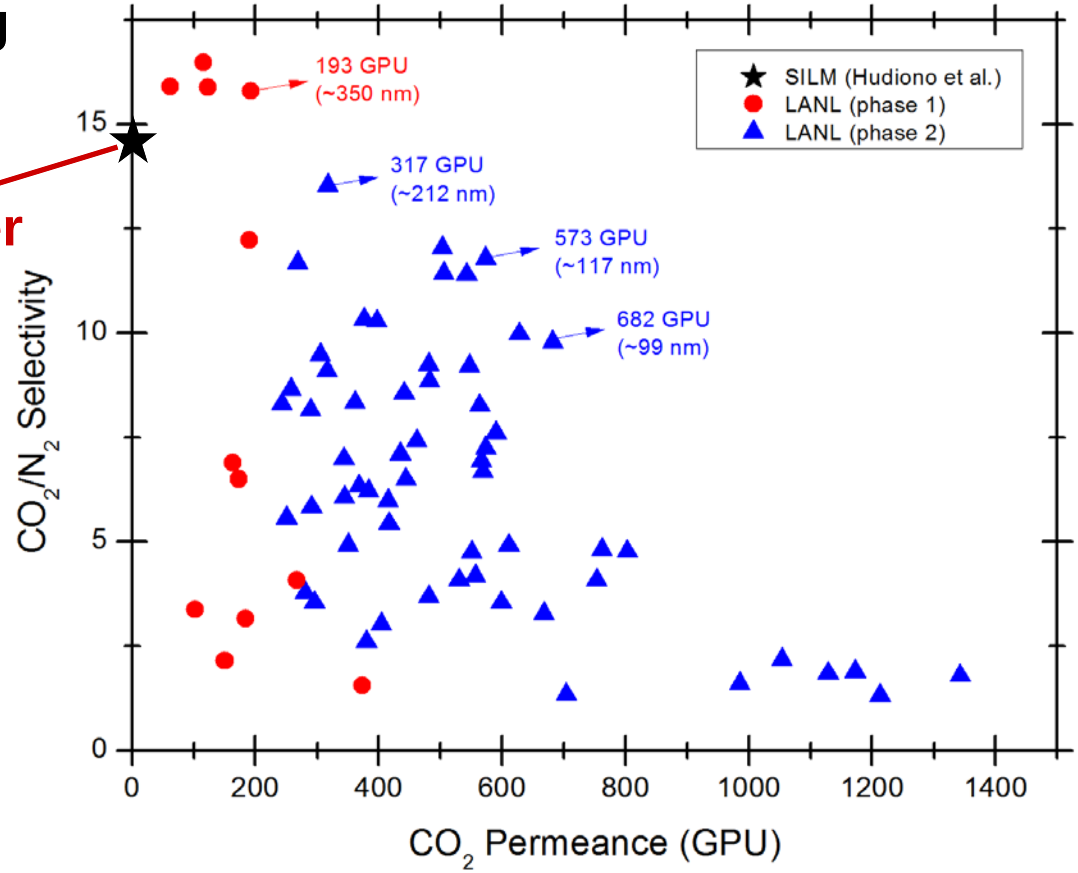


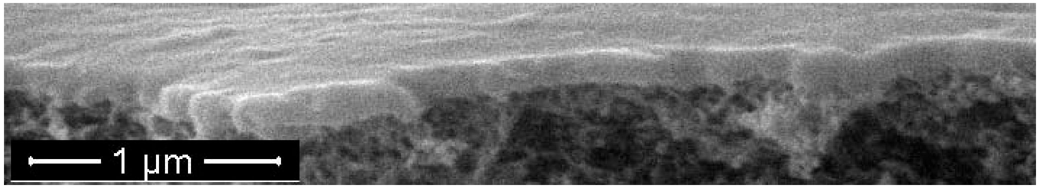
Ultra-thin Membrane Characterization

- **Dramatic influence of coating parameters on membrane performance**

  Permeability = 67.3 barrer

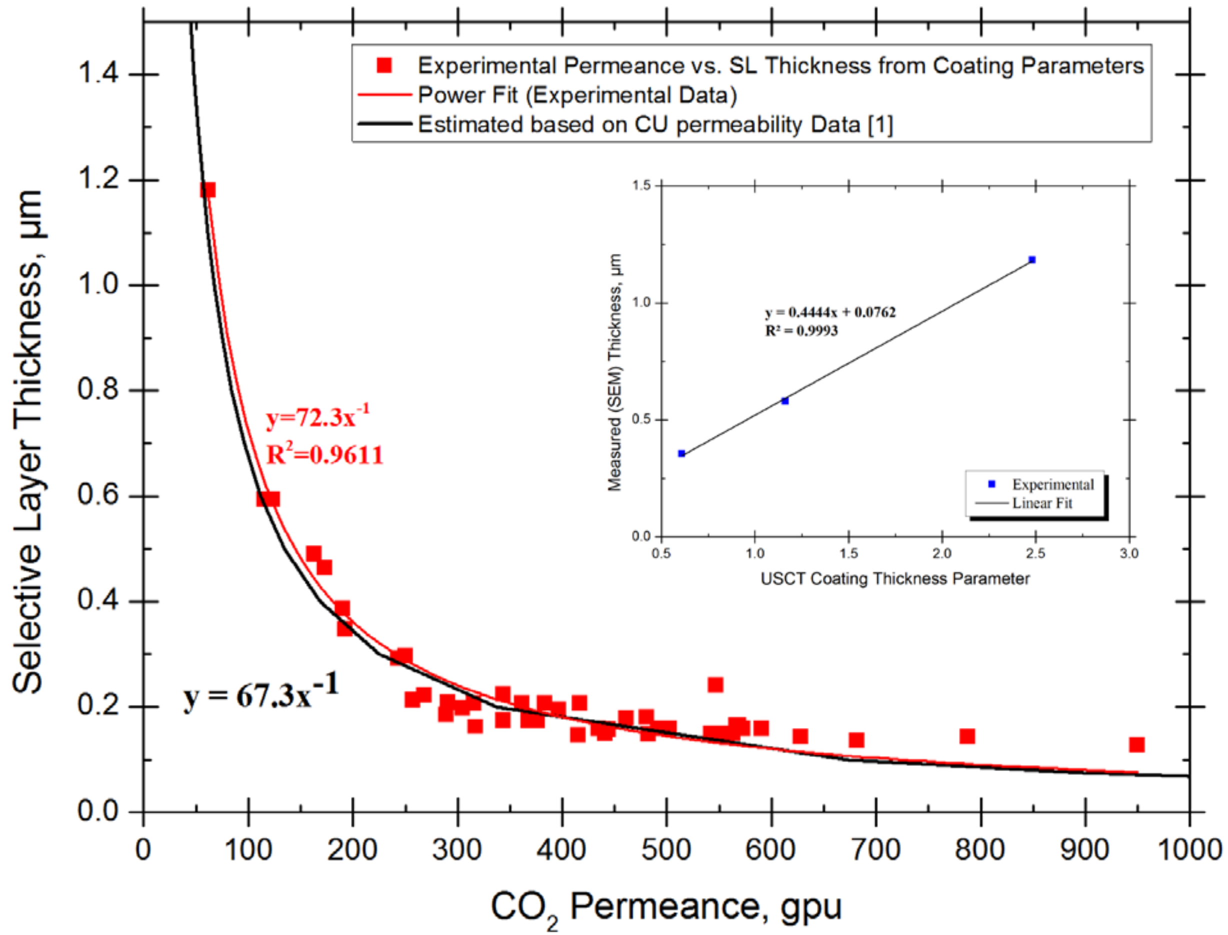
- **Demonstrated defect-free poly(RTIL) composite membrane with CO_2 permeance of 317 GPU – *approximately 212 nm effective thickness***
- **Fabricated numerous membranes with CO_2 permeance ≥ 500 and near ideal CO_2/N_2 selectivity ≥ 10**





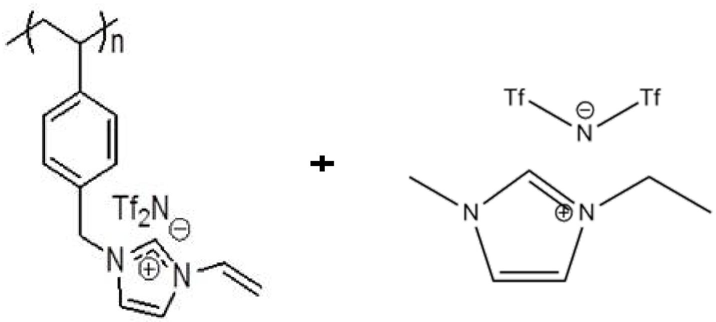
Controlling Membrane Fabrication Process

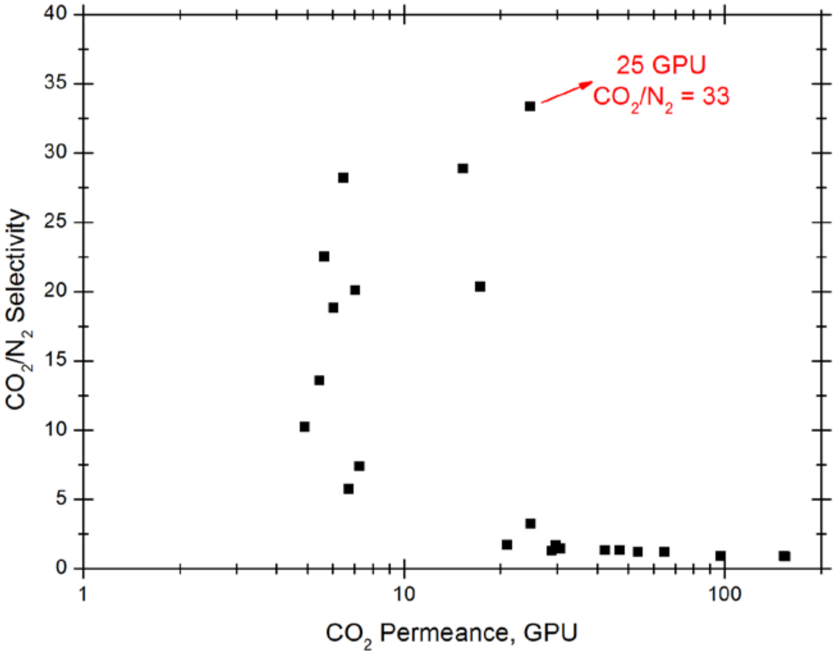
- **Limited SEM thickness data set used for correlation with USCT coating thickness parameter (inset plot)**
- **Excellent correlation achieved between CO_2 permeance and estimated SL thickness**
- **Estimated permeability from composite membranes (72.3 barrer) in good agreement with CU permeability (67.3 barrer). (Membranes with CO_2/N_2 > 5 used in the analysis)**



[1]: Hudiono Y.C. et al., *J. Membr. Sci.* **2011**, *370*, 141-148

Fabrication of PSVI/RTIL Composite Membranes

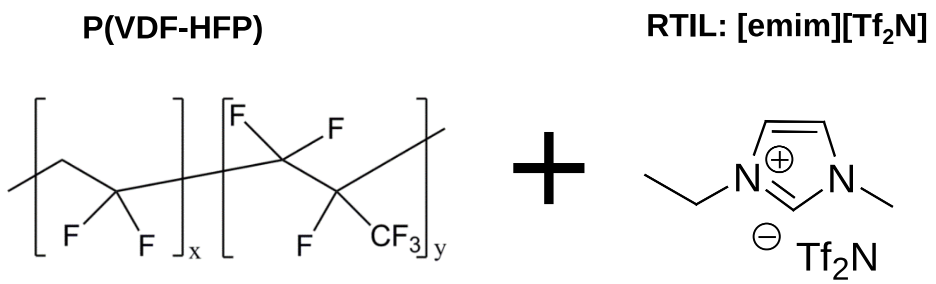


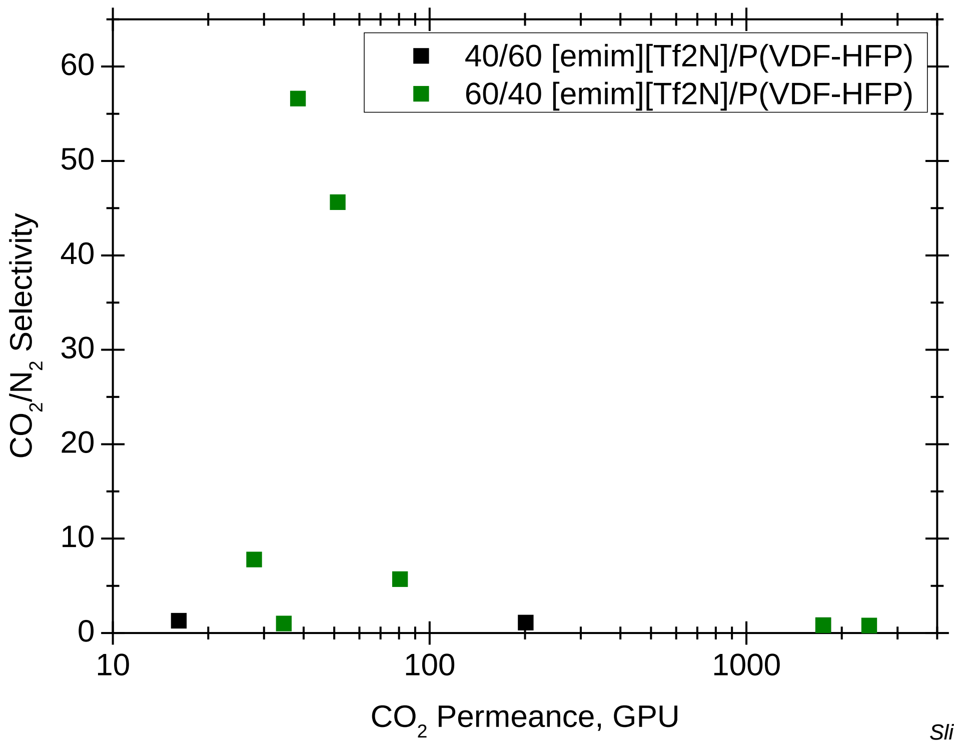


- **High fraction of free RTIL (>50%) required to achieve high permeability**
- **Fabrication of PSVI-based composite membranes with varying RTIL ratios using USCT yields membranes with high CO_2/N_2 selectivity**
- **However, the permeances are much lower than expected from SILM data**
  - **With target thicknesses 1-2 µm, permeances are expected to be in the order of >100 GPU**
  - **Our best membrane fabricated using 80/20 PSVI/emim-Tf_2N, with CO_2/N_2 selectivity of 33, only has CO_2 permeance of 25 GPU (estimated selective layer thickness = 2 µm)**

P(VDF-HFP)/emim-Tf_2N Composite Membranes

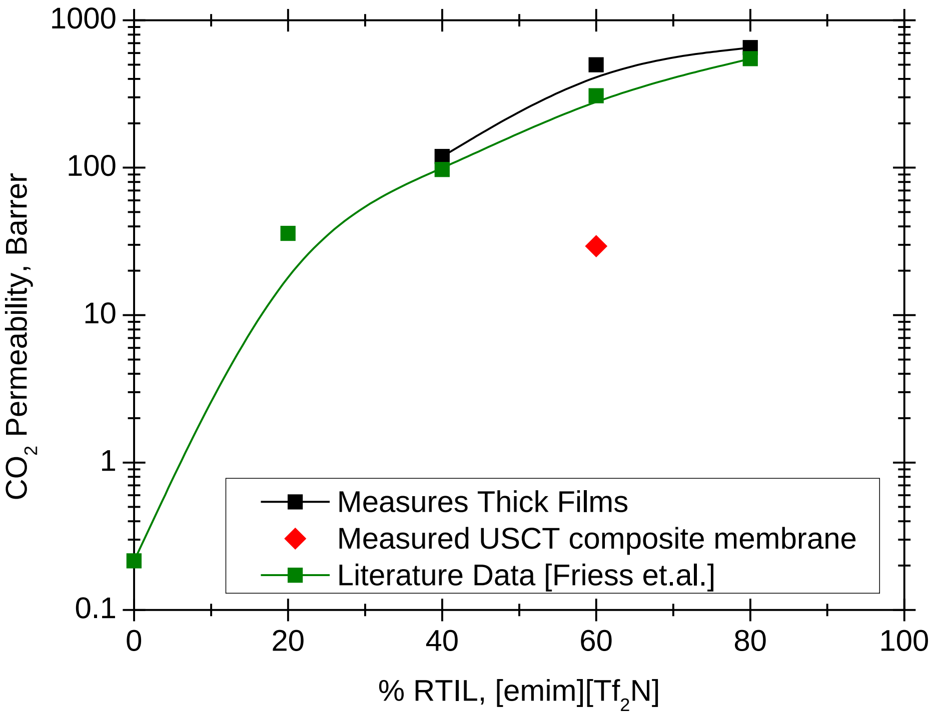
- **Fabricated and evaluated p(VDF-HFP)/emim-Tf_2N composite membranes containing 40 and 60% emim-Tf_2N**
  - **Selective layer thickness varied from 0.2 to 1.8 µm**
  - **High CO_2/N_2 selectivity obtained for 60/40 emim-Tf2N/p(VDF-HFP) composite membrane with 0.9 µm thick selective layer!**
  - **CO_2 permeance lower than that estimated from the CO_2 permeability obtained from bulk p(VDF-HFP)-RTIL composite films**

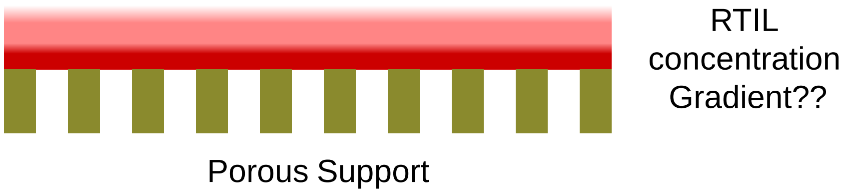




Achieving High Permeance??

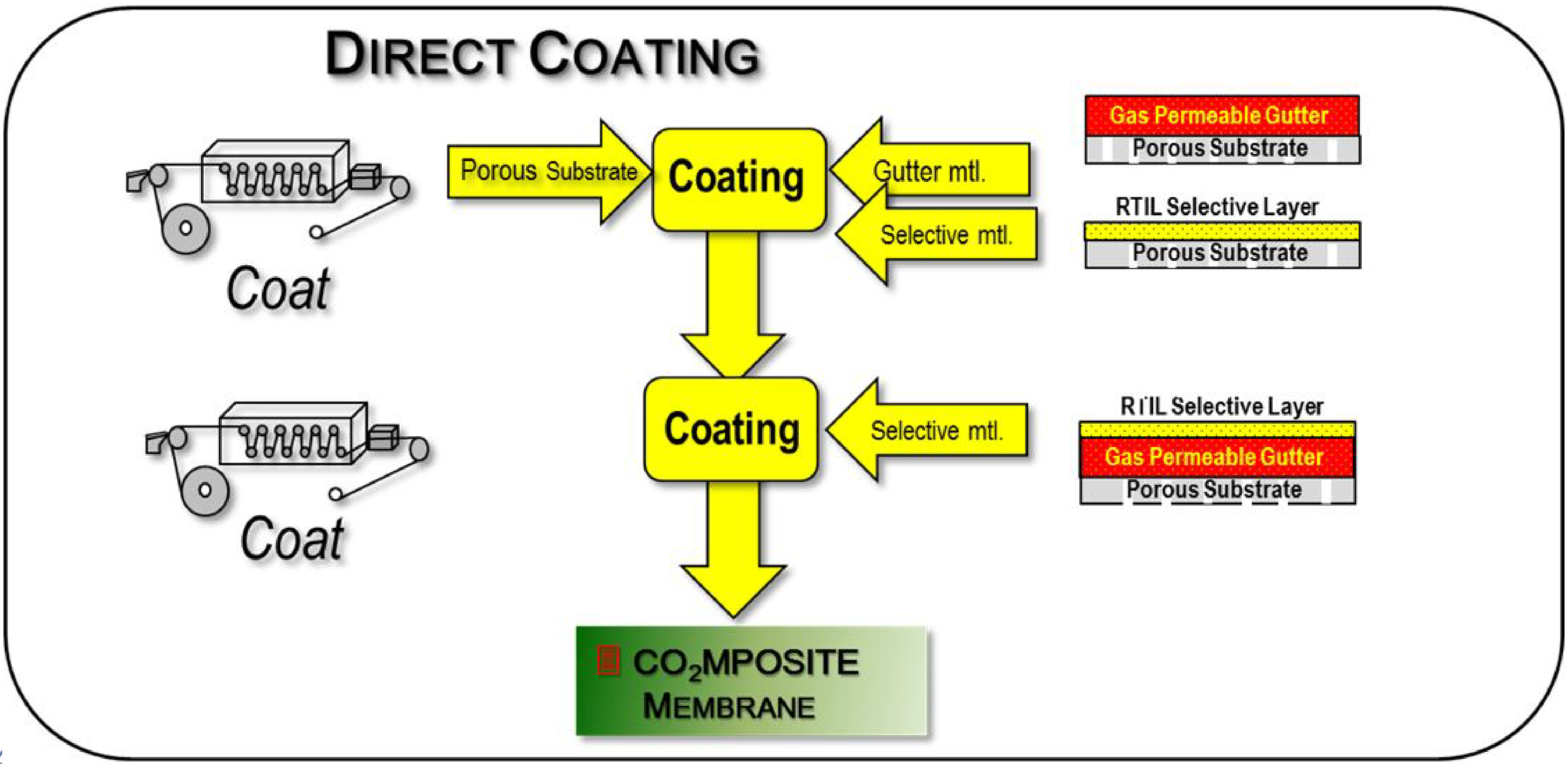
- **Composite membranes fabricated by USCT have significant lower permeance than that estimated from the permeability data.**
  - **Permeability of composite membrane with 60% free RTIL similar to permeability of film containing 20% RTIL**
  - **Possible phase separation or RTIL migration to the support with solvent during coating leading to lower RTIL concentration in the selective layer.**
  - **Pore penetration in the support pores increasing effective thickness.**





Fabrication Approach 2: Roll to Roll Casting

- Direct single or multi-step coating on nano-porous substrate

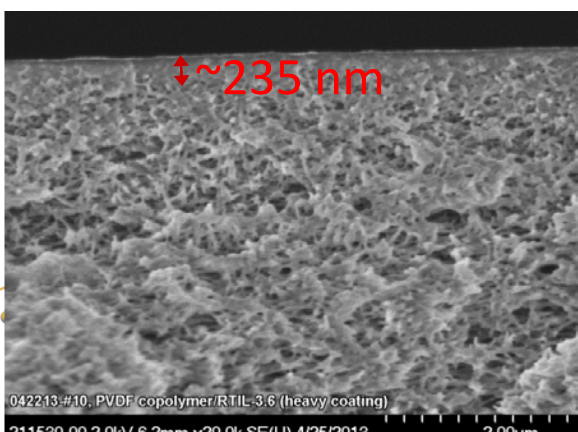


Direct Casting on Porous Substrate

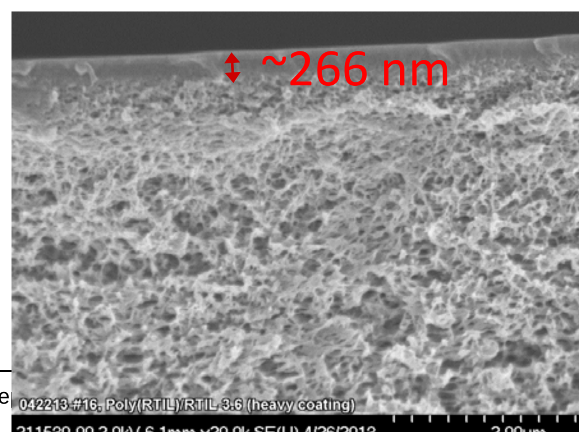
- **Selectivity observed - but low permeance**
  - **SEM cross sections show much thinner coatings than thickness targeted**
  - **Pore infiltration?**
  - **Free RTIL being carried into substrate by solvent?**

Sample	Target Thickness	Est. Obs. Thickness	CO_2 Permeance	N_2 Permeance	CO_2/N_2 Selectivity
10-PVDF Comp.	2.8 um	235 nm	93	30	3.1
11B-PVDF Comp.	1.9 um	235 nm	73	30	2.4
16-PolyRTIL Comp.	2.8 um	266 nm	292	27	11
17-PolyRTIL Comp.	1.5 um	208 nm	292	28	10
20-PolyRTIL Comp.	1.5 um	117 nm	7730	917	8.4
24A-PolyRTIL Comp.	1.5 um	-	459	40	12

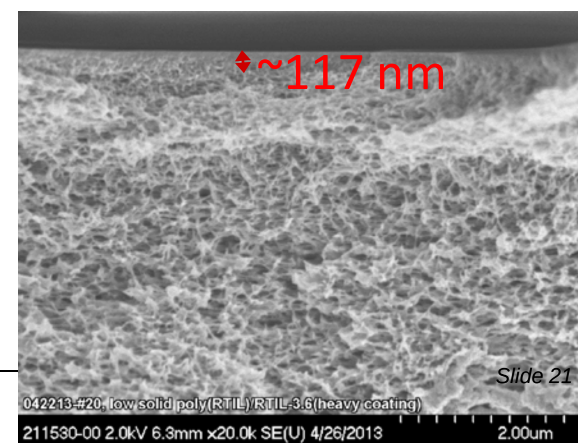
(10) PVDF Composite



(16) PolyRTIL Composite

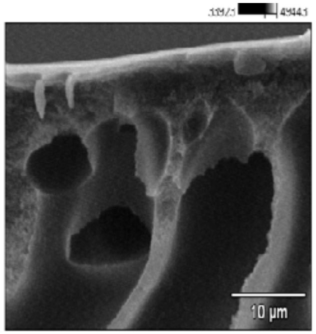


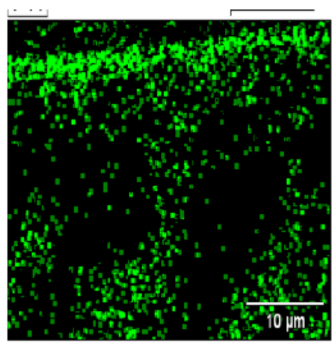
(20) PolyRTIL Composite

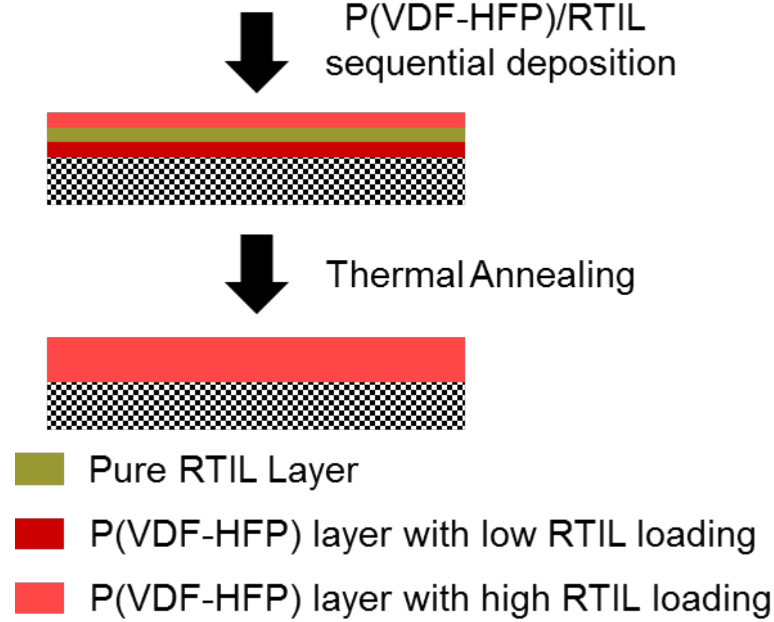


Newly Encountered Challenges for Thin Film Casting

- Discrepancy observed between measured bulk materials and thin film membrane properties
  - Hypothesis: Free RTIL being lost to porous substrate leaving majority polymer in coating
  - Elemental x-ray mapping confirms presence of fluorine in substrate



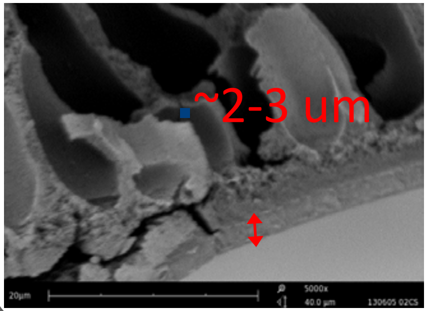




- Future Directions:
  - Optimize processing with RTIL rewetting procedure
  - Analytical characterization to understand RTIL-poly(RTIL) interactions

Preliminary Results: Secondary Coating & Post-Treatment

- **Experiment:** Post-treat 2-3 um PVDF-HFP coating with pure free RTIL to promote diffusion
  Result: Selectivity enhanced to bulk values; permeance appears unchanged



RTIL Post-Treatment	CO_2 Permeance	N_2 Permeance	CO_2/N_2 Selectivity
None	16	16	1.0
50 C, 20 min	16	0.5	33
80 C, 5 min	22	0.7	30

- **Experiment:** Apply secondary polymer/RTIL coating containing 75-80% free RTIL (Thickness ~200-300nm)
  Result: Selectivity enhanced; permeance slightly reduced

Sample	Post-Treatment	CO_2 Permeance	N_2 Permeance	CO_2/N_2 Selectivity
PVDF-HFP Comp. (240 nm)	None	93	30	3.1
	+ 2nd Coating, 5 min at 50 C	32	5.6	5.7
	+ 2nd Coating, 20 min at 50 C	64	6.5	9.8
PolyRTIL Comp. (270 nm)	None	290	27	11
	+ 2nd Coating, 5 min at 50 C	230	12	18
	+ 2nd Coating, 20 min at 50 C	240	14	17

Summary

- Two classes of RTIL-based gel materials with bulk gas transport properties that meet the CO_2/N_2 permeability and selectivity targets were developed.
- Several examples of these two classes of RTIL-based gel materials were successfully cast at a thickness of 100 nm.
- A discrepancy between the bulk and composite membrane gas transport properties was observed.
- Several approaches to address this processing challenge have been developed and are being explored in earnest.
- Thorough analysis of the thin-film membranes produced to date is in progress.
- Preliminary modeling results technological and economic benefits over state-of-the-art CO_2 capture technology
- This work generated 7 published papers + 2 papers just accepted + 2 papers in preparation and 2 patent applications.

Path Forward

- **To Project Completion**
  - Develop a quantitative understanding of how the deposited material is distributed in the composite membrane both within the support and through the selective layer thickness.
  - Multiple Layer coatings and post-processing to increase the permeability and selectivity of the final membrane.
  - Complete parametric studies to further understand the influences of membrane performance characteristics on process economics.
- **Transition to Commercialization**
  - In order to enhance the potential for industrial interest, we will also evaluate the membranes for CO_2/CH_4 separation (natural gas treatment) as requested by a petrochemical company. The selectivity target is CO_2/CH_4 selectivities >20 at low pressure and ambient temperature.

Acknowledgements

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