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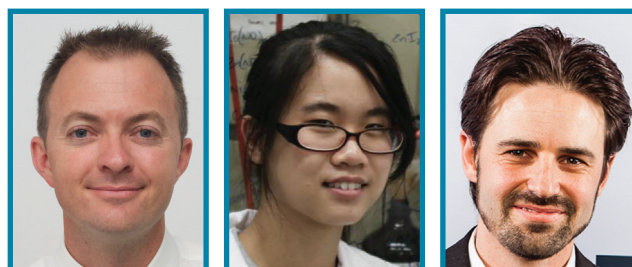
## The carbon sponge: squeezing out captured carbon dioxide

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“...it is clear that genuine breakthroughs in carbon-capture technologies ... will be required to enable power generation from fossil fuels in a carbon constrained future.”

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Carbon-capture technologies for the removal of carbon dioxide from industrial process streams have been intensively researched, both in academia and industry, for several decades. Governments worldwide have devoted enormous sums of research funding to advancing carbon capture technologies, especially to demonstrate them on pre-commercial and, eventually, the commercial scale. The impetus to make these investments are twofold.

First, governments can claim that they are directing resources to efforts that will reduce the carbon emission intensity of existing industries, especially power generation from fossil fuels such as coal. Superficially this is true, as without doubt the successful adoption of carbon capture-technologies in base load power generation from fossil fuels would reduce atmospheric carbon dioxide emissions. However, the fact that the power generation and allied industries are major employers is not lost on political minds, and so directing funding to potentially extending the extent or lifetime of those existing industries has pragmatic benefits too.

The second major reason to support the development of viable carbon capture technologies suitable for power

generation is to protect the other major industries that rely on reliable, low-cost base load electricity generation, such as manufacturing and electro-refining. This is particularly the case in Victoria, Australia, which contains vast brown coal (lignite) reserves that could easily provide another 500 years of low-cost power generation at current consumption rates. If a technological option was available, which allowed for the continued use of brown coal (a very low-cost fuel) to generate electricity with minimal carbon dioxide emissions, then fossil-fuel rich regions such as Victoria could enjoy an enormous competitive advantage in terms of electricity supply costs.

The current state-of-the-art in carbon-capture technologies reveals that no one technology has reached the technological maturity and, more importantly, the required cost per ton of carbon dioxide removed, to be commercially adopted [1,2]. Perhaps the most mature technology that can be used at significant scale is the use of liquid absorbents such as amine solutions, which can scrub carbon dioxide from a mixed gas stream and be regenerated using steam or heat, releasing the carbon dioxide in concentrated form in a separate stream, ready

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for compression, transport and usually some form of sequestration. This approach has been successfully used in the natural gas industry for removing carbon dioxide from largely methane streams, a process called 'sweetening'. However, for power generation units, the size of the capture plant using amine absorbents would be enormous, and the power to operate it could easily consume a significant fraction of the power output of the power station.

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Various membrane technologies have been proposed and validated at small to medium scales. This includes the use of polymeric membranes to remove carbon dioxide from combustion gas streams that have been cooled and cleaned to remove particulates and certain chemical species that are known to damage the membranes. This approach is also capital intensive, as the feed stream is usually available at pressure barely above ambient, which means that various configurations of vacuum pumps and membrane stages are required to obtain sufficient driving force for gas transport across the membrane. Very large membrane areas are inevitably required and, while membranes have the unique advantage that large areas can be packed into relatively compact modules with high area-to-volume ratios, the cost of the membranes becomes prohibitively high. Ceramics, metal oxides and other inorganic membranes in different configurations have also been proposed as carbon-capture technologies, however these usually require the reconfiguration of power-generation technology to use enriched oxygen as the feed gas (which has the benefit of producing a combustion product largely free of nitrogen). Alternatively, the fuel may be gasified to produce a syngas-type mixture, which is then passed through membranes to produce hydrogen and other gas streams suitable for combustion, sequestration or otherwise. While very high performance inorganic membranes have been demonstrated at small scales, the production of defect-free large scale inorganic membranes has proved extremely difficult and is a major limitation to this technology.

Gas adsorption onto solid adsorbents is another long-established technology that is being pursued as a carbon-capture possibility, but again there are significant challenges related to the size and cost of the equipment that would be required to treat the enormous flow rates resulting from power stations.

The inherent parasitic energy loads of many prospective carbon-capture technologies limits the maximum attainable efficiencies. While liquid amines and some membranes are likely to find first-generation adoption, widespread application will be best suited to those technology solutions with drastically lowered parasitic energy loads. Consequently, methods that readily utilize alternative energy sources as part of the process are attractive. With this in mind, we have developed materials that can utilize solar radiation to release captured carbon dioxide.

Metal-organic frameworks (MOFs) are a paradigm-shifting family of materials. Consisting of metal atoms or clusters joined periodically by organic linking species, MOFs are hybrid materials with an ultraporous array of uniform pores in which unprecedented surface areas are housed. These surfaces can be tuned to provide exceptional capacity and selectivity for carbon dioxide adsorption. We have previously shown that MOFs have exceptional gas storage and separation characteristics [3–8], and their use in advanced membrane topologies [9–13].

“ Termed the 'solar sponge', the structure was able to release approximately 64% of the adsorbed carbon dioxide within just a few seconds. ”

Our team utilized a zinc-based MOF constructed from azobenzene and bipyridyl ethane organic linkers, substances known to change shape, or strongly absorb UV light [14]. After adsorption of carbon dioxide, we found that localized bending modes induced within these responsive organic components could instantly induce the release of this adsorbed gas when the samples were exposed to concentrated light while loaded with carbon dioxide. Furthermore, we found that while this was most effective at 365 nm, the absorption maximum for the MOF, the effect was still significant when simple, broadband UV radiation was employed. This gives the best of both worlds in a future application. Termed the 'solar sponge', the structure was able to release approximately 64% of the adsorbed carbon dioxide within just a few seconds.

Our discovery of the use of photo-swing adsorption is a general result that could be applied to all candidate adsorbents 'squeezing' out adsorbed carbon dioxide with application of broad spectrum light.

There are many challenges to using this type of capture process at any significant scale and the authors are currently working through those with colleagues around the world, but regardless of whether this particular breakthrough leads to a commercial reality, it is clear that genuine breakthroughs in carbon-capture technologies, and not just incremental improvements on the existing

technologies, will be required to enable power generation from fossil fuels in a carbon constrained future.

### Financial & competing interests disclosure

The authors acknowledge financial support from the Science and Industry Endowment Fund. The authors are co-applicants on a PCT Patent application entitled 'Gas Separation Process', based on the

process described in this Editorial. The authors have no other relevant affiliations or financial involvement with any organization or entity with a financial interest in or financial conflict with the subject matter or materials discussed in the manuscript apart from those disclosed.

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