

A molecular-scale waterwheel removes carbon dioxide from the air

A chemical trick that harnesses energy from a humidity gradient could become another tool to mitigate climate change.

After centuries of releasing carbon dioxide into the atmosphere, humans are now looking for ways to remove it (see *PHYSICS TODAY*, June 2022, page 26). One obstacle is that despite the climate changes being driven by the rising concentration of CO_2 in the atmosphere, that concentration is still relatively dilute, at about 420 ppm. Dif-

fusion naturally moves molecules from high-concentration areas to low-concentration ones, but extracting CO_2 from air requires a reversal of that process. Separating an already dilute substance from air thus poses thermodynamic and kinetic challenges that can predispose the task to being energy-intensive and slow.

To reverse the typical diffusion process, cells and other biological systems use an efficient trick to move molecules against a concentration gradient. Cells, for example, pump out hydrogen ions to maintain a specific pH. The trick, known as active transport, works in a manner akin to a waterwheel: As one substance moves down its gradient (from high concentrations to low ones), the energy that is released is harnessed to move another substance against its gradient (from low concentrations to high ones).

Ian Metcalfe, of Newcastle University in the UK, and colleagues have now found a way to harness an artificial version of the active transport mechanism to pull CO_2 out of air.¹ Just like with a

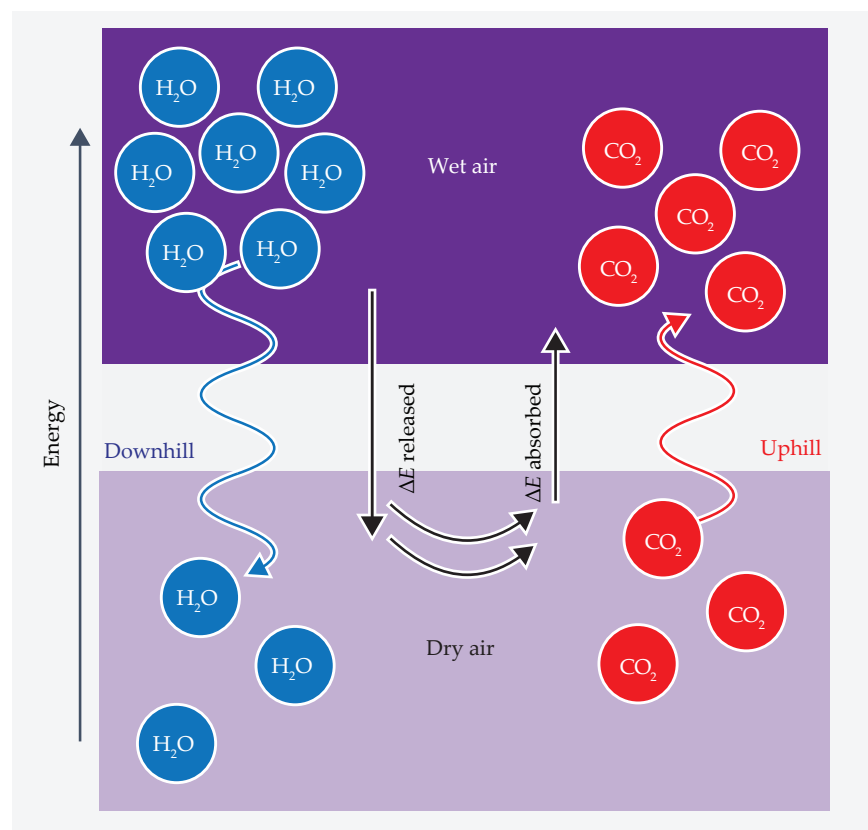


FIGURE 1. WATER MOVES ACROSS A MEMBRANE from wet air to dry air, and the energy ΔE released by the process is harnessed to move carbon dioxide in the opposite direction. (Adapted from ref. 1.)

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waterwheel, the movement of water—in this case, at a molecular level—provides the driving force.

The method uses a difference in humidity between two air masses. The separation is made possible by a membrane containing a common carrier that bonds with either CO_2 or water molecules and shuttles them through the membrane to produce an equal and opposite exchange of the two substances. As shown in figure 1, moisture in an air mass on one side of the membrane causes water to move from the humid side to the dry side, which provides the energy for a corresponding transfer of CO_2 in the opposite direction.

Common carrier

Metcalfe and colleagues had not set out to replicate active transport; rather, they discovered the mechanism through a fortuitous experiment. They were investigating the use of molten-salt membranes for CO_2 separation, a small subset of the immense research field of direct air capture (see *PHYSICS TODAY*, January 2020, page 44). Most experiments performed with such membranes involve some degree of leakage across them. When calculating the effectiveness of a membrane for a given task, researchers typically use a tracer gas to measure the extent of leaks and correct for them. Not satisfied with those typical conditions, Metcalfe and colleagues sought to design a leak-free membrane.

Leaks occur because it is hard to create a perfect seal between a hot membrane and the end of an open-ended tube. The researchers made the leak-free membrane by drilling many small holes into the end of an alumina cylinder that were then filled with a molten salt—in this case, a roughly equal mixture of lithium, sodium, and potassium carbonates. In early experiments led by Sotiria Tsochataridou, a member of the research team and a PhD student at the time, the team noticed that anytime moisture was introduced on one side, that water would transfer across to the dry side, and an equal number of CO_2 molecules would transfer in the opposite direction.

"It was something that I recognized when I saw it, and I thought, this might well be that we've got a common carrier," says Metcalfe about the early experiments. "We've got one species in

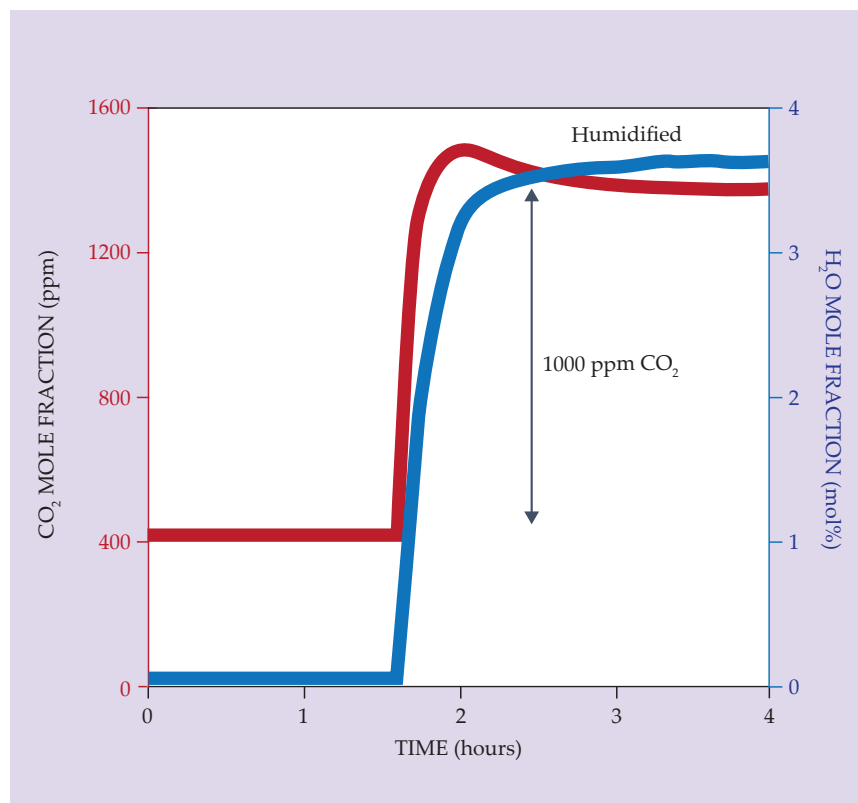


FIGURE 2. CARBON DIOXIDE CONCENTRATION (red line) rises in an air mass when the humidity (blue line) is increased after a period of equilibrium. Researchers took advantage of that relationship and designed a new method to extract CO_2 from the air. (Adapted from ref. 1.)

there that's shuttling backward and forward, and if that's the case, we should be able to do some interesting things with it."

The experiments were exceptional not just because they were leak-free. Alumina is not the typical support material used for molten-salt membranes. Most often, the supports are conductive materials that help the membrane function by transporting charge. It was generally assumed in the community of membrane researchers that without a conductive support material, such membranes would not work. But alumina is not conductive, and it did work.

"We did a really daft experiment that gave us a really interesting result," says Metcalfe. "Everybody else was saying it wouldn't work, but nobody checked."

Equal exchange

Subsequent experiments confirmed the initial suspicion that the membrane contains a common carrier. Unlike a

filter, in which one air mass is pushed through a medium to produce one input stream and one output stream, membrane separation involves two moving air masses and, subsequently, two inputs and two outputs. In membrane research, measurements of all four streams aren't always collected, but in this case, they were a necessary condition for noticing the common-carrier effect.

The experiments begin with streams of dry air on each side of the membrane that contain about 400 ppm of CO_2 , close to the average concentration in today's atmosphere. When the streams have equal flow rates and water vapor is introduced into one of them, water quickly permeates from the humid side to the dry side and rises to 200 ppm. An equal quantity of CO_2 moves from the dry side to the humid side, leaving the dry side at a concentration of 200 ppm of CO_2 and raising the humid side to 600 ppm.

As shown in figure 2, when Metcalfe and colleagues dropped the flow rate

on the humid side by a factor of five, the CO_2 concentration on that side increased by 1000 ppm, five times as much as the increase observed at equal flow rates, to a total of 1400 ppm. Before CO_2 concentrations reach 1400 ppm, though, there's a slight bump to an even higher concentration right after the water is introduced to the stream. That bump is from CO_2 that had been stored in the salt membrane suddenly being kicked out by the flux of water.

Metcalfe then enlisted the help of Patricia Hunt (Victoria University of Wellington in New Zealand) to explore the potential carrier reactions operating in the molten carbonate salts. Using density functional theory, she found that multiple reaction pathways could be at play in the membrane because of the similar chemical stability of several carriers. The carriers are generally composed of clusters of carbonates and lithium or sodium ions in varied proportions. And the carriers are highly selective—they bind with only water or CO_2 , with a slight energetic preference for binding with CO_2 .

The absorption of CO_2 and water into the melt is energetically favored, and the release of those species from the carriers is driven by concentration differences. The rate-limiting step is the release of CO_2 from solution on the humid side. The effective partial-pressure difference of water drives the water-binding process on the humid side and accelerates the release of CO_2 . Because of the prevailing water partial-pressure difference across the interface, absorption of CO_2 on the dry side remains energetically favorable despite the CO_2 partial-pressure difference that develops.

Molten membranes

Although the discovery is a new way to pull CO_2 from the air, the method is far from having the conditions necessary for implementation in a direct air capture system. A CO_2 concentration of 1400 ppm is still much lower than the near-pure concentration of CO_2 necessary for movement into permanent storage, but Metcalfe and colleagues note that the new process could be a valuable preconcentration step that reduces the expense of other downstream extraction methods. Further adjustments to the flow rates and relative

humidity levels could also push that concentration higher.

The extremely dry air used in the experiments is nowhere near the humidity of atmospheric air, even in the driest deserts. For that reason, the researchers also investigated using humidified air on both sides of the membrane while retaining a gradient in the humidity. They found that the membrane works even at humidity levels that reflect natural conditions, although the permeation rates do decrease somewhat. The natural swing of atmospheric humidity from day to night in many regions could provide enough of a gradient for the mechanism to be used for direct air capture.

For the carbonate salts used in the experiment to stay molten, they have to be at least 400 °C, which means the air must also be that hot. That could pose another barrier to economically scaling up the process. But there could be ways to lower the melting point, such as doping the salts with other materials.

Metcalfe is excited about the prospects of refining the method or finding other common carrier materials. "We wanted to try to change the way people think—there are ways to address the thermodynamic and kinetic barriers—and with that inspiration, and perhaps with clever engineering, they can take it further," he says.

Clear benefits of the new approach are that it is fast and highly selective—only water and CO_2 move through the membrane, with no leaks. Though polymer-based membranes make up the bulk of direct air capture membrane research, they are generally plagued by a low selectivity that allows gases besides CO_2 through. The carbonate salts and alumina used for the experiments are also relatively cheap base materials. It's unlikely that any single technology will provide a solution to looming climate change. Metcalfe and colleagues' molten-salt membrane adds a new, efficient tool to the effort.

Laura Fattaruso

Reference

1. I. S. Metcalfe et al., *Nat. Energy* (2024), doi:10.1038/s41560-024-01588-6.



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