Speeding Carbon Dioxide Capture - The Key to Better Energetics

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LLNL-PRES-499751
This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC
Carbonic anhydrase is one of the most rapid enzymes known – it was first discovered in human lungs, where it facilitates $\text{CO}_2$ exhalation.

Carbonic anhydrase appears to have evolved independently five times, and has hundreds of structural variants.
The problem for today – carbon dioxide separation is too slow

- Separating pure CO$_2$ from industrial sources, or from the atmosphere, is a slow chemical reaction

- This requires large process equipment and long times, leading to high costs
  - Separation from natural gas power is 3-4x slower than coal
  - Separation from air is 300x slower than from coal flue gas

- Water-based liquids separate CO$_2$ from other gases with very high efficiency because CO$_2$ is very soluble in water
We have focused on using natural analogues to beat the speed limit

- Faster, rugged catalysts that survive industrial conditions
- Tethering of catalysts to the air-water interface
- Encapsulation to provide high surface area and confine solvent
And we are examining processes that utilize solid bicarbonate

25% exchangeable CO$_2$ by weight
The transfer of CO$_2$ into water or other liquids is almost always dominated by chemical reactions at the liquid interface.

The rate of CO$_2$ uptake directly depends on the near-surface conversion rate of CO$_2$(aq) to another species.

The liquid side "mass transfer limitation" is very large.
First we want a general approach for mimicking enzymes with small molecules - then to apply it to CO$_2$ capture

CA Structure & Function:
His triad, axial –OH, coordinate Zn$^{2+}$ center, key amino acids bind CO$_2$

Mimics:
optimize metal and ligand identity to improve kinetics

Carbonic Anhydrase

Zn$^{2+}$/His triad active site
We have created mimic catalysts that they are stable at 100°C, and their rate increases with temperature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Buffer</th>
<th>Temp (C)</th>
<th>$K_{cat}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(BF$_4$)$_2$ ctrl</td>
<td>Hepes, phenol red, pH = 7.5</td>
<td>$T_r$</td>
<td>7</td>
</tr>
<tr>
<td>Cyclen-Zn</td>
<td>Hepes, phenol red, pH = 7.5</td>
<td>$T_r$</td>
<td>540</td>
</tr>
<tr>
<td>Cyclen-Zn</td>
<td>Hepes, phenol red, pH = 7.5</td>
<td>Post 18 h, 100 C</td>
<td>900</td>
</tr>
<tr>
<td>Cyclen-Zn</td>
<td>AMPSO, thymol blue, pH = 9.0</td>
<td>$T_r$</td>
<td>2500</td>
</tr>
<tr>
<td>Cyclen-Zn</td>
<td>AMPSO, thymol blue, pH = 9.0</td>
<td>Post 18 h, 100 C</td>
<td>2260</td>
</tr>
<tr>
<td>Cyclen-Zn</td>
<td>AMPSO, thymol blue</td>
<td>50C</td>
<td>11,500</td>
</tr>
</tbody>
</table>

Demonstrated stability and enhanced kinetics for cyclen at elevated temperature and pH conditions.
Our mimics are faster at higher temperatures
And stable up to at least 120°C
The catalyst can be formed from zinc carbonate, indicating that carbonate solutions will not scavenge the zinc.
The rate of CO$_2$ uptake directly depends on the near-surface conversion rate of CO$_2$(aq) to another species.

The liquid side “mass transfer limitation” is very large.
The trick is tethering the catalyst to the liquid/gas interface – again nature is our example
Polyethylene glycol (PEG) linkers do not deform the catalysts and appear to be appropriate for tethering to hydrophobic groups.

~50 PEG units keep the catalyst removed from the immediate surface.
Catalysis is not the only speed-enhancer – surface area is critical

We can create encapsulated solvents analogous to alveoli in size and function
**Concept:** Encapsulate liquid solvents such as MEA in a thin, permeable, polymer shell.

**Initial Goals**

- Reduced volatility
- Degradation products contained

**Additional Benefits**

- Increased surface area
- Good interface with capture catalysts
- Facilitates new chemistries, especially high viscosity
We have pursued microcapsules made from a photocurable silicone (Semicosil)

Inner fluid: 5 wt% PEO solution in water with green dye
Middle fluid: Unmodified Semicosil A & B (10:1)
Outer fluid: 2 wt% PVA, 34 wt% H₂O, 64 wt% glycerol

Successful fabrication of microcapsules with Semicol UV curable silicon
Microcapsule production requires balanced fluid properties

Formation of double emulsions within microfluidic device using methods as described by the Weitz group

<table>
<thead>
<tr>
<th>Capillary</th>
<th>ID (µm)</th>
<th>OD (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection</td>
<td>50</td>
<td>1000</td>
</tr>
<tr>
<td>Collection</td>
<td>500</td>
<td>1000</td>
</tr>
<tr>
<td>Square</td>
<td>1000</td>
<td>1200</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Viscosity (cP)</th>
<th>Flow rate (µl h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner Fluid</td>
<td>10-50</td>
<td>200-800</td>
</tr>
<tr>
<td>Middle Fluid</td>
<td>10-50</td>
<td>200-800</td>
</tr>
<tr>
<td>Outer Fluid</td>
<td>100-500</td>
<td>2000-3500</td>
</tr>
</tbody>
</table>

Na₂CO₃/H₂O
Silicone Pre-polymer
PVA Stabilizer
Our current process runs at 250 capsules per second – too fast for this movie!
We have encapsulated multiple solvents in silicone capsules – with and without added catalyst.
Carbonate solvents show carbon capture amounts of over 3 moles CO$_2$ per liter of solvent (13 wt % CO$_2$)

- Plot shows the increase in carbon content as 30 wt % (4m) Na$_2$CO$_3$ reacts with flue gas.
- Calculated carbon capacity is the maximum possible per 1000g H$_2$O in solvent. Still need to get it back out.
- Most of the carbon capacity comes at PCO$_2$>0.001.
- Nahcolite doubles carbon capacity.
Why attempt high pressure recovery with solids present?

- **High PCO2**
  - Less energy to compress CO2
  - Less water boiled
  - Less carbon transfer per unit of solvent

- **Low PCO2**
  - More energy to compress gas
  - More water boiled
  - More carbon transfer per unit of solvent
30 wt % (4M) Sodium Carbonate (1) – Phase behavior

Flue Gas Loading

CO₂+H₂O gas

pH=9.8

pH=8.7

pH=7.3

Flue Gas

log CO₂ pressure (bars)

Temp C

HEATING

LOADING
30 wt % (4M) Sodium Carbonate (3) - Energetics

\[ \Delta H = 28 \text{ kJ} \]

- Carbon capacity compares well with amines
- Energy lower:
  - Lower heat of reaction of CO\(_2\)
  - Can extract CO\(_2\) at high pressure – lowering compression costs
  - Favorable process energetics due to the presence of solid bicarbonate (NaHCO\(_3\))
Speeding carbon dioxide absorption will enable low energy process approaches

- Faster, rugged catalysts that survive industrial conditions
- Tethering of catalysts to the air-water interface
- Encapsulation to provide high surface area and confine solvent, permit solids formation