

SOLAR FUELS

Scalable CO₂-to-oxygenate production

Most electrochemical CO₂ reduction research has been confined to fundamental studies that attempt to understand how to overcome low selectivity and energy efficiency for valuable oxygenated products. Now, a modular, scalable system generates multi-carbon oxygenates with a potential solar-to-alcohol efficiency of more than 8%.

Erin B. Creel and Bryan D. McCloskey

While alternative energy sources have received much attention in attempt to address climate change, the limited number of economically viable approaches to reduce the automotive and chemical industry's reliance on petroleum-derived fuels and feedstocks is still a concern when considering greenhouse gas emission reduction¹. Enabling large-scale, solar-driven conversion of captured CO₂ to valuable multi-carbon products could provide an alternative, renewable route to liquid fuel production, allowing what would otherwise be a harmful greenhouse gas to be used beneficially to help meet energy demands². Despite decades of investigation, CO₂ reduction systems are still primarily confined to the realm of basic research, where work has focused on improving the limited understanding of rational catalyst or system designs that provide excellent multi-carbon product selectivity at reasonable energy efficiencies³. The most common electrochemical CO₂ reduction products observed on many metal electrodes are formate, CO, or hydrogen from the competing water reduction reaction, all of which are not as desirable as hydrocarbon or alcohol products, which can be directly used as fuels or in other high-value applications⁴. Copper is among the very few known electrocatalyst materials capable of catalysing the formation of multi-carbon products, although only at large, efficiency-limiting overpotentials, and with undesirable broad product distributions⁴. The key scientific challenge for CO₂ reduction is the development of new concepts that can achieve high selectivity towards multi-carbon oxygenates, extended system lifetime and enhanced photon-to-product efficiencies.

Now, writing in *Nature Catalysis*, Schmid and colleagues describe⁵ a path towards cost-effective commercialization of CO₂-to-oxygenate conversion using a modular and scalable system (Fig. 1). The researchers use a system in which they harness the known ability of silver electrocatalysts to efficiently form syngas

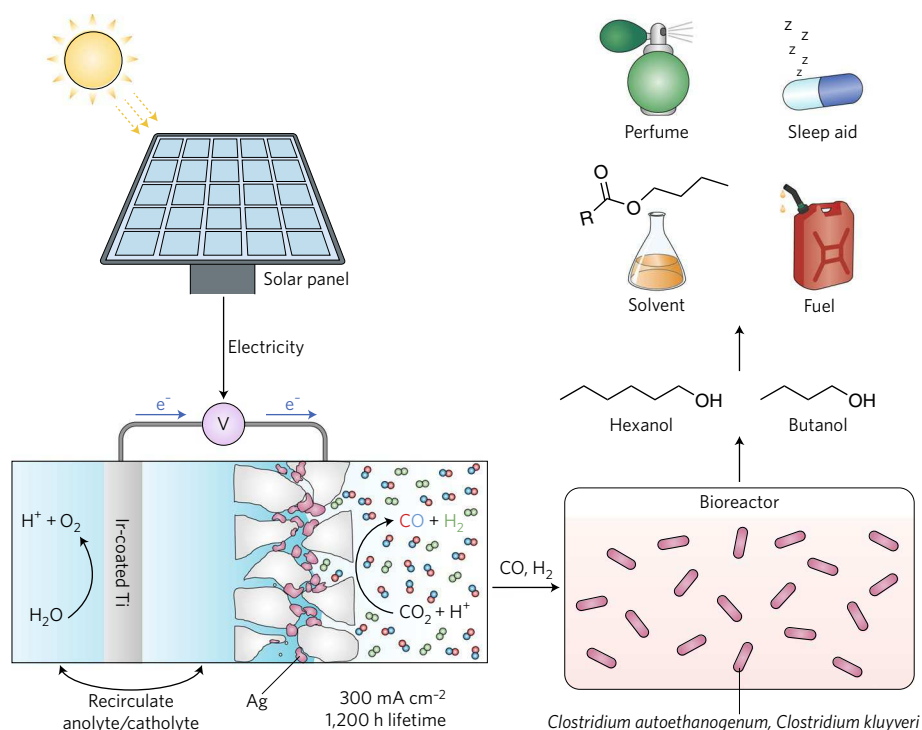


Fig. 1 | Modular and scalable CO₂ reduction process. An electrolyser powered by a photovoltaic cell array converts CO₂ and H₂O into CO and H₂ (drawn without stoichiometric accuracy for simplicity), which are then fed to a bioreactor where they are further converted to the valuable alcohols, hexanol and butanol.

in an electrolyser⁶, and then send the syngas to a bioreactor where fermentation by a mixture of bacteria results in high conversion of CO to acetate and ethanol (when the bacteria pair is *Clostridium autoethanogenum* and *Clostridium ljungdahlii*) or butanol and hexanol (when *C. autoethanogenum* and *Clostridium kluyveri* are used). The electrolyser employs a commercially available porous silver gas diffusion electrode originally developed for the chlor-alkali process, achieving remarkable current densities (up to 300 mA cm⁻²), extended operational lifetime (1,200 hours continuous operation demonstrated) and stable generation of a syngas composed of 65/35 mol% CO/H₂.

In particular, the combined current density and lifetime of the device are extraordinary, and clearly show that further scale-up to larger reactors is possible. The syngas product mixture is then sent to an anaerobic bioreactor, where the production of various valuable oxygenates (alcohols or acetate depending on the bacteria selected), is demonstrated. The researchers argue that, using known photovoltaic efficiencies from commercially available solar cells, overall photon-to-alcohol efficiencies of 8% can be achieved for the butanol/hexanol forming process described, making the process among the most efficient reported for multi-carbon product formation from solar-driven CO₂ reduction.

Previous studies of solar-to-chemical CO₂ reduction systems have focused on a number of methods to integrate various aspects of the modular design used in the present study. For example, microorganism integration into a CO₂ reduction electrochemical cell provides a route to electrochemically ‘pump’ electrons into biological reduction processes, although at unknown ultimate efficiencies⁷. A few interesting studies on CO₂ electrolysis (without a bioreactor) driven either by a photovoltaic cell or a photoanode in a photoelectrochemical configuration have been reported^{8–10}. For example, a recent study conducted at the Joint Center for Artificial Photosynthesis (JCAP) reported 5% solar conversion, producing more than ten hydrocarbon and oxygenate species using a photovoltaic cell coupled to a CO₂ electrolysis cell employing a bimetallic Ag–Cu-based catalyst⁸. Nevertheless, the high current densities of the CO₂-to-syngas electrolyser, combined with a bioreactor that can selectively form C₄/C₆ oxygenates (butanol and hexanol), appear to be clear advantages. Furthermore, separating the functions of the CO₂ reduction system into individual modules — light capture, syngas formation and fermentation to multi-carbon products —

allows each component to be optimized independently, providing a clear path to further gains in efficiency or to the development of processes that form other valuable products. Conversely, in an integrated system, where the photoabsorber, electrocatalysts and bacteria are all contained within the same module, a refinement to one function may negatively impact another function, although continued research into these systems will surely provide breakthroughs for an integrated solar-to-fuels device.

Schmid and co-workers provide a clear vision for the commercialization of CO₂ reduction systems through decentralized modular systems. Future work should address the separation of the products from the bioreactor and integration of a photovoltaic module to evaluate the performance of the system over daily and diurnal cycling of light levels. The development of alternative technologies to the Fischer–Tropsch process that allow energy-efficient, selective and distributed conversion of syngas to other hydrocarbon or oxygenate products would also potentially provide enhancements beyond the reported bioreactor module. This is a call to researchers in the fields of photovoltaics, power conversion, electrochemistry and microbiology to iterate on the promising design presented by Schmid

and colleagues by improving the efficiency of each component. □

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