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Title

Chemical storage of renewable energy.

Permalink

<https://escholarship.org/uc/item/2r394419>

Journal

Science (New York, N.Y.), 360(6390)

ISSN

0036-8075

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Publication Date

2018-05-01

DOI

10.1126/science.aat7918

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Peer reviewed

Electrochemical synthesis of ethylene from CO₂

High rates, selectivity, and stability achieved

By Joel W. Ager¹ and Alexei A. Lapkin²

Conversion of carbon dioxide into fuels and chemicals using renewable energy is a potential pathway to mitigate increasing concentrations of CO₂ in the atmosphere and in the oceans (1). In a process which is essentially the reverse of combustion and is analogous with photosynthesis, CO₂ can be electrochemically reduced (EC-CO₂R) to hydrocarbons using renewable power sources such as wind and solar (2). This would not compete with direct use of renewable energy as electricity, as the objective is to utilize excess capacity in a chemical energy storage system. On page xxx of this issue, Dinh *et al.* demonstrate that ethylene can be generated selectively via EC-CO₂R at rates which could yield a technologically feasible process (3).

The thermodynamics of EC-CO₂R are similar to splitting water into hydrogen and oxygen, which has been done commercially at 80% energetic efficiency (4). However, the unreactive nature of the CO₂ molecule and the demands of controlling multiple electron and proton transfer events (i.e. 12 in the case of ethylene) on the surface of the electrocatalyst make EC-CO₂R considerably more challenging. Remarkably, Cu catalysts bind CO and other reaction intermediates in such a way as to produce C₂ products such as ethylene and ethanol (5). However, it has been difficult to steer the reaction towards any one product. Moreover, most EC-CO₂R studies provide CO₂ to the electrode from aqueous solution, whereby its finite solubility leads to a upper, diffusion-limited current density of few 10's of mA cm⁻², which is far below what would be commercially relevant.

A breakthrough in efficiency can be achieved through intensification of mass transfer within the process. Process Intensification (PI) is an approach in chemical engineering through which many fold increases in product throughput may be attained by eliminating mass and energy transport limitations, and by exploiting potential synergies within a process, such as combining multiple functions (reaction + separation, etc) (6). Use of a gas diffusion electrode (GDE), similar to those used in fuel cells, greatly reduces the mass transfer constraint for CO₂ and has been used to attain very high (>500 mA cm⁻²) current density for

formation of C₁ products such as CO (7). However, careful management of the gas phase CO₂, liquid electrolyte, and solid electrocatalyst is required to maintain selectivity to CO₂R and minimize parasitic reactions such as water reduction.

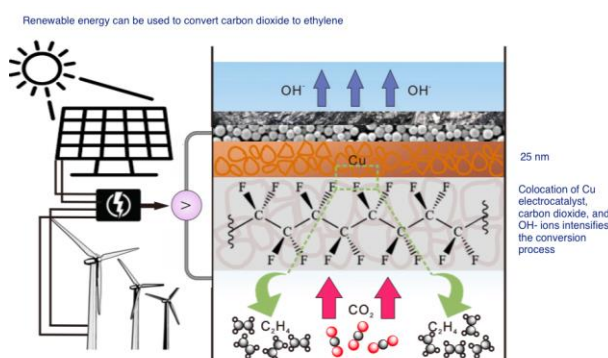
Higher pH conditions are known to increase the yield of C₂ products in EC-CO₂R (8), but CO₂ itself is acidic which sets an upper limit to the pH attainable in a conventional experiment. In contrast, Dinh *et al.* show that very high concentrations of OH⁻ can be maintained at the catalyst surface provided the electrochemical conversion is faster than the homogenous reaction of CO₂ with OH⁻ to form bicarbonate. An optimal balance between these competing processes is attained by the use of very thin, ca. 25 nm, Cu catalyst layers deposited on the gas diffusion electrode (In thicker catalyst layers a region of lower OH⁻

value is smaller than the 60-80% achieved for water splitting, it is comparable to CO₂R cells which make C₁ products such as CO or formate and have lower cathode overpotentials (9).

Although the work of Dinh *et al.* is an important step towards renewable energy chemical storage, challenges remain. The reactor in their work, and indeed nearly all CO₂R reactors in the literature, produce their products either entrained in the CO₂ stream or dissolved in the electrolyte, leaving product separation as an unsolved challenge (10). On a more global basis, it is important to consider the source of the CO₂, i.e. harvested from point sources or directly captured from the air.

There is a lively discussion in the literature regarding the prospective economics of EC-CO₂R (11). While there is consensus that a carbon tax would be required to provide an incentive to CO₂ conversion, there are divergent opinions on the economic viability of the proposed conversion targets (CO and/or syn gas, ethylene, ethanol, etc.). In this context, benchmark demonstrations such as Dinh *et al.* can be used to focus the discussion.

While the products of EC-CO₂R (C₁-C₃ hydrocarbons and oxygenates) are simpler than those of natural photosynthesis (C₅/C₆ sugars) it can be appreciated that they are the most ambitious targets of preparative electrosynthetic chemistry as most work to date (>100 years) has focused on simpler transformations involving far fewer electron transfers (12). Demonstrations such as Dinh *et al.*, combined with the increasing understanding of the mechanism, could lead to EC-CO₂R becoming a commercially viable approach to mitigate rising CO₂ levels on Earth and promoting the use of renewable energy. ■



concentration and also selectivity to ethylene is created). This approach, enhanced by the use of extremely basic conditions (10 M KOH), led to ca. 70% current (Faradaic) efficiency to ethylene at current densities up to 750 mA cm⁻².

An industrially relevant process would need to operate continuously to be economically viable. Dinh *et al.* found that the highly basic conditions they were employing to enhance ethylene yield led to deterioration of the carbon based GDE material within an hour. As an alternative, they then designed an implemented a GDE of base-stable PTFE with Cu nanoparticles as the catalyst with carbon nanoparticles and graphite providing electrical contact. Although a lower current density was achieved (ca. 300 mA cm⁻²), stability over 100 hours was shown.

A full EC-CO₂R system must also oxidize water to oxygen at the anode for sustained operation. Dinh *et al.* performed such a full cell experiment using NiFe to catalyze the oxygen evolution reaction at the anode. A full cell energy conversion efficiency which captures all the losses – overpotentials at the cathode and anode and IR drops in the electrolyte – of 34% was measured. While this

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