Direct Air Capture of CO₂ with Aqueous Peptides and Crystalline Guanidines

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SUMMARY

Negative emission technologies, including direct air capture (DAC) of carbon dioxide, are now considered essential for mitigating climate change, but existing DAC processes tend to have excessively high energy requirements, mostly associated with sorbent regeneration. Here we demonstrate a new approach to DAC that combines atmospheric CO₂ absorption by an aqueous oligopeptide (i.e., glycyglycine) with bicarbonate crystallization by a simple guanidine compound (i.e., glyxal-bis-iminoguanidine). In this phase-changing system, the peptide and the guanidine compounds work in synergy, and the cyclic CO₂ capacity can be maximized by matching the pKₐ values of the two components. The resulting DAC process has a significantly lower regeneration energy compared to state-of-the-art solvent-based DAC technologies.

KEYWORDS

CO₂ capture; direct air capture; amino acids; peptides; guanidines
INTRODUCTION

Removal of carbon dioxide straight from the atmosphere, or direct air capture (DAC),\(^1\) has recently emerged as an important component of our portfolio of negative emission technologies for addressing climate change.\(^2,3\) While a number of promising DAC systems have been demonstrated in the past decade, based on aqueous solvents\(^4\) or solid adsorbents,\(^5,6\) their energy requirements remain relatively high, in the range of 8.4-12.5 and 4-6 GJ/t CO\(_2\), respectively.\(^2\) Unless the energy costs of DAC technologies are significantly reduced, their implementation at the massive scale (GtCO\(_2\)/year) necessary to positively impact the climate will remain economically unfeasible. Considering that most of the energy requirements for DAC (up to 90% of the total energy in the case of aqueous solvents) are associated with sorbent regeneration, developing new DAC processes with reduced regeneration energies are critically needed.\(^2\)

In developing new DAC systems, one can take inspiration from nature. The RuBisCO enzyme, the most abundant protein on earth, found in leaves, selectively fixates CO\(_2\) from air using a lysine amino acid residue that reacts with CO\(_2\) and converts it into carbamate.\(^7,8\) Though the RuBisCO enzyme has evolved to fulfill its biological function of capturing atmospheric CO\(_2\) and converting it into sugars for plant growth, its applicability to DAC processes is severely restricted by the slow CO\(_2\) uptake–trees grow very slowly–the very low CO\(_2\) capacity due to its high molecular weight, and the relatively poor chemical stability inherent to biological structures. Furthermore, RuBisCO includes significant amounts of water that are needed to maintain its structure and activity, which would come with high energy penalty in a DAC regeneration process. Notwithstanding these limitations, the active site of RuBisCO provides valuable design principles that could lead to effective DAC systems if reactive amino acids or small peptides could be incorporated into stable platforms with minimal water inclusion. Indeed, aqueous amino acids have been recently
demonstrated as effective absorbents for DAC, taking advantage of their fast reaction rates with CO₂—on par with, or surpassing more traditional sorbents such as monoethanolamine or NaOH—negligible volatility, non-toxicity, and environmental compatibility.\textsuperscript{9,10} Peptides, on the other hand, have received little attention as DAC sorbents,\textsuperscript{11} though solid peptides have been found effective at CO₂ capture from more concentrated gas streams.\textsuperscript{12-14} However, it remains to be determined if solid peptides can compete with solid-supported amine sorbents in terms of CO₂ capacity, adsorption rate, and chemical stability. One major advantage of peptides is that, with dozens of natural or artificial amino acids readily available, and countless possibilities of combining them into peptides, they offer a structurally diverse platform for designing new DAC systems with optimized CO₂ capacities, absorption rates, and regeneration energies.

Here we demonstrate a new approach to DAC based on aqueous solutions of simple oligopeptides, such as diglycine or triglycine. The CO₂ absorption by the aqueous peptide was combined with a phase-changing process involving bicarbonate crystallization with a simple guanidine ligand, to reduce the energy penalty and chemical degradation expected when heating aqueous peptide solutions. The resulting DAC process has a significantly lower regeneration energy compared to state-of-the-art solvent-based DAC technologies.\textsuperscript{2}

**RESULTS**

**DAC System Design**

The design of the current system is based on our recently demonstrated approach to DAC that combines atmospheric CO₂ absorption by aqueous amino acids, followed by crystallization of bis(iminoguanidine) (BIG) (bi)carbonate salts of very low aqueous solubilities (Figure 1).\textsuperscript{9,10} This phase-changing DAC process combines the benefits of aqueous amino acid solvents, such as fast
reaction rates with CO\(_2\), low volatility, easy scale-up, and environmental compatibility, with the advantage of solid-state adsorbents, such as lower energies and temperatures of regeneration. The ready availability of amino acids, and the simple, modular synthesis of BIGs by imine condensation of dialdehydes with aminoguanidinium salts,\(^{15}\) provides the ultimate designer’s toolbox for DAC systems, where key performance parameters like CO\(_2\) capacity, absorption rate, regeneration energy and temperature, can be optimized by a simple mix and match approach.

![Figure 1. DAC system design, combining aqueous amino acids and peptides (top) with solid BIGs (right). The pK\(_a\) values of the amino acids/peptides, and the regeneration energies of the BIGs, are specified under each structure. An example of a previously demonstrated CO\(_2\)-capture cycle involving glycine (as potassium salt, K\(^+\) not shown) and GBIG, alongside with the associated GBIGH\(_2\)(HCO\(_3\))\(_2\)(H\(_2\)O)\(_2\) crystal structure, are shown in the middle. The amino acid regeneration reaction, the key step in the cycle, is shown on the bottom. The peptides and the GBIG selected for this study are highlighted in yellow.](image)

Of all the BIG compounds under consideration,\(^9\),\(^10\),\(^16\),\(^17\) glyoxal-bis(aminoguanidine) (GBIG) appears most appealing for developing a CO\(_2\) capture technology due to its significantly lower regeneration energy (152 kJ/mol, 3.45 GJ/ton CO\(_2\)),\(^{16}\) rivaling the most energy-efficient DAC sorbents studied to date.\(^2\) As previously demonstrated, and summarized in Figure 1, the CO\(_2\)
capture cycle consists of the following steps: 1) The anionic form of the amino acid (potassium salt of glycine was used in this example) reacts with the CO₂ and converts it into bicarbonate anion via a carbamate intermediate (not shown here); 2) GBIG removes two H⁺ and two HCO₃⁻ ions from solution and crystallizes as GBIGH₂(HCO₃)₂(H₂O)₂, thereby regenerating the anionic form of the amino acid; 3) After the bicarbonate crystals are separated from the aqueous solution, the CO₂ is released and GBIG is regenerated by mild heating of the crystals. This cycle was successfully applied to CO₂ separation from coal-burning flue gas simulants, with sustained cyclic capacities of 0.2-0.3 mol CO₂/mol amino acid over multiple cycles.¹⁸ However, when applied to DAC, a much lower cyclic capacity of 0.08 mol CO₂/mol amino acid was observed with glycine/GBIG (Supplemental Information).

Examination of the amino acid regeneration reaction (Fig. 1) provides a simple explanation for the relatively poor DAC performance of the GBIG/glycine system, and a straightforward strategy to improve it. As this reaction involves proton transfer between the amino acid and GBIG, the corresponding equilibrium constant, $K_{\text{reg}}$, is dependent on the relative pKₐ values of the amino acid and GBIG (pKₐ 7.33 and 8.65),¹⁶ respectively. For the particular case of glycine (pKₐ 9.58), GBIG is not sufficiently basic to deprotonate the amino acid, and the regeneration reaction is inefficient. However, by replacing glycine with less basic amino acids (shown on the right side of Gly in Fig. 1), we hypothesized the regeneration equilibrium would be shifted to the right, leading to a more efficient DAC process.

**Thermodynamic Analysis of the Amino Acid/Peptide Regeneration with GBIG**

The equilibrium constants for the amino acid regeneration reactions by crystallization with GBIG ($K_{\text{reg}}$) was measured for five amino acids and two small peptides: proline (Pro), sarcosine (Sar),
alanine (Ala), glycine (Gly), serine (Ser), glycylglycine (GlyGly), and glycylglycylglycine (GlyGlyGly). Their $pK_a$ values span two and a half units, from 10.47 to 8.02 (Fig. 1). The GlyGly and GlyGlyGly oligopeptides are significantly less basic than the corresponding glycine monomer, which makes them particularly promising candidates for DAC. Longer peptides have also been considered, though their basicities are only incrementally reduced at the expense of significant drops in their aqueous solubilities.

The equilibrium constants for the amino acid regeneration reactions were calculated according to Equation 1, where $AA^-$ and $AA$ are the anionic and neutral (zwitterionic) forms of the amino acid, respectively, and $\gamma_\pm$ and $\gamma_{AA}$ are the activity coefficients of the anions ($AA^-$, $HCO_3^-$) and zwitterions ($AA$), respectively. Details of the methodology used to measure the concentrations involved and calculate $K_{reg}$ can be found in the Supplemental Information. The obtained $K_{reg}$ values for the five amino acids and two peptides investigated are listed in Table 1 and plotted as a function of amino acid/peptide $pK_a$ in Figure 2.

$$K_{reg} = \frac{\gamma_\pm^2 \times [AA^-]^2}{\gamma_{AA}^2 \times [AA]^2 \times \gamma_\pm^2 \times [HCO_3^-]^2} \quad (Eq. 1)$$

<table>
<thead>
<tr>
<th>Amino acid/Peptide</th>
<th>$pK_a$</th>
<th>$\log K_{reg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pro</td>
<td>10.47</td>
<td>0.79 ± 0.18</td>
</tr>
<tr>
<td>Sar</td>
<td>10.29</td>
<td>1.44 ± 0.25</td>
</tr>
<tr>
<td>Ala</td>
<td>9.71</td>
<td>2.92 ± 0.17</td>
</tr>
<tr>
<td>Gly</td>
<td>9.58</td>
<td>2.19 ± 0.15</td>
</tr>
<tr>
<td>Ser</td>
<td>9.15</td>
<td>3.40 ± 0.19</td>
</tr>
<tr>
<td>GlyGly</td>
<td>8.17</td>
<td>4.39 ± 0.29</td>
</tr>
<tr>
<td>GlyGlyGly</td>
<td>8.02</td>
<td>4.95 ± 0.35</td>
</tr>
</tbody>
</table>

Table 1. Equilibrium constants for the amino acid/peptide regeneration reactions with GBIG ($K_{reg}$). Each measurement was done in triplicate, with initial amino acid/peptide concentrations of 0.5 M, and initial $HCO_3^-$ concentrations varying between 0.1 and 0.5 M.
Figure 2. Plot of \( \log K_{\text{reg}} \) vs \( pK_a \) for the amino acid/peptide regeneration reactions with GBIG. The error bars represent the standard deviations calculated from five separate \( K_{\text{reg}} \) measurements corresponding to different initial bicarbonate concentrations in the range of 0.1-0.5 M.

Figure 2 shows there is a good correlation between \( \log K_{\text{reg}} \) and amino acid/peptide \( pK_a \) values, with the less basic amino acids/peptides (lower \( pK_a \)) showing more favorable regeneration with GBIG. The two oligopeptides in particular, GlyGly and GlyGlyGly, were found to be regenerated most efficiently by GBIG, with measured \( \log K_{\text{reg}} \) of 4.39 ± 0.29 and 4.95 ± 0.35, respectively.

Figure 3. van’t Hoff plot for the regeneration reaction of GlyGly with GBIG, in the 15-35 °C temperature range.
The GlyGly regeneration reaction with GBIG was further measured as a function of temperature in the 15-35 °C range. The regeneration reaction is endothermic, with an enthalpy of 66 kJ/mol obtained from the van’t Hoff plot of $-\Delta\ln K_{\text{reg}}$ as a function of 1/T (Figure 3). Thus, an even more efficient regeneration of GlyGly can be achieved by slightly elevating the temperature, which can be easily done by harvesting low-grade heat.

**Direct Air Capture with Glycylglycine and GBIG**

The GlyGly peptide was selected as the sorbent of choice for DAC based on its favorable thermodynamics of regeneration with GBIG and good aqueous solubility (> 1M). The DAC cycle consists of loading a 1 M aqueous solution of the potassium salt of GlyGly with atmospheric CO$_2$ under ambient conditions using a household humidifier,$^9,10$ followed by bicarbonate stripping and regeneration of GlyGly by stirring the loaded solution with solid GBIG. The amount of CO$_2$ in solution, in the form of carbamate and (bi)carbonate anions, was monitored by $^1$H NMR (Figure S1, Supplemental Information) and ion chromatography, respectively. The formation of carbamate was also confirmed by single-crystal X-ray diffraction (Figure S2, Supplemental Information). The loading and regeneration of GlyGly as a function of time are plotted in Figure 4. The average CO$_2$ loading capacity of GlyGly, after 48 hours, is $0.50 \pm 0.03$ mol CO$_2$/mol GlyGly, with about 44% of it as carbamate, and the rest as (bi)carbonate anions. Compared to GlyGly, the CO$_2$ loading capacity of Gly is about 20-30% higher, which can be explained by its higher basicity. However, more important than the loading capacity is the cyclic capacity, which is limited by the regeneration reaction of the amino acid/peptide with GBIG. In this respect, GlyGly, with an average cyclic capacity of $0.16 \pm 0.04$ mol/mol, is twice as efficient as Gly (0.08 mol/mol cyclic capacity) (Figure S3, Supplemental Information).
Figure 4. DAC with GlyGly/GBIG. (a) CO$_2$ loading curve with 1 M potassium glycylglycynate. The error bars are defined as the standard deviations from 4 different loading experiments. (b) Regeneration of GlyGly by stirring a slurry mixture of the CO$_2$-loaded aqueous peptide with solid GBIG, quantified as the total amount of CO$_2$ removed from solution as a function of time. The error bars are defined as the standard deviations from 3 different regeneration experiments.

To test the viability of the overall DAC process with GlyGly/GBIG, we run three consecutive loading/regeneration cycles consisting of the following steps: 1) loading the 1 M potassium glycylglycynate solution with CO$_2$ using the air humidifier; 2) GlyGly regeneration by transferring the loaded solution into a beaker and adding solid GBIG (0.5 mol equiv), then stirring the slurry for 2 h; 3) filtering the suspension to remove the solid carbonate salt and the unreacted GBIG from the regenerated solution; 4) heating the carbonate solid for 2 h at 120 °C to regenerate the GBIG solid; 5) recycling of the regenerated GlyGly solution and solid GBIG. The measured cyclic
capacities for the three consecutive cycles were in the range of 0.12–0.17 mol/mol (Figure 5), comparable with previous amino acid/BIG systems.\textsuperscript{9,10}

![Graph showing cyclic capacities for DAC cycles](image)

**Figure 5.** DAC cyclic capacities (mol CO\textsubscript{2}/mol peptide) measured for consecutive loading/regeneration cycles with GlyGly/GBIG. The error bars are defined as the standard deviations from three separate experiments.

**DISCUSSION**

This study provided the proof of principle for DAC with aqueous peptides and solid BIGs. Similar to amino acids, small peptides, such as GlyGly, can effectively absorb CO\textsubscript{2} from the air and convert it into carbamate and (bi)carbonate anions. The GBIG compound then removes H\textsuperscript{+} and HCO\textsubscript{3}\textsuperscript{−} ions (nominally H\textsubscript{2}CO\textsubscript{3}) from solution and crystallizes as a bicarbonate salt, thereby regenerating the peptide absorbent. This crystallization-based regeneration circumvents the heating of the aqueous peptide, thereby extending its lifetime and lowering the regeneration energy. Finally, the DAC cycle is closed by mild heating of the bicarbonate crystals, which releases the CO\textsubscript{2} and regenerates the GBIG with an energy requirement of only 152 kJ/mol (3.45 GJ/ton CO\textsubscript{2}).\textsuperscript{16}

GBIG is unique among the BIG compounds studied to date for CO\textsubscript{2} capture. Unlike the other BIGs in the series, which crystallize as carbonate salts in the presence of CO\textsubscript{2},\textsuperscript{9,10,17} GBIG forms a bicarbonate salt with the formula GBIGH\textsubscript{2}(HCO\textsubscript{3})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}.\textsuperscript{16} Its crystal structure consists of hydrogen-bonded (HCO\textsubscript{3})\textsubscript{2} dimers, further linked by guanidinium groups and water molecules.
into an extended hydrogen-bonded framework. The lower charge density of the bicarbonate anions, and their self-assembly into ‘anti-electrostatic’ hydrogen-bonded dimers, result in lower Coulombic stabilization of the bicarbonate crystals compared to analogous carbonate salts. Furthermore, there is only one stabilizing water molecule per bicarbonate anion, compared to 2-5 water molecules/CO$_3^{2-}$ found in other BIG carbonate salts. The GBIG bicarbonate crystals are stable enough to drive the separation of CO$_2$ from post-combustion flue gas mixtures (5-13% CO$_2$) with high efficiency. However, on its own, GBIG is hardly effective for DAC. The calculated free energy for the crystallization of GBIGH$_2$(HCO$_3$)$_2$(H$_2$O)$_2$ from air, of $-7.4$ kJ/mol CO$_2$,\textsuperscript{17} indicates a thermodynamically favorable reaction, but not necessarily an effective DAC process. Indeed, when left open to air, an aqueous solution of GBIG led mostly to crystallization of the hydrated free ligand, GBIG·2H$_2$O, which has an aqueous solubility that is very similar to that of the bicarbonate salt. Consequently, water evaporation leads to crystallization of the free ligand before the relatively slow CO$_2$ absorption from air, which is necessary for the GBIG bicarbonate crystallization, can occur.

The combination of aqueous peptides and GBIG provides the synergy required for an efficient DAC process. The peptide solution reacts relatively quickly with the atmospheric CO$_2$, converting it into bicarbonate anions, and lowering the solution pH by more than 3 units, from about 12 to less than 9. Under these conditions, the crystallization of GBIGH$_2$(HCO$_3$)$_2$(H$_2$O)$_2$ becomes favorable as the concentrations of GBIGH$_2^+$ and HCO$_3^-$ become sufficiently high to induce the supersaturation and nucleation of the GBIG bicarbonate salt. The relatively low $pK_a$ of the peptide (8.17 for GlyGly) is a critical parameter for the DAC process with GBIG, as it lowers the pH of the CO$_2$-loaded solution enough to allow for GBIG protonation. In direct contrast, most amino acids are too basic ($pK_a$ 9-10.5) for GBIG, leading to inefficient DAC. For example, aqueous Gly
(pK$_a$ 9.58) absorbs CO$_2$ effectively from air, reaching a pH of about 9.5, but that is too high for GBIG (pK$_a$ 7.33, 8.65) and leads to poor amino acid regeneration and low cyclic capacity (0.08 mol/mol) compared to GlyGly (0.16 mol/mol). We anticipate even higher cyclic capacities can be achieved by selecting small peptides that more closely match the pK$_a$ values of GBIG. Alternatively, de novo design of BIGs with enhanced basicities and propensities to form less soluble, anhydrous (bi)carbonate crystals will lead to more effective and energy-efficient DAC processes.

EXPERIMENTAL PROCEDURES

Resource Availability

Lead Contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the lead contact, Radu Custelcean (custelceanr@ornl.gov).

Materials Availability

This study did not generate new unique materials.

Data and Code Availability

The single-crystal X-ray data were deposited with CCDC (deposition number 2051067).

Full experimental procedures are provided in the Supplemental Information.

SUPPLEMENTAL INFORMATION

Supplemental Experimental Procedures for the thermodynamic analysis, DAC experiments, and X-ray diffraction analysis; Supplemental Figures: NMR spectra, X-ray crystal structure, and comparison of Gly and GlyGly regenerations.
ACKNOWLEDGMENTS

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AUTHOR CONTRIBUTIONS


DECLARATION OF INTERESTS

A US patent (10,583,387), with R.C. and N.J.W. as inventors, covering the DAC system described in this manuscript, has been granted. R.C. seeks to develop and commercialize a DAC technology based on the findings presented in this manuscript.

REFERENCES


