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Direct air capture (DAC) of CO_2 using polyethylenimine (PEI) "snow": a scalable strategy†

Xingguang Xu,*[ab] Matthew B. Myers,*[b] Friso G. Versteeg,[bc] Bobby Pejcic, [ID][b] Charles Heath[b] and Colin D. Wood [ID] *[bd]

We have developed a cross-linked polyethyleneimine non-porous material (PEI "snow") for direct air capture (DAC) of CO_2. This new hydrogel is green, inexpensive, readily scalable and can be fabricated through simple crosslinking of PEI with triglycidyl trimethylol-propane ether (TTE) in 10 minutes. It demonstrates outstanding DAC performance (overall CO_2 uptake efficiency of approximately 50 mg g^{-1} of sorbent) at lab scale (sorbent weight roughly 60 g, air flow rate 2000 ml min^{-1}) and the CO_2 can be desorbed using low-grade waste steam.

Continued CO_2 emissions from various anthropogenic sources has become a major environmental concern, as the increasing atmospheric CO_2 level will inevitably accelerate global warming that can cause immediate and direct changes to the planet.[1] In order to avoid these changes, carbon capture and sequestration (CCS) is one method that has the potential to deal with emitted CO_2.[2] Briefly, anthropogenic CO_2 emissions released from fixed sources are physically or chemically captured and then permanently stored in depleted reservoirs or deep saline aquifers which leads to substantially reduced CO_2 emissions.[3] However, it is costly to install individual carbon removal units for distributed and isolated sources. In addition, the captured CO_2 needs to be transported to the storage site, which also increases the overall costs. In addition, CCS can merely inhibit the further increase in atmospheric CO_2 concentration, making it at best a "carbon neutral technique".[4] Therefore, other carbon removal strategies are worthy of investigation.

a Key Laboratory of Tectonics and Petroleum Resources, Ministry of Education, China University of Geosciences (Wuhan), Wuhan 430074, China. E-mail: xuxingguang@cug.edu.cn

b Energy Business Unit, Commonwealth Scientific Industrial Research Organisation (CSIRO), Kensington, WA 6151, Australia. E-mail: Matt.Myers@csiro.au, Colin.Wood@csiro.au

c Faculty of Science and Engineering, University of Groningen, 9747 AG Groningen, The Netherlands

d Curtin University of Science and Technology, Curtin Oil and Gas Innovation Centre (COGIC), Kensington, WA 6151, Australia

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As a potentially "carbon negative process", direct air capture (DAC), which is not limited by matching emission sources with storage locations, can lower atmospheric CO_2 concentrations to below pre-industrial levels if this approach is widely deployed.[5–7] Therefore, DAC has gained considerable attention from both academia and industry, leading to rapid development in this field. Recently, Carbon Engineering demonstrated that aqueous solutions of strongly basic hydroxide salts were an effective and scalable absorbent for DAC.[8] Generally, these inorganic salts are inexpensive, readily available, and environmentally benign. However, the slow absorption kinetics and the high energy input for regeneration means that opportunities exist to develop new materials.[9] Metal–organic frameworks (MOFs) exhibit superior CO_2 adsorption kinetics due to their high surface areas.[10] A few research groups have reported the effectiveness of MOFs on removing CO_2 from ultra-dilute sources such as air, but they found the CO_2 uptakes of the applied MOFs dramatically decreased under humid conditions.[11,12] As such, high relative humidity (RH) in the air would compromise the performance of most MOF-based sorbents. In addition, the large-scale synthesis of cost-effective MOFs remains a challenge but this is being rapidly addressed.[13] Another emerging material for DAC is supported-amine adsorbents where the functional amines are either impregnated or grafted onto the pore surface of the highly porous supports. They have distinct advantages over inorganic basic salts and MOFs in terms of ease of recycling and insensitivity to water vapor,[14,15] but most suffer from poor structural stability and oxidative degradation. The use of micro-porous organic polymers for DAC material was also reported,[16] but their complicated synthesis and availability can hinder the large-scale deployment but rapid progress is being made in this area.

In a previous work, we reported an effective and robust non porous material for post-combustion capture, namely cross-linked polyethylenimine "snow" (PEI "snow").[17] It demonstrates outstanding CO_2 absorption performance and can be rapidly prepared within 15 minutes through crosslinking PEI with 1,3-butadiene diepoxide (BDDE). In the present study, instead
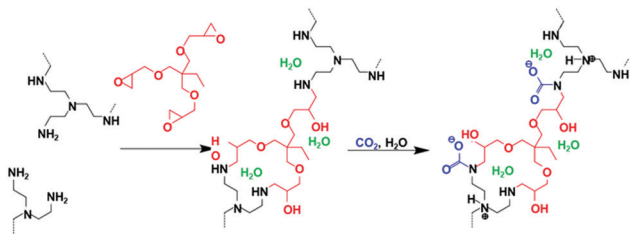
Scheme 1 Synthesis of the PEI snow (first step) and direct air capture of CO_2 by PEI snow (second step). The synthesis was performed at room temperature and could be finalized within 10 minutes.

of using BDDE which is relatively expensive and toxic, we apply a highly reactive and commonly used epoxide crosslinker, namely triglycidyl trimethylolpropane ether (TTE), to fabricate the PEI "snow" for DAC (Scheme 1). This new version of PEI snow will be more feasible for large scale application which is critical for DAC implementation considering the enormous volume of air that needs to be processed worldwide. This is because TTE is significantly cheaper and less toxic than BDDE thereby reducing both the material costs and environmental hazards. Meanwhile, each TTE molecule contains three epoxide groups and as a result a fairly dense 3-D structure of cross-linked PEI will form. Consequently, the spatial density of reactive sites is increased and a greater quantity of CO_2 molecule can be fixed within a unit of time, contributing to a higher CO_2 absorption efficiency.

In this work, PEI with a weight-average molecular weight of 25 000 and PEI solution with a mass percentage of 30.0 wt% were applied unless otherwise specified. It is noted that the updated PEI snow can be prepared within 10 min by adding 6.0 wt% TTE into the PEI solution and grinding the resulting gel (see ESI† for details).

Fig. 1(a) presents the IR spectrum of the crosslinking reaction between TTE and PEI over time. Two characteristic peaks were observed at 3350–3400 cm^{-1} and 1600–1550 cm^{-1} which corresponded to the –NH stretch and –NH bend vibration, respectively. Another two characteristics peaks were found at ~1640 cm^{-1} and 1020–1025 cm^{-1} which corresponded to the –OH bend vibration and –COC– stretch vibration, respectively. In particular, the intensity of the –COC– stretch vibration deceased with reaction time and this is consistent with the consumption of epoxide groups. It was noted that intensities of the characteristic peaks hardly varied after 10 minutes, demonstrating the fast reaction rate and the ease of preparing PEI snow, which is critical for large-scale production. The pristine sample was exposed to pure CO_2 gas flow (100 ml min^{-1}) for 45 minutes and the corresponding IR spectrum of the entire CO_2 absorption process is shown in Fig. 1(b). Peaks were observed at 1549–1557 cm^{-1}, 1413–1414 cm^{-1}, 1348–1363 cm^{-1} and 1286–1307 cm^{-1}, and these correspond to the following vibrations COO– asymmetric stretch, C–N stretch, CO_3^{2-}/HCO_3^- and NCOO– skeletal, respectively. The peak at ~1250 cm^{-1} may be due to the trace amount of remaining TTE. A majority of the peaks occurring between 1550 to 1300 cm^{-1} correspond to the formation of the carbamate species,[18] whereas the IR band at
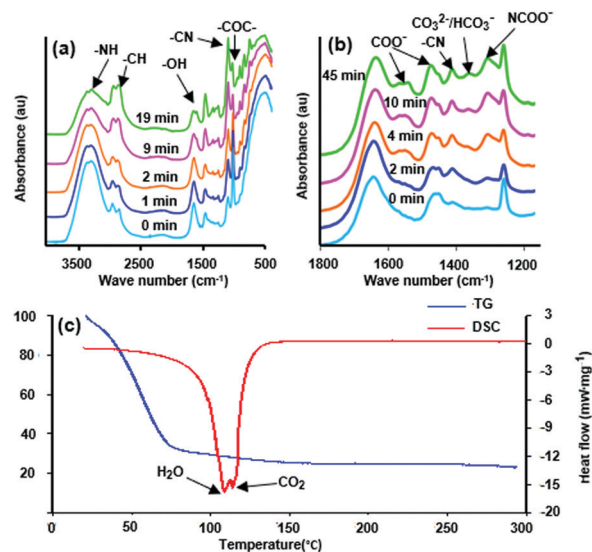

Fig. 1 (a) IR spectrum of the crosslinking reaction between PEI and TTE over time (30 wt% PEI-25 000 and 6.0 wt% TTE); (b) IR spectrum of CO_2 absorption by PEI snow over time (30 wt% PEI-25 000 and 6.0 wt% TTE); (c) TG–DSC of CO_2-loaded PEI sow (30 wt% PEI-25 000 and 6.0 wt% TTE).

~1356 cm^{-1} is most likely due to the generation of carbonate/bicarbonate species. The coexistence of carbamate and carbonate/bicarbonate species suggests that the CO_2 reacted with amino groups at a mole ratio of 2:1 to 1:1 due to the presence of water in the PEI snow, which is important so the material must be hydrated to effectively capture CO_2.[19] This is an additional advantage of the material because it can operate under a range of different humidity conditions. It was evident that the intensities of the characteristic peaks remained constant after 4 min, demonstrating the fast CO_2 absorption kinetics of the new PEI snow.

Afterward, the CO_2-loaded sample was heated using a thermal analyser (STD Q600) under a N_2 atmosphere from room temperature to 300 °C with a heating rate of 5 °C min^{-1}. The TG–DSC results are presented in Fig. 1(c). It was found the dramatic weight loss after 75 °C was mostly attributed to the water evaporation and release of CO_2 upon the heating, which was confirmed by the two indicated endothermic peaks on the DSC curve. The residual sample weight at 300 °C was determined to be 26.4 wt% which was similar to the weight of "dry" PEI snow (i.e. PEI snow subtracting the water content). This demonstrates that once the dehydrated PEI snow was re-hydrated, then its CO_2 absorption capacity would be readily recovered, which revealed its outstanding thermal stability and recyclability.

In order to test the ability of the material for DAC we employed, for the first time, a G2201-i Isotopic Analyzer (PICARRO) to assess the DAC capacity of a CO_2 absorbent under ambient conditions (by measuring the effluent CO_2 concentration). This instrument is able to measure the $\delta^{13}C$-CO_2 within CO_2 and has an operational range of 100–4000 ppm and has a precision of less than 0.12‰, therefore it is ideal for DAC investigations. The ambient air in the lab, rather than a synthetic gas, was pumped into a column that held ~15 g of PEI snow (6.0 wt% TTE and 30 wt% PEI) and the
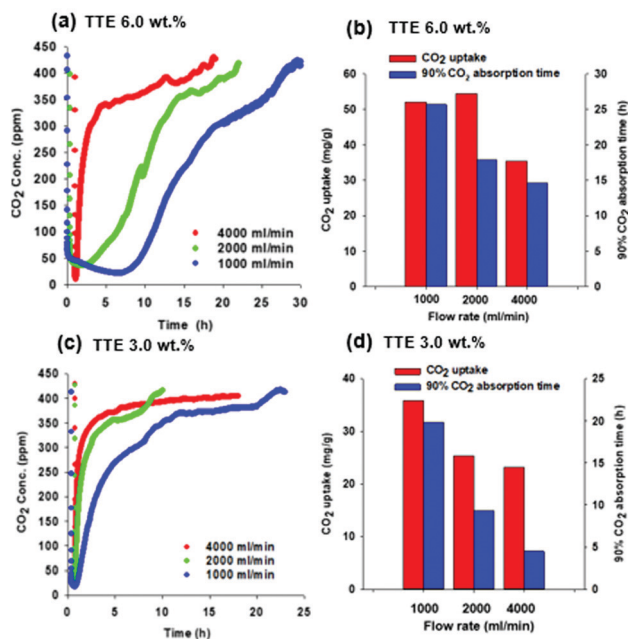
Fig. 2 (a) Outlet CO_2 concentrations of the PEI snow column at various flow rates (30 wt% PEI-25 000 and 6.0 wt% TTE); (b) summary of CO_2 uptakes and $t_{90\%}$ of PEI snow at various flow rates (30 wt% PEI-25 000 and 6.0 wt% TTE); (c) outlet CO_2 concentrations of the PEI snow column at various flow rates (30 wt% PEI-25 000 and 3.0 wt% TTE); (d) summary of CO_2 uptakes and $t_{90\%}$ of PEI snow at various flow rates (30 wt% PEI-25 000 and 3.0 wt% TTE).

outlet CO_2 concentration was continuously monitored and recorded using the Isotopic Analyzer. A detailed schematic and experimental procedures are available in Fig. S1 and S2 (ESI†).

Herein, reasonably high flow rates (1000, 2000, 4000 ml min^{-1}) were applied to mimic an industrial process and the outlet CO_2 concentrations as a function of the air injection time are illustrated in Fig. 2(a). It was seen that, regardless of the air flow rate, the outlet CO_2 level dramatically decreased in the first few minutes of the air injection, demonstrating the high reactivity of the material to CO_2 even at extremely low CO_2 partial pressure, which was mainly attributed to the powdery nature and high amine group density of the PEI snow. At relatively low flow rate (1000 ml min^{-1}), the outlet CO_2 level was lower than 50 ppm for 10 h before it slowly rose to the atmospheric level. When the flow rate was increased to 2000 ml min^{-1}, as expected, the breakthrough occurred significantly earlier because the PEI snow is saturating more quickly, indicating the pronounced effect of flow rate on DAC processes. After the breakthrough, the outlet CO_2 concentration increased in a similar way to that under 1000 ml min^{-1}, and it took around 20 hours to reach 425 ppm. If the flow rate was further increased to 4000 ml min^{-1}, the breakthrough could occur in less than 30 min, after which the outlet CO_2 concentration climbed rapidly. Fig. 2(b) summarizes the CO_2 uptake and the $t_{90\%}$ which represents the time until 90% of the maximal absorption is reached at different flow rates. Clearly, higher flow rates led to shorter $t_{90\%}$ which was desirable for real DAC

applications. However, low CO_2 uptakes were obtained due to insufficient contact between the air and surface amine groups of PEI snow. This strongly suggests that the air was flowing so fast through the tube that it was not really at equilibrium with the gel. Therefore, the CO_2 in the outlet might have risen before the gel had finished absorbing. When it came to the lower flow rates, the CO_2 uptake was 52.4 and 56.7 mg CO_2 per g absorbent for 1000 and 2000 ml min^{-1}, respectively. These values were not among the highest reported values, but reasonable considering that most of the reported DAC experiments were performed at significantly low flow rates.[20–22] Therefore, the CO_2 uptakes of this work might be more representative for industrial scale DAC.

We also evaluated the effect of crosslinker TTE level on the DAC performance of the PEI snow. The results are presented in Fig. 2(c) and (d). It was seen that if the TTE concentration was reduced from 6.0 wt% to 3.0 wt%, the CO_2 uptake became significantly lower. For instance, the CO_2 uptakes of PEI snow with 3.0 wt% and 6.0 wt% TTE at 1000 ml min^{-1} were 36.8 and 52.4 mg CO_2 per g absorbent, respectively. The reasons were two-fold. First, less amount of crosslinker TTE could lower the crosslinking degree, which accordingly decreased the rigidity of PEI snow and negatively affected its powdery nature (Fig. S3, ESI†). As a result, the contact between the air and the PEI snow was compromised, leading to a lower CO_2 absorption efficiency. Secondly, as illustrated in Scheme 1, the lower TTE concentration resulted in less production of hydroxyl groups in the alkanolamines which can promote the CO_2/amine interactions.[23] For these reasons, relatively high TTE cross-linking level was essential for PEI snow to effectively capture CO_2 directly from the air. However, if the TTE concentration was too high, excessive numbers of amine groups would be consumed and this would cause the reduction of the reactive sites for CO_2. Therefore, an optimal crosslinker level should exist and it was generally a function of PEI molecular weight, PEI solution concentration, crosslinker structure and CO_2/amines reaction mechanism. 6.0 wt% was determined to be the optimal TTE level under this experimental condition.

For DAC it is essential to have a material that is capable of many sorption/desorption cycles with low energy requirements and minimal degradation in performance. However, most existing regeneration approaches required high energy input. The PEI snow can be readily regenerated with low-grade steam which may have limited utility otherwise in some instances,[24] thereby the PEI snow could be regenerated in a cost-effective way providing there was a source of steam at the regeneration site. However, the material can also be regenerated with heat, although loss of water would result in a significant energy penalty. The CO_2 can be readily desorbed by heat alone while the PEI snow maintains the water content due to the introduction of the steam and minimizes energy losses to vaporizing water. The experimental details are shown in Fig. S4 (ESI†).

Herein, ten regeneration cycles were performed to evaluate the recyclability of PEI snow for DAC processes. As shown in Fig. 3, the DAC capacity of the PEI snow hardly declined after ten cycles, demonstrating the effectiveness of steam regeneration. The absorption curves of several representative experiments were consistent
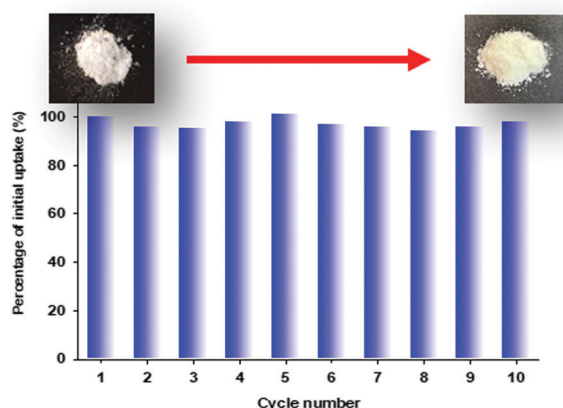
Fig. 3 Regeneration of the PEI snow by heating with steam. Both the CO_2 uptake and the material appearance hardly changed after ten absorption–desorption cycles (30 wt% PEI-25 000 and 6.0 wt% TTE, 2000 ml min^{-1}).

during the regeneration process (Fig. S5, ESI†), which also suggests that the capacity of PEI is maintained. Meanwhile, the appearance and powdery nature of PEI snow were well maintained, indicating the excellent robustness of the PEI snow upon multiple cycles. More importantly, the IR spectrum suggested that its chemical structure was barely affected through the regeneration process which normally harmed the recyclability of amine-based CO_2 absorbents (Fig. S6, ESI†). This implies the small variations in CO_2 uptake across multiple cycles was most presumably due to partial dehydration and not actual degradation of the material. Further studies will focus on more cycles however, these initial results show that the PEI snow exhibited outstanding stability and reliability as a robust DAC material.

In conclusion, this study demonstrates that the PEI snow has potential for DAC. This new version of the PEI snow could be readily prepared in 10 minutes *via* crosslinking PEI with TTE which was relatively green and inexpensive. The tap density of the PEI snow is determined to be 0.5–0.6 cm^3 g^{-1} depending on the crosslinker level, which is decent compared to that of some of the porous materials, so the column size will be reasonable. IR spectroscopy confirmed the rapid crosslinking reaction and fast CO_2 absorption kinetics of PEI snow. The DAC capacity was generally governed by the air flow rate and the crosslinker concentration. The former could influence the air/PEI snow contact, while the latter determined the powdery nature and the hydroxyl level. Although the CO_2 uptake of PEI snow is not remarkably high compared to other reported DAC sorbents (Fig. S7, ESI†), it presented fairly encouraging DAC performance at large scale (Fig. S8, ESI†) and excellent recyclability. Therefore, it may serve as an economically and functionally promising DAC material for field scale application in the future.

Conflicts of interest

There are no conflicts of interest to declare.

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