Title
Chemical storage of renewable energy

Permalink
https://escholarship.org/uc/item/2r394419

Journal
Science, 360(6390)

ISSN
0036-8075

Authors
Ager, Joel W
Lapkin, Alexei A

Publication Date
2018-05-18

DOI
10.1126/science.aat7918

Copyright Information
This work is made available under the terms of a Creative Commons Attribution-NonCommercial-NoDerivatives License, available at https://creativecommons.org/licenses/by-nc-nd/4.0/

Peer reviewed
Electrochemical synthesis of ethylene from \( \text{CO}_2 \)

High rates, selectivity, and stability achieved

By Joel W. Ager and Alexei A. Lapkin

Conversion of carbon dioxide into fuels and chemicals using renewable energy is a potential pathway to mitigate increasing concentrations of \( \text{CO}_2 \) in the atmosphere and in the oceans (1). In a process which is essentially the reverse of combustion and is analogous with photosynthesis, \( \text{CO}_2 \) can be electrochemically reduced (EC-\( \text{CO}_2 \)-R) 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 xxxx of this issue, Dinh et al. demonstrate that ethylene can be generated selectively via EC-\( \text{CO}_2 \)-R at rates which could yield a technologically feasible process (3).

The thermodynamics of EC-\( \text{CO}_2 \)-R 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 \( \text{CO}_2 \) 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-\( \text{CO}_2 \)-R considerably more challenging. Remarkably, Cu catalysts bind CO and other reaction intermediates in such a way as to produce \( \text{C}_2 \) products such as ethylene and ethanol (5). However, it has been difficult to steer the reaction towards any one product. Moreover, most EC-\( \text{CO}_2 \)-R studies provide \( \text{CO}_2 \) 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 \( \text{CO}_2 \) and has been used to attain very high (>500 mA cm\(^{-2}\)) current density for formation of \( \text{C}_1 \) products such as \( \text{CO} \) (7). However, careful management of the gas phase \( \text{CO}_2 \), liquid electrolyte, and solid electrocatalyst is required to maintain selectivity to \( \text{CO}-\text{R} \) and minimize parasitic reactions such as water reduction.

Higher pH conditions are known to increase the yield of \( \text{C}_2 \) products in EC-\( \text{CO}_2 \)-R (8), but \( \text{CO}_2 \) 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 \( \text{OH}^- \) can be maintained at the catalyst surface provided the electrochemical conversion is faster than the homogeneous reaction of \( \text{CO}_2 \) with \( \text{OH}^- \) 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\(^-\) 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 provide electrical contact. Although a lower current density was achieved (ca. 300 mA cm\(^{-2}\)), stability over 100 hours was shown.

A full EC-\( \text{CO}_2 \)-R 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 value is smaller than the 60-80% achieved for water splitting, it is comparable to \( \text{CO}-\text{R} \) cells which make \( \text{C}_1 \) products such as \( \text{CO} \) 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 \( \text{CO}-\text{R} \) reactors in the literature, produce their products either entrained in the \( \text{CO}_2 \) 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 \( \text{CO}_2 \), 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-\( \text{CO}_2 \)-R (11). While there is consensus that a carbon tax would be required to provide an incentive to \( \text{CO}_2 \) 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-\( \text{CO}_2 \)-R (\( \text{C}_2-\text{C}_6 \) hydrocarbons and oxygenates) are simpler than those of natural photosynthesis (\( \text{C}_6\text{H}_{12} \) 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-\( \text{CO}_2 \)-R becoming a commercially viable approach to mitigate rising \( \text{CO}_2 \) levels on Earth and promoting the use of renewable energy.

REFERENCES
3. Dinh et al., Science, this issue