

Careful catalysis converts CO₂ emissions into useful chemicals

'Reduce carbon dioxide emissions by reducing carbon dioxide': at first glance, this doesn't seem particularly insightful, but it's the basis of research recently produced by Samuel Perry at the University of Southampton. Using the carbon dioxide reduction reaction, an electrochemical process with multiple possible products, Perry and his collaborators are working towards an electrode design that can selectively convert CO₂ into ethylene. To accomplish this, he used PIMs, Polymers with Intrinsic Microporosity, which limit the production of side-products like carbon monoxide by hindering bubble formation at the catalyst site. Carbon dioxide emissions from industrial exhausts could be collected and converted into useful products. By reducing carbon dioxide electrochemically, the technology has potential to reduce carbon dioxide emissions.

2019 was the end of the warmest decade on record. Carbon dioxide (CO₂) levels in the atmosphere reached record levels, and meanwhile, emissions show no sign of peaking. Reducing global CO₂ output is a crucial component in conserving a liveable world.

As a result, many countries, notably including all of those in the European Union, are committed to having net zero emissions by 2050. However, many climate models – especially those pathways which meet 1.5 °C warming target – involve utilising carbon-reduction technologies which haven't been invented yet, or at least, are not proven to work at scale.

These technologies aim to reduce greenhouse gas emissions by capturing CO₂ and converting it into other materials. Particularly attractive is the possibility of using the gas as a carbon source for synthesising useful chemicals – this provides an added benefit of reducing our dependency on fossil fuels, which would otherwise be the feedstock for these industrial chemicals.

Converting carbon dioxide into biofuels, for example, could compliment intermittent green energy sources such as wind and solar.

THE CARBON DIOXIDE REDUCTION REACTION

There is a process – the CO₂ Reduction Reaction (CO₂RR) – which does exactly this, converting CO₂ into industrially important substances like methane, ethylene, formate, and carbon monoxide. This is an electrochemical process, meaning that a current is applied using electrodes through a mixture of materials, including carbon dioxide, and the products are evolved at the electrodes. Reduction in the electrochemical sense does not mean lowered, but that CO₂ gains electrons during the reaction in order to reach the end product. This is the opposite of oxidation, which we see when metal rusts or fruit turns brown.

Some of these products are more desirable than others, and some are more easily obtained too. Both carbon monoxide and methane have been demonstrated to work at a reactor scale, meaning that they might be implemented relatively soon. Various other carbon-containing compounds are obtained using different catalysts, which favour different CO₂RR products.

Ethylene, also called ethene or C₂H₄, is one of the more elusive. It is a highly important chemical, able to be converted to many products, but by far its main application is in creating polyethylene, the most commonly-used plastic in the world. Creating ethylene from carbon dioxide has been

demonstrated using copper catalysts, but there are a couple of barriers preventing this technology becoming commercially viable.

BARRIERS TO SCALING UP

The first problem is that the copper-catalysed reaction creates a few other products alongside ethylene, including carbon monoxide, hydrogen gas and methane.

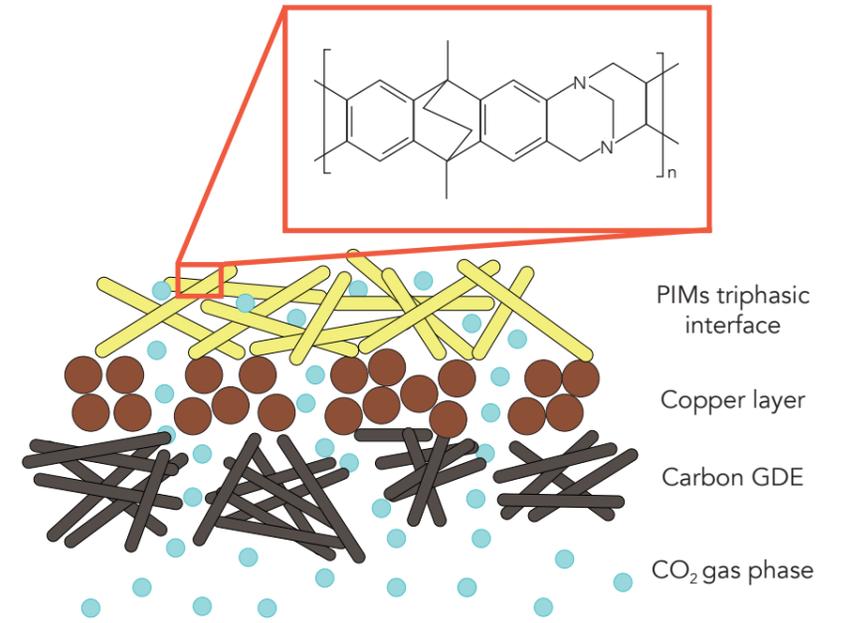
The second is that scaling these reactions up necessitates the use of high currents, which drives a reaction that reduces water, creating even more hydrogen.

These are significant limitations – producing a pure product is essential if this process is going to become economically viable.

MICROPORES: THE KEY TO SELECTIVITY

Can the CO₂RR process be modified in a way which results in high quantities of ethylene? This is the conundrum being tackled by Samuel Perry, Research Fellow at the University of Southampton, UK, with collaborators at the University of Edinburgh, McGill University in Montreal, and the Schaeffler Group based in Germany.

His team is addressing these issues by designing modified copper catalysts which have protective coatings that can convert CO₂ selectively to ethylene. This coating is a thin layer of material deposited onto the catalyst, which coats the electrode.



Using the carbon dioxide reduction reaction, Samuel Perry and collaborators are working towards an electrode design that can selectively convert CO₂ into ethylene. Reproduced from Perry et al. *Chemosphere* 248, 2020 <https://doi.org/10.1016/j.chemosphere.2020.125993> with permission from Elsevier.

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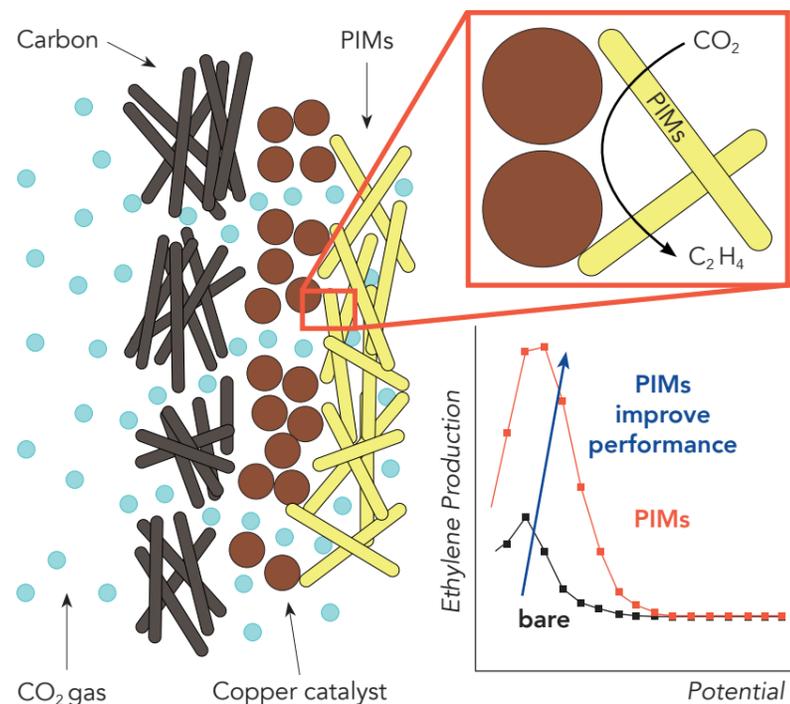
The electrodes used are porous and made from carbon fibre, allowing the gas to diffuse quickly through the electrode, which facilitates a higher rate of reaction. The novel protective coating is made from polymers with intrinsic microporosity

(PIMs), a type of material which – you guessed it – contains very small pores. These pores are so small that bubbles cannot form, the theory being that CO₂ would be trapped close to the catalyst surface allowing for a longer reaction



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Enhancing CO₂ catalysis. Gas diffusion electrodes give rapid CO₂ conversion. Copper nanoparticles are selective for ethylene. Polymers with intrinsic microporosity (PIMs) trap CO₂ and reaction intermediates like CO at the electrode to favour complete conversion. PIMs increases selectivity of copper catalysts. Reproduced from Perry *et al.* *Chemosphere* 248, 2020 <https://doi.org/10.1016/j.chemosphere.2020.125993> with permission from Elsevier.

PIMs improved the selectivity of copper catalysts from 19% to 46% ethylene.

time. Notably, ethylene is a 'two-carbon' product, which involves the formation of carbon-carbon bonding at the catalyst active site. This process happens in a different pathway to the formation of methane, and benefits from extended exposure to the catalyst. The carbon dioxide held in this accessible state is referred to as the "triphasic interface", since the gas (CO₂) is held in a liquid electrolyte solution near a solid catalyst.

TESTING FOR ETHYLENE SELECTIVITY

Having built a set of electrodes and coated them with a thin porous layer of copper nanoparticles, Perry and his team deposited PIMs on the electrodes in various thicknesses, and used them to perform tests to determine if the PIM had an effect on the selectivity of the reaction towards ethylene.

One key metric of success for this experiment PIM is the selectivity towards ethylene. This was measured

by the percentage of product which was ethylene for each PIM thickness electrode. These tests gave a promising result: the PIM does increase selectivity towards ethylene compared to an electrode without any PIM. In fact, PIMs improved the selectivity of copper catalysts from 19% to 46% ethylene. In other words, trapping CO₂ using PIM is effective for producing faster reaction rates and higher selectivity for ethylene.

Carbon monoxide is a key intermediate in the production of ethylene from CO₂, and Perry hypothesises that the micropores in the PIM hinders carbon monoxide release, meaning it can be further reduced to ethylene, increasing the overall yield.

UNEXPECTED EFFECT ON CATALYST STABILITY

Another important factor in determining whether PIM-coated electrodes are suitable for upscaling as a technology is the stability of the catalyst. This is a key challenge in CO₂ reduction, because

of a phenomenon known as electrode flooding, which is when a liquid electrolyte seeps into the porous carbon electrode structure. When this happens, it prevents the carbon dioxide gas from flowing to the catalyst and slows the reaction rate down.

Usually, this problem is mitigated by using hydrophobic components in gas diffusion electrodes, to repel water. However, this is generally not particularly effective: whilst it works well at first, over only a few hours of use the hydrophobicity wears off. It's only a matter of time before the electrode fails due to flooding.

Thicker layers of PIM allow more water to accumulate in the electrode, meaning that the electrode quickly floods. This effect is caused by the PIM being less hydrophobic than an electrode which hasn't been coated.

However, thinner layers of PIM showed a minimal decrease in the hydrophobicity, but still gave all of the catalytic benefits for ethylene production. The thin PIM coating also slowed the rate of hydrophobicity loss, meaning the electrode works for a longer period of time.

DEVELOPING THE CATALYSTS OF THE FUTURE

Whilst the PIM increases the performance of the copper electrode in the CO₂RR, the technology is definitely not perfect yet. Perry outlines that there are further improvements and implementations that would enhance the performance further, including changing the substance that the PIM is made from, especially favouring PIM materials with high hydrophobicity to reduce the chance for electrode flooding. The researchers also suggest that PIM coatings should be tested on catalysts other than pure copper; many types are being tested by other research groups.

This technology represents a sizeable step towards making the electrochemical synthesis of important chemicals and fuels from CO₂ viable in an industrial setting. What makes it particularly exciting is that it could become economically beneficial for industry to reduce carbon dioxide emissions, which in turn would lessen our dependency on fossil fuels, and provide energy security for intermittent green energy sources.



Behind the Research

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Research Objectives

Dr Perry is currently working on experimental and simulated studies into the electrochemical reduction of carbon dioxide. His other research interests include microelectrodes, SECM, biosensors and corrosion.

Detail

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Bio

Samuel Perry is a Research Fellow at University of Southampton with expertise in electrochemical catalysis, surface chemistry, scanning probe electrochemical sensing and numerical modelling. He is a leader for the CO₂ reduction package of the Horizon 2020 CO₂EXIDE project, responsible for directing research, mentoring students and communicating new discoveries.

Funding

This work is supported as part of

the CO₂-based electrosynthesis of ethylene oxide (CO₂EXIDE) project, which receives funding from the European Union's Horizon 2020 research and innovation programme in co-operation with the sustainable process industry through resource and energy efficiency (SPIRE) initiative under grant agreement no. 768789.

Collaborators

- From Southampton University: Sotirios Mavrikis, Pui-Ki Leung, Carlos Ponce de León and Ling Wang for regular project discussions and lots of hard work on related projects
- From Edinburgh University: Richard Malpass-Evans and Neil McKeown for the synthesis of the PIM itself
- From McGill University: Samantha

Gateman and Janine Mauzeroll for the electron microscopy and contact angle measurements

- From Schaeffler Technologies Ag & Co. KG and SIA Schaeffler Baltic: Moritz Wegener and Pävells Nazarovs for preparing the original copper gas diffusion electrodes
- All project partners on the CO₂EXIDE project from University of Science and Technology Kraków, Axiom angewandte Prozesstechnik, Budapest University of Technology and Economics, Energy Institute at the Johannes Kepler University Linz, EPC gGmbH, Fraunhofer IGB, Institute of Solid State Physics of the University of Latvia, Schaeffler Technologies, Siemens and University of Southampton.

References

Perry, S. C., Gateman, S. M., Malpass-Evans, R., Mckeown, N., Wegener, M., Nazarovs, P., Mauzeroll, J., Wang, L., Ponce de León, C. P. (2020). Polymers with intrinsic microporosity (PIMs) for targeted CO₂ reduction to ethylene. *Chemosphere*, 248, 125993. <https://doi.org/10.1016/j.chemosphere.2020.125993>

Perry, S. C., Leung, P-K., Wang, L., Ponce de León, C. P. (2020). Developments on carbon dioxide reduction: Their promise, achievements, and challenges. *Curr Opin Electrochem*, 20:88–98. <https://doi.org/10.1016/j.coelec.2020.04.014>



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Personal Response

In your research, you reference how this reaction can be complimented with oxidation of H₂O into H₂O₂, hydrogen peroxide. Can you describe how this would contribute to a commercial reactor design?

|| In a "standard" electrochemical cell, we have a tendency to just focus on one electrode. In our case this is the negative electrode (cathode), which reduces CO₂. Also in our cell we have a positive electrode (anode), which balances the charge in our cell. If we don't think about the anode in our design, any current passed here is wasted on background reactions. Instead, we can use an anode catalyst that selectively oxidises H₂O to H₂O₂, allowing us to make two useful products for the same amount of energy. This would make the process much more cost effective and energy efficient. ||