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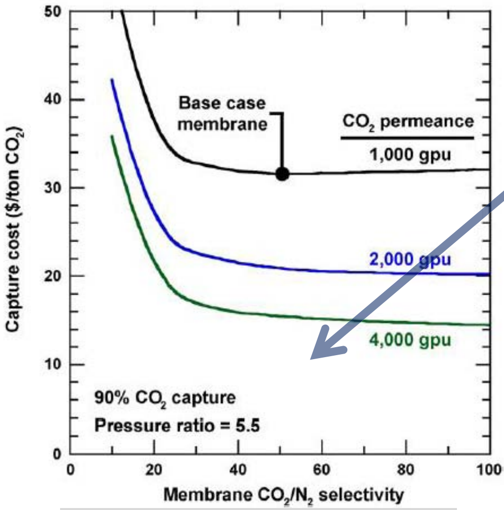
Achieving a 10,000 GPU Permeance for Post-Combustion Carbon Capture with Gelled Ionic Liquid-Based Membranes

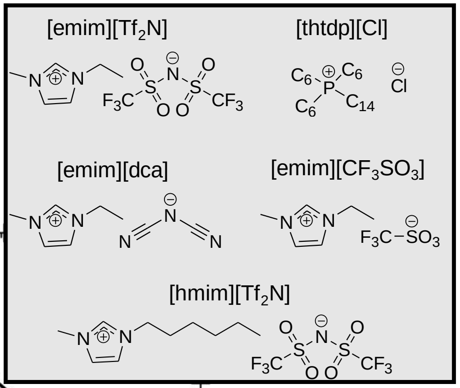


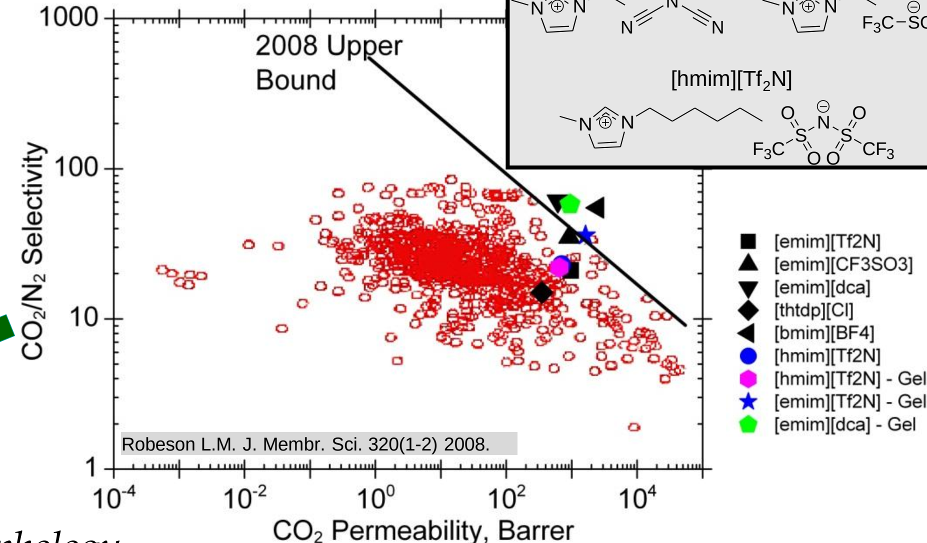
Merkel T.C. *et al*, J. Membr. Sci. 359(1-2) 2010.

10,000 GPU

< $10/ton of CO_2 captured

RTILs have promising permselectivity character and tolerance to flue gas impurities





Robeson L.M. J. Membr. Sci. 320(1-2) 2008.

Challenge:

Material stability: SLM format limitations

Enhancing permeability thru chemistry & molecular morphology

Approach:

Tailored gel-ILs, RTIL/poly(RTIL) composites, incorporation of task specific complexation chemistries

Challenge:

Enhancing permeance through selective layer thickness (SL) minimization

Permeability = 1000 barrer → **Permeance (100 nm thick SL) = 10,000 GPU**

Approach:

Commercially viable fabrication technique development using ultrasonic spray coating technology (USCT) -- enabling controlled ultra-thin SL deposition on commercially attractive support platforms

Membrane Permeance 10,000 GPU & Selectivity > 20

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

Richard D. Noble[1], Douglas L. Gin[1], Kathryn A. Berchtold[2], Rajinder P. Singh[2], Rico Del Sesto[2], and Abhoyjit Bhown[3]
[1]University of Colorado, [2]Los Alamos National Laboratory, and [3]Electric Power Research Institute

Abstract

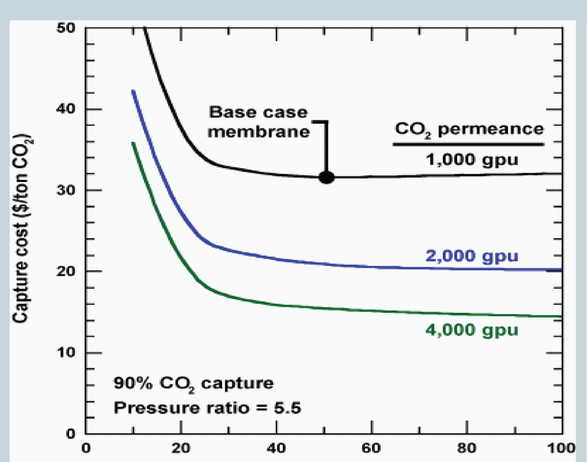
This project entails the development and demonstration of an innovative next-generation membrane technology for selective and energy-efficient carbon dioxide separation from power plant flue gas. We propose to develop gelled ionic liquid membranes and composite membranes containing ionic liquids as well as complexing agents with CO_2/N_2 separation performance in realistic process environments greater than any other membrane system with techno-economics that exceed the current DOE/industry benchmarks. Specific project targets include achievement of a membrane with a CO_2 permeance of 10,000 GPU and a CO_2/N_2 selectivity of at least 20. Membrane performance will be transformationally improved through implementation of material design strategies that enable greatly enhanced and selective CO_2 transport. The impact of these enhancements will be further amplified through the development of commercially viable selective layer fabrication techniques that enable controlled thin film selective layer deposition on commercially attractive support platforms. The achievement of our objectives will result in a non-incremental improvement in the combined economics and performance achievable and the development and demonstration of a new separations tool that meets and *exceeds*, in stepwise fashion, the ARPA-E/DOE-FE/ NETL techno-economic goals for this separation.

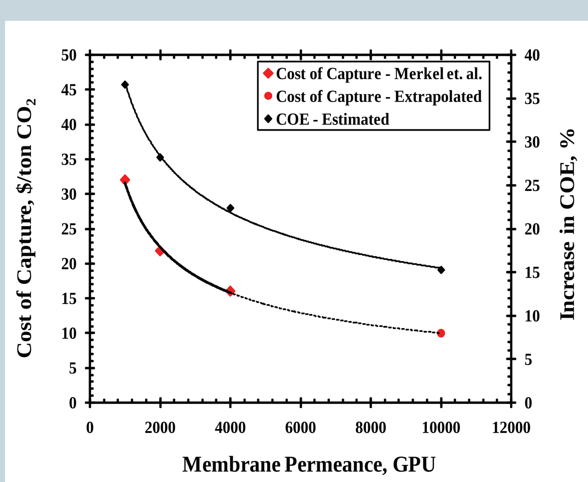
Separation and Capture

- 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

- Recent estimates of COE increases for CO_2 capture using membranes* are substantially lower than current DOE benchmarks
- 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
- However, membrane-based separations platforms afford many inherent advantages over other separations technologies
  - Smaller footprints, simpler operation, better scalability & modularity
- Compelling need for new materials and processing methods to enhance productivity and selectivity

Objectives

- Design mechanically and chemically robust ionic liquid-based selective layers (SLs) having CO_2 permeability exceeding 1000 barrer and a CO_2/N_2 selectivity of at least 20.
- Develop ultrasonic-atomization-based coating technique to fabricate less than 100 nm thick selective layer/microporous support composites.
- Devise technically and economically viable membrane performance characteristics and process scenarios for CO_2 capture from coal derived flue gas.
- Achieve 10,000 GPU membrane permeance & selectivity > 20

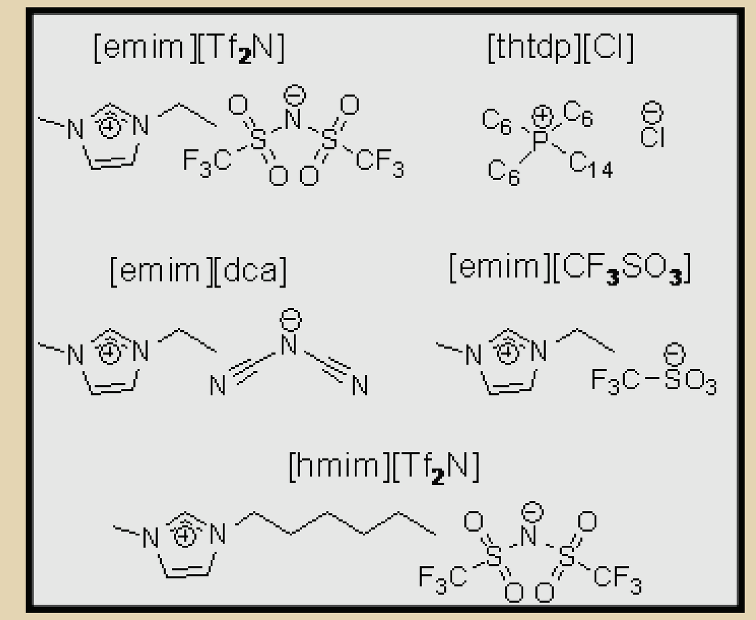
Approach

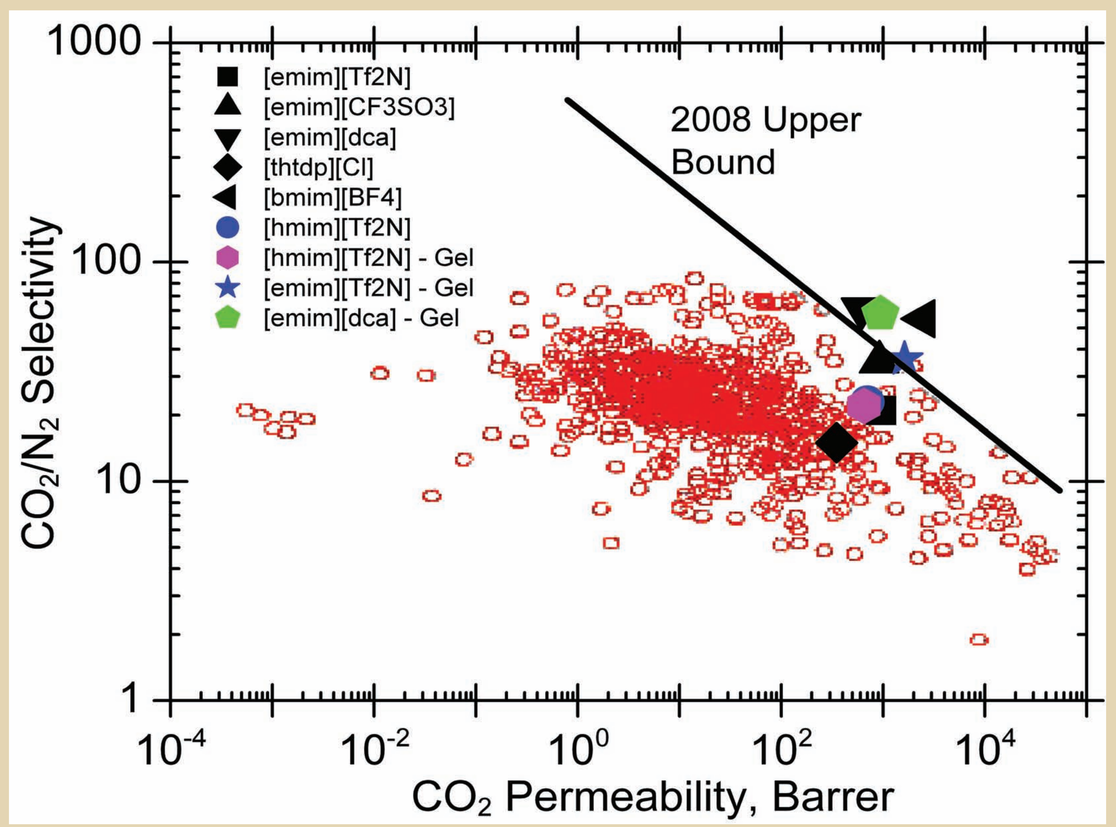
- Selective Layer Design Synthesis & Evaluation
  - Tailored gel-RTILs, RTIL/Poly(RTIL) composites, incorporation of task-specific CO_2 complexation chemistries
- Ultra-Thin Membrane Fabrication, Optimization, & Testing
  - Commercially viable fabrication technique development using ultrasonic spray-coating technology (USCT) -- enables controlled ultra-thin SL deposition on commercially attractive support platforms
- Membrane, Systems, and Economic Analyses

Membrane Selective Layer Design Synthesis & Evaluation

Room-Temperature Ionic Liquids (RTILs)

- RTILs are compounds consisting of entirely ions resembling the ionic melts of metallic salts.
- Liquids at ambient temperature and over a broad temperature range from -96 to 300 °C with practically no vapor pressure.
- Beneficial properties: very high solubility/perm selectivity for CO_2, low flammability, and excellent thermal/chemical stability.
- Easily tailored for specific properties by manipulating/adding functional groups.
- RTILs lack mechanical stability necessary for industrial utilization as thin film gas separation membranes.



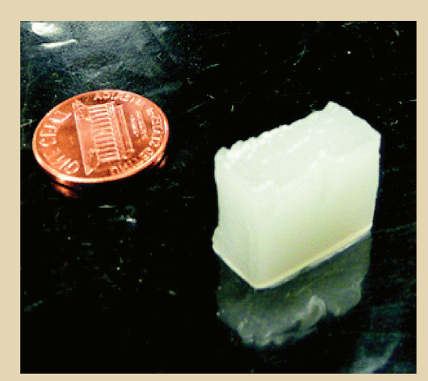


Red circle data from Robeson, Journal of Membrane Science, 320 (2008) p 390.

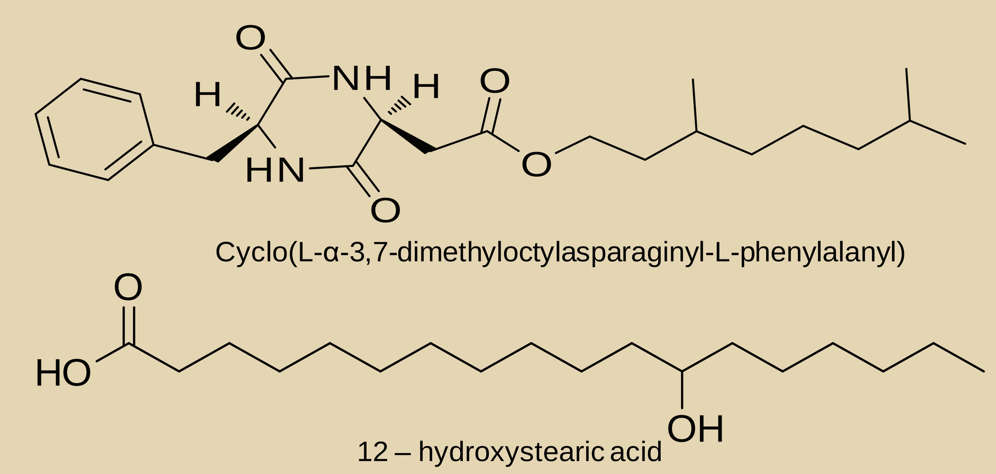
Gel-RTILs

- Gel-RTILs are formed by incorporating low molecular weight organic gelators (LMOGs) into RTILs
  - H-bonding, van der Waals interactions, and *pi-pi* stacking between LMOG and RTIL are responsible for physical gelation.
- Gel-RTIL maintains CO_2 affinity and permeability characteristics of RTILs
  - Low fraction of LMOG required, typically 1-5 wt%.
  - Free RTIL provides provides for fast liquid-like diffusion and enhanced flux
- Increase in mechanical and thermal properties of RTIL upon gelation.
- Gelation is thermo-reversible process with transition temperatures ranging from 20 to 180 °C.
- Demonstrated high permselectivity for CO_2 over other components of coal-fired power plants exhaust gas.

Gel-RTIL

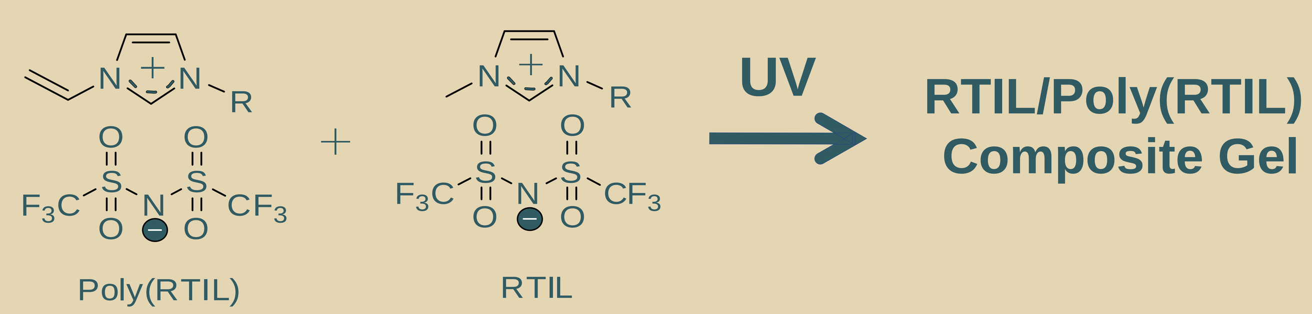


Low Molecular Weight Organic Gelators (LMOGs)

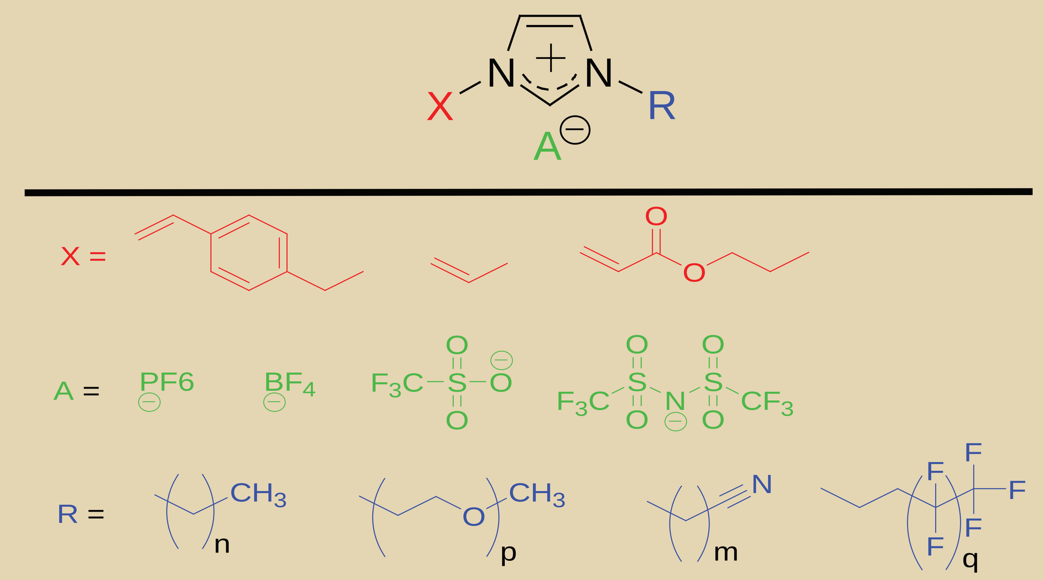


RTIL/Poly(RTIL) Composites

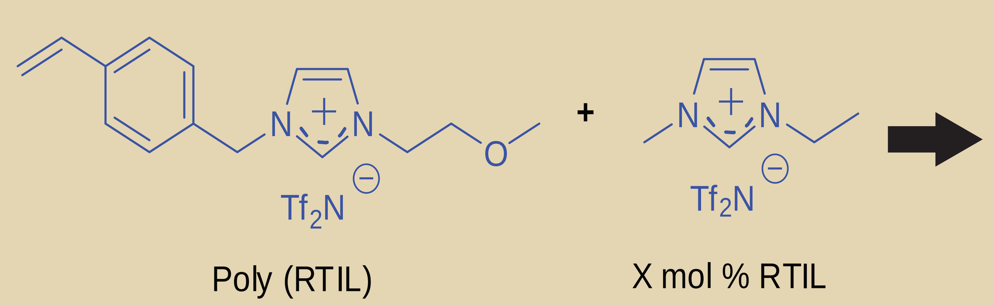
- RTIL/Poly(RTIL) composites are materials formed by *in-situ* polymerization of RTILs containing polymerizable groups with various fractions of non-polymerizable RTIL.
- Resulting solid-liquid composites impart flexibility in controlling the material CO_2/N_2 permselectivity character with mechanical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



General Range of Structures for Polymerizable RTIL Monomers



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



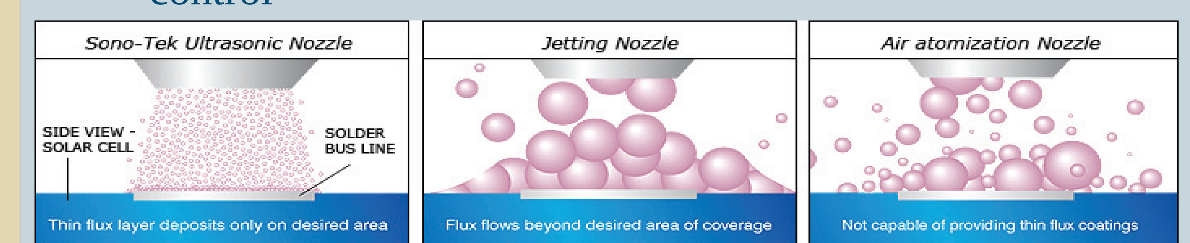
Mol % RTIL	CO_2 Permeability, (barrer)	CO_2/N_2 Selectivity
0	16	41
10	46	36
30	72	36
50	173	36

Ultra-Thin Membrane (Support & Selective Layer) Fabrication, Optimization, and Testing

- Enhance permeance through SL thickness minimization

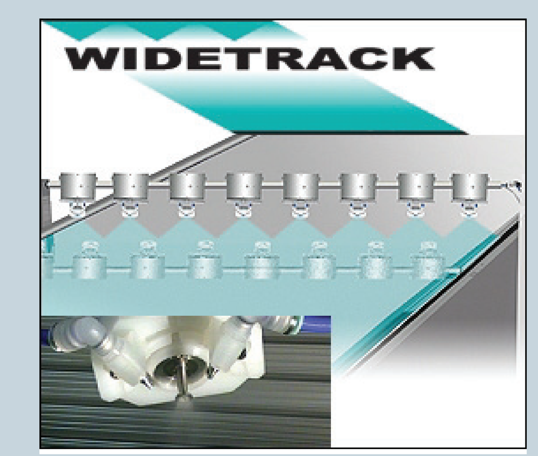
Permeability = 1000 barrer → Permeance (100 nm thick SL) = 10,000 GPU

- Ultrasonic-atomized spray-coating to fabricate ultrathin gel-RTIL and RTIL/Poly(RTIL) composite membranes supported on microporous polymeric substrates.
- Very soft and low-velocity spray droplets reduce pore penetration
- Precise & controllable liquid delivery rates facilitate ultra-thin film deposition.
- High operating temperatures (up to 150 °C) enable phase control



Illustrations from www.sonotek.com

- Varied deposition schemes can be used for further thickness and penetration control
- SL and support surface chemistry provide additional control over film formation.
- Industrial deployment envisioned as spiral-wound modules.



Illustrations from www.sonotek.com

Membrane, Systems, and Economic Analysis

- Use process simulations to set quantifiable targets for membrane properties such as permeability and selectivity desired for CO_2 capture
- Conduct techno-economic analysis of leading membrane candidates arising in this work
- Determine cost of process; benchmark process against other CO_2 capture processes
- Commercialization plan development

Acknowledgments

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