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

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Polymers of intrinsic microporosity (PIM) fibers based on amidoxime and amine functionalities were formulated into high-performance CO_2 adsorbents. Fiber sorbents were composed of a single porous polymer component as well as molecular amines to increase the CO_2 capture kinetics. The highest CO_2 uptake capacity (3.3 wt% CO_2 at 400 ppm) among all PIM-based sorbents to date was reported. Moreover, sorbents exhibited rapid CO_2 adsorption rates (5 min adsorption cycle) and cost efficient regeneration (70°C, no vacuum) which are imperative to reducing the cost of direct air capture.

Introduction

Carbon capture technology has long been considered a viable solution to reduce ever-increasing atmospheric CO_2.[1] Very recently, CO_2 capture directly from the air has been in the spotlight due to its unique potential for reaching Paris Agreement targets.[2] To meet these targets, negative emission technologies are needed in addition to point source capture. However, the cost of direct air capture of CO_2 (DAC) is currently an order of magnitude above that of point source capture.[3] This high cost is due to the very low concentration of CO_2 in the atmosphere (400 ppm). Therefore, developing economical, high-performance sorbent and solvents for DAC and other low concentration CO_2 capture applications has been extremely challenging to date.[4] To adsorb a sufficient level of CO_2 from the air, a library of adsorbents with nucleophilic groups (amines and hydroxides) has been investigated.[5,6] Sorbents such as Mg-MOF-74, aminated silica, and various porous polymer networks (PPNs) have shown high CO_2 capture capacity at low CO_2 partial pressure.[7] However, these high-performance sorbents are mostly in particle form and ultimately need to be processed into geometries such as fibers or pellets to decrease pressure drop, which is detrimental to the DAC energy cost.[8] On the other hand, the kinetic rate of the CO_2 adsorption and desorption is at least as important a parameter for DAC as well as for other CO_2 capture applications.[9] To date, CO_2 capture adsorption and desorption cycles with aminated sorbents frequently exceed two hours.[10] The most expensive part of CO_2 capture is sorbent regeneration. High-temperature desorption not only adds to the total cost of DAC but also leads to an oxidation problem that reduces the sorbent lifetime.

Pursuant to these challenges associated with current DAC materials, we have developed a polymeric fiber sorbent functionalized with amidoxime and molecular amines (Figure 1A). The synthesis of amidoxime-functionalized PIM-1 (PIM-1-AO) was performed by modifying our cost-efficient and scalable method that was reported recently.[11] The polymer sorbent is soluble in common sorbents. Accordingly, the polymers were spun into fibers (Figure 1B) and later functionalized with diethylenetriamine (DETA) and tris(2-aminoethyl)amine (TAEA). The preparation of fiber sorbents, their characterization, and gas sorption tests are reported herein.
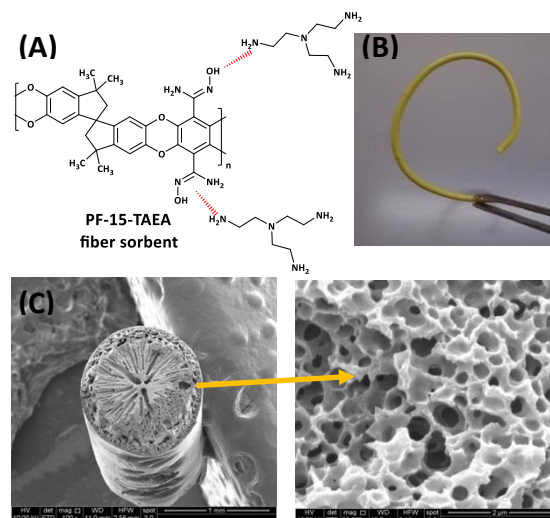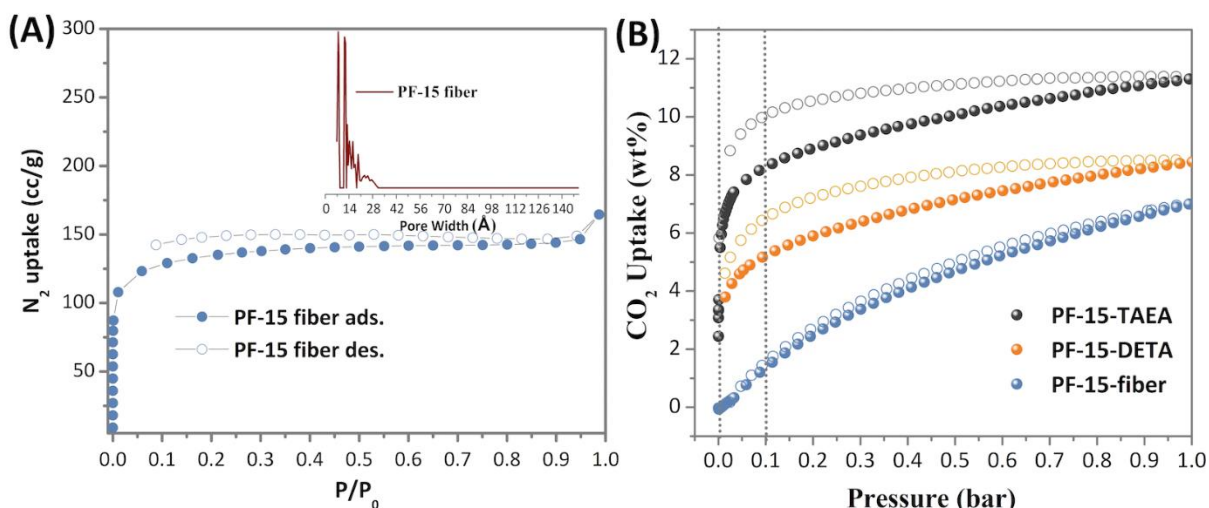

Figure 1. (A) Chemical structure (B) top view and (C) cross-section SEM images of PF-15-TAEA sorbent.

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Figure 2. (A) Nitrogen adsorption and desorption isotherm (77 K) and pore size distribution of PF-15 fiber (inset) and (B) CO_2 adsorption (filled spheres) and desorption (hollow spheres) isotherms of PF-15 (neat), PF-15-DETA and PF-15-TAEA fibers.

Discussion

Polymer fibers were spun from PIM-1-AO, which was prepared by first synthesizing PIM-1 followed by post-synthetic functionalization with amidoxime groups, using our recently reported synthetic procedure (SI section 1).[11] The amidoxime functionalization reaction was performed in methanol to attenuate the degree of the functionalization of the polymers. Unlike other reported methods, this amidoxime functionalization reaction method is more straightforward and low cost as it does not require heat or relatively more expensive solvents such as tetrahydrofuran.[12]

The chemical structure and the functional groups were identified by FT-IR (Figure S1). The IR absorption peaks of –OH/-N-H, nitrile, and N=H were found at 3300–3600, 2240, and 1604 cm^{-1}, respectively, indicating the presence of amidoxime functional groups.[13]

Nitrogen adsorption measurements of PIM-1 and PIM-1-AO confirmed that the porosity and surface area of the polymers are in-line with reported studies, at approximately 749 m^2/g and 493 m^2/g respectively (Figure S2 and S3).

PIM-1-AO fibers were spun into porous fiber form using a conventional non-solvent induced phase separation (NIPS) technique.[14] This was possible because PIM-1-AO can be readily dissolved in N-methyl-2-pyrrolidone (NMP), unlike PIM-1. The dope solutions were extruded through a needle bore into a water bath using a syringe pump, and the resulting fiber was solvent-exchanged with methanol before drying. Cross-sectional SEM characterization showed that the fiber spun from a 15 wt% polymer dope solution has an internally spongy structure (300-400 nm cells) near the shell surface, with larger macroporous channels radiating from the inner core outward, has and with a smaller finger region underneath a non-porous skin layer (Figure 1C and S4). Within the range of dope compositions studied (15-20 wt% polymer), increasing dope concentration leads to less porosity and at 20 wt%, the formation of non-porous regions within the fiber.

Fiber sorbents based on 15% polymer concentration were selected (denoted as PF-15) for amine impregnation, gas adsorption, and kinetics studies. The nitrogen adsorption measurements (Figure 2A) of PF-15 showed that the fibers exhibit 503 m^2/g BET surface area which is very similar to that of their particle form (PIM-1-AO, 493 m^2/g, Figure S3). On the other hand, the pore size distribution of PF-15, calculated by using non-local density functional theory (NLDFT), was found to be mostly microporous (<2 nm) (Figure 2A). However, the pores of PF-15 had slightly larger volume (>2 nm) compared to the pore size distribution of PIM-1-AO.[11]This shift could be attributed to the fiber processing which creates larger pores in the polymer during phase separation of the polymer with water.[15] After confirming the porosity, PF-15 was impregnated with molecular amines diethylenetriamine (DETA) and tris(2-aminoethyl)amine (TAEA). We chose an amine impregnation method which includes decanting most of the unreacted amines from the solution.[16] With this method, excess (unbounded) amine accumulation in the sorbents could be limited as the sorbent only receives amines based on its amine affinity. Molecular amines (DETA and TAEA) were used rather than polyamines such as polyethylene amine (PEI), which is the conventional choice of amine in sorbents.[17] These molecular amines can increase the CO_2 adsorption rate (mmol/g.hr) as well as reduce the energy for desorption.[18] After the amine impregnation, two amine-functionalized sorbents, denoted PF-15-DETA and PF-15-TAEA, were characterized by FT-IR to evince the amine incorporation. IR bands representing amines[11] were visible in the IR spectrum of the sorbents (Figure S5).
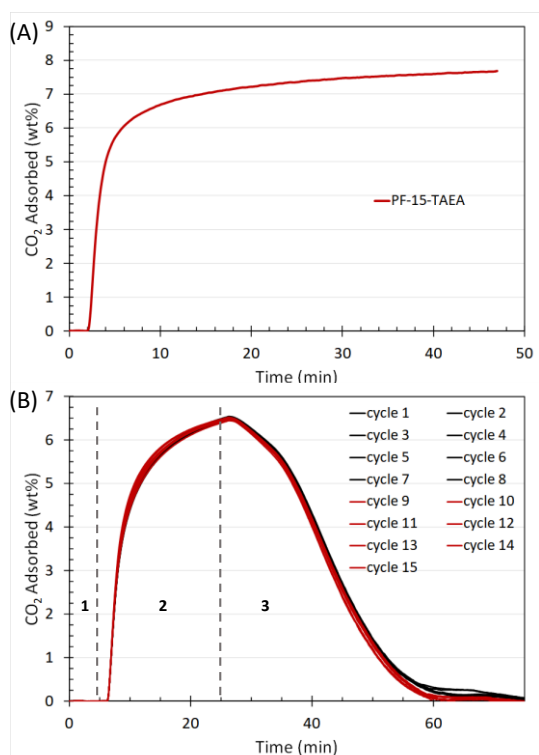
Figure 3. CO_2 uptake in PF-15-TAEA. (A) measured in flowing gas at a total pressure of 100mbar, 25°C. The switch from pure N_2 to 10%CO_2/90%N_2 occurs at 2 min. (B) adsorption / desorption cycles in flowing gas at a total pressure of 1bar. Conditions: (1) pure N_2, 25°C; (2) 10%CO_2/90%N_2; (3) temperature ramp in pure N_2 at 3°C/min to 70-75°C (black) or 75-80°C (red).

The CO_2 adsorption isotherms of the aminated and non-aminated fiber sorbents were compared (Figure 2B). The CO_2 uptake of the particle polymer (PIM-1-AO) (Figure S6) and the fiber PIM-1-AO (PF-15-neat) showed similar CO_2 adsorption capacity.

On the other hand, aminated sorbents, PF-15-DETA and PF-15-TAEA, demonstrated drastically higher CO_2 adsorption capacity. To our knowledge, the CO_2 uptake of PF-15-TAEA is the highest of any PIM-based material reported to date under the same conditions (8.2 wt% or 43 cc/g at 0.1 bar, 298K). We also tested CO_2 adsorption capacity of PF-15-TAEA at very low CO_2 partial pressure and the sorbent showed 3.3 wt% (17 cc/g) CO_2 uptake capacity at 400 ppm CO_2 (298 K), which represents the concentration of CO_2 in the atmosphere.

This remarkable CO_2 uptake performance can be attributed to the high porosity of the PF-15 polymer fiber which allows for high capacity for molecular amines. We have also calculated the isosteric heats of adsorption (Q_{st}) for PF-15 and PF-15-TAEA by using the Clausius-Clapeyron equation (Figure S7).[19] The Q_{st} of PF-15-TAEA is 47 kJ/mol, indicating that it is an effective chemisorbent.

The CO_2 uptake capacity of a sorbent is commonly used metric for performance comparison. However, in real applications the CO_2 capture rate (kinetics) also contributes to the cost efficiency of the sorbent system.[20] The CO_2 adsorption rate is especially important for DAC. Accordingly, we studied the kinetics of PF-15-TAEA (Figure 3A). The mixed gas (10% CO_2 and 90% N_2) CO_2 uptake performance of the sorbent was found to be similar to the pure CO_2 adsorption data. The very low nitrogen uptake of the sorbent is related to the low porosity of the sorbent after amine loading. Remarkably, PF-15-TAEA captures 90% of the total CO_2 capacity within five minutes. The initial CO_2 uptake rate was calculated to be 6 wt%/g/0.1 hr. This initial slope is much higher compared to conventional aminated sorbents.[21]

Intriguingly, the sorbent was regenerable at only 70°C using a nitrogen sweep. In a real system, a steam sweep may be preferred for simple downstream separation of the sweep and product gas. Having a low-temperature regeneration process is expected to greatly reduce the overall carbon capture cost.[22] In addition, the low temperature desorption also reduces the probability of oxidative degradation of sorbents over time. Oxidative aging is a prevalent phenomenon in amine-based sorbents with high temperature (>90°C) regeneration requirements which accelerate the oxidation and decrease the sorbent lifetime.[23,24] The fast kinetics and mild regeneration conditions of PF-15-TAEA can be ascribed to two parameters: (1) The molecular amines are much smaller compared to PEI which enables faster CO_2 diffusion in the sorbent[25], and (2) The relatively low amine concentration in the sorbents. The usual amine loading in CO_2 sorbents is approximately 50 wt%.[26] Therefore it takes more time for CO_2 molecules to diffuse through the packed polymer (PEI) chains. We intentionally used a relatively small amine loading (<20 wt%) to facilitate rapid CO_2 transport in the sorbent.

To probe the sorbent stability, we have cycled the CO_2 sorption of PF-15-TAEA 15 times and the CO_2 uptake of the sorbent remained consistent (Figure 3B). The performance stability of the sorbent may be related to the strong interaction between the amidoxime and amines in the fiber sorbents.[27] Humid CO_2 adsorption tests were also performed for the fibers using several different humidity levels. The CO_2 uptake capacity (7.5 wt% at 10% CO_2, 40% RH, and 298 K) was slightly increased compared with the CO_2 uptake at 0% RH (Figure S8), which is typical for amine-based sorbents.[28]

Conclusions

We have developed novel, soluble, and cost-efficient PIM-1 polymer fiber sorbents for low concentration CO_2 capture. The sorbent is processable into various geometries such as porous monolith fibers, which were demonstrated here. Molecular amines were tethered to sorbents through strongly interacting amidoxime groups. The CO_2 uptake performance of the sorbent fiber not only exceeded previously reported PIM sorbents, but also exhibited rapid and low temperature regeneration, which is vital for direct air capture and other low concentration CO_2 capture applications.

Disclaimer

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter

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