MEMBRANE TECHNOLOGY

Embedded enzymes catalyse capture

Membrane technologies for carbon capture can offer economic and environmental advantages over conventional amine based absorption, but can suffer from limited gas flux and selectivity to CO₂. Now, a membrane based on enzymes embedded in hydrophilic pores is shown to exhibit combined flux and selectivity that challenges the state of the art.

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Global warming represents one of the greatest challenges of the present generation. While a shift to renewable energy is starting to have impact, the consumption of fossil fuels continues to grow, rather than to decline¹. The very large use of fossil fuels worldwide means that CO₂ capture and subsequent utilisation or storage underground must be pursued as one strategy to limit emissions. The classical approach to capturing CO₂ uses a liquid solvent such as monoethanolamine. However, this approach has its problems; it consumes a lot of energy (2.5 to 3.5 GJ/tonne of CO₂ (ref 2)) and amine-based solvents can release carcinogens such as nitrosamines into the atmosphere and into wastewater streams³. An alternative approach is that based on membranes. In such technologies, a membrane material is formed into either hollow fibres or flat sheets that selectively allow CO₂ to pass, while retaining other gas species (Fig. 1a). The approach can compete with solvent processes for CO₂ capture from a cost and energy consumption perspective⁴. Furthermore, the approach uses no harmful solvents. Obviously, this reduces the impacts on human health and the environment, but as electricity providers are not normally experts in chemical processing, it can also be easier for them to implement. Now, writing in *Nature Communications*, Ying-Bing Jiang, C. Jeffrey Brinker and colleagues across the US exploit a naturally occurring enzyme, carbonic anhydrase, confined within a nanoporous silica membrane, to catalyse the recovery of CO₂ from gas mixtures with promising performance⁵.

Two key requirements for membrane materials for CO₂ separation are that they are highly permeable to CO₂ and highly selective for CO₂ over other gases. The membrane developed by Jiang, Brinker and colleagues achieves excellent results in both respects. Their work recognises that achieving high CO₂ flowrates requires not only a material that has an intrinsic affinity for this molecule, but also that this material is formed into a mechanically stable, ultrathin layer. If the layer is too thick, it will provide too much resistance to flow. The researchers manufacture a layer that is very thin (18 nm) by using an oxygen plasma to etch a hydrophilic surface into 8 nm diameter nanopores, which have been formed beforehand by

evaporation-induced self-assembly of block copolymer templated mesoporous silica. The ultrathin hydrophilic portions of the nanopores are then filled with water, which is stabilised by capillary forces of up to 35 atm (Fig. 1b). The remaining length of the mesoporous silica nanopores are hydrophobic and hence remain free for rapid transport of the captured CO₂ away from the surface.

The material developed achieves ultrahigh selectivity for CO₂ through the use of a natural biological molecule – carbonic anhydrase, which is the enzyme used by red blood cells in the human body to capture CO₂. It acts as a catalyst to rapidly convert the molecule into carbonic acid (Fig. 1c). There are many other groups who have been looking at using this enzyme for industrial capture applications⁶⁻⁸ but the unique advantage claimed by Jiang, Brinker and colleagues is that by embedding the enzyme in the nanopores they achieve extremely high enzyme concentrations, ten times greater than can be achieved in an aqueous solution. In their device, the CO₂ is captured by the enzyme, passes across the 18 nm liquid film in the form of carbonic acid and is then released into a product stream – this is known as a facilitated transport mechanism.

A key innovation here is the use of carbonic anhydrase derived from *Desulfovibrio vulgaris*, an extremophile bacteria, which allows stable performance up to 90°C and across a pH range from 2 to 10. Stability in a range of pH environments is important, as the flue gas environment is humid and liquid water carryover can occur – the pH of this water carryover can vary significantly if upstream flue gas desulphurisation or direct contact cooling is used. Thermal stability is also critical, as the incoming gas stream can be elevated in temperature.

The permeance values that the researchers achieve are competitive with state of the art polymeric membranes being tested for carbon capture applications^{4,9}, but with much higher selectivity to CO₂. High selectivity can be important in carbon capture applications where the feed gas pressure is relatively high (greater than 5 atm). This is typical when CO₂ is separated before combustion, as occurs in integrated gasification combined cycle power plants. Jiang, Brinker and colleagues show CO₂/H₂ selectivities of up to 1500, which offer significant promise for such applications. However, it is well known that facilitated transport membranes can lose permeance and selectivity as pressure increases, as the active sites on the feed side of the membrane become saturated¹⁰. Further testing is required to determine whether this occurs in the present case, but the very high enzyme concentrations – and therefore the high concentration of active sites – may prevent a significant loss as saturation of active sites should be minimised.

Although the researchers suggest applications for classical flue gas capture, there are still hurdles to be overcome for such post-combustion carbon capture applications. For example, previous work⁴ has shown that if the selectivity is high, the membrane area required increases, leading to higher capital cost. Inorganic membranes will always be more expensive to manufacture than polymeric membranes and this will exacerbate the capital cost issue. There are other matters that also need to be solved for such approaches to reach commercial implementation. The researchers have shown that the membranes are stable for up to three months in a humidified gas stream, but more extended trials are needed to confirm that membrane lifetimes of several years can be obtained. Trials under real industrial conditions are also needed to confirm that the enzyme is not leached from the substrate, particularly during process upsets, where liquid water can come into contact with the membranes.

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Figure 1 Carbon capture using an enzyme. **(a)** The CO_2 rich feed gas passes across the surface of the membrane and the CO_2 preferentially passes through the 1 micron deep arrays of 8 nm diameter cylindrical silica mesopores embedded within a 50 micron thick porous alumina support, due to the concentration gradient; **(b)** the silica mesopores are hydrophobic (employing trimethylsilyl ($\text{Si}(\text{CH}_3)_3$) surface groups) except for an 18 nm deep region at the pore surface which is hydrophilic due to $\text{Si}-\text{OH}$ surface groups. The carbonic anhydrase (CA) enzyme fills the hydrophilic mesopores and catalyses the capture and dissolution of CO_2 as HCO_3^- ions at the upstream surface and regeneration of CO_2 at the downstream surface. **(c)**

Carbonic anhydrase is a metalloenzyme, typically with a zinc centre co-ordinated to three amino acids such as histidine or cysteine. The capture of CO₂ occurs when the Zn²⁺ ion abstracts a proton from a surrounding water molecule, creating a negatively charged hydroxide ion that can attack the electron deprived carbon atom within a CO₂ molecule to form a bicarbonate (HCO₃⁻) ion. Figure panels a and b are adapted with permission from ref. 5, Macmillan Publishers Ltd (2018).

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