Achieving a 10,000 GPU Permeance for Post-Combustion Carbon Capture with Gelled Ionic Liquid-Based Membranes

Kathryn A. Berchtold[1], Richard D. Noble[2], Douglas L. Gin[2], Rajinder P. Singh[1], Victor A. Kusuma[1], Cynthia F. Welch[1], Will McDanel[2], Phuc Tien Nguyen[2], Matt Cowan[2], Trevor Carlisle[2], Garret Nicodemus[2], A. Lee Miller II[2] and Abhoyjit Bhown[3]

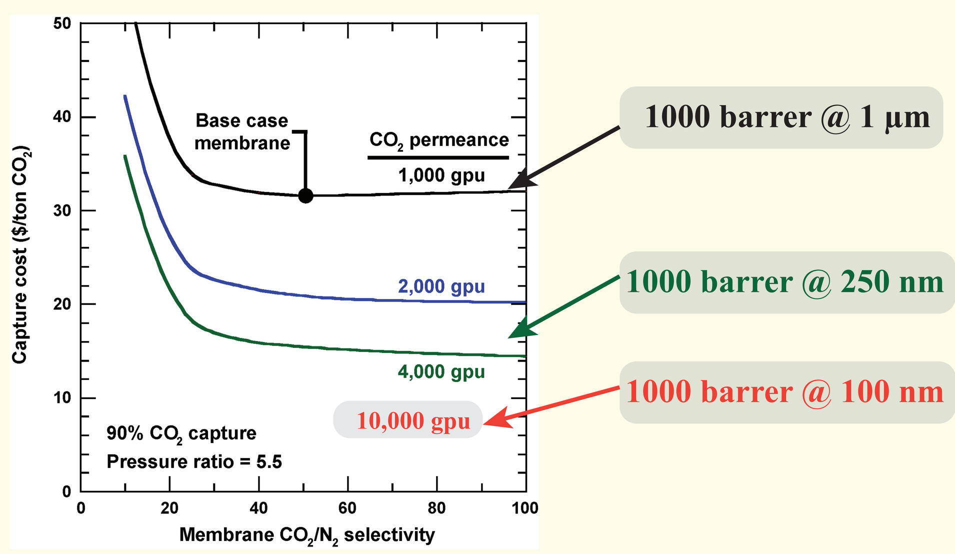
[1]Los Alamos National Laboratory, [2]University of Colorado - Boulder, and [3]Electric Power Research Institute

Motivation

- Current technologies fall substantially short of DOE targets
  - ❑ 2020 DOE NETL Sequestration Program post-combustion capture goal 90% capture with less than a 35% increase in COE
- Industry/DOE benchmark technology for capture of CO_2: Amine Absorption
  - ❑ Parasitic loss: 90% CO_2 capture from flue gas will require approximately 22-30% of the produced plant power
  - ❑ Estimated CO_2 capture cost: \$40-\$100/ton of CO_2 and an increase in the cost of electricity (COE) of 50-90%

Membrane Opportunities

- Estimated CO_2 capture cost using membranes* is substantially lower than current DOE benchmarks
- Advantages of membrane-based separations over other separations technologies
  - ❑ Smaller footprints, simpler operation, better scalability & modularity
- Membrane performance scales linearly with permeance – Less than \$10/ton CO_2 captured at 10,000 GPU (extrapolated)



* Data from Merkel et. al., Journal of Membrane Science, 359 (2010) p 126.

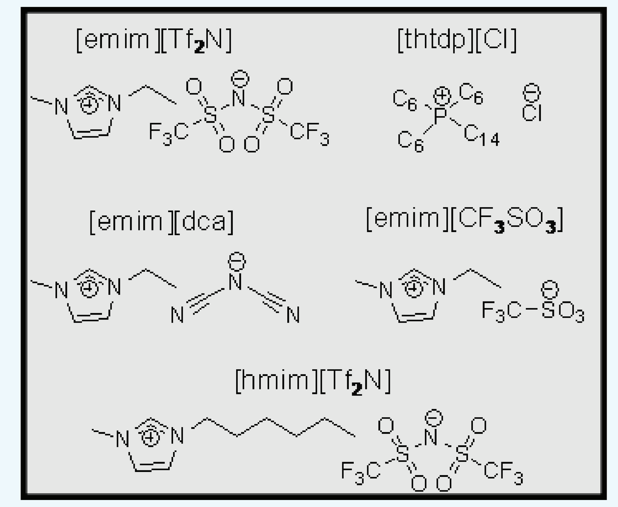
- Existing membrane materials have limited selectivity, productivity, chemical resistance, & mechanical durability
- Compelling need for new materials and processing methods to enhance productivity and selectivity

Objectives & Approach

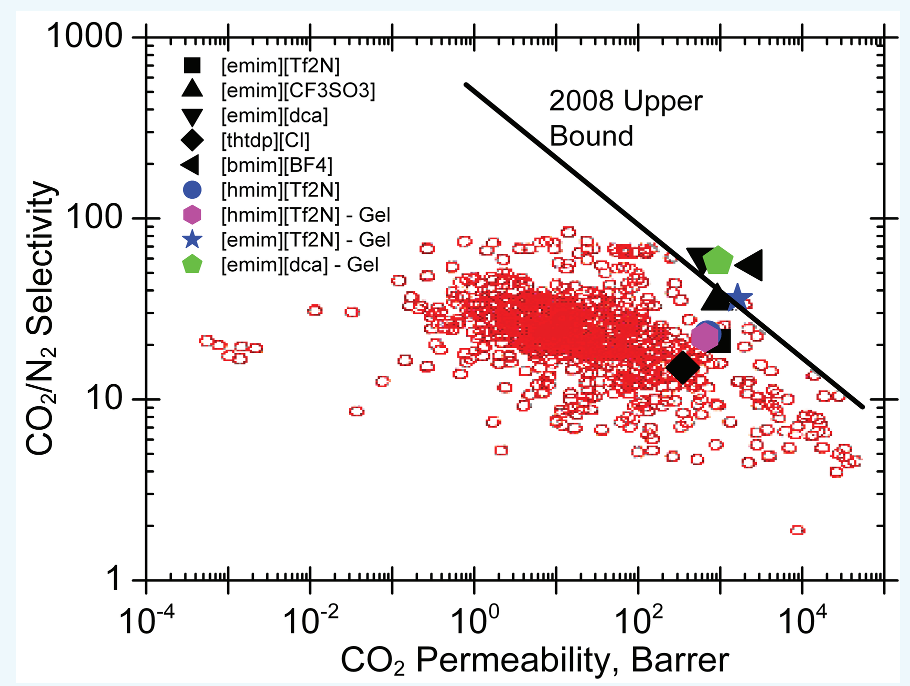
- Design mechanically and chemically robust room temperature ionic liquid (RTIL)-based selective layers (SLs)
  - Evaluate tailored gel-RTILs, RTIL/Poly(RTIL) composites, incorporation of task-specific CO_2 complexation chemistries
  - ❑ CO_2 permeability exceeding 1000 barrer
  - ❑ CO_2/N_2 selectivity of at least 20
- Develop ultrasonic spray coating technology (USCT)
  - Commercially viable development of USCT which enables controlled ultra-thin SL deposition on commercially attractive support platforms
  - ❑ Fabricate < 100 nm thick selective layer/microporous support composites
  - ❑ 1000 barrer and 100 nm thick SL: Permeance = 10,000 GPU
- Devise technically and economically viable membrane performance characteristics and process scenarios for CO_2 capture from coal derived flue gas

Membrane Selective Layer Design Synthesis & Evaluation

- Room-Temperature Ionic Liquids (RTILs)
  - ❑ Compounds entirely consisting of ions resembling the ionic melts of metallic salts
  - ❑ Liquids at ambient temperature and over a broad temperature range from -96 to 300 °C
  - ❑ Negligible vapor pressure
  - ❑ Beneficial properties: high solubility/perm selectivity for CO_2, low flammability, excellent thermal/chemical stability
  - ❑ Easily tailored for specific properties by manipulating/adding functional groups
  - ❑ Lack mechanical stability necessary for industrial utilization as thin film gas separation membranes

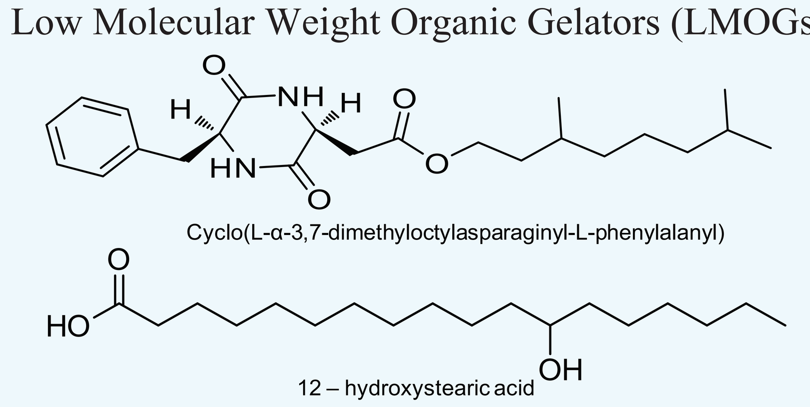


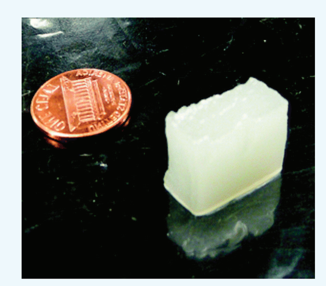
- Gel-RTILs
  - ❑ Formed by incorporating low molecular weight organic gelators (LMOGs) into RTILs
    - Physical gelation: H-bonding, van der Waals interactions, *pi-pi* stacking between LMOG and RTIL
  - ❑ Gel-RTIL maintains CO_2 affinity and permeability characteristics of RTILs
    - Low fraction of LMOG required, typically 1-5 wt%
    - Free RTIL provides for fast liquid-like diffusion and enhanced flux
  - ❑ Increase in mechanical and thermal properties of RTIL upon gelation
  - ❑ Demonstrated high perm-selectivity for CO_2 over other components (coal-fired power plants exhaust gas)



Red circle data from Robeson, Journal of Membrane Science, 320 (2008) p 390.

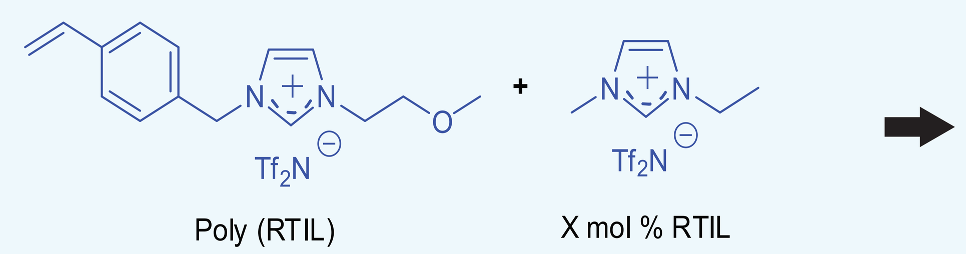
Low Molecular Weight Organic Gelators (LMOGs)





Gel-RTIL

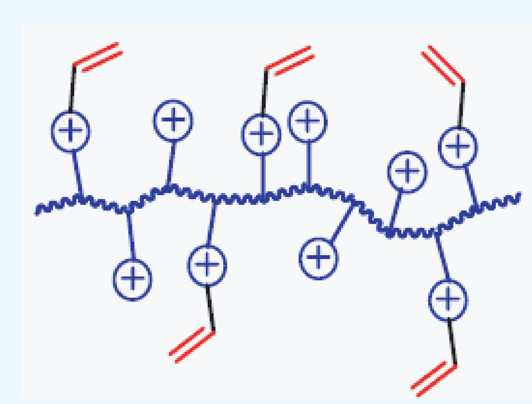
- RTIL/Poly(RTIL) Composites
  - ❑ Materials formed by *in-situ* polymerization of RTILs containing polymerizable groups with various fractions of non-polymerizable RTIL
  - ❑ Resulting solid-liquid composites impart flexibility in controlling the material CO_2/N_2 perm-selectivity character with mechanical integrity imparted by the polymerized component



Mol % RTIL	CO_2 Permeability, (barrer)	CO_2/N_2 Selectivity
0	16	41
10	46	36
30	72	36
50	173	36

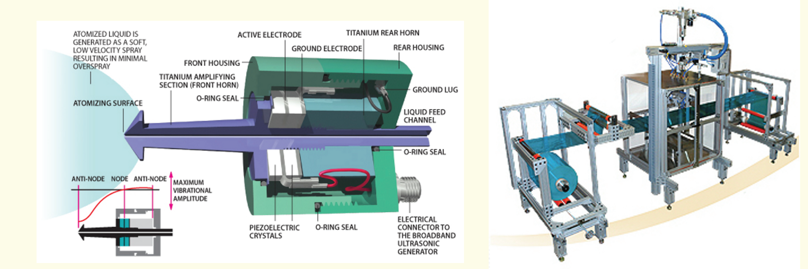
CO_2 permeability enhancements of >10X observed for RTIL/Poly(RTIL) as compared to neat Poly(RTIL)

- Curable Poly(RTIL)s and Composites Thereof
  - ❑ Imidazolium based polymers with reactive "ene" groups for free radical curing reactions with various amounts of non-polymerizable RTIL
  - ❑ Reactive polymer solutions have higher viscosities compared to monomer solutions
  - ❑ Pore penetration can likely be reduced by faster reaction time and use of macromolecules
  - ❑ Composite materials are formed by cross-linking curable polymers in the presence of free RTIL
  - ❑ Unbound RTIL monomer can be doped into system to modify the cross-linking density of the network and thus perm-selectivity characteristics



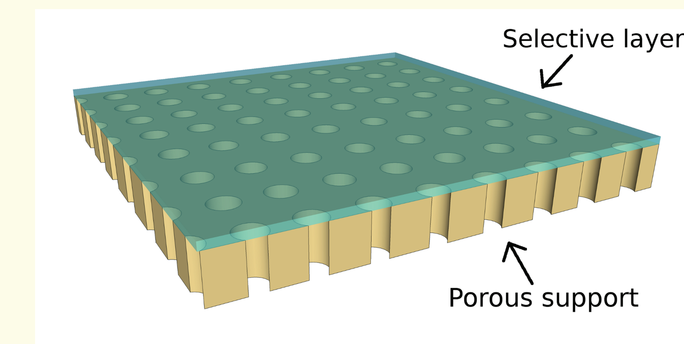
Ultra-Thin Membrane Fabrication, Optimization, and Testing

- Ultrasonic atomization based material deposition process on microporous polymeric substrates for fabrication of commercially attractive composite membranes
  - ❑ Proven technology for industrial-scale thin film applications
  - ❑ Large-scale custom thin film deposition systems employing ultrasonic atomization technology readily achievable
  - ❑ Industrial deployment envisioned as spiral-wound modules
  - ❑ Tailorable, precisely controlled, repeatable deposition characteristics
  - ❑ Soft, low-velocity spray reduces pore penetration into support substrates

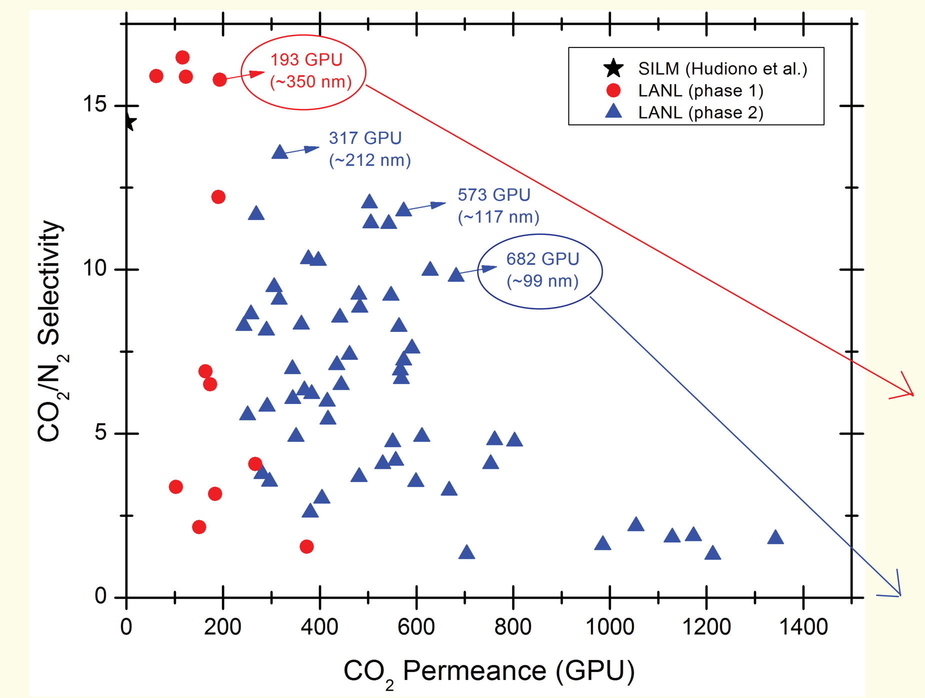


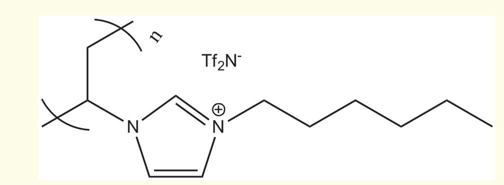
Illustrations from www.sonotek.com

- Development and optimization of ultrasonic coating technique (USCT)
  - ❑ Achieve formation of an ideal selective layer on highly porous support
    - Dense, ultra-thin, cohesive selective layer with minimal pore penetration and good adhesion to support layer
  - ❑ Tune coating parameters to effect and control coating layer formation
    - System control parameters include: liquid flow rate, spray geometry, coating profile, raster speed, substrate temperature, *in-situ* IR and UV irradiation

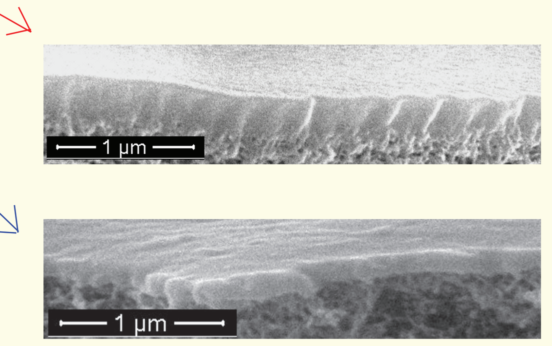


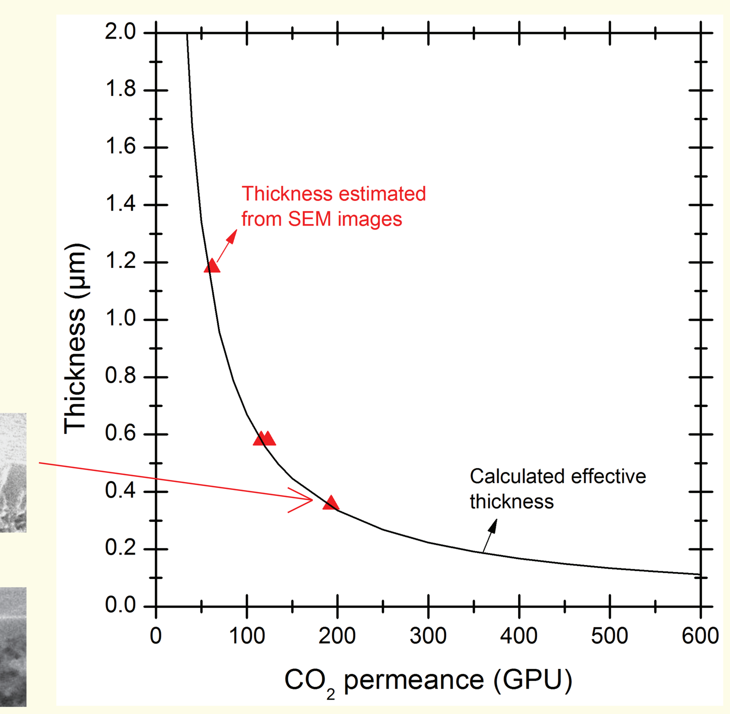
- Fabrication of a poly(RTIL) composite membrane using USCT - Example Case
  - ❑ Poly(RTIL) selective layers were deposited on commercially attractive porous substrates using USCT
  - ❑ Dense, sub-micron thick selective layers were successfully applied to substrate with minimal pore penetration
  - ❑ 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
  - ❑ Ongoing work to further optimize USCT parameters to allow formation of defect-free selective layer with thickness ~100 nm.





poly(vhim)[Tf2N]
Lit. CO_2 permeability: 67.3 barrer
Lit. CO_2/N_2 selectivity: 14.5



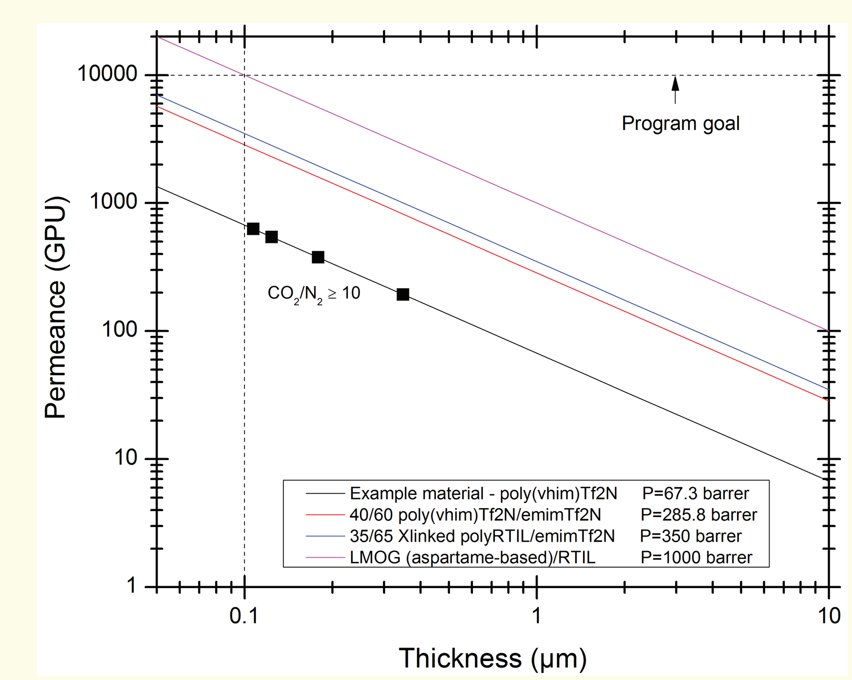


Data of poly(vhim)Tf2N SILM from Hudiono et al, Journal of Membrane Science, 370 (2011) p 141.

- Program Goal Achievement: Improved Materials/Processes

Development of RTIL-based selective layer materials with:
- improved CO_2 permeability (P > 1000 barrer);
- material properties amenable to robust, stable, continuous film formation and application in flue gas environments; &
- an ultra-thin (≤ 100nm) membrane fabrication technology

will lead to achievement of project targets.



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