

Scalable and Highly Porous Membrane Adsorbents for Direct Air Capture of CO₂

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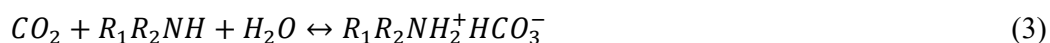
KEYWORDS: *direct air capture, polyethylenimine, membrane adsorbent, CO₂ sorption, porous support*

ABSTRACT: Direct air capture (DAC) of CO₂ is a carbon-negative technology to mitigate carbon emissions, and it requires low-cost sorbents with high CO₂ sorption capacity that can be easily manufactured on a large scale. In this work, we develop highly porous membrane adsorbents comprising branched polyethylenimine (PEI) impregnated in low-cost, porous Solupor supports. The effect of the PEI molecular mass and loading on the physical properties of the adsorbents is evaluated, including porosity, degradation temperature, glass transition temperature, and CO₂ permeance. CO₂ capture capacity from simulated air containing 400 ppm CO₂ in these sorbents is thoroughly investigated as a function of temperature and relative humidity (RH). Polymer dynamics was examined using differential scanning calorimetry (DSC) and broadband dielectric spectroscopy (BDS), showing that CO₂ sorption is limited by its diffusion in these PEI-based sorbents. A membrane adsorbent containing 48 mass% PEI (800 Da) with a porosity of 72% exhibits a CO₂ sorption capacity of 1.2 mmol/g at 25 °C and RH of 30%, comparable to the state-of-the-art adsorbents. Multi-cycles of sorption and desorption were performed to determine their regenerability, stability, and potential for practical applications.

■ INTRODUCTION

Direct air capture (DAC) has emerged as a critical approach to reducing CO₂ content and ultimately mitigating the long-lasting effect of CO₂ in the atmosphere.^{1, 2} The main challenge to the DAC is the low CO₂ content (~400 ppm) in the air and thus associated high cost.^{3, 4} For example, the CO₂ content in the air is 300 times more dilute than in coal-fired power plant flue gas (~12%). State-of-the-art technologies for DAC are based on solvents or sorbents, such as aqueous hydroxide solutions and solid amine sorbents.⁵⁻⁷ The hydroxide solutions have a high capacity for CO₂ sorption. However, sorbent regeneration can be costly due to heating and water evaporation.⁸

Solid sorbents offer the possibility of low energy input, low operating costs, and good scalability. Amine groups are the key to achieving high CO₂ sorption capacity and high selectivity over the major components in the air (such as N₂ and O₂).^{9, 10} Equations 1 and 2 elucidate the reaction mechanisms between the primary and secondary amines and CO₂. Under dry conditions, these amines react with CO₂ and form ammonium carbamate.^{7, 11} The maximum molar ratio of CO₂/N can be as high as 0.5 and can increase to 1.0 in the presence of moisture, as shown in Equation 3. Equation 4 also shows that tertiary amines can react with CO₂ at a 1:1 molar ratio in the presence of water vapor:



Amine groups can be incorporated into solid sorbents by impregnation in porous supports.^{6, 7, 12} A variety of inorganic porous supports have been explored to incorporate amines including fume silica,¹³ silica monoliths,¹⁴ ordered mesoporous silica such as MCM-41 with regular cylindrical mesopores¹⁵ and SBA-15 with both mesopores and intrawall pores,¹⁶

mesoporous γ alumina,¹⁷ and metal-organic frameworks (MOFs).¹⁸⁻²⁰ CO₂ sorption capacity as high as 1 – 3 mmol/g was reported for simulated air. The sorption is often subject to slow kinetics due to CO₂ diffusion, and the pore structure and chemistry exert significant influence on CO₂ sorption capacity and kinetics.^{21, 22} The strong interactions between amines and CO₂ may also retard CO₂ diffusion at low temperatures.^{23, 24} For example, CO₂ sorption in a polyethylenimine (PEI)-modified silica is higher at 75 °C than 25 °C because of the faster diffusion at the higher temperature.^{13, 25} These inorganic supports are relatively expensive to produce at a large scale. By contrast, polymeric supports (such as expanded poly(tetrafluoroethylene)²⁶ and hollow fiber membranes (HFM)²⁷⁻²⁹) have been explored as they can be low-cost and routinely produced on a large scale. Nevertheless, porous supports can be continuously optimized to lower adsorbent costs, a key component determining the DAC costs.

In this study, we develop a scalable, highly porous membrane adsorbent platform, where branched PEI is impregnated into commercial flatsheet Solupor support (20-100 μ m), as shown in Fig. 1. Solupor support is made of high-density polyethylene (HDPE), and it has a porosity of 88%, a pore size of 0.9 μ m, and good chemical and mechanical stability.³⁰ It is produced at a low cost and large scale as battery spacers, and its high porosity renders a high surface area and increases the accessibility of the amines to CO₂. Two branched PEIs with molecular mass (M_w) of 800 and 25,000 g/mol are used to elucidate their effect on CO₂ sorption capacity and long-term stability.^{31, 32} The sorbents are denoted as SPEI800- x or SPEI25k- x , where x (mass%) is the PEI mass percentage in the samples. The effect of the PEI M_w and content on porosity, CO₂ permeance, and amine sorption efficiency is investigated. CO₂ sorption capacity was thoroughly evaluated as a function of temperature and relative humidity (RH) in both series of SPEIs, and their long-term stability was examined by multi-cycles of sorption and desorption. Compared with many PEI-based sorbents reported in the literature,

our highly porous adsorbents are based on commercially available low-cost supports and can be produced using existing membrane fabrication equipment and allow for similar CO₂ capture as packed bed systems or plate-and-frame modules while significantly reducing pressure drop and accelerating the sorption and desorption. Our membrane adsorbents demonstrate a CO₂ sorption capacity of 1.2 mmol/g sorbent with simulated air, comparable to state-of-the-art sorbents, making them attractive, considering their low cost and easy production scale-up. Moreover, this study, for the first time, shows that the impregnated PEI thin films have reduced chain dynamics using differential scanning calorimetry (DSC) and broadband dielectric spectroscopy (BDS), validating that the CO₂ sorption is limited by its diffusion in these amine-based DAC sorbents.

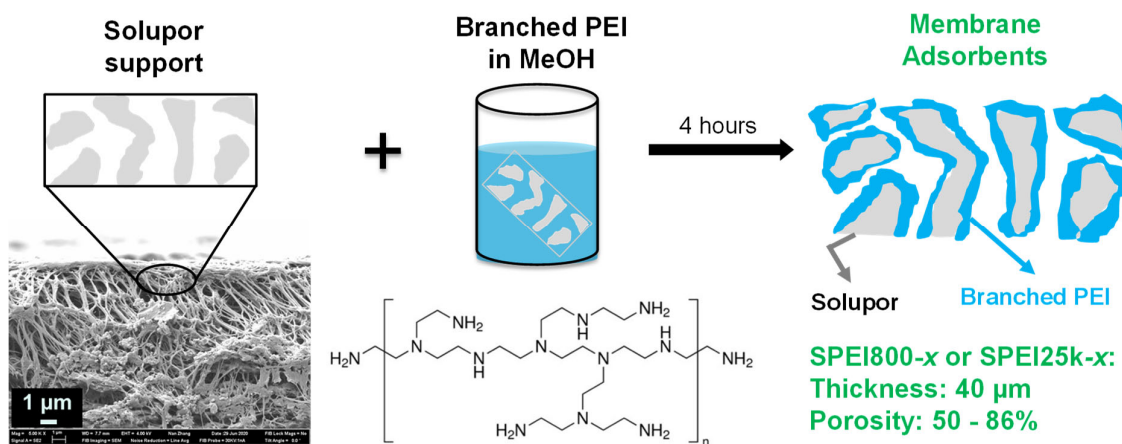


Figure 1. Schematic of preparation of membrane adsorbents (SPEI800-x or SPEI25k-x) via wet impregnation, including a cross-sectional SEM image of the Solupor support with a pore size (d_p) of 0.9 μm and a thickness of 40 μm.

■ RESULTS AND DISCUSSION

Physical Properties of Membrane Adsorbents. The PEI loading in membrane adsorbents was determined by the mass increase after the PEI impregnation. Figure 2a shows that the PEI loading increases before leveling off with increasing PEI concentration (w_{PEI}) in the methanol solutions. As the PEI800 concentration increases from 1 to 15 w/v% (g per 100 ml methanol), the x increases from 18% to 63% (Table S1), indicating successful loading of

PEI in the Solupor. Additionally, once the w_{PEI} is above 5 w/v%, its further increase does not significantly increase the PEI loading in the adsorbents. Assuming that the Solupor support is fully filled by the solution before drying for the PEI to coat the pore surface, the x can also be estimated using the following equation:

$$x = \frac{\phi_{SS} \times w_{PEI}}{\rho_{SS} + \phi_{SS} \times w_{PEI}} \times 100\% \quad (5)$$

where ϕ_{SS} is the porosity of the Solupor support (0.88), and ρ_{SS} is the density of the Solupor support (0.13 g/cm³). As shown in Figure 2a, Equation 5 underestimates the loading for both series of adsorbents, probably because the PEI may also deposit on the Solupor surface.

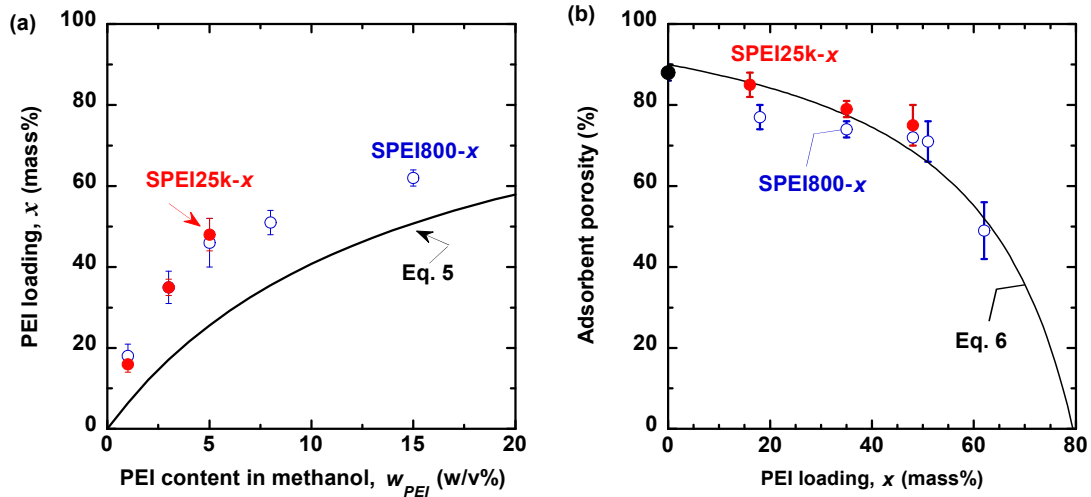


Figure 2. Modeling of the PEI loading (determined by the mass increase after impregnation) and porosity (determined by the solvent uptake) of the SPEIs. (a) Correlation between x and PEI concentration in the methanol solutions (w_{PEI}). (b) Correlation between the membrane porosity and x . The error bar is the standard deviation of 3 samples or more.

The membrane porosity was determined using the n-decane sorption experiments. Figure 2b demonstrates that the membrane porosity decreases with increasing PEI loading as the pores are filled up by PEI. For example, SPEI800-18 exhibits a porosity of 76%, much higher than SPEI800-63 (49%). Similar behavior has also been observed for PEI impregnated in other supports, such as SBA-15¹⁶ and MIL-101(Cr).¹⁷ The porosity of the membrane adsorbents (ϕ_{MA}) can also be estimated by Equation 6:

$$\phi_{MA} = \phi_{SS} - \frac{x\rho_{SS}}{(1-x)\cdot\rho_{PEI}} \quad (6)$$

As shown in Figure 2b, there is a remarkable agreement between the calculated and measured porosity.

Figures 3a and S1a display the thermograms of thermalgravimetric analysis (TGA) for Solupor, SPEI800-18, and PEI800. The Solupor support degrades at ≈ 490 °C, consistent with the degradation temperature of HDPE.³³ The pure PEI800 starts to degrade at 150 °C.³⁴ By contrast, the SPE800-18 exhibits the first degradation step from 220 to 450 °C, indicating improved thermal stability because of Solupor confinement. The mass loss of the SPEI800-18 at 450 °C is 14%, consistent with the PEI loading (18%) determined from the mass increase during the impregnation, and similar behaviors have been observed for other SPEI samples (Table S1). The second degradation step of the SPE800-18 occurs at 450 °C because of the degradation of Solupor.

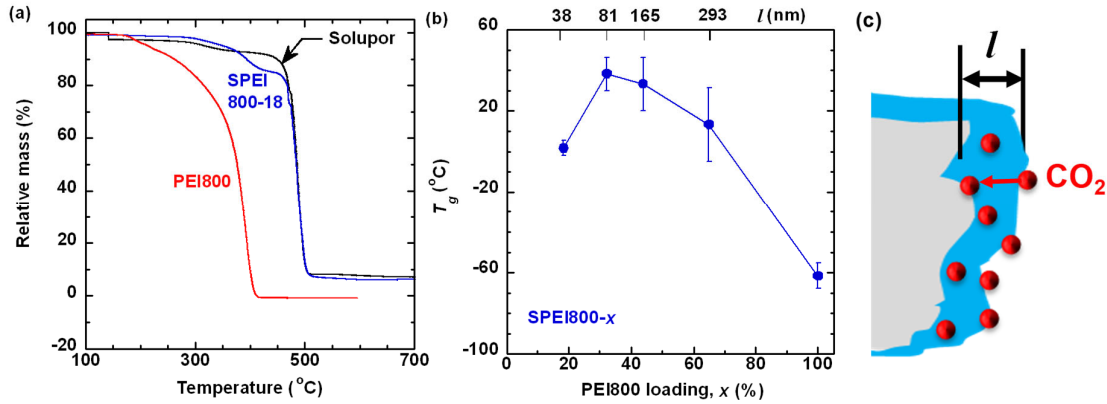


Figure 3. (a) TGA thermograms of Solupor and SPEI800-18. (b) Effect of the PEI loading and film thickness on T_g . (c) Schematic demonstrating CO₂ diffusion into PEI film. The error bar in (b) is the standard deviation for 3 samples or more.

Figure 3b shows that the glass transition temperature (T_g) of the PEI in the SPEI800 increases with increasing loading before decreasing. For example, SPEI800-18 exhibits a T_g of 0 °C, much higher than that of PEI800 (-65 °C). The uncertainty is higher for SPEI800-49 and SPEI800-63 due to the random distribution of PEI800 in the pores at higher loadings.³⁵ To

elucidate this behavior, the average thickness of the PEI film on the pore wall, l (nm), is estimated by Equation 7:

$$l = \frac{x}{(1-x) \cdot \rho_{PEI} \cdot A_{SS}} \quad (7)$$

where A_{SS} is the surface area of the Solupor measured by the Brunauer, Emmett and Teller (BET) method (5.8 m²/g). Notably, the thickness cannot be directly measured due to the complexity of the porous structures. Therefore, the l values from Equation 7 are the only way to indicate the PEI layer thickness, which increases from 38 to 293 nm as the loading increases from 18% to 62%. Figure 3b shows that the pore wall can significantly influence the polymer chain dynamics of the thin PEI films,^{36, 37} consistent with the improved thermal stability of the Solupor-confined PEI (Figure 3a).

Table S1 also shows that increasing the x decreases pure-gas CO₂ permeance at 35 °C. For example, introducing 46% PEI800 in Solupor decreases CO₂ permeance from 1.8×10⁶ to 2.3×10⁴ GPU (1 GPU = 10⁻⁶ cm³(STP) cm⁻² s⁻¹ cmHg⁻¹). Nevertheless, the membrane adsorbents still exhibit very high gas permeance, which is needed for the air to flow through the sorbent at low pressure drops.

CO₂ Sorption and Behaviors of SPEIs. The CO₂ sorption in the SPEIs was tested with simulated dry air containing 400 ppm CO₂ for 4 h at 25 °C. Figure 4a shows that increasing the PEI loading increases CO₂ sorption capacity before leveling off for both series of samples. For example, increasing x from 18% to 48% increases CO₂ sorption capacity by 57% from 0.30 to 0.47 mmol/g for SPEI800, while SPEI25k-48 exhibits CO₂ sorption capacity only 25% higher than SPEI25k-16. Increasing x above 35% for SPEI25k and above 48 for PEI800 does not enhance CO₂ sorption capacity because of the limited CO₂ transport caused by the decreased porosity (Figure 2b) and increased PEI thickness (Figure 3b). Similar behavior has also been reported with computational simulations.¹⁵

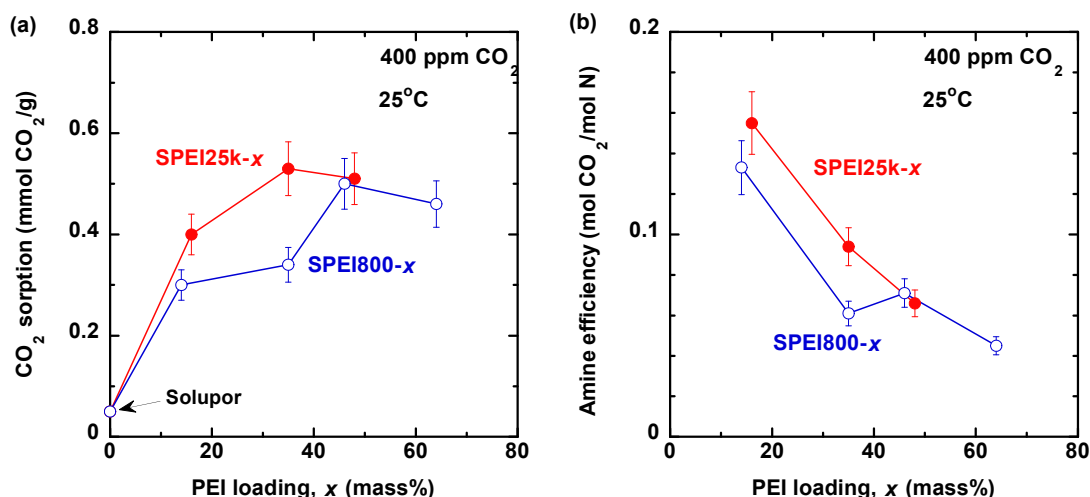


Figure 4. Effect of the PEI loading on (a) CO₂ sorption capacity and (b) amine efficiency when tested with 400 ppm CO₂ in air and 25 °C (dry gas). The error bars are estimated by the error propagation method.³⁸

The amine efficiency for CO₂ sorption (mol CO₂/mol N) can be calculated by assuming that only primary (1°) and secondary (2°) amines are active for CO₂ sorption under dry conditions (Equations 1 and 2). The branched PEI (including PEI800 and PEI25k) contains 1 mol N^{1°,2°} per 62.3 g of PEI. As shown in Figure 4b, the amine efficiency of both SPEI25k and SPEI800 decreases from ≈ 0.15 to ≈ 0.07 mol CO₂/mol N as x increases from 18% to 48%. The amine efficiency is significantly below the theoretical value of 0.5 mol CO₂/mol N, indicating that not all amine groups are accessible for CO₂ sorption because of the CO₂ transport limit during the testing time (4 h). For example, the PEI800 is glassy at the testing temperature (25 °C) in SPEI800-35 ($T_g = 38$ °C) and SPEI800-48 ($T_g = 35$ °C), leading to low CO₂ diffusivity and limited access of CO₂ to the amine groups in the PEI films (Figure 3c).

Figure 5a exhibits that increasing the sorption temperature from 25 to 50 °C drastically increases the CO₂ sorption capacity of SPEI800 for 4-h testing. For example, increasing the temperature from 25 to 50 °C increases CO₂ sorption capacity by 72% from 0.47 to 0.81 mmol CO₂/g in SPEI800-48, and by 36% from 0.53 to 0.72 mmol CO₂/g for SPEI25k-48 (Figure 5b). The comparison indicates that the temperature effect is more significant for the lower

molecular weight PEI with lower viscosity. On the other hand, CO₂ sorption in SPEI25k-48 is below 0.1 mmol/g at 65 °C and eventually decreases to below zero after 4 h due to the degradation of PEI25k at 65 °C in the presence of O₂.

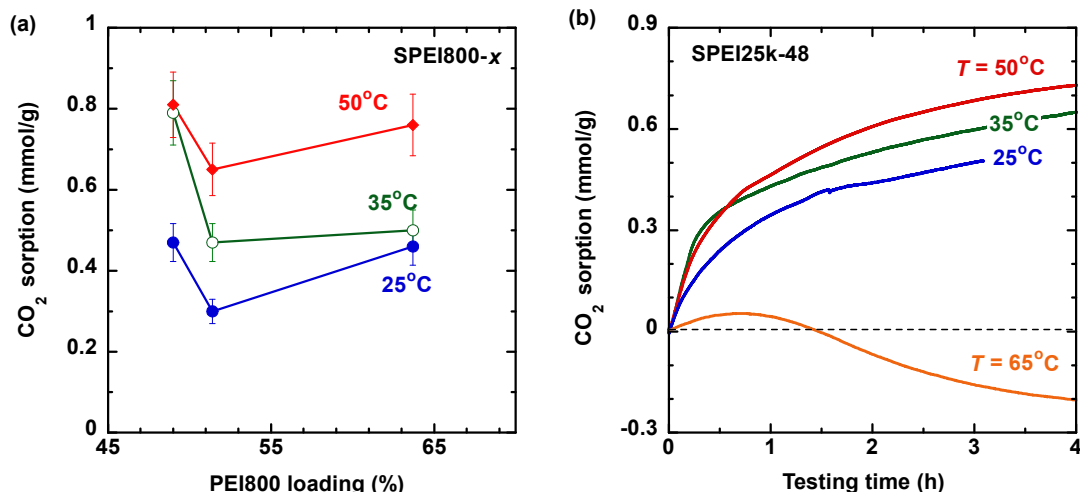


Figure 5. (a) Effect of temperature on CO₂ sorption capacity in SPEI800 when tested with air containing 400 ppm CO₂. (b) CO₂ sorption kinetics of SPEI25k-48 at 25, 35, 50, and 65 °C. The error bars in Figure 5a are estimated by the error propagation method.³⁸

The increase in the measured CO₂ sorption with increasing temperature contradicts the notion that gas sorption at equilibrium decreases with increasing temperature. This behavior can be ascribed to the non-equilibrium CO₂ sorption caused by the restricted CO₂ diffusion in amines. As CO₂ reacts with the amine groups on the surface of the PEI films, it cross-links the PEI and lowers CO₂ diffusion in the PEI films to access other amine groups (Figure 3c). Increasing the temperature from 25 to 50 °C lowers the CO₂ content on the PEI surface and accelerates the CO₂ diffusion into the PEI films, resulting in higher CO₂ sorption. On the other hand, the effect of equilibrium solubility becomes dominant at 65 °C, decreasing the measured CO₂ sorption. The effect of diffusion-limited sorption is also evident when increasing the sorption time from 4 to 9 h increases CO₂ sorption capacity (Figure S2). Additionally, the SPEI25k-48 exhibits slower CO₂ sorption than SPEI800-48 because of the higher viscosity of PEI25k.

To validate the effect of the CO₂ sorption on the PEI chain dynamics, thermal properties were measured using DSC for three samples, including fresh PEI25k, PEI25k after CO₂ sorption, and regenerated PEI25k. The CO₂ sorption increases the T_g of the PEI, which agrees with neutron scattering experiments and computer simulations.^{35, 39}

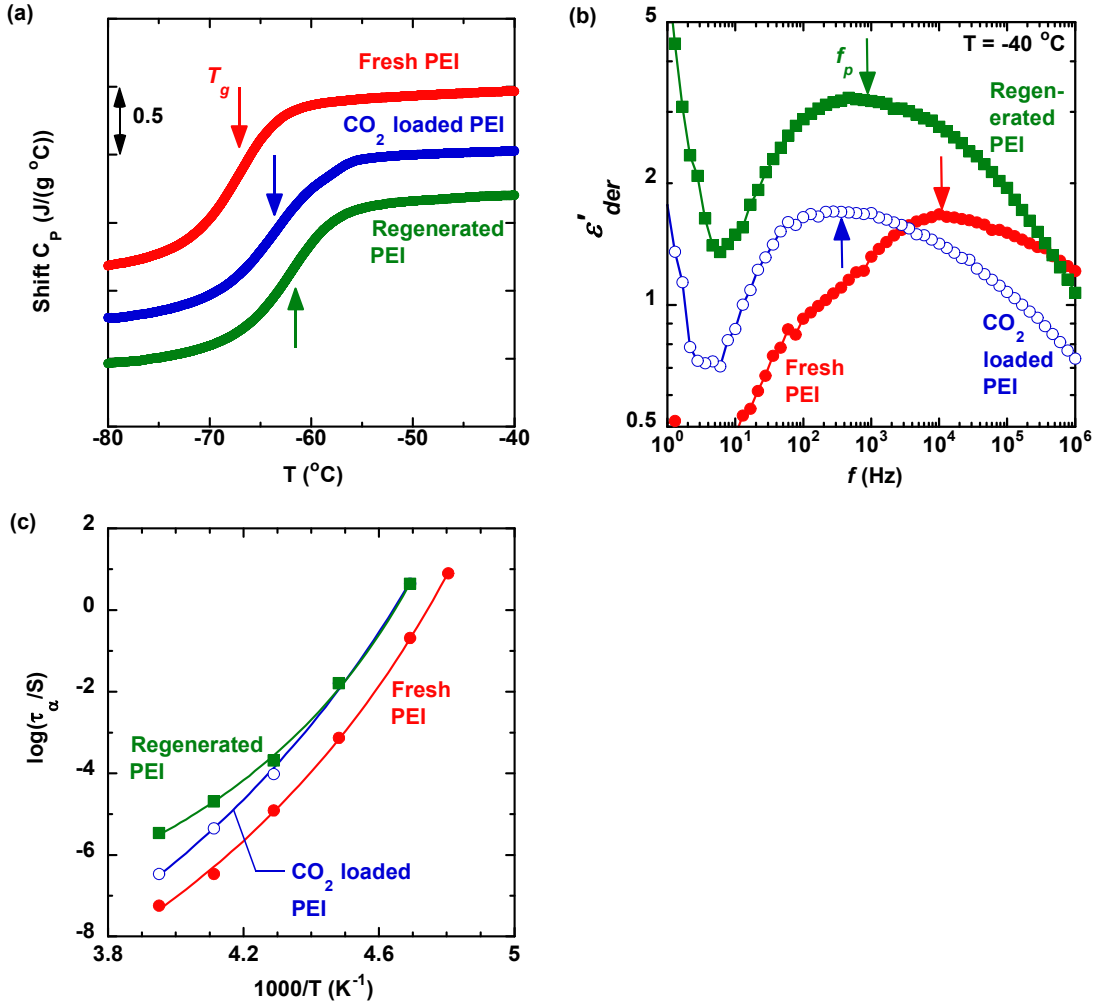


Figure 6. Comparison of polymer chain dynamics of fresh PEI25k, CO₂ loaded PEI25k, and regenerated PEI25k, including (a) DSC thermograms and (b) dielectric derivative spectra (ϵ'_{der}) at -40 °C. The arrows point to the position of T_g in (a) and the peak frequency (f_p) associated with the segmental dynamics in (b). (c) Segmental relaxation estimated through $\tau_\alpha = \frac{1}{2\pi f_p}$ at different temperatures. The lines provide the VFT fit to each sample.

Figure 6b shows a comparison of dielectric derivative spectra, $\epsilon'_{der} = -\frac{\pi}{2} \frac{\partial \epsilon'}{\partial \ln f}$ with ϵ'

being the dielectric storage permittivity and f the frequency of fresh PEI, CO₂ loaded PEI, and

regenerated PEI. The arrows point to the characteristic segmental relaxation peaks of the PEI, and their structural relaxation can thus be estimated as $\tau_\alpha = \frac{1}{2\pi f_p}$. Both CO₂-loaded and regenerated PEI exhibit much slower segmental relaxation with a significant broadening than the fresh PEI, implying the sorbent changes during sorbent regeneration. The results demonstrate that air-sorption and sorbent regeneration strongly affect the polyamine dynamics.

Figure 6c summarizes the temperature dependence of the τ_α for the three samples, where the symbols are from experiments, and the lines are the best fits of the Vogel-Fulcher-Tammann (VFT) equation. The T_g values from the VFT fit at $\tau_\alpha = 100$ s match well with those from the DSC measurements, which further confirms the peak assignment of our BDS measurements. We notice a shoulder peak at lower frequencies for all three samples. The physical origin of this peak remains unclear at this moment, which could be due to H-bonding association/dissociation in PEI among primary or secondary amine groups. The slow dynamics modes have also been observed in amine-based associative polymers through reversible H-bonding interactions.⁴⁰

Effect of RH on CO₂ Sorption. Figure 7a illustrates the complicated effect of RH (15% and 30%) on the CO₂ sorption in SPEI800-48. The introduction of 15% RH increases the CO₂ sorption capacity at 25 °C from 0.47 to 1.0 mmol/g because of the additional reaction with the tertiary (3°) amine in the presence of water (Equations 3 and 4). Moreover, water swells the PEI network, permitting CO₂ access to additional amine sites. However, a further increase of the RH to 30% increases the CO₂ sorption capacity to only 1.2 mmol/g (12% improvement) at 25 °C, probably due to the competitive sorption between water and CO₂ with accessible amine groups and the swelling of the PEI and thus blocked pores in the SPEIs.¹⁵

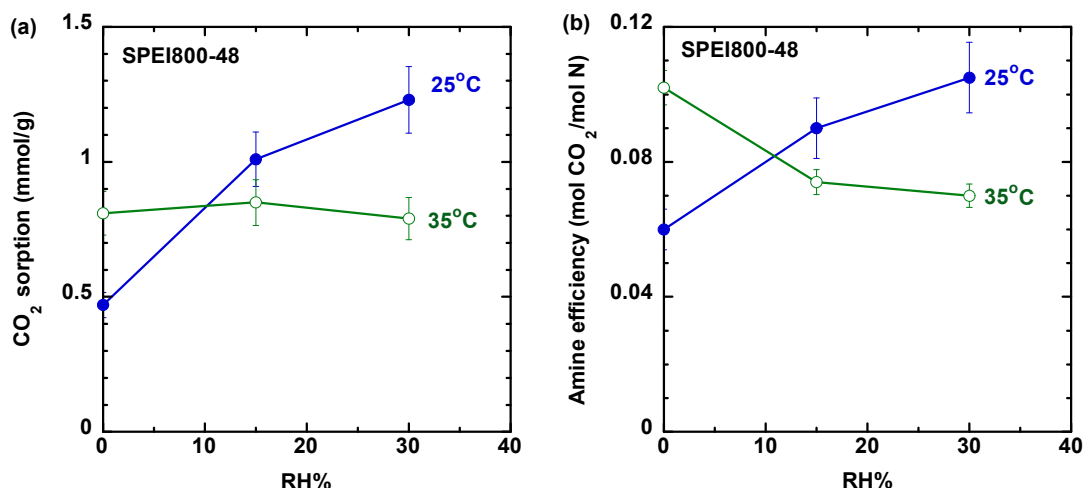


Figure 7. Effect of RH% on (a) CO₂ sorption capacity and (b) amine efficiency at 25 and 35 °C when tested with the air containing 400 ppm CO₂. The error bars are estimated by the error propagation method.³⁸

By contrast, the RH minimally affects the CO₂ sorption capacity at 35 °C, decreasing the amine efficiency presumably caused by the stronger binding between amine and H₂O at 35 °C. The amine efficiency under humidified conditions was calculated assuming 1 mol N^{1°,2°,3°} per 42.8 g of PEI instead of 1 mol N^{1°,2°} per 62.3 g of PEI under dry condition. Figure 7b shows that the amine efficiency at 25 °C increases by $\approx 72\%$ from 0.061 to 0.10 mol CO₂/mol N, suggesting that all amine types can sorb CO₂. Interestingly, the amine efficiency at 35 °C is higher than that at 25 °C under dry conditions but 34% lower with 30% RH, signifying the complexity of CO₂ sorption behavior in the PEI-based membrane adsorbents.¹⁵

Regeneration Stability of Membrane Adsorbent. Sorbent regeneration ability is a key factor determining the DAC costs.⁴¹ Regenerability is often characterized by the change in CO₂ sorption capacity during multiple sorption/desorption cycles. Figure 8a-b exhibits the sample mass as a function of time during the cycles for SPEI800-48 and SPEI25k-48, respectively, and their corresponding CO₂ sorption capacity for each cycle is summarized in Figure 8c. The SPEI25k-48 demonstrates a stable working capacity of 0.47 mmol/g after 3 cycles with minimal mass loss after desorption at 110 °C. By contrast, the CO₂ sorption

capacity of SPEI800-48 decreases by 29% from 0.66 to 0.47 mmol/g with a noticeable mass loss after each desorption step due to the evaporation and oxidative degradation of PEI800 by a trace amount of O₂. After 5 cycles, SPEI800-48 exhibits a stable working capacity of 0.37 mmol/g.

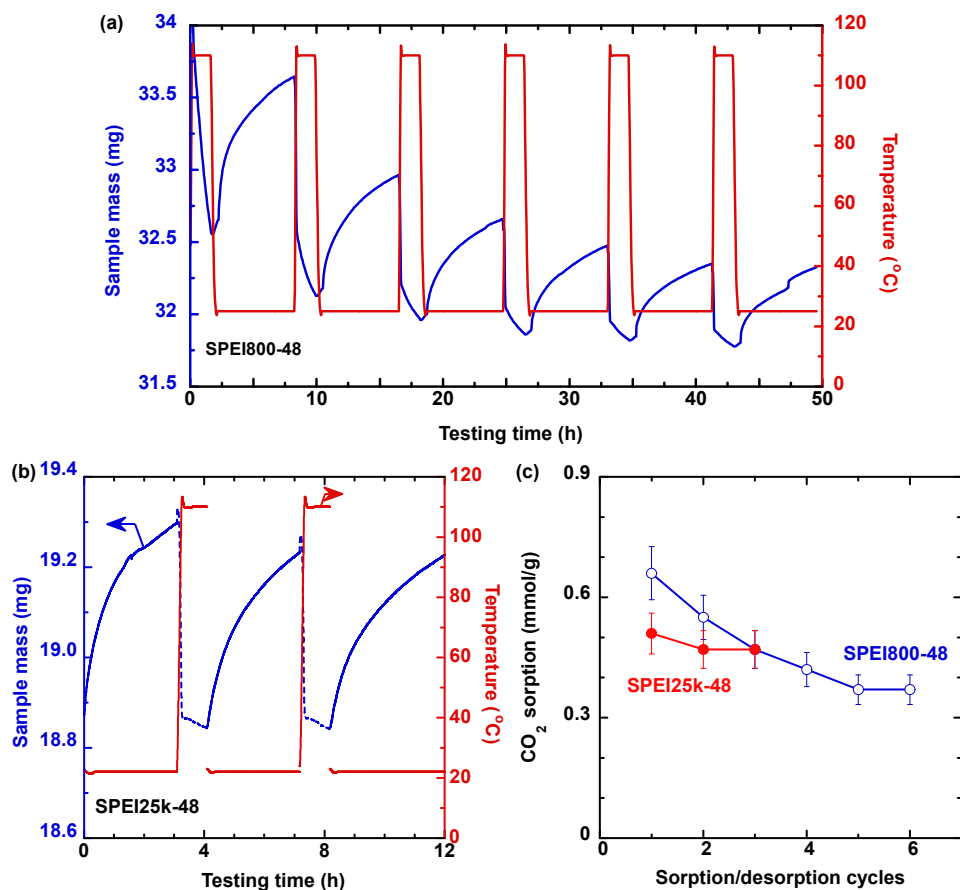


Figure 8. Sample mass of (a) SPEI800-48 and (b) SPEI25k-48 during sorption/desorption cycles, and (c) CO₂ sorption capacity for each cycle. The sorption was at 25 °C for 4 h with 400 ppm CO₂ in air, and the desorption was at 110 °C for 1 h under N₂ purge. The error bars in Figure 8c are estimated by the error propagation method.³⁸

SPEI800-48 was evaluated for 18 cycles of accelerated sorption and desorption to determine its regenerability (Figure S3). The sorption was conducted at 25 °C with 400 ppm CO₂ in air for 2 h, and the desorption was performed at 110 °C under N₂ for 15 min. SPEI800-48 exhibits a stable working capacity of ≈ 0.10 mmol/g after 10 cycles, indicating a slow sorption kinetic of this membrane adsorbent.

■ CONCLUSION

We develop low-cost and scalable membrane adsorbents for DAC of CO₂ based on a commercially available, thermally stable flatsheet polymeric substrate (Solupor). Branched PEIs with molecular masses of 800 and 25k g/mol were successfully impregnated into the pores, and the loading is determined by weight and TGA and agrees well with the PEI concentration in the solutions and the measured porosity. Interestingly, the impregnated PEI forms thin films on the pore walls and exhibits much higher T_g and better thermal stability than the bulk PEI. CO₂ sorption by these membrane adsorbents is limited by its diffusion, and increasing the PEI loading increases CO₂ sorption capacity but decreases amine efficiency because of the thicker PEI layers. Increasing the temperature from 25 to 50 °C enhances the CO₂ sorption capacity by 72% in SPEI800-48 because of the enhanced diffusivity at 50 °C. SPEI800-48 exhibits the highest sorption capacity of 1.2 mmol/g at 25 °C and 30% RH with the air containing 400 ppm CO₂, and such a sorption capacity is comparable with state-of-the-art commercial sorbents. SPEI25k-48 exhibits a stable working capacity of 0.47 mmol/g after 3 cycles, while SPEI800-48 exhibits a working capacity of 0.37 mmol/g. This work demonstrates the potential of low-cost polymeric substrates to prepare PEI-based adsorbent with low resistance to airflow and comparable CO₂ sorption capacity.

■ EXPERIMENTAL SECTION

Materials. Branched PEI800, branched PEI25k, and n-decane were obtained from Sigma Aldrich (St. Louis, MO). Methanol was purchased from Fisher Scientific International (Pittsburgh, PA). Cylinders of N₂, zero-grade air, and air containing 1200 ppm CO₂ were obtained from Airgas (Radnor, PA).

Preparation of Membrane Adsorbents. Membrane adsorbents with different loadings of PEI in Solupor were prepared using a wet impregnation method.³⁰ First, a desired amount of PEI was dissolved in methanol, which can then easily wet the hydrophobic Solupor support. Second, a Solupor sample with an initial mass of m_0 (mg) was immersed in the solution overnight. Third, the impregnated support was removed from the solution, dried in the air, and dried under a vacuum overnight at 22 °C. The impregnated support was measured to have a mass of m_1 (mg). Different PEI loadings were obtained by varying the PEI concentration in the methanol solutions. The PEI loading, x (mass%), was calculated using in Equation 8:

$$x = \frac{m_1 - m_0}{m_1} \times 100\% \quad (8)$$

Physical Properties Characterization. Thermal stability and PEI content in the sorbents were determined by TGA (TG 209 F1, Netzsch GmbH & Co., Germany) under the N₂ atmosphere. The samples were first equilibrated at 100 °C for 1 h and then heated to 800 °C at 10 °C/min. The T_g of the samples was determined using DSC (Q2000, TA Instruments, New Castle, DE). The samples were first equilibrated at -90 °C for 10 mins and then heated to 80 °C at 10 °C/min, and the second heating thermogram was used to derive T_g .

BDS was employed to characterize the influence of CO₂ sorption and sorbent regeneration on the dynamics of PEI. Three samples were measured for comparison, including the fresh PEI, the CO₂-loaded PEI, and the regenerated PEI after CO₂ sorption and desorption. Specifically, a thin film of PEI was filled in a hollow Teflon spacer with an outer diameter of 25 mm and an inner diameter of 14 mm. The PEI-filled Teflon spacer was then sandwiched by two gold electrodes with a diameter of 20 mm and transferred into a ZGS sample holder connected to Novocontrol Concept 40. The ZGS sample holder was then placed in an environmental chamber with a temperature accuracy of ± 0.1 °C controlled by a Quatro System. Each measurement covers a frequency range of $10^7 - 10^2$ HZ and a temperature range from -100 to 40 °C upon heating at an interval of 5 °C and from 40 to -100 °C upon cooling at an

interval of 20 °C. The spectra of the heating and cooling processes were compared to confirm the reproducibility of the measurements. Before each measurement, a thermal annealing of 20 mins was applied to ensure thermal equilibrium.

The membrane morphology was characterized by FIB-SEM (Auriga CrossBeam, Carl Zeiss, Germany). BET surface area was determined using N₂ adsorption isotherm (Tri-Star II, Micromeritics, Norcross, GA). The sorbent porosity, ϕ_{MA} (%), was determined by n-decane uptake using the following equation:

$$\phi_{MA} = \frac{m_2 - m_1}{\rho_L} \frac{1}{V_{MA}} \quad (9)$$

where m_1 and m_2 are the sample mass before and after the n-decane uptake. ρ_L (g/cm³) is the density of n-decane (0.73 g/cm³), and V_{MA} (cm³) is the volume of the sorbent sample. Pure-gas CO₂ permeance was determined using a constant-pressure and variable-volume apparatus at 15 psig and 35 °C.³⁷

Characterization of DAC Performance by TGA. The CO₂ sorption capacity of the membrane adsorbents was determined using TGA. First, a sample of 30 – 45 mg was heated to 110 °C at 10 °C/min under an N₂ environment (90 cm³/min) and then kept for 1 h to remove H₂O and CO₂. The flow rate is sufficiently high to minimize concentration polarization on the sample surface. Second, the sample was cooled to the desired sorption temperatures of 25, 35, or 50 °C and then kept at the temperature for 20 min. Third, the gas was switched to the simulated air containing 400 ppm CO₂ while retaining the gas flow rate at 90 cm³/min. Finally, after 4-h sorption, the sample was heated to 110 °C under N₂ for CO₂ desorption.

To investigate the effect of humidity on CO₂ sorption capacity, the sample was first allowed to saturate with water vapor for 2 h at the desired RH% under N₂ atmosphere. Then 400 ppm CO₂ was introduced to TGA at the same RH% by passing a gas stream through a temperature-controlled gas bubbler. The stability and regenerability of the adsorbent were also evaluated by multiple cycles of sorption/desorption.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org>.

TGA thermograms; physical properties; CO₂ sorption with time

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Author Contributions

All authors contributed to the scientific discussion and manuscript preparation. H.L. and T.T. conceived the approach and conducted experimental designs. T.T. and S.S. fabricated and characterized materials. T.T. wrote the first draft of the manuscript, and all authors contributed to manuscript editing. H.L. supervised the project.

Notes

The authors declare no competing financial interest.

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Graphic Abstract

Scalable and Highly Porous Membrane Adsorbents for Direct Air Capture of CO₂

