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What would it take for renewably-powered electrosynthesis to displace petrochemical processes?

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Abstract: Electrocatalytic transformation of CO₂ and H₂O into chemical feedstocks offers the potential to reduce carbon emissions by shifting the chemical industry away from fossil fuel dependence. We provide a technoeconomic and carbon emission analysis of possible products, offering targets that would need to be met for economically compelling industrial implementation to be achieved. We provide a comparison of the projected costs and CO₂ emissions across electrocatalytic, biocatalytic, and fossil-fuel derived production of chemical feedstocks. We find that, for electrosynthesis to become competitive with fossil-fuel derived feedstocks, electrical-to-chemical conversion efficiencies need to reach at least 60%, and renewable electricity prices need to fall below 4 cents/kWh. We discuss the possibility of combining electro- and bio-catalytic processes, using sequential upgrading of CO₂ as a representative case. We describe the technical challenges and economic barriers to marketable electrosynthesized chemicals.

One Sentence Summary: An assessment of the performance and cost required for electrocatalytic CO_2 conversion technologies to enable the cost-effective renewably-powered synthesis of chemical feedstocks.

The dependence on fossil fuel feedstocks of the chemical industry presents an important emissions challenge. For example, in Europe, 26 chemical compounds account for 75% of the total energy use within the chemical sector (including energy used as feedstock) and contribute more than 90% of the European chemical sector GHG emissions (150 Mt or 0.6% of the world's total emissions). If the sector continues on its current growth trajectory, these chemical feedstocks will result in emissions of 200 Mt CO₂ equivalents by 2050.(1) The demand for emissions-heavy petrochemicals such as ethane and naphtha continues to grow given the downstream use of these feedstocks to manufacture consumer goods such as personal care items, food preservatives, fertilizers and furnishings that will be needed in higher quantities to supply a growing worldwide middle class.(2) A less CO₂ emissions intensive alternative to produce chemical feedstocks must be found in order to mitigate future CO₂ emissions.

Renewable electrosynthesis could potentially target high-value chemicals (e.g. ethylene, ethanol) as a market-entry strategy since these important chemical products rely today on energy intensive thermochemical routes: high-temperature and high-pressure processes. High-value renewables-derived commodity chemicals could provide a step in the direction of implementing electrosynthesis technologies at scale, thereby improving manufacturing methods and efficiency – in essence, to advance along the learning curve of the technology maturation process. This strategy avoids short-term direct competition with fuels derived from shale gas (i.e., targeting methane).(*3*) However, we do note that the costs of many commodity chemicals are tied to natural gas, as natural gas is a major feedstock.

In the long term, it will be essential to target commodity chemical processes that can be implemented at the gigatonne scale in order to make meaningful carbon emissions reductions.(4) For example, today formic acid represents too small a global market, and a complete transition to its CO₂ emissions-neutral production would result in only meagre global carbon emissions reductions, though, this could change in the future if advances in formic acid fuel cells or the use of formic acid as a hydrogen carrier continue. Industrially more mature electrocatalytic technologies such as chloralkali cells, hydrogen electrolyzers, and fuel cells provide examples and directions for the roadmap to advance from the laboratory to commercial scales for electrochemical synthesis.

Renewable-energy-powered electrochemical CO₂ reduction to chemicals could be implemented to take advantage of point-sources of relatively pure CO₂ emissions, such as those released from cement manufacturing, breweries and distilleries, or from various fuel processing facilities. Electrosynthesis of commodity chemicals can be done at the point of use, requiring less handling and distribution infrastructure than is necessary for fuels production. However, some key challenges include matching the manufacturing scales of downstream chemicals and the emissions of point sources, flexible on-demand production, and cost-effective scale-up. This optimization problem will rely heavily on the type and scale of CO₂ sources. Additionally,

complicated supply chain management needs to be accounted for – transport and storage costs between CO₂ emissions point-sources and end-product users needs to be considered.

Electrosynthesis must first be scaled and validated under practical conditions for thousands of hours of chemical production. Then, carbon-based fuels can be targeted, providing a strategy for long-term (i.e., seasonal) energy storage.(5) The time-varying and unpredictable nature of renewable low-carbon emission energy sources such as wind and solar limits their deployment in the replacement of fossil-fuel-fired power plants. Batteries and other energy storage (such as compressed gas or flywheels) may provide short-term storage solutions on the scale of hours or even days, but there is still a need for month-to-month season storage. Existing electricity grid infrastructure is not well designed to absorb excess renewable power generation, resulting in a mismatch of supply and demand: during periods of peak generation, excess supply commonly leads to negative electricity prices in some markets today.(6) This variability (non-dispatchability) challenge limits the widespread adoption of low-carbon energy sources to reach the terawatt scale. Electrosynthesized fuels (if they can become competitive in price to low cost natural gas) could provide a route to turn renewable electricity into stable chemical form for storage and transport, enabling increased penetration and dispatchability of renewable sources.

Here we consider what it would take to displace fossil-fuel sources as the chemical supply for small molecule chemical feedstocks. Independent of energy source for transformation, petroleum is ultimately not a sustainable resource for our chemical needs: the extraction and processing of fossil-fuels consumes energy (1200 million tonnes of oil equivalent in 2017) and emits CO₂ (1500 million tonnes of CO₂ per year in 2017)(7) We present prospective pathways towards industrial implementation and a technoeconomic assessment (TEA) and simple life cycle analysis (LCA) of the most promising products. We discuss the opportunities for electrocatalysis in the sustainable production of some important chemical compounds. First, we discuss the renewable production of alcohols. The sustainable production of olefins is then discussed, with a focus placed on renewable ethylene and plastics recycling. We then discuss the potential of coupled synthesis gas and biocatalytic approaches as a pathway to higher order valuable commodity chemicals. We ask, quantitatively, what it would take to disrupt the chemical production sector, and thus offer target figures of merit. We conclude with challenges to overcome for electrocatalytic technology to be successful.

Electrocatalysis: A versatile network of chemical transformation

Electrochemical activation and conversion of CO_2 and water into hydrocarbons and oxygenates could potentially offer a sustainable route to produce many of the world's most needed commodity chemicals (**Fig. 1a**). Coupling renewable sources of energy (solar, wind, hydro) with electrochemical reduction of CO_2 to chemicals, if done efficiently, could address the non-dispatchable nature of renewables by providing storage in chemical bonds. Electrocatalysis also provides a route to transforming carbon resources into chemicals without the need to burn carbon fuels, assuming the CO_2 is taken from air. At present, direct air CO_2 capture is far from industrially mature, but recent work has shown a pathway to a cost of \$94 to \$232 per tonne CO_2 from the atmosphere(8) with start-up companies such as <u>Carbon Engineering</u> and <u>Climeworks</u> having secured funding to scale CO_2 capture processes to industrially relevant levels. However, electrocatalysis is currently limited to C_1 - C_3 chemical production for two major reasons. The first is that higher carbon species require more proton-coupled electron transfers, leading to a highly complex reaction pathway and poor product selectivities.(9) The second is that there is a diminishing energy return per number of electrons transferred as the carbon number increases.(10)

There exist commercial electrochemical technologies that offer a blueprint for CO₂ electroconversion. Of these options, water electrolyzers that produce hydrogen and oxygen are the most analogous and industrially mature, with companies such as Siemens, Proton OnSite, Teledyne, Nel Hydrogen, and Hydrogenics selling commercial-scale electrolyzers. The global water electrolysis market is expected to grow from \$8.5B USD today to \$11B USD by 2023, driven mostly by the chemical industry's desire for emissions-free sources of hydrogen.(11) While electrochemical hydrogen production today accounts for 4% of total hydrogen production (the remainder from steam reforming of natural gas coal gasification), this represents 8 GW of electrolysis capacity – a significant scale.(12) The total market is \$115B and expected to reach \$155B by 2022, with up to 8% of the growth coming from electrolysis.(12) Natural gas as a feedstock is currently cheap because of the shale gas revolution in North America. However, in the long term, electrolysis may be a more sustainable process. The energy landscape is evolving quickly with renewables gaining market share. If technological challenges are overcome, electrochemical processes based on renewable electricity may become more cost effective. In addition to water electrolysis, the research community has also been focusing on photoelectrochemical water splitting as a means of decentralized energy conversion and storage.(13, 14) The topic of hydrogen evolution has been covered in many excellent reviews(5, 15–18) and will not be further explored here.

Electrochemical carbon dioxide reduction (CO₂R) has seen a dramatic increase in research activity over the last few years. It offers a prospectively sustainable pathway for producing fuel and chemical feedstocks through the electrochemical conversion of an undesirable greenhouse gas. The Faradaic efficiencies (**Fig. 1b**) and energy conversion efficiencies (**Table 1**) towards many CO₂R products have increased steadily over the last 3 decades. Current densities have also increased to >100 mA/cm² (**Fig. 1b**) due to the adoption of gas diffusion electrodes that overcome the CO₂ solubility limit in aqueous electrolytes. Production of simpler C1 products such as CO and formic acid was possible with high initial selectivity even on simple metal foils. However, more sophisticated catalyst, electrolyte, and cell engineering was required to make significant improvements in selectivity for C2 products, due to the difficulty of C-C coupling. Additionally, efficient product separation and recycling of unreacted CO₂ is another practical concern that could be mitigated by improvements in catalyst selectivity. The topic of materials design for CO₂R electrocatalysis has also been covered

extensively by multiple reviews. (19–26) Here we instead focus on the barriers this technology would have to surmount to disrupt the chemical industry.

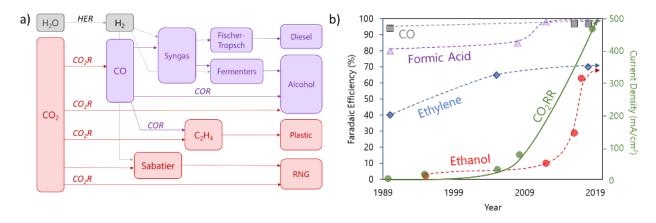


Figure 1 | Pathways and selectivities for renewable chemical synthesis. (a) Possible renewable-energy powered routes to commodity chemicals driven by electrocatalysis from H_2O (grey) and CO_2 (purple, red) as feedstocks. (b) Highest reported Faradaic efficiencies for carbon monoxide (grey squares), formic acid (purple triangle), ethylene (blue diamond), and ethanol (red circles) and corresponding current densities (green) over the past three decades (Table S3).

Catalyst	Electrolyte	Product	Cell Voltage (V)	Current Density (A/cm²)	Faradaic Efficiency (%)	Energy Conversion Efficiency (%)
Cu(<i>27</i>)	7 М КОН	Ethylene	2.4	110	70	34
Au(<i>28</i>)	2 M KOH	Carbon Monoxide	2.0	99	98	64
Ag(<i>29</i>)	1 M KOH	Carbon Monoxide	3.0	350	101	45
Ag(<i>30</i>)	0.5 M K ₂ SO ₄ : 1 M KHCO ₃	Carbon Monoxide	2.9	197	87	50
Ag(31)	0.1 M K ₂ SO ₄ : 1.5 M KHCO ₃	Carbon Monoxide	4.7	233	78	25
Sn(<i>32</i>)	0.5 M KCl	Formate	4.0	163	84	32
Pb(<i>33</i>)	0.5 M H ₂ SO ₄	Formate	2.8	50	95	49
Sn(<i>34</i>)	0.5 M KHCO ₃ + 2 M KCl	Formate	3.1	133	83	33
Pt(<i>35</i>)	Polymer Electrolyte	Hydrogen	1.2 – 2.2	0.6 – 2	100	57 – 74
Pt(<i>35</i>)	Alkaline	Hydrogen	1.5 – 2.0	0.2 - 0.4	100	52 – 69

Table 1. Current state of CO₂ electrolyzers in comparison with hydrogen electrolyzers and their figures of merit.

Pathways toward industrial implementation

Decades of research have proven effective in developing efficient catalysts for the electrochemical generation of hydrogen and oxygen from water to the point of commercialization. Because these electrochemical transformations require, in principle, similar components to CO₂R, lessons learned from the engineering scale-up and device design of hydrogen electrolyzers can be of great utility.

Several factors uniquely position the electrochemical conversion of CO₂ for accelerated technological development. First, the products of CO₂R already exist within many petrochemical supply chains, and therefore the chemical industry infrastructure is more readily prepared to adapt to CO₂R. Second, the need to reduce emissions along with the gradual adoption of carbon capture technologies is resulting in large energy consumers and carbon emitters facing the challenge of what to do with the CO₂ once it is captured.(*10*) CO₂R provides a way to recover value from what would otherwise be a tremendous sunken cost. The <u>Carbon XPRIZE</u> is a \$20M competition to capture and convert the most CO₂ and is jointly funded by COSIA, a consortium of large oil producers.(*36*)

Governments worldwide have identified climate change initiatives as having high priority. For example, China, the world's largest energy consumer and carbon emitter, recently announced \$360 billion in renewable energy by 2020 in effort to reduce carbon emissions.(*37*) Canada is implementing a carbon pricing policy federally with a current price of \$10/tonne CO₂ and a steady rise to \$50/tonne CO₂ nationwide by 2022. <u>Mission Innovation</u>, a 22-country global initiative to accelerate clean energy innovation, has named (i) CO₂ Capture and Utilization, (ii) Clean Energy Materials and (iii) Converting Sunlight as topics of their distinct innovation challenges.

Despite a favorable ecosystem for renewable chemical feedstocks, there still exist challenges and risk towards industrial scale up. For example, electrolytes must be optimized with careful consideration of cost, environmental impact, and availability to reach the scales necessary for meaningful emissions reductions. Public policy of CO₂ utilization technologies needs to be carefully crafted and social acceptance of the field needs to be managed. Carbon taxes, nationwide caps on CO₂ emissions, and certifications of CO₂-derived products are examples of public policy tools. From a societal acceptance point of view, greater education on the differences between carbon capture and sequestration and carbon capture and utilization is needed. Most importantly, catalysts and system efficiencies for this technology need to be vastly improved to be economically viable with minimal or no government subsidies (as it is difficult to rationalize sustainable business models based on subsidies and policies that can be easily changed).

There exist many technoeconomic analyses of solar fuels that have analyzed the needed Faradaic efficiencies and energy efficiencies required to match fossil-fuel derived sources.(10, 38–42) Among them, the largest influence on the levelized cost of production has consistently been the price of electricity. Building upon previous studies, we have calculated the cost of electrosynthesized hydrogen, carbon monoxide, ethanol, and ethylene as a function of the energy conversion efficiency and electricity cost (**Fig. 2**) to provide a comparison to current market prices. We also provide a sensitivity analysis on production cost as a function of carbon-emissions free electricity source, showing nuclear and geothermal as currently the most cost

competitive (Fig. S2, refer to supplementary text for calculation details). We do note that commodity chemical prices are highly variable with respect to geographic region and feedstock, a challenge that will be expanded upon later. Using optimistic assumptions based on industrially mature polymer electrolyte membrane (PEM) water electrolyzer specifications, we show that when electricity costs fall below 4 cents/kWh and energy efficiency is at least 60%, all products become competitive with current market prices for these products derived from fossil-fuel sources. We note that these calculations assume amortization over a plant lifetime of 30 years, a common period for industrial power plants.(43) Replacing initial capital-intensive infrastructure would carry additional costs. To put this into perspective, the best systems today have demonstrated full cell energy efficiencies of approximately 40 to 50% for CO, approaching cost competitive targets. Considering that CO₂R to CO technologies are in the early stages of development, it is expected that with further catalyst and electrochemical cell designs, improved performance can be obtained. From an electricity cost perspective, renewable prices continue to plummet. Between 2010 and 2017 average global utility-scale solar plants fell 73% to 10 cents/kWh and onshore wind fell by 23% to 6 cents/kWh, with some projects consistently delivering electricity for 4 cents/kWh.(44) Recent onshore wind power auctions in Brazil, Canada, Germany, India, Mexico, and Morocco have shown levelized electricity costs as low as 3 cents/kWh, within the range of profitability of electrosynthesized chemicals.(44) Costs have fallen due to increased economies of scale, greater competition, and advances in the manufacturing of crystalline silicon. This cost decrease in renewable technologies provide an optimistic and aggressive goal for electrocatalytic technologies.

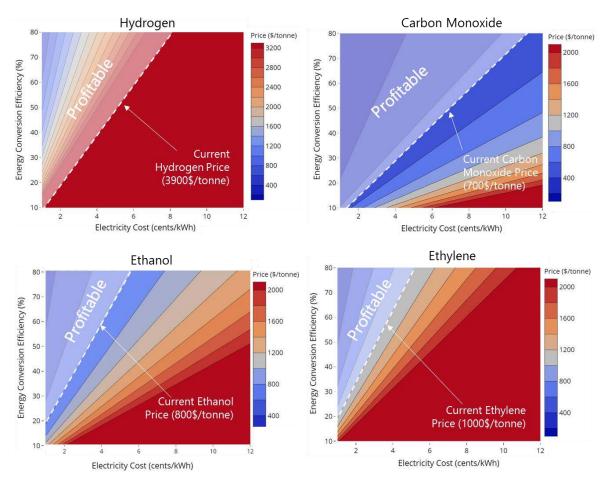


Figure 2| Production costs of electrosynthesized chemicals. Technoeconomic analysis of hydrogen, carbon monoxide, ethanol, and ethylene costs as a function of electrolyzer energy conversion efficiency and electricity costs. Assumes a pure CO₂ price of \$30/ton, Faradaic efficiency of 90%, current density of 500 mA/cm², electrolyzer cost of \$300/kW, and plant lifetime of 30 years. The area above the white dotted line in lighter color indicates profitable production costs based on average global prices. We note that regional differences on market prices exist due to the nature of fossil fuel feedstocks.

To quantify the potential impact that electrochemical synthesis of common carbonbased commodity chemicals has on carbon emissions, we performed a life cycle assessment for formic acid, carbon monoxide, ethylene, and ethanol. Of these products, ethylene has the largest global market size at \$230B and the highest impact on emissions reductions, potentially reducing 862 MT CO₂ equivalents (CO₂e) per year (**Fig. 3a**), suggesting it is an attractive target for meaningful CO₂ emissions reductions. The electricity grid carbon intensity (the amount of carbon dioxide emitted per kWh of electricity generated) and the energy conversion efficiency were found to be the most sensitive factors affecting overall CO₂ emissions (**Fig. 3b-e**). Assuming a plant capacity of 500 MW, an average grid carbon intensity for the USA (0.45 kg CO₂e/kWh in 2016),(45) and an energy conversion efficiency of 70%, all products result in either neutral (ethylene) or net negative (ethanol, carbon monoxide, and formic acid) carbon emissions.

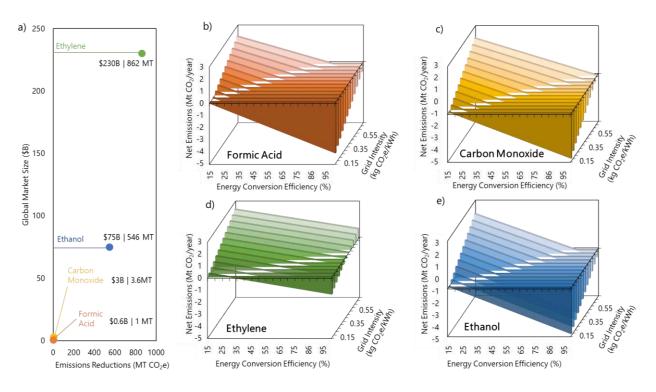


Figure 3. The emissions impact of electrosynthesized chemicals. (a) Market size and total emissions reductions of ethylene(*46*), ethanol(*47*), carbon monoxide(*48*), and formic acid(*49*). Carbon emissions assessment of (b) formic acid, (c) carbon monoxide, (d) ethylene, and (e) ethanol. Assumes a plant capacity of 500 MW, global warming potential (GWP) of formic acid and carbon monoxide of 1 kg CO₂/kg product, and GWP of ethylene and ethanol of 5.75 kg CO₂/kg product. Emissions reductions are calculated as a product of global production and GWP.

To benchmark these results, we provide a comparison of electrocatalytic, biocatalytic, and traditional fossil fuel derived processes for ethylene, carbon monoxide, ethanol, and formic acid production (Table 2). Bio-ethylene production using bio-ethanol precursors is economically competitive in Brazil due to the ample availability of cheap sugarcane feedstock.(50) Petrochemical ethylene is produced mainly from steam cracking of fossil fuels. (51) The majority of carbon monoxide is produced as a component of syngas through coal gasification or steam methane reforming.(52) Ethanol is primarily produced through fermentation of sugars or corn.(53) Formic acid is primarily produced through chemical processes using tertiary amines.(54) We find that when using optimistic targets (electricity cost = 4 cents/kWh, Faradaic efficiency = 90%, energy conversion efficiency = 70%), electrocatalysis is cost-competitive with fossil fuel derived sources and more economical than biocatalytic processes. We nonetheless note that whereas fossil fuel derived chemical production are well-established processes, advances in biocatalytic processes have potential to steadily drive down production costs and carbon emissions. For example, the US Department of Energy has set the goal of biofuel production cost at \$1/gasoline gallon equivalent (currently \$2.68/gge) with GHG reductions of 50% by 2020.(55)

Additionally, we find that electrocatalysis, when powered by renewable electricity, has the lowest carbon emissions of all processes and could potentially prove carbon-negative for production of carbon monoxide, ethanol, and formic acid. With these targets in mind, we now outline electrocatalysis as a means for the sustainable production of alcohols, olefins, and syngas.

Product	Technology	Production Cost (\$/tonne)	Carbon Emissions (tonne CO2e/tonne prod)
Ethylene	Electrocatalytic	1100	-0.01
	Biocatalytic(50)	1200 - 2600	2.5
	Fossil Fuel Derived(<i>56,</i> <i>57</i>)	600 - 1300	6
Carbon Monoxide	Electrocatalytic	200	-0.85
	Biocatalytic	-	-
	Fossil Fuel Derived(52, 54)	150	0.05
Ethanol	Electrocatalytic	515	-1.00
	Biocatalytic(58, 59)	670	2.1
	Fossil Fuel Derived	-	-
Formic Acid	Electrocatalytic	108	-1.63
	Biocatalytic	-	-
	Fossil Fuel Derived(<i>54,</i> <i>60</i>)	570	0.01

Table 2. Comparison of production cost and carbon emissions across various catalytic processes.

*Electrocatalysis assumes Faradaic efficiencies of 90%, electricity costs of 4 cents/kWh, energy conversion efficiency of 70%, capacity factor of 0.9, and grid intensities of 0.35 kg CO₂e/kWh.

Direct electrochemical conversion of CO₂ to alcohols

Among the various oxygenates that can be produced directly from electrochemical CO₂R or through sequential reaction pathways, alcohols are attractive for their utility as chemical precursors, drop-in fuels, and solvents. The global market for alcohols is in excess of \$75B USD,(*61*) suggesting that sustainable pathways towards methanol and higher (C₂₊) alcohols could provide alternative environmentally friendly routes to these high-demand products. Methanol is primarily synthesized through circuitous oxidation and reduction processes, by first reforming natural gas sources to syngas and converting this reaction mixture.(*62*) A few recent studies have reported high selectivity for direct CO₂R to methanol(*63–65*), suggesting that can accomplish a direct synthesis. Alternatively, a number of recent studies have reported high selectivity for direct CO₂R to methanol, and lower but non-negligible selectivity to n-propanol.(*66–71*)

Traditionally, higher alcohols are predominantly made through the fermentation of sugars(53, 72) or conversion of petrochemicals(73). The food vs. fuel dilemma is still a long-standing social issue for the fermentation of foods or feeds. Biocatalysis is highly selective at making C2+ products and alcohols, but the economics of this process are dependent on the cost of sugar for fermentation. Production rates from biocatalysis are typically slower, are water intensive, and highly sensitive to the overall health of the microorganisms. Significant advances have been made improving these processes in recent years, and progress is expected to continue.

Direct synthesis of higher alcohols from syngas is a desirable alternative for both environmental and economic reasons. However, there are currently no thermochemical catalysts with the appropriate performance for industrial implementation of higher alcohol synthesis from syngas, motivating continued research in this area.(73)

Electrocatalysis has the advantage of productivity with a modular and scalable approach to producing small C_1 - C_3 molecules and H_2 . Although some of these electrocatalytic technologies are still in the development stage, the already promising selectivity indicates that there may be intrinsic advantages to electrochemical processes for the synthesis of methanol and higher alcohols, although product separation remains a challenge. While there is clearly potential for electrochemical CO_2R and/or COR technologies to have a large impact on global alcohol industries, we note that many alcohols such as methanol and ethanol (**Table 2**) can be produced at costs of <\$1/kg through current industrial processes.(*74*) Therefore, market penetration will be initially and possibly continually very difficult, except in specialized applications that may need the flexibility of modular reactors.

Ethylene derivatives and sustainable plastic production

Ethylene is produced at an annual rate of 150 million tonnes per year globally, the most of any organic chemical compound. It is a versatile building block used in the petrochemical industry. The majority of ethylene is used as a chemical intermediate for the preparation of some of the world's most heavily used plastics, including polyethylene (116 million tonnes/year), polyvinyl chloride (38 million tonnes/year) and polystyrene (25 million tonnes/year)(*51*); the compound is also used for the production of anti-freeze and detergents, and in the agricultural sector as a fruit ripener. Ethylene has traditionally been produced by the energy intensive steam cracking of naphtha obtained from crude oil; however, in recent years the shale gas boom has led to an abundance of inexpensive feedstocks that have spurred capital investment in the US to build many new ethane crackers or retro-fit existing steam cracking facilities to accommodate light gas feeds.(*75*)

Ethylene is a prime example of a petrochemical commodity – priced on feedstock cost and consistency of supply. In North America, where ethylene is primarily produced from cracking of inexpensive and abundant ethane from shale gas reserves, prices can be as low as \$250/tonne. However, in regions such as Europe and Asia where naphtha is the main feedstock, ethylene cost can be as high as \$1200/tonne.(46) In these regions, where the price of the feedstock such as naphtha is volatile, electrocatalytic conversion may have a greater chance of gaining a foothold on the market.

Although alternative routes for ethylene production are under development, including catalytic dehydrogenation of light alkanes, Fischer-Tropsch synthesis, or oxidative coupling of methane, these processes each rely on fossil fuel feedstocks and remain uneconomical or require further development. The development of catalysts and reactor designs that can simultaneously achieve high energy efficiencies, selectivity, conversion rates and long-term operational durability is the key outstanding challenge in this field. Over the past several years, many advances have contributed to a deeper fundamental understanding of electrochemical CO_2 reduction, such as the impact that the electrolyte (pH(*76*, *77*), ions,(*78*, *79*) additives,(*80*)), surface structure(*81–84*), and alloying(*85*) can have on copper catalyst activity and selectivity towards C-C coupled products such as ethylene. Only more recently has this knowledge been translated to practical flow cell CO_2 reduction devices that have attained current densities on the order of > 100 mA/cm² towards ethylene.(*76*, *86*)

One possible use case of electrochemical CO_2 conversion is the sustainable production of ethylene and polyethylene. In this case, post-consumer plastic could be recycled by incineration where energy (heat) capture(87) could ideally be coupled with electrochemical reduction of the combustion products (CO_2) to close the carbon cycle. This could mitigate plastic waste accumulation in landfills or in the environment which is estimated at more than 4,900 million tonnes and counting,(51) and ultimately provide a pathway for converting polyethylene back into sustainable ethylene at the end of its useful lifetime. Electrocatalysis could enable the production of ethylene from CO_2 emissions and/or from post-consumer plastic, rather than from fossil-feedstocks, resulting in different economics than in the established petrochemical industry.

Sequential pathways to higher chemicals via syngas electrosynthesis and biocatalysis

There exist many sequential reaction pathways for converting CO_2 to chemicals and fuels, such as single- (C₁) or multi-carbon (C₂₊) oxygenates and hydrocarbons. Leveraging these reaction sequences, one approach is to first convert CO_2 into stable intermediate species that can be further upgraded to the desired product(s) using biocatalysts such as enzymes and bacteria.

Among suitable reaction intermediates, CO stands out as it is a common gaseous precursor for numerous thermochemical, biological, and electrochemical processes. Mixtures of CO with H_2 (syngas) can serve as feedstocks for Fischer-Tropsch (FT)(88) synthesis or fermentation(89, 90) processes that are implemented today. For example, FT production of diesel is an industrially mature process with plants operating at 11.5 tonne/day production, an energy conversion efficiency of 51%, and greenhouse gas emissions of 3.8 tonne $CO_2/tonne product$ — resulting in diesel costs of \$240 to \$525/tonne.(*91*) Biocatalytic syngas fermentation with enzymes and bacteria can produce more valuable chemicals such as acetic acid, butyric acid, ethanol, butanol, and biodegradable polymers such as polyhydroxyalkanoates (PHAs). For a 1 tonne/year production facility with a biocatalytic syngas conversion of 90% and emissions of 0.26-0.45 tonne $CO_2/tonne$ product, the cost of PHA production is \$1650/tonne.(*92, 93*) The contrast between these two syngas utilization routes highlights the advantages and challenges of biocatalytic vs. FT routes. FT synthesis operates at much higher rates of production and is less expensive for fuel production but has greater carbon emissions, while biocatalytic routes are lower volume, lower emission, and target more expensive speciality chemicals. Integrating electrocatalytic and biocatalytic process in the short-term represents a promising approach due to the matching of production rates and higher value of the end-product.

The syngas precursors used in conventional industrial processes are almost exclusively produced by steam methane reforming that, depending on the method, can co-generate different molar ratios of CO and H_2 .(94) Although these processes are relatively cost-effective and extensive process optimization has been applied to minimize greenhouse gas emissions, the exclusive reliance on fossil fuel sources motivates the development of more sustainable syngas production pathways.

One such sustainable pathway to CO is electrochemical CO₂R, where ideally a high yield near-ambient process could generate a stream of CO from CO₂, H₂O and electricity. Because CO is gaseous under ambient conditions, a selective CO₂R process would enable direct CO evolution and downstream use from an aqueous electrolyzer device. In the case of syngas, H₂ production is complementary and not parasitic to CO₂R, allowing for co-generation as HER and CO₂R have comparable half-cell potentials under nearly identical electrochemical conditions. Although syngas production from CO₂ electrolysis with controlled CO:H₂ ratios is possible,(*95*) techno-economic analysis favors the highest possible selectivity to CO, which is , the more valuable product.(*41*) Co-generation of CO and H₂ could nonetheless be advantageous for situations where it is essential to have on-site and on-demand syngas production from a single reactor.(*31*)

To date, electrochemical CO₂R has been demonstrated with high selectivity and/or reaction rates to CO and syngas in CO₂ electrolyzers.(*31, 95–98*) A recent breakthrough in this area was achieved by a collaboration of Siemens, Covestro, and Evonik. The team demonstrated a system whereby solar-powered electrochemical reduction of CO₂ into syngas was then followed by fermentation with bacteria to selectively produce butanol or hexanol, depending on the type of anaerobic digester used.(*31*) Stable CO₂ reduction was carried out at industrially relevant current densities (300 mA cm⁻²) with near 100% Faradaic efficiency for syngas (CO + H₂). Following this significant applied advance, Siemens and Evonik recently announced in a joint press release a plan to build a test plant that with the goal of 20,000 tonnes production capacity for butanol and hexanol.(*99*)

This example presents an exciting future avenue for commodity chemical production – the coupling of biocatalytic processes with electrocatalytic processes (**Fig. 4**). There has been some initial promising work in this area interfacing biological systems with inorganic systems for solar fuels and fertilizer production.(*100, 101*) The current state of the art couples water splitting electrocatalysts with engineered bacteria to convert CO_2 into polymers and alcohols,(*102, 103*) or nitrogen into ammonia.(*104*) These efforts have focused mainly on the electrochemical production of H₂ as input for bacteria, or with electrochemical production of acetate as input for bacteria.(*101, 105*)

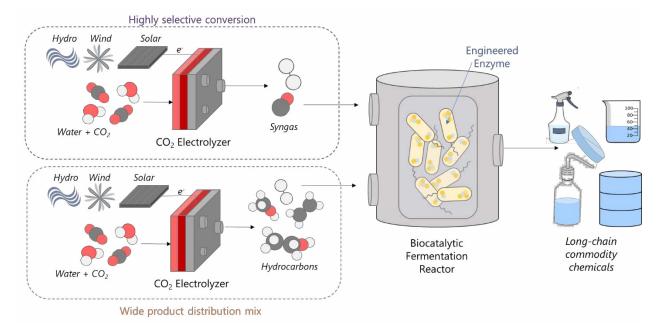


Figure 4. Bio+electrocatalytic pathways towards long-chain commodity chemicals. Today, CO₂ may be converted to syngas at very high selectivity using silver or gold-based catalysts (purple box). Alternatively, CO₂ can also be converted into a wide range of hydrocarbon and oxygenate products using copper-, tin-, or palladium-based catalysts (orange box). These products can then be used as inputs for genetically engineered enzymes and bacteria to convert to more complex commodity chemicals.

Although we have chosen to highlight CO in this section as a promising intermediate, we also note that there are other possible sequential reaction pathways from the myriad of oxygenated intermediates that can be produced from CO_2R . Other commonly observed oxygenates from electrochemical CO_2R , such as formate, can be used as the sole carbon sources for microorganisms or enzymes to selectively upgrade into the desired oxygenates and hydrocarbons.(*106, 107*)

The field of electrocatalysis, especially with copper-based catalysts, has recently been focusing on engineering catalysts to make one specific high-value product as selectively as possible. This approach lowers the product separation costs and makes the overall process more economical. One opportunity for the biocatalytic community will be to engineer microorganisms that can tolerate the electrolyte and a diverse CO_2R liquid product mix (**Fig. 4**). If engineered microorganisms can be used to process a less selective input mix from CO₂R (ethanol, acetate, formate, methanol) and then upgrade the combined feedstocks into higher value commodity chemicals, then electrocatalytic selectivity and energy intensive separation processes would no longer be a limiting constraint. High production electrocatalysis combined with highly selective biocatalysis may offer a practical pathway to combine integrated renewable energy production with chemicals manufacturing.

Technical challenges and market barriers

Even with recent progress, there exist technological challenges and significant market entry barriers that need to be overcome for electrosynthesis of commodity chemicals to become industrially competitive.

From a technical standpoint, scientific research has focused largely on aqueous CO_2R systems that are limited due to the solubility of CO₂ in water. To address this issue, there has been a push towards flow-cell and gas diffusion type architectures that operate at more industrially relevant current densities (>100 mA/cm²).(74, 108) Continued research on highcurrent density electrolyzer architectures is needed to increase the energy conversion efficiency. Product separation is another technical cost that needs to be addressed. (109) For example, in petrochemical ethylene production, the cryogenic separation of ethylene and ethane is capital intensive (~50% of capital) and consumes a large amount of energy.(110) Electrochemical CO₂R produces does not produce ethane, avoiding expensive cryogenic separation. Instead, membrane-based porous materials for ethylene separation have recently achieved high selectivity, indicating progress toward lower-cost, more efficient separation processes(111) that could potentially be used for product separation from CO_2R . Furthermore, the technology developed for carbon capture materials (112) could also be used for separation of unreacted CO₂ from ethylene (an easier separation than olefin/paraffin separations) in the output stream. Recent work on optimizing single-pass conversion at high selectivity(113) also show promise in reducing separation costs downstream.

An additional technical challenge is the need for chemical plants to run continually for both capital efficiency and process safety – highlighting the need for non-intermittent electricity. If an electrochemical plant operates continuously, then its capital utilization is a high 100% (loading factor), and the system does not require design for time-varying biases. However, renewable baseloads typically command higher electricity market prices, since they are in effect dispatchable. On the other hand, if an electrochemical plant is to utilize low-cost intermittent renewable electricity (e.g. solar with a typical capacity factor .22), the contribution of capital cost is increased (**Fig. S2**), and the system must tolerate dramatic swings (including to unbiased conditions) in driving voltage. As seen in **Fig. S2**, since capital cost is expected to play a notable but not dominant role in total renewable chemicals cost, moving from capacity factor 1 to 0.22 leads to a 20% increase in chemicals cost. Hydroelectric and geothermal power plants are examples of renewable baseloads that may mitigate this risk. Additionally, greater advances in lowering the capital expenditure costs could potentially sustain lower capacity factors.

Finally, lower costs of grid-scale energy storage, driven by the decrease in Li-ion technology, is bringing hour-by-hour storage within reason, and future lower-cost grid scale batteries could further enable electrochemical processes as well.

The manufacturing scale and installed capacity for commodity chemicals like ethylene also present significant barriers for a new technology to penetrate these saturated, complex, and capital-intensive markets. The case can be made for electrochemical technologies to supplement existing fossil-fuel processes by retrofitting existing plants, decreasing the financial burden of shutting down expensive existing assets. Retrofitting power plants carries a nontrivial capital cost, but has been already been successfully demonstrated with post-combustion carbon capture technologies. (114) Electrochemical technologies may also provide lower cost to add chemical production capacity going forward, supplementing the existing industry as the market continues to grow. Furthermore, electrochemical production costs are dependent mainly on the price of electricity, providing a more stable feedstock price than naphtha feedstocks that are more sensitive to price fluctuations. Ultimately, a focus on C-C bond formation and subsequent C2+ products provides a technological basis to target higher value chemicals. The source and costs of renewable electricity is another factor to consider when discussing scale (see Fig. 2, Fig. S1). Electrocatalytic technology may find a source of cheap electricity from areas with excess hydroelectric capacity such as in Northeastern Canada. Transportation costs between large CO₂ emitters and C2 and C3 production facilities is also another challenge, although we note that petrochemical plants for C2 and C3 production are in themselves point sources of CO_2 emissions. For example, the NOVA Chemicals Joffre petrochemical plant in Alberta is the 15th largest industrial CO₂ point source in Canada, emitting 3,087 kilotonnes of CO₂ in 2016.(115) In Canada, the petrochemical industry is located in three main clusters near Calgary (AB), Sarnia (ON), and Montreal (QC). CO2 point sources in the Alberta oilsands are co-located with the petrochemical plants while CO₂ point sources from Canadian manufacturing, cement, and steel mills in Ontario are also located near Sarnia. It should be pointed out that by no means are all C2 and C3 production sites located near CO2 point sources. The cost of CO_2 transportation is estimated to be \$10/tonne of CO_2 for 200 km, rising to \$44/tonne for 12,000 km.(116)

Another consideration is future societal acceptability. As the consequences of climate change grow more severe, governments and the public will demand more of the private sector to cut emissions and decarbonize. The economic argument presented here is based on pure cost of production and does not include carbon pricing schemes or the demands of shareholders on large carbon emitters. For example, in 2018 there were 53 carbon pricing initiatives worldwide that covered 11 GtCO₂e, representing 19.8% of the global GHG emissions. (*117*) The total value of carbon pricing initiatives was valued at \$82B USD in 2018 and these initiatives are only continuing to grow – enhancing the economic case for electroconversion of CO₂.

Finally, there is an open question of how feedstock needs may change in the future, and how future electrolyzer technologies will fit in, beyond competing head-to-head against the current paradigm as discussed above. As technologies are advanced in all sectors simultaneously, the needs of future society will evolve as well. For instance, R&D efforts in using carbon as a building material could lead to a future where carbon replaces a large proportion of steel and cement, two industries with remarkably large CO₂ footprints. Electrolyzer technologies that readily convert CO₂ into carbon using low-carbon electricity would naturally dovetail with such a future building industry, allowing for sustainably produced building materials provided on-site at the point-of-construction.

Outlook

The transformation of the chemical production industry to emissions-free processes will rely on a variety of technologies working in combination. Electrocatalysis can be implemented throughout the chemical supply chain, ranging from electrosynthesis of basic building blocks, to higher-value fine chemicals in combination with biocatalytic processes, to supplementing traditional thermocatalysis pathways. The economics of electrocatalytic processes will be highly dependent on the availability and price of renewable electricity, the regional cost of feedstock and traditional petrochemical manufacture, the maturity of carbon capture technologies, and the social, political and economic incentives to transition to low-carbon processes.

As electrochemical technologies mature and the understanding of transforming small abundant molecules deepens, the possibilities to produce renewable chemicals increases. Hydrogen electrolyzers represent the first generation of these clean fuel technologies; CO_2 electrolyzers are poised to be the second generation for production of fuels and chemicals, and the nascent field of N₂ reduction to ammonia may represent the future of renewable fertilizer production.

There still remain many scientific and engineering challenges for this technology to truly penetrate the petrochemical market, but the advances in recent years suggests that these challenges can be overcome. As society evolves with new paradigms of operation, continued market opportunities will likely emerge. Regardless of the technical challenges, considerable economic barriers also exist within the complex, established, and highly connected petrochemical industry. Despite these challenges, the adoption and growth of renewable energy technologies such as solar and wind provide a promising pathway to follow.

References

- A. Boulamanti, J. A. Moya Rivera, "Energy efficiency and GHG emissions: Prospective scenarios for the Chemical and Petrochemical Industry - European Commission" (2017), , doi:10.2760/20486.
- International Energy Agency, Oil 2018: Analysis and Forecasts to 2023. *Mark. Rep. Ser.* (2018) (available at https://www.iea.org/Textbase/npsum/oil2018MRSsum.pdf).

- 3. Q. Wang, X. Chen, A. N. Jha, H. Rogers, Natural gas from shale formation The evolution, evidences and challenges of shale gas revolution in United States. *Renew. Sustain. Energy Rev.* **30**, 1–28 (2014).
- 4. A. Majumdar, J. Deutch, Research Opportunities for CO2 Utilization and Negative Emissions at the Gigatonne Scale. *Joule*. **2** (2018), pp. 805–809.
- 5. J. H. Montoya *et al.*, Materials for solar fuels and chemicals. *Nat. Mater.* **16**, 70–81 (2017).
- 6. Y. Parag, B. K. Sovacool, Electricity market design for the prosumer era. *Nat. Energy*. **1**, 16032 (2016).
- Araceli Fernandez Pales, P. Levi, "The future of petrochemicals towards more sustainable plastics and fertilisers - International Energy Agency" (2018), , doi:10.1002/0470842555.ch45.
- 8. D. W. Keith, G. Holmes, D. St. Angelo, K. Heidel, A Process for Capturing CO2 from the Atmosphere. *Joule*. **2**, 1573–1594 (2018).
- 9. M. J. Orella, Y. Román-Leshkov, F. R. Brushett, Emerging opportunities for electrochemical processing to enable sustainable chemical manufacturing. *Curr. Opin. Chem. Eng.* **20** (2018), pp. 159–167.
- 10. O. S. Bushuyev *et al.*, What Should We Make with CO2and How Can We Make It? *Joule*. **2** (2018), pp. 825–832.
- 11. "Water Electrolysis Market Research Report Global Forecast to 2023" (2017), (available at https://www.marketresearchfuture.com/reports/water-electrolysis-market-4133).
- 12. E. Taibi *et al., Hydrogen from renewable power: Technology outlook for the energy transition* (2018; www.irena.org).
- B. A. Pinaud *et al.*, Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry. *Energy Environ. Sci.* 6, 1983 (2013).
- C. C. L. McCrory *et al.*, Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *J. Am. Chem. Soc.* **137**, 4347– 4357 (2015).
- 15. Z. W. She *et al.*, Combining theory and experiment in electrocatalysis: Insights into materials design. *Science (80-.).* **355**, eaad4998 (2017).
- 16. M. Gong, D. Y. Wang, C. C. Chen, B. J. Hwang, H. Dai, A mini review on nickel-based electrocatalysts for alkaline hydrogen evolution reaction. *Nano Res.* **9**, 28–46 (2016).
- 17. F. Safizadeh, E. Ghali, G. Houlachi, Electrocatalysis developments for hydrogen evolution reaction in alkaline solutions A Review. *Int. J. Hydrogen Energy*. **40**, 256–274 (2015).
- 18. M. Zeng, Y. Li, Recent advances in heterogeneous electrocatalysts for the hydrogen

evolution reaction. J. Mater. Chem. A. 3, 14942–14962 (2015).

- 19. Q. Lu, J. Rosen, F. Jiao, Nanostructured metallic electrocatalysts for carbon dioxide reduction. *ChemCatChem.* **7**, 38–47 (2015).
- G. O. Larrazábal, A. J. Martín, J. Pérez-Ramírez, Building Blocks for High Performance in Electrocatalytic CO2 Reduction: Materials, Optimization Strategies, and Device Engineering. J. Phys. Chem. Lett. 8 (2017), pp. 3933–3944.
- 21. R. Kortlever, J. Shen, K. J. P. Schouten, F. Calle-Vallejo, M. T. M. M. Koper, Catalysts and Reaction Pathways for the Electrochemical Reduction of Carbon Dioxide. *J. Phys. Chem. Lett.* **6**, 4073–4082 (2015).
- 22. J. Qiao, Y. Liu, F. Hong, J. Zhang, A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. *Chem. Soc. Rev.* **43**, 631–675 (2014).
- 23. C. Costentin, M. Robert, J.-M. Savéant, Catalysis of the electrochemical reduction of carbon dioxide. *Chem. Soc. Rev.* **42**, 2423–2436 (2013).
- 24. J. Wu, Y. Huang, W. Ye, Y. Li, CO2 Reduction: From the Electrochemical to Photochemical Approach. *Adv. Sci.* **4** (2017), p. 1700194.
- 25. Z. Sun, T. Ma, H. Tao, Q. Fan, B. Han, Fundamentals and Challenges of Electrochemical CO2Reduction Using Two-Dimensional Materials. *Chem.* **3** (2017), pp. 560–587.
- L. Zhang, Z.-J. Zhao, J. Gong, Nanostructured Materials for Heterogeneous Electrocatalytic CO 2 Reduction and their Related Reaction Mechanisms. *Angew. Chemie Int. Ed.* 56, 11326–11353 (2017).
- 27. C.-T. Dinh *et al.*, CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science*. **360**, 783–787 (2018).
- S. Verma *et al.*, Insights into the Low Overpotential Electroreduction of CO2to CO on a Supported Gold Catalyst in an Alkaline Flow Electrolyzer. *ACS Energy Lett.* 3, 193–198 (2018).
- 29. S. Ma *et al.*, Carbon nanotube containing Ag catalyst layers for efficient and selective reduction of carbon dioxide. *J. Mater. Chem. A.* **4**, 8573–8578 (2016).
- 30. E. J. Dufek, T. E. Lister, S. G. Stone, M. E. McIlwain, Operation of a Pressurized System for Continuous Reduction of CO2. *J. Electrochem. Soc.* **159**, F514–F517 (2012).
- 31. T. Haas, R. Krause, R. Weber, M. Demler, G. Schmid, Technical photosynthesis involving CO2 electrolysis and fermentation. *Nat. Catal.* **1**, 32–39 (2018).
- D. T. Whipple, E. C. Finke, P. J. A. Kenis, Microfluidic Reactor for the Electrochemical Reduction of Carbon Dioxide: The Effect of pH. *Electrochem. Solid-State Lett.* 13, B109 (2010).
- 33. X. Lu, D. Y. C. Leung, H. Wang, J. Xuan, A high performance dual electrolyte microfluidic reactor for the utilization of CO 2. *Appl. Energy*. **194**, 549–559 (2017).

- H. Li, C. Oloman, Development of a continuous reactor for the electro-reduction of carbon dioxideto formate – Part 1: Process variables. J. Appl. Electrochem. 36, 1105–1115 (2006).
- 35. M. Carmo, D. L. Fritz, J. Mergel, D. Stolten, A comprehensive review on PEM water electrolysis. *Int. J. Hydrogen Energy.* **38** (2013), pp. 4901–4934.
- 36. E. Kahler, \$20M NRG COSIA Carbon XPRIZE finalists announced; teams ready to test transformative CO2 technologies at Alberta's carbon conversion centre | Canada's Oil Sands Innovation Alliance COSIA. *COSIA*. **Press Rele** (2018), (available at https://www.cosia.ca/resources/news-releases/20m-nrg-cosia-carbon-xprize-finalists-announced-teams-ready-test).
- 37. D. Zhang *et al.*, Present situation and future prospect of renewable energy in China. *Renew. Sustain. Energy Rev.* **76** (2017), pp. 865–871.
- 38. M. R. Shaner, H. A. Atwater, N. S. Lewis, E. W. McFarland, A comparative technoeconomic analysis of renewable hydrogen production using solar energy. *Energy Environ. Sci.* **9**, 2354–2371 (2016).
- S. Verma, B. Kim, H.-R. "Molly" R. M. Jhong, S. Ma, P. J. A. A. Kenis, A gross-margin model for defining technoeconomic benchmarks in the electroreduction of CO2. *ChemSusChem*. 9, 1972–1979 (2016).
- 40. J. M. Spurgeon, B. Kumar, A comparative technoeconomic analysis of pathways for commercial electrochemical CO 2 reduction to liquid products. *Energy Environ. Sci.* **11**, 1536–1551 (2018).
- 41. M. Jouny, W. W. Luc, F. Jiao, A General Techno-Economic Analysis of CO 2 Electrolysis Systems. *Ind. Eng. Chem. Res.* **57**, 2165–2177 (2018).
- 42. C. Palmer, F. Saadi, E. W. McFarland, Technoeconomics of Commodity Chemical Production using Sunlight. *ACS Sustain. Chem. Eng.* **6**, 7003–7009 (2018).
- 43. S. K. Sanyal, Cost of Geothermal Power and Factors that Affect It. *World Geotherm. Congr. 2005*, 24–29 (2005).
- I. Renewable Energy Agency, "Renewable power: Climate-safe energy competes on cost alone" (2018), (available at https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2018/Dec/IRENA_COP24_costs_update_2018.p df).
- 45. Environmental Protection Agency, eGRID Summary Tables 2016. *eGRID* (2016) (available at https://www.epa.gov/sites/production/files/2018-02/documents/egrid2016_summarytables.pdf).
- 46. S. Lewandowski, in *IHS Markit* (2016; https://cdn.ihs.com/www/pdf/Steve-Lewandowski-Big-Changes-Ahead-for-Ethylene-Implications-for-Asia.pdf).
- 47. Transparency Market Research, "Global Ethanol Market: Advancement in Production

Technologies to boost Market, notes TMR" (2018), (available at https://www.transparencymarketresearch.com/pressrelease/ethanol-market.htm).

- Orbis Research, "Global (North America, Europe and Asia-Pacific, South America, Middle East and Africa) Carbon Monoxide Market 2017 Forecast to 2022 | Orbis Research" (2018), (available at https://www.orbisresearch.com/reports/index/global-northamerica-europe-and-asia-pacific-south-america-middle-east-and-africa-carbonmonoxide-market-2017-forecast-to-2022).
- 49. Mordor Intelligence, "Formic Acid Market Segmented by Grade Type, Application, and Geography Growth, Trends & Forecasts (2019-2024)" (2018), (available at https://www.mordorintelligence.com/industry-reports/formic-acid-market).
- 50. M. Broeren, Production of Bio-ethylene. *IEA-ETSAP IRENA© Technol. Br. 13*, 9 (2013).
- 51. R. Geyer, J. R. Jambeck, K. L. Law, Production, use, and fate of all plastics ever made. *Sci. Adv.* **3**, e1700782 (2017).
- 52. M. Blesl, D. Bruchof, Syngas Production from Coal. *Energy Technol. Netw.*, 1–5 (2010).
- 53. M. Balat, H. Balat, Recent trends in global production and utilization of bio-ethanol fuel. *Appl. Energy.* **86**, 2273–2282 (2009).
- 54. A. Sternberg, C. M. Jens, A. Bardow, Life cycle assessment of CO2-based C1-chemicals. *Green Chem.* **19**, 2244–2259 (2017).
- U.S. Department of Energy, "Strategic Plan for a thriving and sustainable bioeconomy" (2016), (available at https://www.energy.gov/sites/prod/files/2017/09/f36/beto_strategic_plan_december_2 016.pdf).
- 56. A. Boulamanti, J. A. Moya, Production costs of the chemical industry in the EU and other countries: Ammonia, methanol and light olefins. *Renew. Sustain. Energy Rev.* **68** (2017), pp. 1205–1212.
- 57. M. Ruth, A. D. Amato, B. Davidsdottir, Carbon Emissions from U.S. Ethylene Production under Climate Change Policies. *Environ. Sci. Technol.* **36**, 119–124 (2002).
- 58. International Energy Agency (IEA), Production costs of alternative transportation fuel & influence of crude oil price and technology maturity, 1–51 (2013).
- 59. W. E. Tyner, F. Taheripour, Q. Zhuang, D. Birur, U. Baldos, "Land Use Changes and Consequent CO2 Emissions due to US Corn Ethanol Production: A Comprehensive Analysis" (2010), (available at www.gtap.org.).
- 60. M. Pérez-Fortes, J. C. Schöneberger, A. Boulamanti, G. Harrison, E. Tzimas, Formic acid synthesis using CO2as raw material: Techno-economic and environmental evaluation and market potential. *Int. J. Hydrogen Energy*. **41**, 16444–16462 (2016).
- 61. Statista, Market value of alcoholic beverages, 2015/2022. Consum. Goods FMCG (2015),

(available at https://www.statista.com/statistics/696641/market-value-alcoholicbeverages-worldwide/).

- 62. J. P. Lange, Methanol synthesis: A short review of technology improvements. *Catal. Today.* **64**, 3–8 (2001).
- 63. X. Sun *et al.*, Molybdenum-Bismuth Bimetallic Chalcogenide Nanosheets for Highly Efficient Electrocatalytic Reduction of Carbon Dioxide to Methanol. *Angew. Chemie - Int. Ed.*, 1–6 (2016).
- 64. Q. Yun, Q. Lu, X. Zhang, C. Tan, H. Zhang, Electrochemical Reduction of CO2 to CH3OH on hierarchical Pd/SnO2 nanosheets with abundant Pd-O-Sn interfaces. *Angew. Chemie* (2018), doi:10.1002/ange.201706426.
- E. E. Barton, D. M. Rampulla, A. B. Bocarsly, Selective solar-driven reduction of CO2 to methanol using a catalyzed p-GaP based photoelectrochemical cell. *J. Am. Chem. Soc.* 130, 6342–6344 (2008).
- 66. C. W. Li, J. Ciston, M. W. Kanan, Electroreduction of carbon monoxide to liquid fuel on oxide-derived nanocrystalline copper. *Nature*. **508**, 504–7 (2014).
- Y. Song *et al.*, High-Selectivity Electrochemical Conversion of CO2to Ethanol using a Copper Nanoparticle/N-Doped Graphene Electrode. *ChemistrySelect*. 1, 6055–6061 (2016).
- 68. D. Raciti *et al.*, Low-Overpotential Electroreduction of Carbon Monoxide Using Copper Nanowires. *ACS Catal.* **7**, 4467–4472 (2017).
- Y. Liu *et al.*, Selective Electrochemical Reduction of Carbon Dioxide to Ethanol on a Boron- and Nitrogen-Co-doped Nanodiamond. *Angew. Chemie - Int. Ed.* 56, 15607–15611 (2017).
- T. T. H. Hoang *et al.*, Nanoporous Copper-Silver Alloys by Additive-Controlled Electrodeposition for the Selective Electroreduction of CO2to Ethylene and Ethanol. *J. Am. Chem. Soc.* 140, 5791–5797 (2018).
- T.-T. Zhuang *et al.*, Steering post-C-C coupling selectivity enables high efficiency electroreduction of carbon dioxide to multi-carbon alcohols. *Nat. Catal.* 1, 421–428 (2018).
- 72. M. Melikoglu, V. Singh, S. Y. Leu, C. Webb, C. S. K. Lin, in *Handbook of Biofuels Production: Processes and Technologies: Second Edition* (2016), pp. 237–258.
- 73. H. T. Luk, C. Mondelli, D. C. Ferré, J. A. Stewart, J. Pérez-Ramírez, Status and prospects in higher alcohols synthesis from syngas. *Chem. Soc. Rev.* **46**, 1358–1426 (2017).
- 74. D. M. Weekes, D. A. Salvatore, A. Reyes, A. Huang, C. P. Berlinguette, Electrolytic CO 2 Reduction in a Flow Cell. *Acc. Chem. Res.* **51**, 910–918 (2018).
- 75. I. Amghizar, L. A. Vandewalle, K. M. Van Geem, G. B. Marin, New Trends in Olefin

Production. *Engineering*. **3**, 171–178 (2017).

- 76. C.-T. T. Dinh *et al.*, CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science (80-.).* **360**, 783–787 (2018).
- L. Wang, S. A. Nitopi, E. Bertheussen, M. Orazov, C. G. Morales-, Electrochemical Carbon Monoxide Reduction on Polycrystalline Copper : Effects of Potential, Pressure and pH on Selectivity towards Multi-Carbon and Oxygenated Products. ACS Catal. 8, 7445–7454 (2018).
- 78. Y. Hori, in *Modern Aspects of Electrochemistry* (2008; http://link.springer.com/10.1007/978-0-387-49489-0_3), pp. 89–189.
- 79. J. Resasco *et al.*, Promoter Effects of Alkali Metal Cations on the Electrochemical Reduction of Carbon Dioxide. *J. Am. Chem. Soc.* **139**, 11277–11287 (2017).
- Z. Han, R. Kortlever, H.-Y. Chen, J. C. Peters, T. Agapie, CO 2 Reduction Selective for C ≥2 Products on Polycrystalline Copper with N-Substituted Pyridinium Additives. ACS Cent. Sci. 3, 853–859 (2017).
- C. Hahn *et al.*, Engineering Cu surfaces for the electrocatalytic conversion of CO 2 : Controlling selectivity toward oxygenates and hydrocarbons. *Proc. Natl. Acad. Sci.* 114, 5918–5923 (2017).
- 82. P. De Luna *et al.*, Catalyst electro-redeposition controls morphology and oxidation state for selective carbon dioxide reduction. *Nat. Catal.* **1**, 103–110 (2018).
- 83. A. Verdaguer-Casadevall *et al.*, Probing the Active Surface Sites for CO Reduction on Oxide-Derived Copper Electrocatalysts. *J. Am. Chem. Soc.* **137**, 9808–9811 (2015).
- Y. Hori, I. Takahashi, O. Koga, N. Hoshi, Selective Formation of C2 Compounds from Electrochemical Reduction of CO₂ at a Series of Copper Single Crystal Electrodes. *J. Phys. Chem. B.* 106, 15–17 (2002).
- 85. E. L. Clark, C. Hahn, T. F. Jaramillo, A. T. Bell, Electrochemical CO2Reduction over Compressively Strained CuAg Surface Alloys with Enhanced Multi-Carbon Oxygenate Selectivity. J. Am. Chem. Soc. **139**, 15848–15857 (2017).
- T. T. H. Hoang, S. Ma, J. I. Gold, P. J. A. Kenis, A. A. Gewirth, Nanoporous Copper Films by Additive-Controlled Electrodeposition: CO2Reduction Catalysis. *ACS Catal.* 7, 3313–3321 (2017).
- 87. A. Brems, R. Dewil, J. Baeyens, R. Zhang, Gasification of plastic waste as waste-to-energy or waste-to-syngas recovery route. *Nat. Sci.* **05**, 695–704 (2013).
- 88. M. E. Dry, The Fischer-Tropsch process: 1950-2000. *Catal. Today*. **71**, 227–241 (2002).
- S. Wainaina, I. S. Horváth, M. J. Taherzadeh, Biochemicals from food waste and recalcitrant biomass via syngas fermentation: A review. *Bioresour. Technol.* 248, 113–121 (2018).

- 90. P. C. Munasinghe, S. K. Khanal, Biomass derived syngas fermentation into biofuels: Opportunities and challenges. *Bioresour. Technol.* **101**, 5013–5022 (2010).
- O. P. R. van Vliet, A. P. C. Faaij, W. C. Turkenburg, Fischer-Tropsch diesel production in a well-to-wheel perspective: A carbon, energy flow and cost analysis. *Energy Convers. Manag.* 50, 855–876 (2009).
- 92. D. Choi, D. C. Chipman, S. C. Bents, R. C. Brown, A techno-economic analysis of polyhydroxyalkanoate and hydrogen production from syngas fermentation of gasified biomass. *Appl. Biochem. Biotechnol.* **160**, 1032–1046 (2010).
- 93. M. Akiyama, T. Tsuge, Y. Doi, Environmental life cycle comparison of polyhydroxyalkanoates produced from renewable carbon resources by bacterial fermentation. *Polym. Degrad. Stab.* **80**, 183–194 (2003).
- 94. J. R. Rostrup-Nielsen, J. Sehested, J. K. Noerskov, Hydrogen and Synthesis Gas by Steamand CO2 Reforming. *ChemInform.* **34** (2003), doi:10.1002/chin.200317288.
- 95. M. B. Ross *et al.*, Tunable Cu Enrichment Enables Designer Syngas Electrosynthesis from CO2. *J. Am. Chem. Soc.* **139**, 9359–9363 (2017).
- R. He *et al.*, Achieving the Widest Range of Syngas Proportions at High Current Density over Cadmium Sulfoselenide Nanorods in CO2 Electroreduction. *Adv. Mater.* **30**, 1–7 (2018).
- 97. P. Kang, Z. Chen, A. Nayak, S. Zhang, T. J. Meyer, Single catalyst electrocatalytic reduction of CO2 in water to H2 + CO syngas mixtures with water oxidation to O2. *Energy Environ. Sci.* **7**, 4007–4012 (2014).
- H.-R. "Molly" R. M. Jhong, S. Ma, P. J. Kenis, Electrochemical conversion of CO2 to useful chemicals: Current status, remaining challenges, and future opportunities. *Curr. Opin. Chem. Eng.* 2, 191–199 (2013).
- Siemens, Evonik, Press Joint Press Release Evonik and Siemens to generate high-value specialty chemicals from carbon dioxide and eco-electricity. *Jt. Press Release* (2018), (available at https://www.siemens.com/press/pool/de/pressemitteilungen/2018/corporate/PR20180 10135COEN.pdf).
- K. K. Sakimoto, N. Kornienko, P. Yang, Cyborgian material design for solar fuel production: The emerging photosynthetic biohybrid systems. *Acc. Chem. Res.* 50 (2017), pp. 476–481.
- S. N. Nangle, K. K. Sakimoto, P. A. Silver, D. G. Nocera, Biological-inorganic hybrid systems as a generalized platform for chemical production. *Curr. Opin. Chem. Biol.* 41 (2017), pp. 107–113.
- 102. C. Liu, B. C. Colón, M. Ziesack, P. A. Silver, D. G. Nocera, Water splitting-biosynthetic system with CO2 reduction efficiencies exceeding photosynthesis. *Science (80-.).* **352**,

1210–1213 (2016).

- X. Chen, Y. Cao, F. Li, Y. Tian, H. Song, Enzyme-Assisted Microbial Electrosynthesis of Poly(3-hydroxybutyrate) via CO2Bioreduction by Engineered Ralstonia eutropha. ACS Catal. 8, 4429–4437 (2018).
- 104. C. Liu, K. K. Sakimoto, B. C. Colón, P. A. Silver, D. G. Nocera, Ambient nitrogen reduction cycle using a hybrid inorganic–biological system. *Proc. Natl. Acad. Sci.* **114**, 6450–6455 (2017).
- 105. K. K. Sakimoto *et al.*, Physical Biology of the Materials-Microorganism Interface. *J. Am. Chem. Soc.* **140** (2018), pp. 1978–1985.
- 106. O. Yishai, S. N. Lindner, J. Gonzalez de la Cruz, H. Tenenboim, A. Bar-Even, The formate bio-economy. *Curr. Opin. Chem. Biol.* **35**, 1–9 (2016).
- 107. Y. X. Huang, Z. Hu, An integrated electrochemical and biochemical system for sequential reduction of CO2to methane. *Fuel*. **220**, 8–13 (2018).
- 108. B. Endrődi *et al.*, Continuous-flow electroreduction of carbon dioxide. *Prog. Energy Combust. Sci.* **62** (2017), pp. 133–154.
- J. B. Greenblatt, D. J. Miller, J. W. Ager, F. A. Houle, I. D. Sharp, The Technical and Energetic Challenges of Separating (Photo)Electrochemical Carbon Dioxide Reduction Products. *Joule*. 2, 1–40 (2018).
- 110. R. B. Eldridge, "Olefin/Paraffin Separation Technology: A Review" (1993), (available at https://pubs.acs.org/sharingguidelines).
- 111. L. Li *et al.*, Ethane/ethylene separation in a metal-organic framework with iron-peroxo sites. *Science*. **362**, 443–446 (2018).
- 112. J. G. Vitillo, B. Smit, L. Gagliardi, Introduction: Carbon Capture and Separation. *Chem. Rev.* **117**, 9521–9523 (2017).
- 113. D. S. Ripatti, T. R. Veltman, M. W. Kanan, Carbon Monoxide Gas Diffusion Electrolysis that Produces Concentrated C2 Products with High Single-Pass Conversion. *Joule* (2018), doi:10.1016/J.JOULE.2018.10.007.
- 114. K. Stéphenne, in *Energy Procedia* (Elsevier, 2014; https://www.sciencedirect.com/science/article/pii/S1876610214024576), vol. 63, pp. 6106–6110.
- 115. Environment and Climate Change Canada, "Overview of 2015 Reported Emissions April 2017 Facility Greenhouse Gas Emissions Reporting" (2017), (available at https://www.canada.ca/en/environment-climate-change/services/climatechange/greenhouse-gas-emissions/facility-reporting/overview-2016.html).
- 116. International Energy Agency (IEA), "Ship Transport of CO2" (2004), (available at https://ieaghg.org/docs/General_Docs/Reports/PH4-30 Ship Transport.pdf).

- 117. OECD, Effective Carbon Rates 2018 Pricing carbon emissions through taxes and emissions trading: Core results from the Effective Carbon Rates database (forthcoming) (2018), , doi:10.1787/9789264305304-en.
- 118. C. He, F. You, Shale Gas Processing Integrated with Ethylene Production: Novel Process Designs, Exergy Analysis, and Techno-Economic Analysis. *Ind. Eng. Chem. Res.* **53**, 11442–11459 (2014).
- B. D. James, J. M. Moton, Techno-economic Analysis of PEM Electrolysis for Hydrogen Production. *Dep. Energy* (2014) (available at https://www.energy.gov/sites/prod/files/2014/08/f18/fcto_2014_electrolytic_h2_wkshp _colella1.pdf).
- 120. U.S. Energy Information Administration, Electric Power Monthly: with data for May 2018, 1–222 (2018).
- 121. U. Energy Information Administration, "Annual Energy Outlook 2018 with Projections to 2050" (2018), , doi:10.2172/1019039.
- 122. IEA, Global Trends and Outlook for Hydrogen (2017) (available at http://ieahydrogen.org/pdfs/Global-Outlook-and-Trends-for-Hydrogen_Dec2017_WEB.aspx).
- 123. P. Luckow *et al.*, 2015 Carbon Dioxide Price Forecast. *Synap. Energy Econ. Inc.*, 1–39 (2015).
- 124. U.S. Department of Energy, DOE Technical Targets for Hydrogen Production from Electrolysis. *Energy.gov* (2015), pp. 1–7.
- 125. R. Bhandari, C. A. Trudewind, P. Zapp, Life cycle assessment of hydrogen production via electrolysis A review. *J. Clean. Prod.* **85** (2014), pp. 151–163.
- 126. J. David, H. Herzog, The cost of carbon capture, 13–16 (2000).
- 127. S. Combustion, E. Factors, Emission Factors for Greenhouse Gas Inventories, 1–5 (2014).
- 128. S. Ikeda, T. Takagi, K. Ito, Selective formation of formic acid, oxalic acid, and carbon monoxide by electrochemical reduction of carbon dioxide. *Bull. Chem. Soc. Jpn.* **60**, 2517–2522 (1987).
- 129. H. Noda *et al.*, Electrochemical Reduction of Carbon Dioxide at Various Metal Electrodes in Aqueous Potassium Hydrogen Carbonate Solution. *Bull. Chem. Soc. Jpn.* **63**, 2459–2462 (1990).
- 130. C. Delacourt, P. L. Ridgway, J. B. Kerr, J. Newman, Design of an Electrochemical Cell Making Syngas (CO+H2) from CO2 and H2O Reduction at Room Temperature. *J. Electrochem. Soc.* **155**, B42 (2008).
- 131. Y. Chen, C. W. Li, M. W. Kanan, Aqueous CO2 reduction at very low overpotential on oxide-derived Au nanoparticles. *J. Am. Chem. Soc.* **134**, 19969–72 (2012).

- 132. A. Klinkova *et al.*, Rational Design of Efficient Palladium Catalysts for Electroreduction of Carbon Dioxide to Formate. *ACS Catal.* **6**, 8115–8120 (2016).
- 133. Y. Hori *et al.*, "deactivation of copper electrode" in electrochemical reduction of CO2. *Electrochim. Acta*. **50**, 5354–5369 (2005).
- 134. K. Hara, A. Kudo, T. Sakata, M. Watanabe, High efficiency electrochemical reduction of carbon dioxide under high pressure on a gas diffusion electrode containing Pt catalysts. *J. Electrochem. Soc.* **142**, L57–L59 (1995).
- 135. K. P. Kuhl *et al.*, New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy Environ. Sci.* **5**, 7050 (2012).
- 136. D. Ren, B. S. H. Ang, B. S. Yeo, Tuning the Selectivity of Carbon Dioxide Electroreduction toward Ethanol on Oxide-Derived CuxZn Catalysts. *ACS Catal.* **6**, 8239–8247 (2016).

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Supplementary Materials: Figures S1 and S2 Tables S1 to S3

References (118-136)

Supplementary Materials for: What would it take for renewably-powered electrosynthesis to displace petrochemical processes?

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Techno-Economic Assessment

The techno-economic assessment model provides a total plant gate levelized cost of production in the units of \$ per ton of product (ethanol, hydrogen, carbon monoxide, and ethylene). The costs are broadly categorized into capital costs and operating costs. The capital costs are limited to the cost of the electrolyzer and do not include the costs of infrastructure or other equipment costs. The plant lifetime is assumed to be 30 years. The operating costs consist of the electricity costs, separation costs, plant operation costs, and costs of goods sold (COGS) costs which are mainly the cost of CO₂ gas. All currencies are in USD unless explicitly stated otherwise.

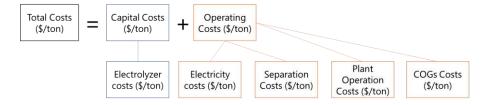


Figure S1. Definition of costs covered within the techno-economic assessment.

A plant is assumed to convert 200 tons of CO_2 a day into carbon monoxide or ethylene, referenced to the production of ethylene from Bakken shale gas formations.(*118*) Hydrogen is produced from a production capacity of 50 tons per day referenced to a central facility as outlined in the Department of Energy's H2A Analysis.(*119*) Plant lifetime is assumed to be 30 years, which is an average of the high (40 years) and low (20 years) H₂ volume projection scenarios as outlined in the DOE H2A Analysis.(*119*) We assume a capacity factor of 80% which is an optimistic renewables scenario based primarily on nuclear and geothermal power generation.(*120*) A separation constant of \$0.001/kg, a capital recovery factor of 0.08, and a product fraction of 0.10 (kg/kg mixture) were all used to model the plant.

The spot price of ethanol is taken to be \$800 per ton as taken from the 2018 Annual Energy Outlook form the US Energy Information Administration.(*121*) The spot price of hydrogen is taken at 3.90/kg (3900/ton) as defined in a International Energy Agency outlook report on hydrogen.(*122*) The spot price of CO was 1200/ton(73) and the spot price of ethylene is taken as 1000/ton.(45) The spot price for pure CO₂ as a feedstock (COGS costs) is \$30 per ton.(*123*)

The Faradaic efficiency is assumed to be 90% and the electrolyzer system capital cost was chosen to be \$300/kW which is 2020 DOE target for water electrolysis hydrogen production and corresponds to an electrolyzer operating at 600 mA/cm² current density.(*124*) The energy conversion efficiency is defined as the ratio: [applied potential minus overpotential] divided by applied potential. A separating constant of 0.001 \$/kg and a product fraction of 0.1 kg product/ kg of mixture was used. The operational cost was taken to be 10% of the electricity costs.

The costs-of-goods-sold are defined as primarily the cost of CO₂. The COGs per ton of product sold is defined as:

$$COGS(\$/ton) = \frac{Cost \ of \ CO_2 \ (\frac{\$}{ton})}{Production \ Volume \ (ton)}$$
(1)

Where production volume is:

$$Production Volume (ton) = \frac{CO_2 Converted *Product Molecular Weight *Faradaic Efficiency}{CO_2 Molecular Weight *Product Ratio*100}$$
(2)

The total electricity costs are:

$$Electricity \ cost \ (\$/ton) = \frac{Energy \ Consumed \ (kW) * Electricity \ cost \ (\frac{cents}{kWh}) * 24hours}{Production \ volume \ (ton) * (100 \frac{cents}{dollar})}$$
(3)

Where the energy consumed is:

Energy consumed (kW) = Production volume * Product energy density * Energy conversion efficiency (4)

The separation cost is:

$$Separation \ cost \ (\$/ton) = \frac{Separating \ Constant}{Product \ Fraction}$$
(5)

The capital cost is:

$$Capital \ cost \ \left(\frac{\$}{ton}\right) = \frac{Energy \ consumed \ \ast \ Electrolyzer \ cost \ \ast \ Capital \ Recovery \ Factor}{Capacity \ Factor \ \ast \ 365 \ days \ \ast \ Production \ Volume}$$

The total plant-gate levelized cost is then described as:

 $Total Cost \left(\frac{\$}{ton}\right) = CapitalCost + ElectricityCost + SeparationCost + OperationalCost + CostofCO2$ (6)

An example calculation for carbon monoxide with an energy conversion efficiency of 30% and an electricity price of 2 cents/kWh is listed below:

 $Production Volume (ton/day) = \frac{200 \frac{ton}{day} CO_2 \text{ converted } * 28 \frac{g}{mol} * 90\% FE}{44 \frac{g}{mol} * 100} = 114 \text{ tons/day}$

 $Energy\ Consumed\ (kW) = \frac{114\frac{ton}{day} * 1000\frac{kg}{ton} * 2.81\frac{kWh}{kg} * 100}{24\frac{hours}{day} * 30\%\ ECE} = 44686\ kW$

$$Capital \ Cost \ (\$/ton) = \frac{44686 \ kW \ast 300 \frac{\$}{kW} \ast 0.8}{0.8 \ast 365 \ days \ast 114 \ ton/day} = \frac{\$32.30}{ton}$$

$$Electricity\ cost\ (\$/ton) = \frac{44686\ kW \ast 24\ hours \ast 2\frac{cents}{kWh}}{100\frac{cents}{\$} \ast 114\frac{tons}{day}} = \frac{\$187.26}{ton}$$

Separation cost (\$/ton) =
$$\frac{\frac{\$0.001}{kg}}{0.01 \frac{kg}{kg \text{ mixture}} * 1000 \frac{kg}{ton}} = \frac{\$10}{ton}$$

Operational cost(
$$\frac{10\%}{ton} = 10\% * \frac{187.26}{ton} = \frac{18.73}{ton}$$

$$COGS \ cost \ (\$/ton) = \frac{\frac{\$200}{ton}}{114 \frac{tons}{day}} = \frac{\$0.26}{ton}$$

$$Total\ cost\ \left(\frac{\$}{ton}\right) = \frac{\$32.20}{ton} + \frac{\$187.26}{ton} + \frac{\$10.00}{ton} + \frac{\$18.73}{ton} + \frac{\$0.26}{ton} = \frac{\$284.55}{ton}$$

Table S1: Product Specific Constants

	Ethanol	Ethylene	Carbon Monoxide	Hydrogen
Stoichiometric Ratio	2.00	2.00	1.00	0.50
Number of Electrons Transferred	12.00	12.00	2.00	2.00
Product molecular weigh (g/mol)	46.07	28.00	28.00	2.00
Energy density of the product (MJ/kg)	7.44	47.19	10.11	33.00
Reactant Molecular weight (g/mol)	44.00	44.00	44.00	18.00

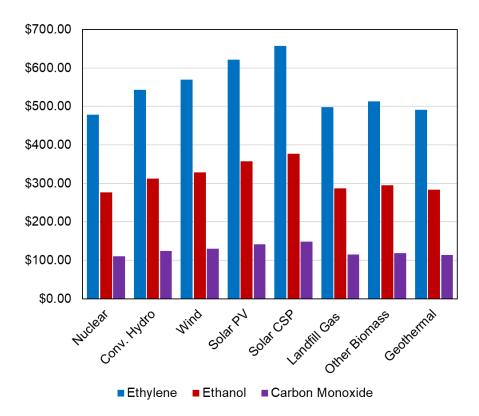


Figure S2. Cost of production according to different capacity factors corresponding to various renewable energy sources.(*120*) Assumes a pure CO_2 price of \$30/ton, Faradaic efficiency of 90%, energy conversion efficiency of 70%, electricity price of 2c/kWh, electrolyzer cost of \$300/kW, and plant lifetime of 30 years.

Carbon Emissions Life-Cycle Assessment

The technology considered is a CO_2 conversion system which operates at room temperature and ambient pressure. The only energy requirements are in electrical energy to power the electrochemical conversion of CO_2 . We assume that the electrolyte may be recycled with the replenishment of water being the only recurring operating activity, representing insignificant CO_2 emissions. We categorize electrolyte as a portion of the capital equipment of the life-cycle assessment and thus outside the boundaries of the current LCA model which focuses instead on the emissions from the operation of CO_2 conversion. The carbon footprint of the conversion process itself is negligible, and the majority of emissions come from the capture process and the electricity generation. When coupled with renewable energy generation, this process has a net zero carbon footprint when the product is a fuel for long term energy storage. If the product generated is a plastic or chemical feedstock then the carbon footprint is net negative as the CO₂ is sequestered into a solid consumer good and can no longer be emitted into the atmosphere. Constants of the model are provided in **Table S2**. The CO₂ emissions avoided are calculated by multiplying the annual global production volume of each product by that product's global warming potential (GWP).

The life cycle analysis seeks to provide a description of the technology process from material extraction to operations and end-of-life of the facility. In the case of this specific technology, the operation will account for the majority of the GWP. The GWP is defined as the ratio of mass of CO₂ (emitted) to mass of product.

Since there has been no CO₂ electrolyzer technology yet proven at scale, we reference the Life Cycle Analysis of an analogous technology, namely hydrogen electrolyzers.(*125*) It was found that the GWP contribution of the eletrolyzer unit itself is relatively small (approximately only 4%) while the majority (~96%) is from the electricity generation and product compression/transportation.(*125*) We expect similar numbers for CO₂ electrolyzer technologies. As CO₂ electrolzyer technologies rely heavily upon hydrogen electrolyzer architectures, we also find that the electrolytic technology is only more favourable from an emissions perspective if renewable energy is used. Furthermore, since the emissions related to building the electrolyzer is minimal in comparison to the energy usage required for operation over a 20 year lifetime, we do not consider this in our LCA.

Product constants are provided in **Table S2**. We assume a plant electricity capacity of 500 kW and a capacity factor of 0.9. The net CO_2 emissions are then calculated as a function of electrical-to-chemical conversion efficiency, simply called the conversion efficiency, and the grid intensity.

The calculations of the net CO₂ emissions are described below:

Net Emissions = Conversion Emissions per year – Baseline Emissions per year	(1)
Baseline Emissions = Production volume $*$ GWP of product + CO_2 converted	(2)
CO_2 converted per year = CO_2 per kg product * Production volume	(3)
$Production Vol. = \left(\frac{Plant \ Electricity \ Cap.*Conversion \ Eff.}{Product \ Energy \ Density}\right) * 8760h/yr * Capacity \ Factor$	(4)
$Conversion \ Emissions = \frac{Conversion \ Emission}{kg \ product} * CO_2 \ converted \ per \ year$	(5)
$\frac{ConversionEmissions}{kg \ product} = (CO_2 \ Conversion \ Em. + Prod. \ Sep. \ Em.) * Grid \ Intensity$	(6)
Product Separations $Emissions = \frac{CO_2}{kg \ product} * Cost \ of \ Prod. Sep.$	(7)

$$CO_2 Conversion Emissions = \frac{Product EnergyDensity}{\frac{CO_2}{kg \ product}*Conversion \ efficiency}}$$
(8)

Constants	Ethylene	Carbon Monoxide	Formic Acid	Ethanol
Product Energy Density (kWh/kg)	13.96	2.8	1.5	7.4
CO ₂ per kg Product (kg CO ₂ / kg)	1.57	1.57	0.957	0.95
Cost of CO ₂ /Product Separation				
(kWh/kg)(<i>126</i>)	0.354	0.354	1	1
GWP of Product (kg CO ₂ / kg)(127)	5.75	1	1	5.75
Global Volume (M tonnes/year)	150	3.6	0.8	95
CO ₂ Emissions Avoided (MT CO ₂ e/year)	863	3.6	0.8	546.25

Table S2: Product Constants for the carbon emissions life-cycle assessment.

Table S3: Maximum reported Faradaic efficiency and corresponding current densities over time.

Year	Product	Faradaic efficiency (%)	Current Density (mA/cm ²)	Reference
1987	CO	35	N/A	(128)
1990	CO	80	6	(129)
2008	CO	85	80	(130)
2012	CO	98	10	(131)
1987	Formic acid	87	N/A	(128)
1990	Formic acid	94	6	(129)
2016	Formic acid	97	22	(132)
1990	Ethylene	40	6	(129)
2005	Ethylene	65	35	(133)
2018	Ethylene	70	473	(75)
1995	Ethanol	2	19	(134)
2012	Ethanol	10	10	(135)
2016	Ethanol	29	8	(136)
2016	Ethanol	63	2	(66)

References:

- 118. C. He, F. You, Shale Gas Processing Integrated with Ethylene Production: Novel Process Designs, Exergy Analysis, and Techno-Economic Analysis. *Ind. Eng. Chem. Res.* **53**, 11442–11459 (2014).
- B. D. James, J. M. Moton, Techno-economic Analysis of PEM Electrolysis for Hydrogen Production. *Dep. Energy* (2014) (available at https://www.energy.gov/sites/prod/files/2014/08/f18/fcto_2014_electrolytic_h2_wkshp _colella1.pdf).
- 120. U.S. Energy Information Administration, Electric Power Monthly: with data for May 2018, 1–222 (2018).
- 121. U. Energy Information Administration, "Annual Energy Outlook 2018 with Projections to 2050" (2018), , doi:10.2172/1019039.

- 122. IEA, Global Trends and Outlook for Hydrogen (2017) (available at http://ieahydrogen.org/pdfs/Global-Outlook-and-Trends-for-Hydrogen_Dec2017_WEB.aspx).
- 123. P. Luckow *et al.*, 2015 Carbon Dioxide Price Forecast. *Synap. Energy Econ. Inc.*, 1–39 (2015).
- 124. U.S. Department of Energy, DOE Technical Targets for Hydrogen Production from Electrolysis. *Energy.gov* (2015), pp. 1–7.
- 125. R. Bhandari, C. A. Trudewind, P. Zapp, Life cycle assessment of hydrogen production via electrolysis A review. *J. Clean. Prod.* **85** (2014), pp. 151–163.
- 126. J. David, H. Herzog, The cost of carbon capture, 13–16 (2000).
- 127. S. Combustion, E. Factors, Emission Factors for Greenhouse Gas Inventories, 1–5 (2014).
- 128. S. Ikeda, T. Takagi, K. Ito, Selective formation of formic acid, oxalic acid, and carbon monoxide by electrochemical reduction of carbon dioxide. *Bull. Chem. Soc. Jpn.* **60**, 2517–2522 (1987).
- 129. H. Noda *et al.*, Electrochemical Reduction of Carbon Dioxide at Various Metal Electrodes in Aqueous Potassium Hydrogen Carbonate Solution. *Bull. Chem. Soc. Jpn.* **63**, 2459–2462 (1990).
- 130. C. Delacourt, P. L. Ridgway, J. B. Kerr, J. Newman, Design of an Electrochemical Cell Making Syngas (CO+H2) from CO2 and H2O Reduction at Room Temperature. *J. Electrochem. Soc.* **155**, B42 (2008).
- 131. Y. Chen, C. W. Li, M. W. Kanan, Aqueous CO2 reduction at very low overpotential on oxide-derived Au nanoparticles. *J. Am. Chem. Soc.* **134**, 19969–72 (2012).
- 132. A. Klinkova *et al.*, Rational Design of Efficient Palladium Catalysts for Electroreduction of Carbon Dioxide to Formate. *ACS Catal.* **6**, 8115–8120 (2016).
- 133. Y. Hori *et al.*, "deactivation of copper electrode" in electrochemical reduction of CO2. *Electrochim. Acta*. **50**, 5354–5369 (2005).
- 134. K. Hara, A. Kudo, T. Sakata, M. Watanabe, High efficiency electrochemical reduction of carbon dioxide under high pressure on a gas diffusion electrode containing Pt catalysts. *J. Electrochem. Soc.* **142**, L57–L59 (1995).
- 135. K. P. Kuhl *et al.*, New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. *Energy Environ. Sci.* **5**, 7050 (2012).
- 136. D. Ren, B. S. H. Ang, B. S. Yeo, Tuning the Selectivity of Carbon Dioxide Electroreduction toward Ethanol on Oxide-Derived CuxZn Catalysts. *ACS Catal.* **6**, 8239–8247 (2016).