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REVIEW SUMMARY

ELECTROCHEMISTRY

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

Phil De Luna*, Christopher Hahn*, Drew Higgins*, Shaffiq A. Jaffer, Thomas F. Jaramillo†, Edward H. Sargent†

BACKGROUND: As the world continues to transition toward carbon emissions–free energy technologies, there remains a need to also reduce the carbon emissions of the chemical production industry. Today many of the world's chemicals are produced from fossil fuel–derived feedstocks. Electrochemical conversion of carbon dioxide (CO_2) into chemical feedstocks offers a way to turn waste emissions into valuable products, closing the carbon loop. When coupled to renewable sources of electricity, these products can be made with a net negative carbon emissions footprint, helping to sequester CO_2 into usable goods. Research and development into electrocatalytic materials for CO_2 reduction has intensified in recent years, with advances in selectivity, efficiency, and reaction rate progressing toward practical implementation. A variety of chemical products can be made from CO_2, such as alcohols, oxygenates, synthesis gas (syngas), and olefins—staples in the global chemical industry. Because these products are produced at substantial scale, a switch to renewably powered production could result in a substantial carbon emissions reduction impact. The advancement of electrochemical technology to convert electrons generated from renewable power into stable chemical form also represents one avenue to long-term (e.g., seasonal) storage of energy.

ADVANCES: The science of electrocatalytic CO_2 reduction continues to progress, with priority given to the need to pinpoint more accurately the targets for practical application, the economics of chemical products, and barriers to market entry. It will be important to scale CO_2 electrolyzers and increase the stability of these catalysts to thousands of hours of continuous operation. Product separation and efficient recycling of CO_2 and electrolyte also need to be managed. The petrochemical industry operates at a massive scale with a complicated global supply chain and heavy capital costs. Commodity chemical markets are difficult to penetrate and are priced on feedstock, which is currently inexpensive as a result of the shale gas boom. CO_2 capture costs from the flue or direct air and product separation from unreacted CO_2 are also important to consider. Assuming that the advancement of electrocatalytic technologies continues apace, what will it take to disrupt the chemical production sector, and what will society gain by doing so?

This review presents a technoeconomic and carbon emissions assessment of CO_2 products such as ethylene, ethanol, and carbon monoxide, offering target figures of merit for practical application. The price of electricity is by far the largest cost driver. Electrochemical production costs begin to match those of traditional fossil fuel–derived processes when electricity prices fall below 4 cents per kWh and energy conversion efficiencies reach at least 60%. When powered by renewable electricity, these products can be made with a net negative carbon emissions footprint. A comparative analysis of electrocatalytic, biocatalytic, and fossil fuel–derived chemical production shows that electrocatalytic production has the potential to yield the greatest reduction in carbon emissions, provided that a steady supply of clean electricity is available. Additionally, opportunities exist to combine electrochemical conversion of CO_2 with a range of other thermo- and biocatalytic processes to slowly electrify the existing petrochemical supply chain and further upgrade CO_2 into more useful chemicals. Technical challenges such as operating lifetime, energy efficiency, and product separation are discussed. Supply chain management of products and entrenched industrial petrochemical competition are also considered.

OUTLOOK: There exists increasingly widespread recognition of the need to transition to carbon emissions–free means of chemical production. CO_2 pricing mechanisms are being developed and are seeing increased governmental support. The nascent carbon utilization economy is gaining traction, with startup companies, global prizes, and industrial research efforts all pursuing new carbon conversion technologies. Recent advances in electrochemical CO_2 reduction through the use of gas diffusion electrodes are pushing current densities and selectivities into a realm of industrial use. Despite this progress, there remain technical challenges that must be overcome for commercial application. Additionally, market barriers and cost economics will ultimately decide whether this technology experiences widespread implementation. ■

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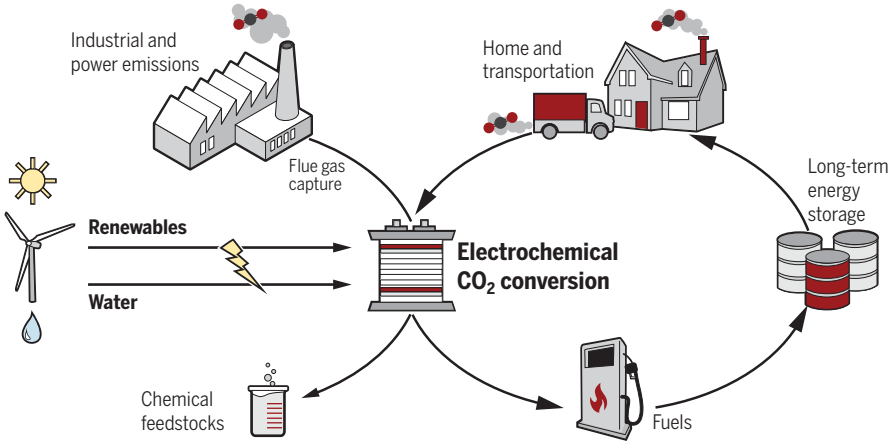

Electrochemical CO_2 conversion. Reduction of CO_2 using renewably sourced electricity could transform waste CO_2 emissions into commodity chemical feedstocks or fuels.

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REVIEW

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

Phil De Luna[1,2,3]*, Christopher Hahn[2,4]*, Drew Higgins[2,4,5]*, Shaffiq A. Jaffer[6], Thomas F. Jaramillo[2,4]†, Edward H. Sargent[7]†

Electrocatalytic transformation of carbon dioxide (CO_2) and water 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 also provide a comparison of the projected costs and CO_2 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 per kilowatt-hour. We discuss the possibility of combining electro- and biocatalytic processes, using sequential upgrading of CO_2 as a representative case. We describe the technical challenges and economic barriers to marketable electrosynthesized chemicals.

The dependence of the chemical industry on fossil fuel feedstocks presents an important emissions challenge. For example, in Europe, 26 chemical compounds account for 75% of total energy use within the chemical sector (including energy used as feedstock) and contribute more than 90% of European chemical sector greenhouse gas emissions [150 million tonnes (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 of CO_2 equivalents (Mt CO_2e) 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 larger quantities to supply a growing worldwide middle class (*2*). A less CO_2 emissions–intensive alternative to produce chemical feedstocks must be found in order to mitigate future CO_2 emissions.

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Renewable electrosynthesis could potentially target high-value chemicals (e.g., ethylene, ethanol) as a market-entry strategy because these important chemical products rely today on energy-intensive thermochemical routes such as 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 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 achieve meaningful carbon emissions reductions (*4*). For example, today formic acid represents a small global market, and a complete transition to its CO_2 emissions–neutral production would result in only meager global carbon emissions reductions; however, 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 road map to advance from the laboratory to commercial scales for electrochemical synthesis.

Renewable energy–powered electrochemical CO_2 conversion to chemicals could be implemented to take advantage of point sources of relatively pure CO_2 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 CO_2 sources. Additionally, complicated supply chain management needs to be accounted for; transport and storage costs between CO_2 emissions point sources and end-product users need 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 seasonal 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 (nondispatchability) challenge limits the widespread, terawatt-scale adoption of low-carbon energy sources. Electrosynthesized fuels (if they can become competitive in price versus low-cost natural gas) could provide a route to turn renewable electricity into stable chemical forms 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 Mt of oil equivalent in 2017) and emits CO_2 (1500 Mt of CO_2 per year in 2017) (*7*). We present prospective pathways toward industrial implementation as well as a technoeconomic assessment and simple life-cycle analysis 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 (syngas) and biocatalytic approaches as a pathway to higher-order valuable commodity chemicals. We ask, quantitatively, what it would

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take to disrupt the chemical production sector, and thus offer target figures of merit. We conclude with challenges that must be 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, hydroelectric) with electrochemical reduction of CO_2 to chemicals, if done efficiently, could address the nondispatchable 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 toward a cost of \$94 to \$232 per tonne of CO_2 from the atmosphere (*8*), with startup companies such as Carbon Engineering and Climeworks having secured funding to scale CO_2 capture processes to industrially relevant levels. However, electrocatalysis is currently limited to C1 to C3 chemical production for two major reasons: (i) Higher carbon species require more proton-coupled electron transfers, leading to a highly complex reaction pathway and poor product selectivities (*9*), and (ii) 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 CO_2 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 \$8.5 billion (USD) today to \$11 billion by 2023, driven mostly by the chemical industry's desire for emissions-free sources of hydrogen (*11*). Although electrochemical hydrogen production today accounts for 4% of total hydrogen production (with the remainder from steam reforming of natural gas and coal gasification), this represents 8 GW of electrolysis capacity (*12*, *13*). The total market is \$115 billion and is expected to reach \$155 billion 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 (*14*, *15*). The topic of hydrogen evolution has been covered in many excellent reviews (*5*, *16*–*19*) and will not be further explored here.

Electrochemical carbon dioxide reduction (CO_2R) has seen a marked increase in research activity over the past 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) toward many CO_2R products have increased steadily over

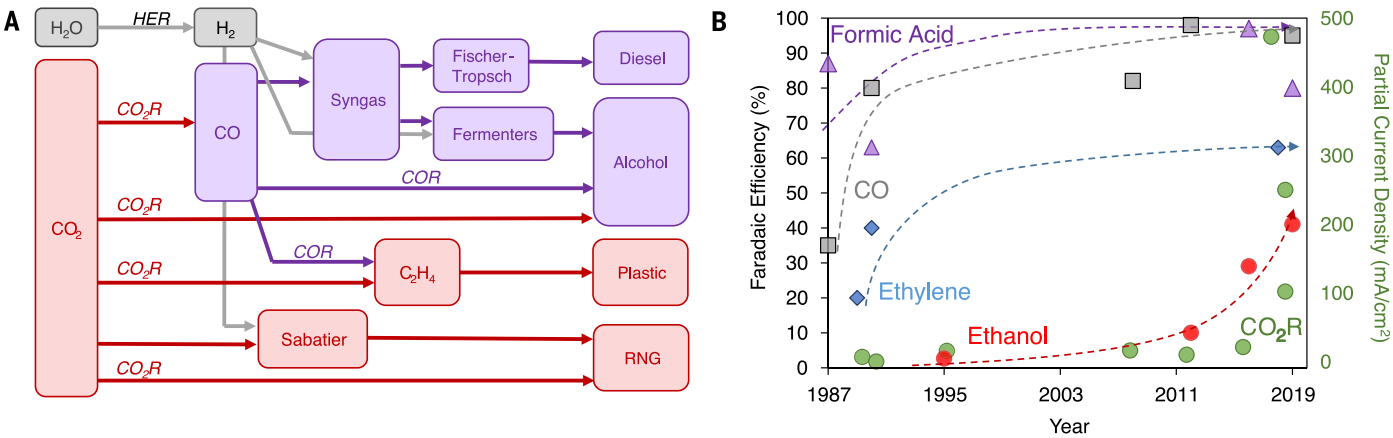

Fig. 1. Pathways and selectivities for renewable chemical synthesis. (**A**) Possible renewable energy–powered routes to commodity chemicals driven by electrocatalysis from H_2O (gray) and CO_2 (purple, red) as feedstocks. (**B**) Highest reported Faradaic efficiencies for carbon monoxide (gray squares), formic acid (purple triangles), ethylene (blue diamonds), and ethanol (red circles) and corresponding current densities (green) over the past three decades (table S3).

Table 1. Current state of CO_2 electrolyzers in comparison with hydrogen electrolyzers and their figures of merit.

Catalyst	Electrolyte	Product	Cell voltage (V)	Current density (mA/cm^2)	Faradaic efficiency (%)	Energy conversion efficiency (%)
Cu (*61*)	7 M KOH	Ethylene	2.4	110	70	34
Au (*107*)	2 M KOH	Carbon monoxide	2.0	99	98	64
Ag (*108*)	1 M KOH	Carbon monoxide	3.0	350	101	45
Ag (*109*)	0.5 M K_2SO_4: 1 M $KHCO_3$	Carbon monoxide	2.9	197	87	50
Ag (*81*)	0.1 M K_2SO_4: 1.5 M $KHCO_3$	Carbon monoxide	4.7	233	78	25
Sn (*110*)	0.5 M KCl	Formate	4.0	163	84	32
Pb (*111*)	0.5 M H_2SO_4	Formate	2.8	50	95	49
Sn (*112*)	0.5 M $KHCO_3$ + 2 M KCl	Formate	3.1	133	83	33
Pt (*113*)	Polymer electrolyte	Hydrogen	1.2 to 2.2	600 to 2000	100	57 to 74
Pt (*113*)	Alkaline	Hydrogen	1.5 to 2.0	200 to 400	100	52 to 69

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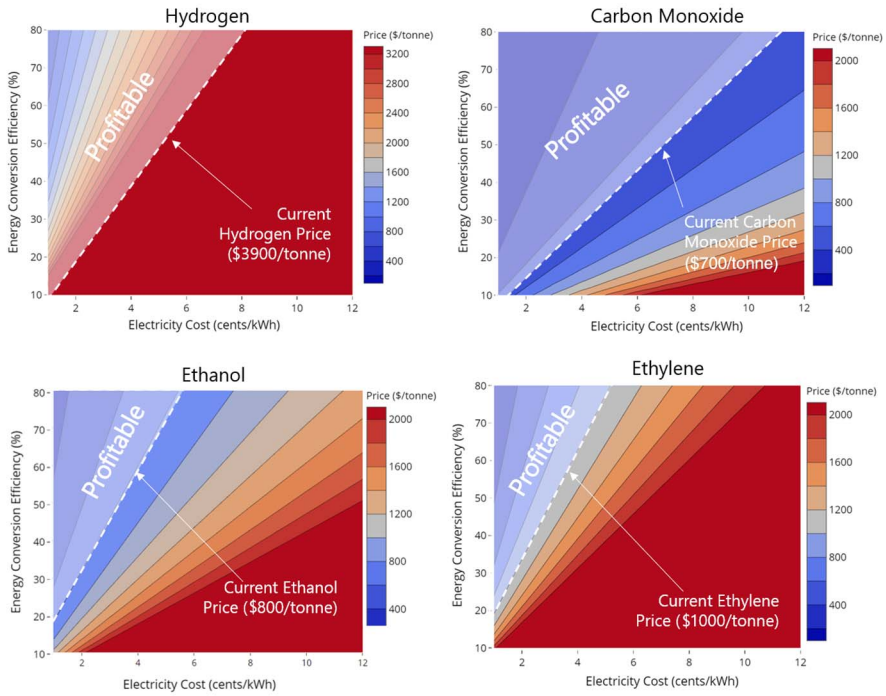

Fig. 2. Production costs of electrosynthesized chemicals. The graphs show technoeconomic analyses of hydrogen, carbon monoxide, ethanol, and ethylene costs as a function of electrolyzer energy conversion efficiency and electricity costs. We assume a pure CO_2 price of $30/tonne, Faradaic efficiency of 90%, current density of 500 mA/cm^2, electrolyzer cost of $300/kW, and plant lifetime of 30 years. The area above the white dashed line in lighter color indicates profitable production costs based on average global prices. We note that regional differences in market prices exist because of the nature of fossil fuel feedstocks.

the past 30 years. Current densities have also increased to >100 mA/cm^2 (Fig. 1B) as a result of the adoption of gas diffusion electrodes that overcome the CO_2 solubility limit in aqueous electrolytes. Production of simpler C1 products such as CO and formic acid has become possible with high initial selectivity even on simple metal foils. However, more sophisticated catalyst, electrolyte, and cell engineering is required to make substantial improvements in selectivity for C2 products because of the difficulty of C-C coupling. Additionally, efficient product separation and recycling of unreacted CO_2 is another practical concern that could be mitigated by improvements in catalyst selectivity. The topic of materials design for CO_2R electrocatalysis has also been covered extensively by multiple reviews (*20*–*27*). Here, we instead focus on the barriers that this technology would have to surmount to disrupt the chemical industry.

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 CO_2R, 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 CO_2 for accelerated technological development. First, the products of CO_2R already exist within many petrochemical supply chains, and therefore the chemical industry infrastructure is more readily prepared to adapt to CO_2R. 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 CO_2 once it is captured (*10*). CO_2R provides a way to recover value from what would otherwise be a tremendous sunk cost. The Carbon XPRIZE is a $20 million competition to capture and convert the most CO_2 and is jointly funded by COSIA, a consortium of large oil producers (*28*).

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 investments by 2020 in an effort to reduce carbon emissions (*29*). Canada is implementing a carbon pricing policy federally with a current tax of $10/tonne CO_2 and a steady rise to $50/tonne CO_2 nationwide by 2022. Mission Innovation, a 22-country global initiative to accelerate clean energy innovation, has named CO_2 Capture and Utilization, Clean Energy Materials, and Converting Sunlight as topics of innovation challenges.

Despite a favorable ecosystem for renewable chemical feedstocks, industrial scale-up still entails challenges and risks. 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 concerning CO_2 utilization technologies needs to be carefully crafted and social acceptance of the field needs to be managed. Carbon taxes, nationwide caps on CO_2 emissions, and certifications of CO_2-derived products are examples of public policy tools. From a societal acceptance point of view, people need to be educated about how carbon capture and sequestration is different from carbon capture and utilization. Most important, catalysts and system efficiencies for this technology need to be vastly improved to be economically viable with minimal or no government subsidies (because it is difficult to rationalize sustainable business models based on subsidies and policies that can be easily changed).

Many technoeconomic analyses of solar fuels have analyzed the needed Faradaic efficiencies and energy efficiencies required to match fossil fuel–derived sources (*10*, *30*–*34*). Among them, the largest influence on the levelized cost of production (the net present value of the cost of electricity over the lifetime of the asset) has consistently been the price of electricity. Building on 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; see supplementary text for calculation details). We note that commodity chemical prices are highly variable with respect to geographic region and feedstock (see below). 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. These calculations assume amortization over a plant lifetime of 30 years, a common period for industrial power plants (*35*). 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 CO_2R 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

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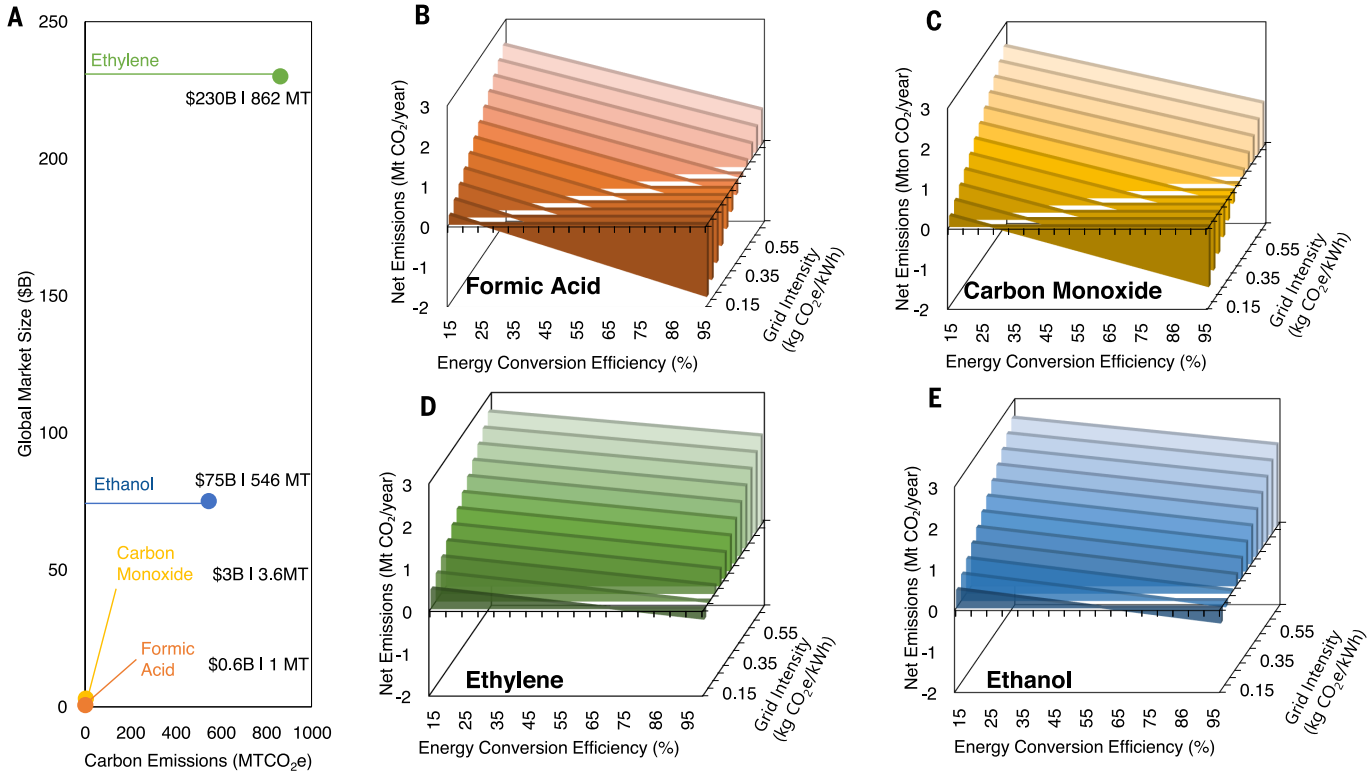

Fig. 3. The emissions impact of electrosynthesized chemicals. (**A**) Market size and fossil-based carbon cradle-to-grave emissions of ethylene (*60*), ethanol (*104*), carbon monoxide (*105*), and formic acid (*106*). (**B** to **E**) Carbon emissions assessment of (B) formic acid, (C) carbon monoxide, (D) ethylene, and (E) ethanol. We assume a plant capacity of 500 MW, global warming impact (GWI) of formic acid (2.00), carbon monoxide (0.57), ethylene (1.1), and ethanol (−0.5) in units of kg CO_2/kg product. Emissions reductions are calculated as a product of global production and GWI.

(*36*). 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 (*36*). Costs have fallen as a result of increased economies of scale, greater competition, and advances in the manufacturing of crystalline silicon. This cost decrease in renewable technologies provides an optimistic and aggressive goal for electrocatalytic technologies.

To quantify the potential impact of electrochemical synthesis of common carbon-based commodity chemicals 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 $230 billion and the highest current production emissions of 862 Mt CO_2e per year (Fig. 3A); these numbers suggest that renewably synthesized ethylene is an attractive target for meaningful global warming impact reduction (*37*). 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 CO_2 emissions (Fig. 3, B to E). We note that capital expenditure factors such as construction and electrode materials were not considered. Assuming a plant capacity of 500 MW, an average grid intensity for the European Union (0.295 kg CO_2e/kWh in 2016) (*38*), and an energy conversion efficiency of 70%, carbon monoxide and formic acid result in carbon emissions that are lower than fossil fuel–derived sources. In order for products to reduce carbon emissions compared to current production, the grid carbon intensity needs to be 0.11 kg CO_2e/kWh or lower. It should be noted that an energy conversion efficiency of 70% has not yet been demonstrated for all products considered herein.

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 because of the ample availability of cheap sugarcane feedstock (*39*). Petrochemical ethylene is produced mainly from steam cracking of fossil fuels (*40*). The majority of carbon monoxide is produced as a component of syngas through coal gasification or steam methane reforming (*41*). Ethanol is primarily produced through fermentation of sugars or corn (*42*). Formic acid is primarily produced through chemical processes using tertiary amines (*43*). 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 processes are well established, advances in biocatalytic processes have the potential to steadily drive down production costs and carbon emissions. For example, the U.S. Department of Energy has set the goal of biofuel production cost at $1 per gasoline gallon equivalent (currently $2.68/gge) with greenhouse gas reductions of 50% by 2020 (*44*).

With these targets in mind, we now outline electrocatalysis as a means for the sustainable production of alcohols, olefins, and syngas.

Direct electrochemical conversion of CO_2 to alcohols

Among the various oxygenates that can be produced directly from electrochemical CO_2R 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 $75 billion (*45*), which suggests that sustainable pathways toward 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 (*46*). A few recent studies have reported high selectivity for direct CO_2R to methanol (*47*–*49*), and further evaluation may yield valuable design

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principles for electrocatalytic systems that can accomplish a direct synthesis. Alternatively, a number of recent studies have reported high selectivity for direct CO_2R and carbon monoxide reduction (COR) to ethanol, and lower but nonnegligible selectivity to n-propanol (50–55).

Traditionally, higher alcohols are predominantly made through the fermentation of sugars (42, 56) or conversion of petrochemicals (57). The food versus 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, water-intensive, and highly sensitive to the overall health of the microorganisms. Important advances have been made toward 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 (57).

Electrocatalysis has the advantage of productivity with a modular and scalable approach to producing small C1 to C3 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 (58). 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 Mt/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 Mt/year), polyvinyl chloride (38 Mt/year), and polystyrene (25 Mt/year) (40); the compound is also used for the production of antifreeze and detergents, and in the agricultural sector as a fruit ripener. Ethylene has traditionally been produced by 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 United States to build many new ethane crackers or retrofit existing steam cracking facilities to accommodate light gas feeds (59).

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 (60). In these regions, where the price of the feedstock 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 (FT) 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, high 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 (61, 62), ions (63, 64), additives (65)], surface structure (66–69), and alloying (70) can have on copper catalyst activity and selectivity toward 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/cm^2 toward ethylene (61, 71).

One possible use 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 (72) 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 4900 Mt and counting (40), and ultimately could 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.

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

Product	Technology	Production cost ($/tonne)	Carbon emissions (tonne CO_2e/tonne produced)
Ethylene	Electrocatalytic	1100	3.07
	Biocatalytic (39)	1200 to 2600	−0.5
	Fossil fuel–derived (114, 115)	600 to 1300	1.1
Carbon monoxide	Electrocatalytic	200	−0.23
	Biocatalytic	—	—
	Fossil fuel–derived (116)	150	0.57
Ethanol	Electrocatalytic	515	1.79
	Biocatalytic (117, 118)	670	−0.5
	Fossil fuel–derived	—	—
Formic acid	Electrocatalytic	108	−0.22
	Biocatalytic	—	—
	Fossil fuel–derived (43, 119, 120)	570	2.00

*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 0.295 kg CO_2e/kWh.

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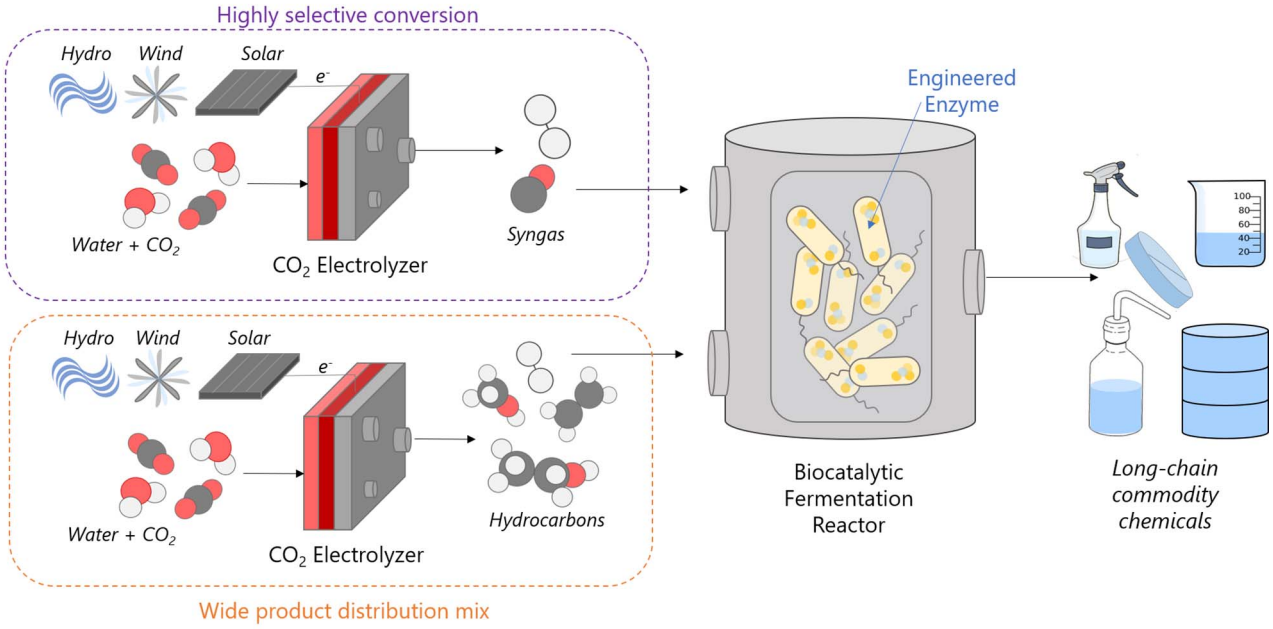

Fig. 4. Bio+electrocatalytic pathways toward long-chain commodity chemicals. Today, CO_2 may be converted to syngas at very high selectivity using silver- or gold-based catalysts (top left). Alternatively, CO_2 can be converted into a wide range of hydrocarbon and oxygenate products using copper-, tin-, or palladium-based catalysts (bottom left). These products can then be used as inputs for genetically engineered enzymes and bacteria to convert to more complex commodity chemicals.

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 FT (*73*) synthesis or fermentation (*74*, *75*) processes that are implemented today. For example, FT production of diesel is an industrially mature process with plants producing 11.5 tonnes/day, an energy conversion efficiency of 51%, and greenhouse gas emissions of 3.8 tonnes CO_2/tonne product, resulting in diesel costs of \$240 to \$525/tonne (*76*). 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 to 0.45 tonnes CO_2/tonne product, the cost of PHA production is \$1650/tonne (*77*, *78*). The contrast between these two syngas utilization routes highlights the advantages and challenges of biocatalytic versus FT routes. FT synthesis operates at much higher rates of production and is less expensive for fuel production but has greater carbon emissions, whereas biocatalytic routes operate at lower volume, produce fewer emissions, and target more expensive specialty 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 (*79*). 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 CO_2R, where ideally a high-yield near-ambient process could generate a stream of CO from CO_2, H_2O, and electricity. Because CO is gaseous under ambient conditions, a selective CO_2R process would enable direct CO evolution and downstream use from an aqueous electrolyzer device. In the case of syngas, H_2 production is complementary and not parasitic to CO_2R, allowing for co-generation because HER and CO_2R have comparable half-cell potentials under nearly identical electrochemical conditions. Although syngas production from CO_2 electrolysis with controlled CO:H_2 ratios is possible (*80*), technoeconomic analysis favors the highest possible selectivity to CO, which is the more valuable product (*33*). Co-generation of CO and H_2 could nonetheless be advantageous for situations where it is essential to have on-site and on-demand syngas production from a single reactor (*81*).

To date, electrochemical CO_2R has been demonstrated with high selectivity and/or reaction rates to CO and syngas in CO_2 electrolyzers (*80*–*84*). 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 CO_2 into syngas was followed by fermentation with bacteria to selectively produce butanol or hexanol, depending on the type of anaerobic digester used (*81*). Stable CO_2 reduction was carried out at industrially relevant current densities (300 mA cm^{-2}) with near 100% Faradaic efficiency for syngas (CO + H_2). Following this applied advance, Siemens and Evonik recently announced a plan to build a test plant with the goal of 20,000 tonnes of annual production capacity for butanol and hexanol (*85*).

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 (*86*, *87*). The current state of the art couples water-splitting electrocatalysts with engineered bacteria to convert CO_2 into polymers and alcohols (*88*, *89*) or nitrogen into ammonia (*90*). These efforts have focused mainly on the electrochemical production of H_2 or acetate as input for bacteria (*87*, *91*).

Although we have chosen to highlight CO 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 source for microorganisms or enzymes to selectively upgrade into the desired oxygenates and hydrocarbons (*92*, *93*).

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

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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 CO_2R (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 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 as a result of the solubility of CO_2 in water. To address this issue, there has been a push toward flow-cell and gas diffusion–type architectures that operate at more industrially relevant current densities (>100 mA/cm^2) (*58*, *94*). Continued research on high-current density electrolyzer architectures is needed to increase the energy conversion efficiency. Product separation is another technical cost that needs to be addressed (*95*). 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 (*96*). Electrochemical CO_2R does not produce ethane, thereby 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 (*97*) that could potentially be used for product separation from CO_2R. Furthermore, the technology developed for carbon capture materials (*98*) could also be used for separation of unreacted CO_2 from ethylene (an easier separation than olefin/paraffin separations) in the output stream. Recent work on optimizing single-pass conversion at high selectivity (*99*) also shows promise in reducing separation costs downstream. It should be noted that there is very limited durability data of CO_2 electrolyzers, as this field is still nascent. Another technical challenge will be to show operating stability over thousands of hours for this technology to be economical.

An additional technical challenge is the need for chemical plants to run continually for both capital efficiency and process safety, highlighting the need for nonintermittent electricity. If an electrochemical plant operates continuously, then its capital utilization is 100% (loading factor), and the system does not require design for time-varying biases. However, renewable baseloads typically command higher electricity market prices, because they are in effect dispatchable. On the other hand, if an electrochemical plant is to use low-cost intermittent renewable electricity (e.g., solar with a typical capacity factor of 0.22), the contribution of capital cost is increased (fig. S2) and the system must tolerate drastic swings (including to unbiased conditions) in driving voltage. As seen in fig. S2, because capital cost is expected to play a notable but not dominant role in total renewable chemicals cost, reducing the capacity factor from 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 cost of Li-ion technology, are 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 such as ethylene also present 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, thereby 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 (*100*). 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 are another factor to consider when discussing scale (see Fig. 2 and fig. S1). Electrocatalytic technology may find a source of cheap electricity from areas with excess hydroelectric capacity, such as northeastern Canada. Transportation costs between large CO_2 emitters and C2 and C3 production facilities are 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 CO_2 point source in Canada, emitting >3 Mt of CO_2 in 2016 (*101*). In Canada, the petrochemical industry is located in three main clusters near Calgary, Sarnia (Ontario), and Montreal. CO_2 point sources in the Alberta oil sands are colocated with the petrochemical plants, whereas CO_2 point sources from Canadian manufacturing, cement, and steel mills in Ontario are also located near Sarnia. However, not all C2 and C3 production sites are located near CO_2 point sources. The cost of CO_2 transportation is estimated to be \$10/tonne CO_2 for 200 km, rising to \$44/tonne for 12,000 km (*102*).

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 Gt CO_2e, representing 19.8% of global greenhouse gas emissions (*103*). The total value of carbon pricing initiatives was valued at \$82 billion in 2018, and these initiatives are only continuing to grow, enhancing the economic case for electroconversion of CO_2.

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 CO_2 footprints. Electrolyzer technologies that readily convert CO_2 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 and could include electrosynthesis of basic building blocks, higher-value fine chemicals in combination with biocatalytic processes, and supplementation of 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 of 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 our knowledge of transforming small, abundant molecules deepens, the possibilities of producing renewable chemicals will multiply. 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 N_2 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 suggest that these challenges can be overcome. As society evolves with new paradigms of operation, continued market

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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.

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