Electronic Supplementary Information

Single polymer sorbent fibers for high performance and rapid direct air capture

Ali K. Sekizkardes a,b,* , Victor Kusuma a,b, Jeffrey T. Culp a,b, Patrick Muldoon a,b, James Hoffman a, Janice A. Steckel a and David Hopkinson a

a. U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, Pennsylvania 15236
b. NETL Support Contractor, 626 Cochrans Mill Road, P.O. Box 10940, Pittsburgh, Pennsylvania 15236
* ali.sekizkardes@netl.doe.gov

Table of Contents

Section S1: Materials, methods and preparations..........................................................................................3
  Chemicals and Experimental Techniques........................................................................................................3
  Synthesis of PIM-1............................................................................................................................................3
  Synthesis of PIM-1-AO...................................................................................................................................3
  Preparation of PF-15-TAEA fibers and PF-15-DETA sorbents..................................................................4

Section S2: Materials Characterizations .........................................................................................................5

  Figure S1: H NMR spectrum of PIM-1........................................................................................................5
  Figure S2: 1H NMR spectrum of PIM-1-AO fiber (PF-15). .................................................................6
  Figure S3. FT-IR spectra of neat PIM-1 and amidoxime functionalized PIM-1 polymer particle (PIM-1) fiber (PF-15). ......................................................................................................................7
  Figure S4: BET surface area calculation of PIM-1.....................................................................................8
  Figure S5. BET surface area calculation of PIM-1-AO...........................................................................9
  Figure S6 Cross sectional SEM images of the fibers. Dope compositions: 15wt%, 17.5wt% and 20wt%..................................................................................................................................................11
  Figure S7 FT-IR spectra of PF-15 and its aminated sorbents PF-15-TAEA and PF-15-DETA...........................12

Section 3. CO₂ sorption studies ....................................................................................................................13
  Figure S8: CO₂ adsorption/desorption isotherm of PIM-1-AO..............................................................13
Figure S10: CO$_2$ adsorption (blue circles) and desorption (grey circles) isotherms of PF-15-TAEA.................................................................15

Figure S11: CO$_2$ adsorption (gray) isotherm of mesoporous silica control sample purchased from Sigma Aldrich ..............................................16

Figure S12: Isosteric heats of adsorption ($Q_{st}$) for CO$_2$ of PF-15-TAEA..............17

Figure S13: CO$_2$ uptake in neat TAEA measured in flowing gas at a total pressure of 100 mbar with 90% N$_2$. .........................................................18

Figure S14: Humid CO$_2$ adsorption and desorption cycles for PF-15-TAEA........19

Figure S15: Breakthrough curves of H$_2$O (red), N$_2$ (light green), Ar (blue) and CO$_2$ (dark green) of the sorbent PF-15-TAEA under simulated wet air conditions: 400 ppm CO$_2$ concentration and 50 % RH at 25 ºC. .................................20

Table S2. CO$_2$ adsorption performance comparison for top performing sorbents .................................................................21

References..............................................................................................................................................21

*
Section S1: Materials, methods and preparations

Chemicals and Experimental Techniques
All chemicals were purchased from Sigma Aldrich and were used without any further purification. Hydroxyl amine solution (50 wt% in water) was purchased from Sigma Aldrich (catalogue number: 438227-250ML). PIM-1 was synthesized based on the previous reports.\textsuperscript{1,2} Surface area measurements were performed using a Micromeritics 3Flex. Volumetric CO\textsubscript{2} uptake adsorption and desorption isotherms were collected by Micromerics (3Flex) and Quantachrome (1C). Fourier transform infra-red (FT-IR) spectra were collected by using a Bruker Vertex 70. Gravimetric adsorption measurements for CO\textsubscript{2} were done using a Hiden IGA 003 system equipped with mass flow controllers for preparing volumetric mixtures of CO\textsubscript{2} and N\textsubscript{2}. The volume of the sample chamber is approximately 300mL. Total flow rates were set at 200mL/min for measurements at 100mbar and 300mL/min for mixed CO\textsubscript{2}/N\textsubscript{2} measurements at 1bar. Temperature ramps for regeneration were accomplished with a dedicated furnace using a ramp rate of 3°C/min and rapidly cooled back to room temperature using an internal fan. Adsorption measurements during the adsorption/regeneration cycling experiments were done at room temperature which varied between 22°C-26°C over the total course of the tests. Tests using humidified gas mixtures were performed at 25°C. The temperature of the sample and humidifier were controlled with a circulating bath. The relative humidity was established by blending a humidified N\textsubscript{2} stream with dry N\textsubscript{2} via mass flow controllers. The humidified N\textsubscript{2} and dry CO\textsubscript{2} streams combined in the sample chamber.

Synthesis of PIM-1
PIM-1 was synthesized by the experimental method reported by Budd et al.\textsuperscript{2} 3,3,3\textquoteleft,3\textquoteleft- tetramethyl-1-1\textquoteleft-spirobisindane-5,5\textquoteleft,6,6\textquoteleft-tetrol (26.48 mmol, 9.02 g) and 2,3,5,6-tetrafluorophthalonitrile (26.48 mmol, 5.31 g) were dissolved in dry dimethylformamide (DMF) (120 mL). K\textsubscript{2}CO\textsubscript{3} was added to the solution and the reaction was stirred at 58°C for two days. Deionized water (500 mL) and 300 mL methanol were added after cooling the reaction mixture and the product was separated by filtration. Further purification was performed by reprecipitation from a CHCl\textsubscript{3} solution with MeOH and a bright yellow solid product was produced after thermal activation at 120°C.

Synthesis of PIM-1-AO
As-synthesized PIM-1 (4 g) was added in methanol under stirring. Hydroxylamine (40 ml) was added to the solution and the reaction was stirred at room temperature for five days. The product was mixed with methanol and water, and it was activated at 120°C under vacuum.
Preparation of PF-15-TAEA fibers and PF-15-DETA sorbents
The polymer dope solutions were made by dissolving PIM-1-AO powder 15 wt% in NMP at room temperature under magnetic stirring. No special treatment to remove water was done to the NMP. The dope solution was loaded into a syringe pump which dispenses the dope directly into a jar of DI water at room temperature with no air gap. The dope was fed through a 1/8” OD PTFE tubing terminated with an 18-gauge blunt-tip needle at the rate of 0.8 ml/min. The nascent fiber was allowed to form in the water as it sinks to the bottom of the jar; no tension was applied. As a rule of thumb, the jar contained at least 1 L of water per 10 ml of dope solution.
As-spun fibers were solvent exchanged with methanol two times over 3 days and thermally activated at 120 CPF-15 fibers were added in 15 mL hexane solution. Amines were added to the solution and left for infusion for a day. The solution was decanted and the sorbent product was filtered and washed with hexane. The product was thermally activated at 85°C under vacuum prior to characterization studies.
Section S2: Materials Characterizations

Figure S1: H NMR spectrum of PIM-1.
Figure S2: $^1$H NMR spectrum of PIM-1-AO fiber (PF-15).

Polymer samples were dissolved in DMSO and characterized by $^1$H-NMR in order to confirm and quantify the extent of conversion of PIM-1 to amidoxime PIM-1 (PIM-1-AO). In particular, integration of the hydroxyl hydrogen peak (~9.5 ppm, 2H) and the cleanly-resolved phenyl hydrogen peak (~7.8 ppm) of PIM-1-AO give 2.00 and 2.03, respectively, indicating near full conversion of PIM-1 to PIM-1-AO.
Figure S3. FT-IR spectra of neat PIM-1 and amidoxime functionalized PIM-1 polymer particle (PIM-1) fiber (PF-15).
Figure S4: BET surface area calculation of PIM-1.
Figure S5. BET surface area calculation of PIM-1-AO.
Tables S1: BET surface, pore size and pore volume of the sorbents.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>BET surface area (m²/g)</th>
<th>pore size (Angstrom)</th>
<th>pore volume (cm³/g)</th>
<th>amine loading (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIM-1-A0</td>
<td>493</td>
<td>10.4</td>
<td>0.27</td>
<td>n/a</td>
</tr>
<tr>
<td>PF-15</td>
<td>503</td>
<td>10.8</td>
<td>0.25</td>
<td>n/a</td>
</tr>
<tr>
<td>PF-15-TAEA</td>
<td>8</td>
<td>25-60</td>
<td>0.03</td>
<td>21</td>
</tr>
</tbody>
</table>
Figure S6 Cross sectional SEM images of the fibers. Dope

- 13.5 wt%
- 15 wt%
- 17.5 wt%
compositions: 15wt%, 17.5wt% and 20wt%.
Figure S7 FT-IR spectra of PF-15 and its aminated sorbents PF-15-TAEA and PF-15-DETA.
Section 3. CO\textsubscript{2} sorption studies

Figure S8: CO\textsubscript{2} adsorption/desorption isotherm of PIM-1-AO.
Figure S9: CO$_2$ adsorption isotherm of PF-15-TAEA from 0 ppm to 1000 ppm.
Figure S10: CO\textsubscript{2} adsorption (blue circles) and desorption (grey circles) isotherms of PF-15-TAEA

This isotherm was collected with a Quantachrome 1C volumetric sorption analyzer. The same PF-15 TAEA sample was also used for the CO\textsubscript{2} adsorption measurement collected on the Micromeritics (3Flex) instrument that is presented in Figure 2b of the manuscript. Prior to the measurement, the sample was degassed at 75 °C for 1 hour under vacuum.
Figure S11: CO$_2$ adsorption (gray) isotherm of mesoporous silica control sample purchased from Sigma Aldrich.
Figure S12: Isosteric heats of adsorption ($Q_{st}$) for CO$_2$ of PF-15-TAEA.
Time CO₂ uptake (wt%)
Figure S13: CO₂ uptake in neat TAEA measured in flowing gas at a total pressure of 100 mbar with 90% N₂.
Figure S14: Humid CO$_2$ adsorption and desorption cycles for PF-15-TAEA

**The testing sequence:** The sections are labeled according to the percentage of humidified N$_2$ used in each cycle. A cycle consists of starting in dry N$_2$ at 25°C, then (A) switching to humidified N$_2$ for 30 minutes, (B) switching back to dry N$_2$ for 30 minutes, then (C) switching back to humidified N$_2$ for 30 minutes, then (D) adding in 10% dry CO$_2$ to the humidified N$_2$ stream for 30 minutes, then (E) switching back to dry N$_2$ for 30 minutes, then (F) ramping temperature to 75°C to complete regeneration, then (G) cooling back to 25°C, then (H) repeating the cycle using a new percentage of wet N$_2$ (see section labels above the chart for % humid N$_2$). For the final cycle from t = 900min, (I) switching from 100% dry N$_2$ to dry 10% CO$_2$ / 90% dry N$_2$ then (J) switching back to 100% dry N$_2$ and heat to regenerate the sorbent.
Figure S15: Breakthrough curves of H₂O (red), N₂ (light green) and CO₂ (blue) of the sorbent PF-15-TAEA under simulated wet air conditions: 400 ppm CO₂ concentration and 50 % RH at 25 °C. The data was collected by Micromeritics Instrument Co.
Table S2. CO₂ adsorption performance comparison for top performing sorbents

<table>
<thead>
<tr>
<th>Sorbent name</th>
<th>Class of sorbent/amine</th>
<th>CO₂ uptake at 400 ppm (mmol/g)</th>
<th>CO₂ uptake at 0.10 bar (mmol/g)</th>
<th>CO₂ capture rate (mmol/g·min⁻¹)</th>
<th>Regeneration Temperature</th>
<th>Sorption capacity loss over cycles</th>
<th>Sorbent formation/processibility</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-808-Gly</td>
<td>MOF/glycine</td>
<td>n/a</td>
<td>0.54*</td>
<td>0.007 (0.15 bar CO₂)</td>
<td>140 °C</td>
<td>no loss</td>
<td>particle/no</td>
<td>1</td>
</tr>
<tr>
<td>MOF-808-Gly</td>
<td>MOF/Lycene</td>
<td>n/a</td>
<td>1.04</td>
<td>n/a</td>
<td>140 °C</td>
<td>no loss</td>
<td>particle/no</td>
<td>1</td>
</tr>
<tr>
<td>MIL-101(Cr) 30 wt%TEPA</td>
<td>MOF/tetraethylpentamine</td>
<td>0.39</td>
<td>n/a</td>
<td>0.022 (400 ppm CO₂)</td>
<td>60 °C</td>
<td>no loss</td>
<td>particle/no</td>
<td>2</td>
</tr>
<tr>
<td>MIL-101(Cr) 50 wt%PEI</td>
<td>MOF/PEI</td>
<td>1.81</td>
<td>n/a</td>
<td>0.016 (400 ppm CO₂)</td>
<td>60 °C</td>
<td>no loss</td>
<td>particle/no</td>
<td>2</td>
</tr>
<tr>
<td>Mg2(dobpdc)-mmen</td>
<td>MOF/mmen</td>
<td>-</td>
<td>3.3</td>
<td>-</td>
<td>120 °C</td>
<td>no loss</td>
<td>particle/no</td>
<td>3</td>
</tr>
<tr>
<td>FCTF-1</td>
<td>COF/triazine</td>
<td>-</td>
<td>0.73</td>
<td>-</td>
<td>vacuum</td>
<td>no loss</td>
<td>particle/no</td>
<td>4</td>
</tr>
<tr>
<td>EB-PEI/SiO₂</td>
<td>Silica/PEI</td>
<td>-</td>
<td>2.2</td>
<td>-</td>
<td>120 °C</td>
<td>no loss</td>
<td>particle/no</td>
<td>5</td>
</tr>
<tr>
<td>h-PEI/SBA15-130</td>
<td>Silica/PEI</td>
<td>-</td>
<td>-</td>
<td>0.08 at 400 ppm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>NOHM-PEI</td>
<td>Polymer/PEI</td>
<td>1.05</td>
<td>-</td>
<td>0.004 at 400ppm</td>
<td>120 °C</td>
<td>no loss</td>
<td>particle/no</td>
<td>7</td>
</tr>
<tr>
<td>PF-15-TAEA</td>
<td>Polymer/TAEA</td>
<td>0.8</td>
<td>1.93</td>
<td>0.45 (0.1 bar CO₂)</td>
<td>70 °C</td>
<td>no loss</td>
<td>fiber/yes</td>
<td>this work</td>
</tr>
<tr>
<td>21 wt.%PEI-PIM-1</td>
<td>Polymer/PIM-1</td>
<td>0.2</td>
<td>1.24 (0.15 bar)</td>
<td>-</td>
<td>110 °C</td>
<td>10%</td>
<td>fiber/yes</td>
<td>8</td>
</tr>
<tr>
<td>SBA-15/PEI</td>
<td>Silica/PEI</td>
<td>1.58</td>
<td>-</td>
<td>0.014 (400 ppm CO₂)</td>
<td>-</td>
<td>-</td>
<td>particle/no</td>
<td>6</td>
</tr>
<tr>
<td>Silica/PEI</td>
<td>Commercial sorbent</td>
<td>-</td>
<td>2.36</td>
<td>0.004</td>
<td>110 °C</td>
<td>30%</td>
<td>particle/no</td>
<td>9</td>
</tr>
<tr>
<td>Climeworks Sorbent</td>
<td>Silica, cellulose acetate, amines</td>
<td>0.65</td>
<td>-</td>
<td>-</td>
<td>80-130 °C</td>
<td>-</td>
<td>fiber/yes</td>
<td>10,11</td>
</tr>
</tbody>
</table>

References

4) Y. Zhao, K. X. Yao, B. Teng, T. Zhang and Y. Han, Energy Environ. Sci., 2013, 6, 3684.