Gelled Ionic Liquid-Based Membranes

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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$_2$ selectivity ≥ 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$_2$ selectivity ≥ 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

Selective Layer Material Design and Synthesis

CO₂ Permeance ≥ 5,000 GPU
CO₂/N₂ selectivity ≥ 20

Ultra-Thin Membrane Fabrication

Systems Process Modeling
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.

  \[
  \text{Permeance} = \frac{\text{Permeability}}{\text{Thickness}} = \frac{\text{Flux}}{\Delta p}
  \]

- **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”

**Preliminary Economic Evaluation**

**Task 1: Benchmarking with MTR results**

Single counter current sweep stage

<table>
<thead>
<tr>
<th>Case</th>
<th>Membrane area (MM m²)</th>
<th>Total power MTR* (MW)</th>
<th>Total power This work (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry feed</td>
<td>4.3</td>
<td>46.4</td>
<td>44.6</td>
</tr>
<tr>
<td>Wet feed</td>
<td>3.9</td>
<td>47.2</td>
<td>53.1</td>
</tr>
</tbody>
</table>

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

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**: 97
  - **This work**: 102
Bulk RTIL Membrane Materials Overview

**Gelled RTIL**

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

Evolution of Materials

<table>
<thead>
<tr>
<th>Bulk Material:</th>
<th>Gelled RTIL</th>
<th>Linear Poly(RTIL)/RTIL</th>
<th>Photo-curable Poly(RTIL)/RTIL</th>
<th>PVDF-co-HFP/RTIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTIL Loading (wt%):</td>
<td>98</td>
<td>40</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>CO₂ Permeability (barrers):</td>
<td>950</td>
<td>105</td>
<td>650</td>
<td>650</td>
</tr>
<tr>
<td>CO₂/N₂ Selectivity:</td>
<td>21</td>
<td>21</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Physical Properties:</td>
<td>Mechanically weak</td>
<td>Brittle</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>
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

Both images taken at same magnification
Ultra-thin Membrane Characterization

- Dramatic influence of coating parameters on membrane performance
  - Permeability = 67.3 barrer

- Demonstrated defect-free poly(RTIL) composite membrane with CO₂ permeance of 317 GPU – approximately 212 nm effective thickness

- Fabricated numerous membranes with CO₂ permeance ≥ 500 and near ideal CO₂/N₂ 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)

\[ y = 72.3x^{-1} \quad R^2 = 0.9611 \]

\[ y = 67.3x^{-1} \]

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 CO₂/N₂ 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-Tf₂N, with CO₂/N₂ selectivity of 33, only has CO₂ permeance of 25 GPU (estimated selective layer thickness = 2 µm)

All data: \( \Delta p = 1 \text{ bar}, T = 25^\circ\text{C} \)
P(VDF-HFP)/emim-Tf$_2$N Composite Membranes

Fabricated and evaluated p(VDF-HFP)/emim-Tf$_2$N composite membranes containing 40 and 60% emim-Tf$_2$N

- Selective layer thickness varied from 0.2 to 1.8 µm
- High CO$_2$/N$_2$ selectivity obtained for 60/40 emim-Tf$_2$N/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?

<table>
<thead>
<tr>
<th>Sample</th>
<th>Target Thickness</th>
<th>Est. Obs. Thickness</th>
<th>CO₂ Permeance</th>
<th>N₂ Permeance</th>
<th>CO₂/N₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-PVDF Comp.</td>
<td>2.8 um</td>
<td>235 nm</td>
<td>93</td>
<td>30</td>
<td>3.1</td>
</tr>
<tr>
<td>11B-PVDF Comp.</td>
<td>1.9 um</td>
<td>235 nm</td>
<td>73</td>
<td>30</td>
<td>2.4</td>
</tr>
<tr>
<td>16-PolyRTIL Comp.</td>
<td>2.8 um</td>
<td>266 nm</td>
<td>292</td>
<td>27</td>
<td>11</td>
</tr>
<tr>
<td>17-PolyRTIL Comp.</td>
<td>1.5 um</td>
<td>208 nm</td>
<td>292</td>
<td>28</td>
<td>10</td>
</tr>
<tr>
<td>20-PolyRTIL Comp.</td>
<td>1.5 um</td>
<td>117 nm</td>
<td>7730</td>
<td>917</td>
<td>8.4</td>
</tr>
<tr>
<td>24A-PolyRTIL Comp.</td>
<td>1.5 um</td>
<td>-</td>
<td>459</td>
<td>40</td>
<td>12</td>
</tr>
</tbody>
</table>

- (10) PVDF Composite
- (16) PolyRTIL Composite
- (20) PolyRTIL Composite

†~235 nm
‡~266 nm
‡~117 nm
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

<table>
<thead>
<tr>
<th>RTIL Post-Treatment</th>
<th>CO₂ Permeance</th>
<th>N₂ Permeance</th>
<th>CO₂/N₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>16</td>
<td>16</td>
<td>1.0</td>
</tr>
<tr>
<td>50 C, 20 min</td>
<td>16</td>
<td>0.5</td>
<td>33</td>
</tr>
<tr>
<td>80 C, 5 min</td>
<td>22</td>
<td>0.7</td>
<td>30</td>
</tr>
</tbody>
</table>

• Experiment: Apply secondary polymer/RTIL coating containing 75-80% free RTIL (Thickness ~200-300nm)

**Result:** Selectivity enhanced; permeance slightly reduced

<table>
<thead>
<tr>
<th>Sample</th>
<th>Post-Treatment</th>
<th>CO₂ Permeance</th>
<th>N₂ Permeance</th>
<th>CO₂/N₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF-HFP Comp.</td>
<td>None</td>
<td>93</td>
<td>30</td>
<td>3.1</td>
</tr>
<tr>
<td>(240 nm)</td>
<td>+ 2ⁿᵈ Coating, 5 min at 50 C</td>
<td>32</td>
<td>5.6</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>+ 2ⁿᵈ Coating, 20 min at 50 C</td>
<td>64</td>
<td>6.5</td>
<td>9.8</td>
</tr>
<tr>
<td>PolyRTIL Comp.</td>
<td>None</td>
<td>290</td>
<td>27</td>
<td>11</td>
</tr>
<tr>
<td>(270 nm)</td>
<td>+ 2ⁿᵈ Coating, 5 min at 50 C</td>
<td>230</td>
<td>12</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>+ 2ⁿᵈ Coating, 20 min at 50 C</td>
<td>240</td>
<td>14</td>
<td>17</td>
</tr>
</tbody>
</table>
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

- DOE – Advanced Research Project Agency - Energy (ARPA-e)
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- Total S.A.

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