Direct Air Capture Using Trapped Small Amines in Hierarchical Nanoporous Capsules on Porous Electrospun Fibers

DE-FE0031969
Miao Yu
University at Buffalo, The State University of New York
Project Overview

Funding: $800,000 from DOE; $200,000 Cost Share

Overall Project Performance Dates: 2/1/2021-7/31/2022

Project Participants:

University at Buffalo
ASU
gti®

Overall Project Objectives:
Develop an innovative sorbent structure of trapped small amines in hierarchical nanoporous capsules (HNC) embedded in porous electrospun fibers (PEF) for direct air capture (DAC). This involves the tailoring of both sorbent and PEF materials to achieve a compact system for DAC with high capacities for CO₂ at concentrations typically available in air and at near ambient conditions.
Technology Background

Transformational Adsorbent Utilizing Small Trapped Amines

**Dry condition:** 0.5 mol CO$_2$ per mole of N

\[
\text{CO}_2 + 2\text{RNH}_2 \leftrightarrow \text{RNH}_3^+ + \text{RNHCOO}^- \\
\text{CO}_2 + 2\text{R}_2\text{RNH} \leftrightarrow \text{R}_2\text{RNH}_2^+ + \text{R}_1\text{R}_2\text{NHCOCO}^- 
\]

**Moisture condition:** 1 mol CO$_2$ per mole of N

\[
\text{CO}_2 + \text{R}_2\text{RNH}_2 + \text{H}_2\text{O} \leftrightarrow \frac{\text{R}_2\text{RNH}_2^+\text{HCO}_3^-}{\text{bicarbonate}} \leftrightarrow \frac{\text{R}_2\text{RNH}_2^+\text{CO}_3^{2-}}{\text{carbonate}} \\
\text{CO}_2 + \text{R}_2\text{R}_3\text{N} + \text{H}_2\text{O} \leftrightarrow \text{R}_2\text{R}_3\text{NH}^+\text{HCO}_3^- \leftrightarrow \text{R}_2\text{R}_3\text{NH}^+\text{CO}_3^{2-} 
\]
Comparison with amine-based sorbents reported in the literature

Amine-based sorbents reported in the literature

Superior projected performance of the proposed sorbent

![Comparison with amine-based sorbents reported in the literature](image)
Uniform microporous coating with micropores

Technical and economic advantages
- Fast reaction kinetics and high amine efficiency
- High CO₂ adsorption capacity and good stability
- High sorbent loading on PEFs and fast exposure of sorbent material to air;
- Low energy penalty from the low support fraction/high sorbent loading;

Challenges of our technology
- Precise control of the surface coating pores to prevent amine loss
- High loading of sorbent particles in PEFs
Technical Approach/Project Scope

Experimental design and work plan

<table>
<thead>
<tr>
<th>Member</th>
<th>Specific project roles/responsibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbent</td>
<td>• Project management and planning</td>
</tr>
<tr>
<td>Development</td>
<td>• Sorbent material development</td>
</tr>
<tr>
<td>Task 2 –</td>
<td>• PEF embedded sorbent direct air capture of CO₂ tests</td>
</tr>
<tr>
<td>Development</td>
<td>• Supporting high-level process design and analysis</td>
</tr>
<tr>
<td>Porous electrospun fiber</td>
<td>• PEF development</td>
</tr>
<tr>
<td>Development</td>
<td>• Supporting high-level process design and analysis</td>
</tr>
<tr>
<td>Task 3 –</td>
<td>• High-level process design and analysis</td>
</tr>
<tr>
<td>Development</td>
<td>• Direct air capture of CO₂ testing</td>
</tr>
<tr>
<td>Task 4 –</td>
<td>• High-level process design and analysis</td>
</tr>
<tr>
<td>Direct air capture</td>
<td>• High-level process design and analysis</td>
</tr>
<tr>
<td>Task 5 –</td>
<td>• High-level process design and analysis</td>
</tr>
<tr>
<td>High-level</td>
<td>• High-level process design and analysis</td>
</tr>
<tr>
<td>process design/analysis</td>
<td>• High-level process design and analysis</td>
</tr>
</tbody>
</table>

Project schedule

- **Month 6:** Achieve microporous coating pore size <0.7 nm and amine loss <5% after 10 heating-cooling cycles (M2.1)
- **Month 13:** Achieve >75% sorbent loading in PEF and CO₂ capacity loss <10% relative to powder sorbents (M3.2)
- **Month 15:** Achieve CO₂ equilibrium capacity >8 mmol/g sorbent at ambient temperatures and pressures (M2.3)
- **Month 15:** Achieve CO₂ working capacity >4.5 mmol/g fiber sorbent material and t₁/₂ <30 min (M4.1)

Project success criteria

- Achieve CO₂ working capacity of 3.5-5 mmol/g fiber sorbent material and t₁/₂ <30 min
- CO₂ working capacity loss <10% and t₁/₂ increase <10% after cyclic testing
- Issue high-level process design/analysis topical report
- Submit Final Technical Report
## Risks and mitigation strategies

<table>
<thead>
<tr>
<th>Perceived Risk</th>
<th>Risk Rating</th>
<th>Mitigation/Response Strategy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Technical/Scope Risks:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potential amine loss during regeneration</td>
<td>Low</td>
<td>Low 1) Optimize microporous coating pore size before amine loading; select amines with larger size 2) Increase ALD cycles during sealing process to reduce pore mouth size 3) Optimize liquid precursor composition for liquid interfacial reaction to better control coating pore size</td>
</tr>
<tr>
<td>Sorbent CO₂ adsorption capacity not sufficiently high or kinetics not sufficiently fast</td>
<td>Low</td>
<td>High Low 1) Increase amine loading to increase amine group density, especially primary amine group density; 2) Optimize coating pore size to allow faster diffusion;</td>
</tr>
<tr>
<td>Air flow pressure drop not sufficiently low in the sorbent DAC process</td>
<td>Low</td>
<td>Mod Low 1) Optimize fiber sorbent packing density to balance air flow and CO₂ capacity per volume; 2) Optimize sorbent bed configuration</td>
</tr>
<tr>
<td><strong>Cost/Schedule Risks:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delay of tasks</td>
<td>Low</td>
<td>Low Early and frequent meetings will be held to avoid delay of tasks. The project team will monitor the staffing/equipment needs closely</td>
</tr>
<tr>
<td><strong>Financial Risks:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The shortfall of cost share</td>
<td>Low</td>
<td>Low UB is committed to providing the required cost share</td>
</tr>
<tr>
<td><strong>Management, Planning, and Oversight Risks:</strong></td>
<td></td>
<td>Minimal – UB, ASU and GTI are implementing project management systems to minimize management risks.</td>
</tr>
</tbody>
</table>
Progress and Current Status of Project

Liquid-liquid interfacial reaction to form microporous coating

Factors influencing coating pore size:

i) Organic precursor composition (different glycols, water percentage in glycols, etc.)
ii) Calcination conditions (temperature, gas environment, etc.)
Deposition of microporous coating by liquid phase interfacial reaction

1. Amine loading followed by coating pore narrowing

   - Original SBA-15
   - EG loading (impregnation)
   - Pore-filled SBA-15
   - Interfacial reaction (+TiCl₄)
   - Pore-sealed SBA-15
   - ALD layer
   - Amine-sealed SBA-15

2. Direct encapsulation

   - Original SBA-15
   - EG, H₂O, amine loading
   - Pore-filled SBA-15
   - Interfacial reaction (+TiCl₄)
   - Pore-sealed SBA-15
   - Dry and calcination
Coated SBA-15 prepared by precursor loading via *vapor condensation*

**Percentage of H₂O in ethylene glycol**

- 250 °C
- 280 °C
- 320 °C
- 350 °C
Coated SBA-15 prepared by pore filling via **vapor condensation**

\[
Dye\ Rejection = \frac{\text{Supernatant Absorbance}}{\text{Stock Solution Absorbance}} \times 100\%
\]

**Note**: CV rejection by pristine SBA-15 is 5%.
Coated SBA-15 prepared by precursor loading via *liquid phase*

<table>
<thead>
<tr>
<th>Sample #</th>
<th>H$_2$O Concentration in Ethylene Glycol (wt.%)</th>
<th>Liquid to Pore Ratio (LPR)</th>
<th>CV (~1.3 nm) Rejection (%)</th>
<th>O-xylene (0.69 nm) uptake (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.8</td>
<td>55</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>61</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>1.2</td>
<td>75</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>1.5</td>
<td>64</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.8</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>1</td>
<td>65</td>
<td>11</td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>1.2</td>
<td>70</td>
<td>11</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>1.5</td>
<td>80</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>0.8</td>
<td>42</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>1</td>
<td>45</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>1.2</td>
<td>47</td>
<td>19</td>
</tr>
<tr>
<td>12</td>
<td>20</td>
<td>1.5</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>13</td>
<td>30</td>
<td>0.8</td>
<td>37</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>30</td>
<td>1</td>
<td>48</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
<td>1.2</td>
<td>68</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>30</td>
<td>1.5</td>
<td>45</td>
<td>-</td>
</tr>
</tbody>
</table>
Plans for future testing/development

- **Microporous coating**: Further modify samples with microporous coating by molecular layer deposition in order to fine tune the coating pore size; detailed characterization of the coating pore size and sorbent pore volume and composition;

- **Amine loading and sealing**: Develop effective amine loading and sealing processes on samples with microporous coating; conduct amine loss evaluation;

- **Porous electrospun fibers (PEF) loaded with sorbent**: Optimize electrospinning conditions to incorporate sorbent materials and characterize composite sorbent structure;

- **CO₂ sorption performance evaluation**: Measure CO₂ adsorption capacity and kinetics for both powder form and fiber form; measure CO₂ working capacity under cyclic operation conditions and evaluate stability of the PEF sorbent.
Summary

- Microporous coating deposition processes based on both vapor condensation and liquid filling were developed;
- CV rejection suggested microporous coatings with pore size smaller than 1.3 nm were successfully deposited;
- O-xylene uptake indicated <0.7 nm coating pores were formed under optimized coating preparation condition
Appendix
Organization Chart

- **DOE NETL**
  - **Project Manager**
  - **Project Oversight**
    - **UB**
      - Ms. Martina Tsai
        - Contract administrator
    - **Prof. Miao Yu-PI**
      - Coordinate project activities
      - Project management
      - Sorbent development
    - **GTI**
      - Dr. Shiguang Li
        - GTI site project management
      - Dr. Weiwei Xu
        - High-level process design and analysis
    - **GTI**
      - Dr. Howard Meyer
        - Project QA/QC
    - **ASU**
      - Dr. Bin Mu
        - Porous electrospun fiber development