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Perspective

Barriers and opportunities for the deployment of CO_2 electrolysis in net-zero emissions energy systems

Omar J. Guerra,[1,*] Hussain M. Almajed,[2,3] Wilson A. Smith,[1,2,3,4] Ana Somoza-Tornos,[2,4] and Bri-Mathias S. Hodge[1,2,5]

SUMMARY

As energy systems across the globe transition toward net-zero emissions, the decarbonization of hard-to-decarbonize sectors, e.g., industry and transportation, is becoming more crucial. Renewable power-driven carbon dioxide (CO_2) electrolysis has the potential to facilitate this transition by (1) substituting carbon-intensive petrochemical and fuel production and (2) using CO_2 otherwise emitted from industrial processes or CO_2 from the atmosphere; however, because of existing technical and economic challenges, the industrial deployment of this technology is not yet imminent. Here, we present an overview of CO_2 electrolysis technologies to identify key hurdles in view of the industrial deployment of this technology in net-zero emissions energy systems. From the technology standpoint, catalysts should be developed with enhanced activity, selectivity, and stability/durability as well as membranes and reactors that prevent carbonate formation or crossover, achieve higher reaction rates, e.g., >1 A/cm^2, and demonstrate long-term stability, e.g., >5 years. Conversely, from the system integration standpoint, impurity-tolerant CO_2 electrolysis systems need to be developed and tested under relevant conditions, e.g., CO_2 streams with traces of impurities (NO_x, SO_x, O_2, N_2, H_2S, etc.). Additionally, the quantification of pros and cons of different integration pathways for CO_2 capture and CO_2 electrolysis requires further research. Moreover, the integration with variable renewable power sources—e.g., wind and solar photovoltaic power—and electricity markets requires a better understanding. For instance, the value of CO_2 electrolysis flexibility in view of variable renewable power supply or dynamic electricity prices is not well understood.

INTRODUCTION

Driven by a variety of factors, including the need to stabilize anthropogenic carbon emissions, falling costs of renewable energy, and social pressures, many companies and local, regional, and national governments have committed to reach net-zero carbon emissions in the energy system by 2050.[1] Achieving this goal at scale is a daunting task, which will require significant efforts to reduce carbon emissions in hard-to-decarbonize energy sectors, e.g., the transportation and industrial sectors.[2,3] For instance, achieving a global net-zero energy system by 2050 could require the cumulative reduction of 8 Gt carbon dioxide (CO_2) and 6.5 Gt CO_2 in the industrial and transportation sectors, respectively, from 2020 to 2050[4] (Figure 1A). Moreover, approximately 7.6 Gt CO_2 would need to be captured and stored

CONTEXT & SCALE

The deployment of CO_2 electrolysis, i.e., powered by renewable or low-carbon energy sources, could facilitate the transition toward net-zero emissions energy systems by (1) replacing carbon-intensive petrochemical and fuel production and (2) using otherwise emitted CO_2 from industrial processes or CO_2 from the atmosphere. However, although significant advances have been achieved in the selectivity, i.e., Faradaic efficiency, and production rate, i.e., current density, of both low- and high-temperature CO_2 electrolysis, the large-scale industrial deployment of this technology is not yet imminent. Rapid industrial adoption of these technologies is a critical step toward reducing cumulative CO_2 emissions from the chemical industry and thus mitigating the worst impacts of climate change. To this end, catalysts with improved activity, selectivity, and stability/durability as well as membranes and reactors that prevent carbonate formation or crossover, achieve higher reaction rates, e.g., >1 A/cm^2 and demonstrate long-term stability, e.g., >5 years, should be developed. Moreover, the integration of CO_2 electrolysis

or used in 2050, including 5.2 Gt CO_2 from emitting point sources—i.e., fossil fuel combustion, ammonia and bioethanol plants, and industrial processes[4]—and 1.0 Gt CO_2 from the air, i.e., via direct air capture (DAC)[4] (Figure 1A). In this context, CO_2 electroreduction to chemicals and fuels could facilitate the pathway toward a net-zero energy system by (1) replacing conventional carbon-emitting fuel and petrochemical processes and (2) using CO_2 either removed from the atmosphere or prevented from reaching the atmosphere, as shown in Figure 2. For instance, based on 2019 global consumption data (Figure 1B), producing carbon monoxide (CO), formic acid, ethylene, and ethanol via CO_2 electrolysis has the potential to use approximately 1 Gt CO_2 per year (Figure 1C), which is equivalent to 100% of the projected CO_2 required to be captured via DAC or 19% of the projected CO_2 capture requirements from fossil fuel combustion and industrial processes in 2050. Note that fossil-fuel-based CO, formic acid, and ethylene, as well as biocatalytic ethanol, are carbon intensive (Figure 1C). Thus, if driven by renewable or low-carbon power sources, CO_2 electrolysis could reduce the carbon footprint of chemicals and fuels, which could facilitate the decarbonization of the transportation and industrial sectors. Regarding market opportunities for CO_2 electrolysis-based chemicals and fuels, both commodity price and consumption (demand) are important. For instance, formic acid has a higher market price than CO but a relatively low demand, implying a potential rapid market saturation[5] (Figure 1B). Note that these decisions will be location dependent and can vary based on the current market prices for each bulk chemical, e.g., the average prices for CO in Canada, Germany, and Japan are 15% lower, 62% higher, and 102% higher than the 2016–2020 average US price, respectively.[6] From a market potential standpoint, commodities with both relatively high prices and demand are attractive targets for CO_2 electrolysis-based production, e.g., ethylene, ethanol, and methanol[10–13] (which arguably could be used to produce sustainable aviation fuel,[14,15] among other products, expanding the market for CO_2 electrolysis products); however, despite recent progress on the fundamental and mechanistic scientific understanding,[16–19] catalyst and reactor design,[20–23] and scale-up[24,25] and commercialization[26–29] of CO_2 electrolysis, large-scale industrial deployment of this technology is not yet imminent. Indeed, techno-economic analyses suggest that significant capital and operating cost reductions are required for CO_2 electrolysis to be profitable or cost competitive with traditional fossil-based or biocatalytic production processes, particularly for C_{2+} products, e.g., ethylene and ethanol[30–32] (Figure 1D). Note that electricity prices and consumption are key cost drivers for CO_2 electrolysis.[33,34] Additionally, C_{2+} products tend to have a lower maximum CO_2 mitigation potential, in grams of CO_2 per kWh, than C_1 products (Figure 1D), which could make CO_2-electrolysis-based ethylene and ethanol production costs more sensitive to electricity prices than CO and formic acid. Yet, the production cost and cost drivers for a given CO_2 electrolysis-based product strongly depend on both the modeling approach, e.g., simulation versus optimization analysis or empirical versus first-principle process models, and the assumptions around technology cost, electricity prices, and technology performance, as measured by current density, energy efficiency, Faradaic efficiency, cell voltage, and CO_2 single-pass conversion.[9,33,34] Additionally, policy mechanisms and/or financial incentives—e.g., production tax credits, carbon pricing, and mandates—could facilitate the earlier economic competitiveness of CO_2 electrolysis pathways.[9,30] Note that CO_2 electrolysis can open avenues for the decentralized production of chemicals, which could make the corresponding supply chain more resilient to disruptions.[35] However, the centralized or decentralized production of chemicals is an open question that depends on many factors, including availability of CO_2 sources, availability of cheap renewable power sources, spatial distribution of demand for chemicals, etc.

with CO_2 capture processes, renewable power sources, and/or electricity markets requires a better understanding.

[1]National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401, USA

[2]Renewable and Sustainable Energy Institute, University of Colorado, Boulder, CO 80309, USA

[3]Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO 80309, USA

[4]Delft University of Technology, Department of Chemical Engineering, Van der Maasweg, 92629 HZ Delft, the Netherlands

[5]Department of Electrical, Computer & Energy Engineering, University of Colorado, Boulder, CO 80309, USA

*Correspondence: omarjose.guerrafernandez@nrel.gov

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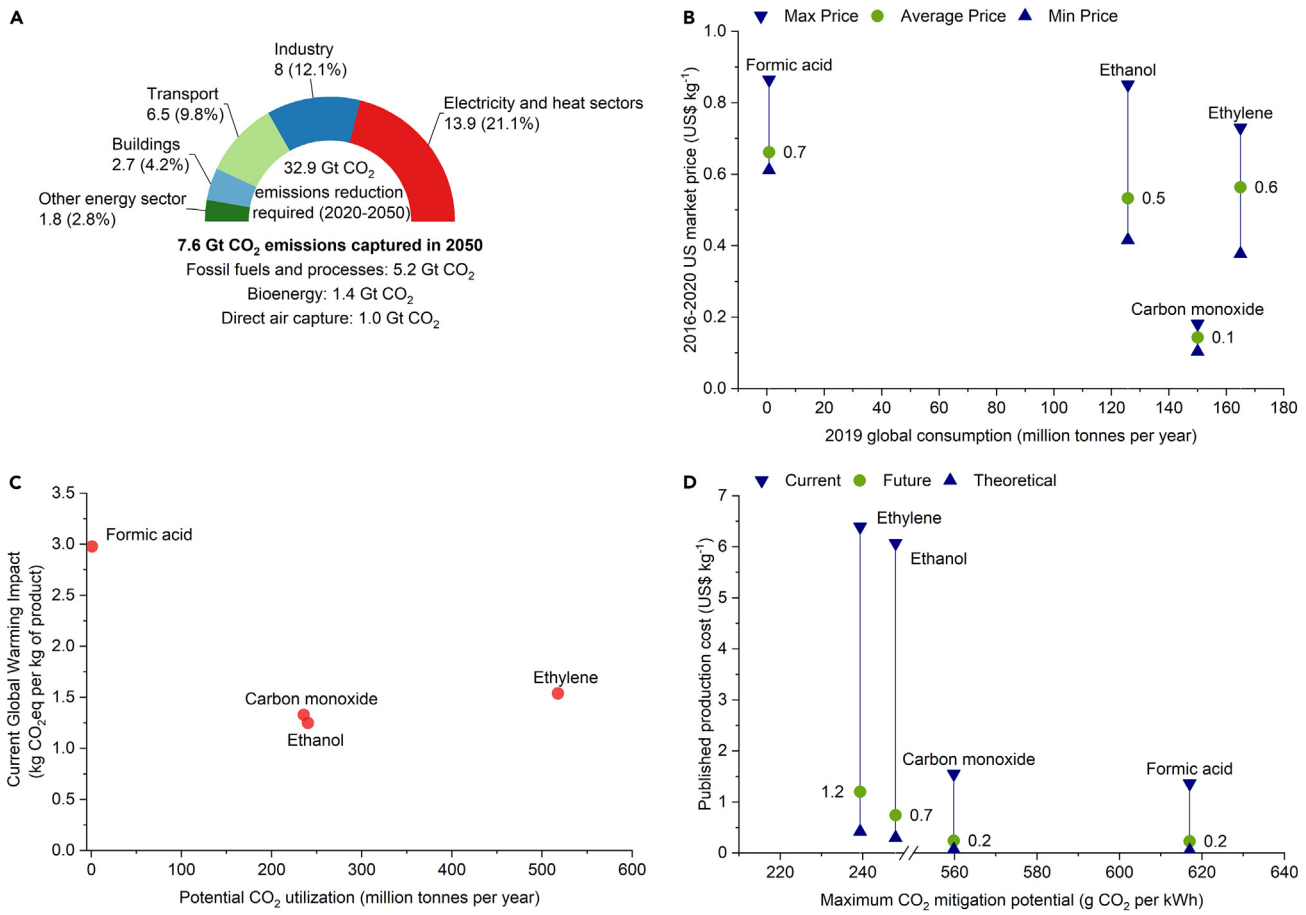

Figure 1. Carbon emissions in view of a net-zero global energy system by 2050, chemicals and fuels emissions and market data, and estimated CO_2 electrolysis production cost for different chemicals and fuels

(A) Required carbon emissions reduction by sector from 2020 to 2050 and required carbon emissions captured by 2050.[4]

(B) Year 2019 global consumption and 2016–2020 US market prices for selected chemicals and fuels.[5,6]

(C) Global warming impact[7,8] for fossil-based or biocatalytic production and potential CO_2 utilization for selected chemicals and fuels. Potential CO_2 utilization for a given product is calculated based on the global consumption and the ratio of the associated molecular weights.

(D) Estimated production costs[9] and maximum CO_2 mitigation potential, i.e., calculated based on the enthalpy of reaction and the reaction coefficients, for selected chemicals and fuels.

This manuscript provides an overview of CO_2 electrolysis in view of net-zero energy systems, as illustrated in Figure 2. First, we provide a detailed description of different figures of merit relevant for the energy systems integration of CO_2 electrolysis, as well as proposed industrial benchmarks and the corresponding status quo of the technology for both low-temperature and high-temperature electrolysis. Additionally, we illustrate how each figure of merit could affect the total system cost for CO_2 electrolysis, when possible. We then summarize recent advances and remaining research gaps in catalysts and membranes for CO_2 electrolysis, and we discuss progress toward practical reactor and process designs. An overview of the opportunities and challenges associated with the integration of CO_2 capture and CO_2 electrolysis is then presented. Finally, we discuss the integration pathways for CO_2 electrolysis, renewable energy sources, and electricity markets, including a discussion around the variability of renewable power sources, the dynamics of electricity prices, and the flexibility of CO_2 electrolyzers. Note that, as far as we are aware, this is the first article that provides a holistic overview of CO_2 electrolysis in view of net-zero emissions energy systems, including not only the advances and challenges in catalysis,

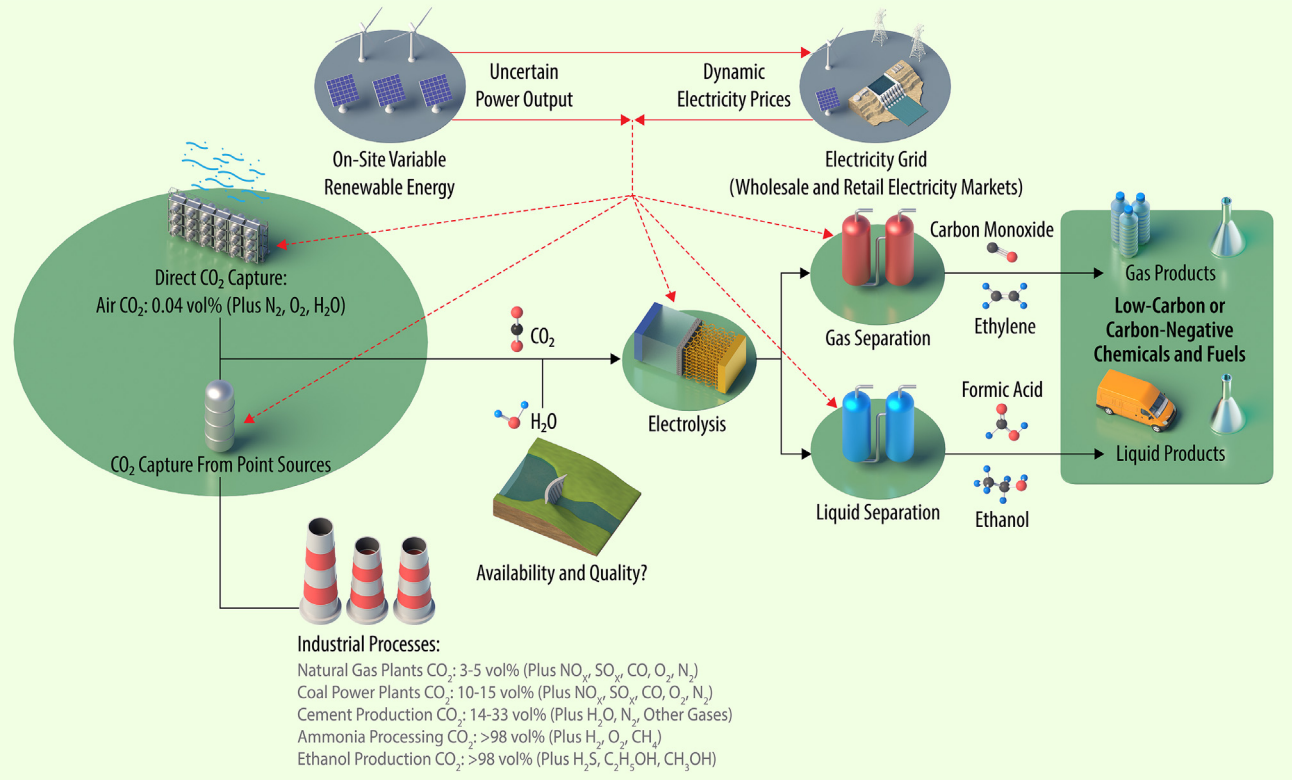

Figure 2. Role of CO_2 electrolysis in future net-zero energy systems
The composition of different CO_2 streams[76,106] is included.

membranes, and reactors but also the integration with CO_2 capture, variable renewable energies, and electricity markets.

FIGURES OF MERIT, INDUSTRIAL BENCHMARKS, AND STATUS QUO OF CO_2 ELECTROLYSIS

Concerning CO_2 electrolysis thermodynamics and cell designs, total energy demand, i.e., enthalpy of formation ($\Delta H_f = \Delta G_f + T\Delta S_f$), can be supplied via either electrical energy, i.e., the Gibbs free energy of formation (ΔG_f) term, or heat, i.e., the entropy portion ($T\Delta S_f$), in which T is temperature, and ΔS_f is the entropy of formation. Thus, depending on the reaction, at elevated temperatures, a larger fraction of the total energy demand could be provided via heat supply. This represents an opportunity to use the Joule heat—heat that is inevitably generated when electricity is passed through a nonzero resistance cell,[36,37] which reduces the electricity consumption (increases energy efficiency). Moreover, the reversible cell voltage—the minimum required cell voltage or Nernst cell voltage—as expressed by $E_{rev} = \frac{-1}{nF}\Delta G_f$, in which n = number of electrons involved in the reaction, and F = Faraday's constant, tends to decrease with temperature (depending on the reaction). Therefore, depending on the desired product, it could be advantageous to operate CO_2 electrolyzers at higher temperatures. Note that the reversible cell voltage, E_{rev}, is different from the thermoneutral voltage ($E_{tn} = \frac{-1}{nF}\Delta H_f$), which represents the minimum voltage required to supply the energy demand via only electricity, without net heat inflow or outflow.[36,38] Additionally, $E_{rev} - E_{tn}$ represents the overvoltage needed to account for the entropic portion of the energy demand of the global reaction.[38] In general, electrolysis cells have at least three elements: two

electrodes (cathode and anode) connected via an electrolyte.[37] Depending on the electrolyte and operating temperature, electrolysis technologies can be classified as follows: low temperature (25°C–80°C), e.g., electrolyte based on aqueous solutions, and high temperature (>600°C), e.g., electrolyte based on solid ceramic material (solid oxide cell) or carbonate melt (molten carbonate cells).[21,22,37] For CO production, high-temperature electrolysis could perform better than low-temperature electrolysis in terms of Faradaic efficiency, power consumption, and energy efficiency; however, low-temperature electrolysis could be more suitable for the direct production of formic acid and C_{2+} chemicals, which have not yet been synthesized directly via high-temperature electrolysis.[37] Thus, the appropriate CO_2 electrolysis technology depends on the desired product(s) and operating conditions, among other factors. Note that the scope of this perspective is to review CO_2 electrolysis due to its potential integration with energy systems. Thus, other pathways for the CO_2 reduction (i.e., microbial electrosynthesis, biological conversion, and thermochemical conversion[5]) are excluded.

Effective CO_2 electrolysis systems might require fast reaction rates, high selectivity, low power consumption, high CO_2 utilization, and operational stability.[20,29,38] Both the catalyst and the electrolyzer play a role in achieving these requirements,[5,21,23] but the quantification of these characteristics can be a challenge. Thus, different figures of merit have been proposed to quantify the operational performance of CO_2 electrolysis systems, including current density, Faradaic efficiency, cell voltage, long-term stability, and single-pass conversion.[5,21,37] Note that the use of a given figure of merit depends on the particular scientific community. For example, Faradaic efficiency is widely used by the low-temperature CO_2 electrolysis community but rarely mentioned by the high-temperature CO_2 electrolysis community, which uses the area-specific resistance as a figure of merit.[37] The following sections are devoted to the definition of figures of merit relevant for the energy systems integration of CO_2 electrolysis and the corresponding industrial benchmark and state of the art.

Figures of merit and industrial benchmark

Cell voltage

The cell voltage (v_{cell}) represents the potential applied across the electrolyzer. The cell voltage can be calculated as a function of the thermoneutral voltage (E_{tn}),[39,40] the cathodic and anodic overvoltage associated with kinetic activations (E_{act}),[41,42] the overvoltage caused by existing ohmic resistances in the electrolyzer (E_{ohm}),[42,43] and the cathodic and anodic overvoltage caused by mass transport limitations (E_{mt}),[44,45] as expressed by Equation 1.[25,33,38] Electrolyzer power consumption (P) depends on both the cell voltage and current flow, e.g., $P = I.v_{cell}$, where I is the total current flow. Thus, reducing the cell voltage is critical to reducing the power consumption and electricity costs for both low-temperature and high-temperature CO_2 electrolysis systems.[22,46] For practical applications of CO_2 electrolysis, e.g., using the oxygen (O_2) evolution reaction as the anodic process and based on the competitiveness with hydrogen evolution reaction, the cell voltage is likely to be lower than 3 V[46] or the overpotential lower than ~0.4 V, depending on the product.[38]

$$v_{cell} = E_{tn} + E_{act} + E_{ohm} + E_{mt} \quad \text{(Equation 1)}$$

Current density

The current density (j) is defined as the electron flux (current flow), I in milliamperes, per unit of geometric area of the electrode, A, in cm^2, as expressed by Equation 2. Maximizing the current density minimizes the required electrolyzer size and,

consequently, capital cost; however, depending on the catalyst and the electrolyzer configuration, increasing the current density tends to increase the required overpotentials (and thus the required cell voltage), e.g., as described by the specific current-voltage or polarization curve,[37,38,47] which increases the power consumption and thus electricity cost (operating cost). Therefore, effective electrolysis systems should be designed and operated to balance the benefits of high current densities and low cell voltages. Note that, in general, high-temperature CO_2 electrolysis can achieve higher current densities at lower cell voltages than low-temperature CO_2 electrolysis[22] and has a higher technology-readiness level (TRL),[37] but performance, degradation, and scale-up remain major challenges for wider adoption.[22] Moreover, for a fixed cell voltage, the current density is a function of catalyst intrinsic activity, load, and utilization, as well as the removal rate of products and the transport rate of reactants.[38] Typical current densities for proton-exchange membrane hydrogen electrolyzers (>1,000 mA/cm^2) could be used to define a benchmark for CO_2 electrolysis.[38] Note that this benchmark could depend on the specific CO_2 electrolysis product.[38] For instance, based on a techno-economic analysis, the current density target was estimated to be 250 mA/cm^2, 100 mA/cm^2, 300 mA/cm^2, and 600 mA/cm^2 for CO, formic acid, ethylene, and ethanol, respectively.[32]

$$j = \frac{I}{A} \qquad \text{(Equation 2)}$$

Faradaic efficiency

The Faradaic efficiency (FE_i in %) denotes the ratio of the charge used to form a given product to the total charge input into the system, e.g., Q in C, as expressed by Equation 3. Terms z_i, n_i, and F denote the number of electrons transferred per molecule of product i, the amount of moles of product i formed, and the Faraday constant, 96,485 C/mol, respectively. The Faradaic efficiency is a measure of the selectivity of the electrochemical process. Thus, higher Faradaic efficiencies could reduce the cost of downstream separation and the energy requirements for CO_2 electrolysis.[23] Therefore, a value of 80% has been proposed as an industrial benchmark for the Faradaic efficiency of CO_2 electrolysis products.[38] Note that the partial current density for a given product, e.g., j_i, can be calculated as a function of the Faradaic efficiency and the total current density, as expressed by $j_i = \frac{I.(FE_i/100)}{A}$. Additionally, the energy efficiency, E_{eff}, can be calculated as a function of the Faradaic efficiency, the cell voltage, and the thermoneutral voltage, $E_{eff} = \frac{\sum_i E_{tni}.FE_i}{v_{cell}}$, in which E_{tni} represents the thermoneutral voltage for product i.

$$FE_i = \frac{z_i.n_i.F}{Q}.100 \qquad \text{(Equation 3)}$$

Single-pass conversion

Single-pass conversion or carbon efficiency, ξ_{CO_2}, is defined as the ratio of total carbon converted into products, $\sum_i C_i.n_i$ (C_i is the number of carbons in product i), to the total carbon entering the system, $CO_{2\,in}$ (number of moles of CO_2 entering the system), as expressed by Equation 4.[37,48] For gas products and flow electrolyzers, the concentration is determined by the single-pass conversion.[48,49] Thus, high single-pass conversions are desired to minimize product separation costs.[48,49] Low single-pass conversions are often caused by carbonate formation in alkaline flow cells or crossover in neutral membrane electrode assemblies (MEAs).[50,51] One alternative to address this issue is to use a two-step process configuration, including the CO_2 electroreduction to CO in a solid oxide cell[50,52] or a non-alkaline electrolyzer[53] followed by CO electroreduction to C_{2+} products in a MEA.[50,52,53] Concerning required single-pass conversions for practical applications of CO_2

electrolysis, e.g., based on the cost competitiveness with conventional processes, 30% and 15% single-pass conversions have been proposed as industrial benchmarks for C_1 (CO and formic acid) and C_2 (ethylene and ethanol) products, respectively.[32]

$$\xi_{CO_2} = \frac{\sum_i C_i . n_i}{CO_{2in}} \quad \text{(Equation 4)}$$

Long-term stability

Mechanical, thermal, and chemical stabilities are required for the long-term stability of both low- and high-temperature CO_2 electrolyzers.[22,54] Long-term stability is expected to have a significant impact on the economics of electrolyzers.[32,55] For example, regardless of the per-unit capital cost and based on a 10% discount rate, increasing the lifetime from 3 to 5 years or from 3 to 10 years will reduce the annualized electrolyzer capital cost by ~34% and ~60%, respectively. Durability tests that are performed under potentiostatic (constant voltage) or galvanostatic (constant current density) conditions[37] have demonstrated a stack lifetime of 2.5 years (21,900 h) for high-temperature CO_2 electrolysis.[22] In contrast, there is a need to demonstrate the stability of low-temperature CO_2 electrolyzers beyond 1,000 h,[21,56] which has been demonstrated for formic acid only.[57] The fuel-forming electrode is one of the main sources of degradation in the solid oxide cell technology,[22] and catalyst failure, cathode flooding, and carbonate salt formation are the primary limiting factors for the long-term stability of low-temperature electrolyzers.[21] Moreover, for commercial applications, a 5-year lifetime has been proposed as a benchmark for the long-term stability of CO_2 electrolyzers.[32]

Status quo of CO_2 electrolysis

Although significant progress has been made in improving the performance of CO_2 electrolysis technologies, most efforts have been devoted to achieving high Faradaic efficiencies, e.g., >67% for CO and formic acid, and current densities, e.g., from hundreds of mA/cm^2 to more than 1 A/cm^2 (see Figure 3). Indeed, some studies do not report single-pass conversion or the operational stability of the tested CO_2 electrolysis system. Thus, it is imperative that new studies on CO_2 electrolysis report not only the Faradaic efficiency and current density but also the cell voltage, single-pass conversion, and operational stability. For example, regardless of the product, the operational stability of CO_2 electrolysis systems has been largely overlooked. Nevertheless, operational stability is key for the industrial deployment of CO_2 electrolysis systems because degradation has a direct impact on the lifetime and economics of industrial processes. The development of accelerated degradation testing methods could help to assess the long-term stability of CO_2 electrolysis systems.[20,30] On the other hand, the cell voltage has a direct impact on power consumption and electricity costs, which affects the operating cost. Therefore, more attention should be paid to reducing the cell voltage of CO_2 electrolysis.[46] To this end, the testing of new anodic chemistries, e.g., organic oxidation, to replace the O_2 evolution reaction could be crucial.[39,40,58,59] However, the coupling of the electrolysis systems has some practical issues related to product scale between the subsystems and deserves further attention.[60] Note that total electricity cost depends on both electricity consumption, which could be reduced by decreasing the cell voltage while keeping high current densities, and electricity prices, which could be reduced by optimizing the integration of CO_2 electrolysis systems with renewable power sources and electricity markets. However, although significant attention has been given to the cell voltage, little attention has been given to the integration of CO_2 electrolysis systems with renewable power sources and electricity markets. This topic is addressed in this manuscript. Additionally, the single-pass conversion of CO_2 has

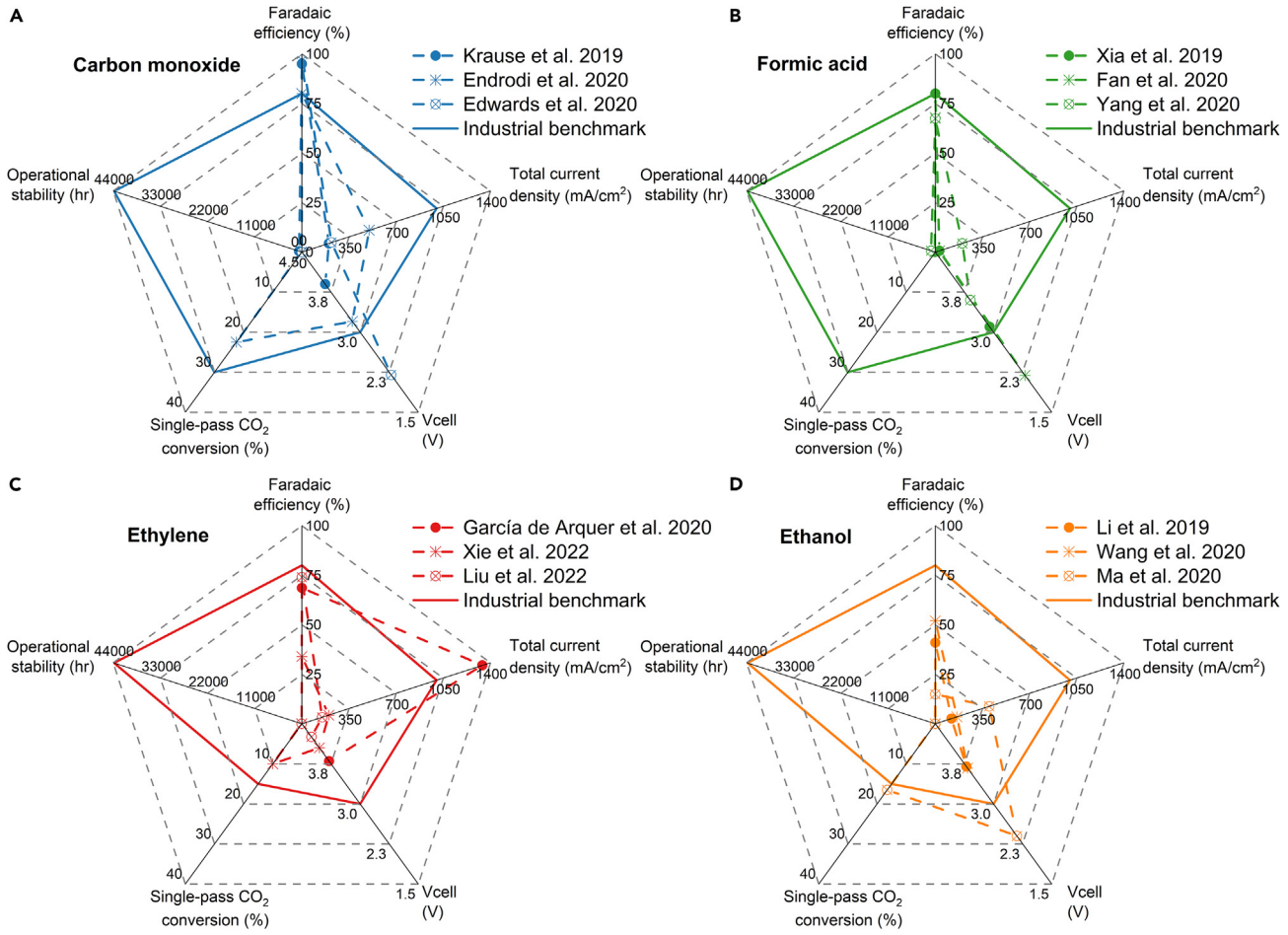

Figure 3. Representative state-of-the-art metrics for relevant CO_2 electrolysis products

(A) Figures of merit for CO.[139–141]

(B) Figures of merit for formic acid.[57,142,143]

(C) Figures of merit for ethylene.[144–146]

(D) Figures of merit for ethanol.[147–149] The corresponding industrial benchmarks are included as a reference. Note that the cell voltage axis is in reverse order. Note that we only included studies that report most of the five figures of merit defined in this section. However, there are studies that report a better performance for a given figure of merit, e.g., 100% Faradaic efficiency, but do not report two or more than two of the other figures of merit. As a reference, we provide some metrics for high-temperature CO_2 electroreduction to CO. Ebbesen et al.[150]: voltage = 1.0 V, area-specific resistance = 0.3 Ω cm^2, Faradaic efficiency = 100%, and energy efficiency = 92%. Kaplan et al.[151]: voltage = 1.1 V, area-specific resistance = 1.9 Ω cm^2, Faradaic efficiency > 96%, and energy efficiency = 74%.

a direct effect on the product separation energy requirements and costs, i.e., the lower the single-pass conversion is, the higher the product separation energy requirements and costs are.[48,61] Therefore, different approaches have been proposed to increase the single-pass conversion of CO_2 electrolysis,[61] including CO_2 electrolysis in acid media,[62] CO_2 regeneration from carbonate,[63] two-step CO_2 electrolysis (CO_2 electroreduction to CO followed by CO electroreduction to C_{2+} products),[52] and direct electrolysis from CO_2 capture liquids.[64] As far as we are aware, however, there is no single CO_2 electrolysis system that performs well not only in terms of Faradaic efficiency and current density but also in terms of cell voltage, single-pass conversion, and operational stability, as evidenced by the representative state-of-the-art metrics from the literature (see Figure 3). Indeed, there is a trade-off between high single-pass conversion of CO_2 and high current density operation due to CO_2 starvation.[65]

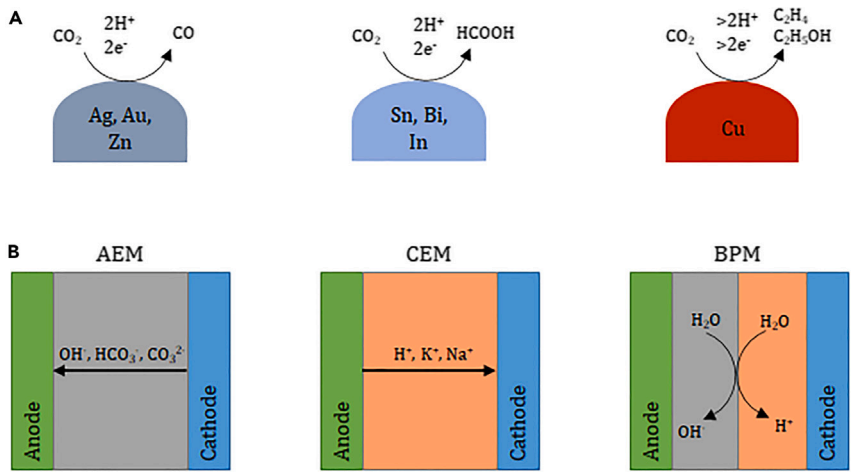

Figure 4. Catalysts and membranes for CO_2 electrolysis

(A) Catalysts for CO_2 electroreduction to CO, formic acid, and C_{2+} products.

(B) Membranes for CO_2 electrolysis.

CATALYSTS, MEMBRANES, AND REACTORS FOR CO_2 ELECTROLYSIS

Catalyst for CO_2 electrolysis

Catalysts play a critical role in the electroreduction of CO_2 to value-added products. Similar to other catalytic processes, the key metrics to evaluate catalysts in CO_2 electrolysis are activity, which is measured by current density or turnover frequency, selectivity, which is measured by Faradaic efficiency, and stability/durability, which is measured by time.[16,17]

Catalyst activity

Early studies on CO_2 electrolysis were performed in aqueous electrochemical cells, typically in an H cell configuration.[28,66] In these architectures, CO_2 is bubbled and saturated in electrolytes, which are then directly reduced at the catalyst surface. Although these initial studies were and still are critical in our understanding of catalyst selectivity for CO_2 electrolysis, the low solubility of CO_2 in typical electrolytes (~34 mM) means that current densities are limited to 30–40 mA/cm^2.[28,66] Recent progress has seen the use of gas diffusion electrodes (GDEs) and MEAs, which can feed pure or humidified CO_2 directly to a catalyst, increasing reaction rates to hundreds of mA/cm^2 and in some cases exceeding 1 A/cm^2.[20,21,67] This improvement can have a significant impact on the scalability of CO_2 electrolyzers, especially when achieved at low cell voltages.

Catalyst selectivity

Although the reduction of CO_2 can make up to 18 unique products, systematic studies of catalysts during the past few decades have revealed that certain products can be made selectively from certain families of catalysts. For example, it has been shown that Ag, Au, and Zn are highly selective for the formation of CO, whereas Sn, In, and Pb selectively produce formate/formic acid (see Figure 4A).[21,68] Uniquely, Cu has been found to be the only base metal catalyst to produce higher-order hydrocarbons (see Figure 4A).[17,69] In recent years, researchers have found new catalysts, such as NiP, that can also produce hydrocarbon products,[70] albeit at much lower current densities and with lower selectivities than Cu or modified Cu electrodes.

Although much initial basic research on CO_2 electrolysis has focused on metallic catalysts and their intrinsic activity and selectivity toward various products, recent

attention has been paid to how to steer selectivity by tailoring the microenvironment around the catalytic active site.[69,71,72] One of the primary ways this has been done is by tailoring the electrolyte, or by incorporating ion-conducting polymers (ionomers) that act as both a binder for catalyst particles but also tune fluxes and concentration gradients near the catalyst.[69,71] By moving beyond the catalyst, these recent approaches have shown that multiple materials can be used to tune the catalytic microenvironment, which might be a more robust way to tune selectivity beyond an intrinsic catalytic site. It is worth noting, however, that product selectivities above 80% are likely sufficient for scalable CO_2 electrolyzers, particularly for the production of C_1 products (i.e., CO and formic acid).[32]

Catalyst stability/durability

Perhaps the most important metric in electrocatalysis and CO_2 electrolysis is stability or durability. Although many catalysts and electrode assemblies exist that can achieve high activity and selectivity, it is imperative that these metrics can be maintained for thousands of hours at industrially relevant conditions (i.e., voltage, current, pressure, flow, etc.).[17,28] Because most foundational work in the CO_2 electrolysis field has focused on activity (current density), selectivity (Faradaic efficiency), and energy efficiency (voltage), less effort has been focused on how to maintain these metrics for long periods of time. Further, in assessing the ability of CO_2 electrolysis to integrate with industrial systems and a renewable power grid, even less attention has been paid to system durability, which is measured by fluctuating changes in input power. The ability for electrochemical systems to operate under variable power loads offers flexibility for renewable electricity integration in ways that thermochemical-based technologies might not be able to offer. Therefore, future work is needed to see how CO_2 electrolysis systems respond to variable electricity supplies.

Membranes for CO_2 electrolysis

Although catalysts receive the most research focus in the CO_2 electrolysis field because of their importance in providing active sites for selective chemical transformations, the other components of an electrolyzer play as important of a role as the catalyst itself in determining the activity, selectivity, and durability of a catalyst.[20,54] Ion exchange membranes play a vital role in many electrochemical processes, separating products from the anode and cathode in addition to providing ion conductivity between the two electrodes. Cation exchange membranes (CEMs), anion exchange membranes (AEMs), and bipolar membranes (BPMs) have all been used in CO_2 electrolysis[20,61] (Figure 4B) and offer different advantages and disadvantages based on electrolyte composition/pH, desired product, and reactor architecture. CEMs can be useful to keep a high proton flux toward the catalyst, especially for restricting carbonate formation, but the low local pH can degrade electrodes and promote hydrogen evolution in gaseous CO_2 electrolysis.[20] AEMs are used to move hydroxide ions away from the catalyst microenvironment to reduce the number of homogeneous reactions they can have with CO_2, e.g., forming carbonate.[20] BPMs can better prevent crossover than monopolar membranes but suffer from large ohmic resistances that decrease the overall energy efficiency of the device.[20] Indeed, BPM voltage contribution was estimated to be 2.56 ± 0.28 V at a current density of 200 mA/cm^2, which was about 57% of the total cell voltage.[46] Replacing the BPM with an AEM shows a membrane voltage contribution of 0.71 ± 0.10 V.[46] Such a high difference can impact the scalability of CO_2 electrolysis tremendously due to the high dependency of electrolysis systems on electricity prices.[31,33] To put this change into perspective, a 200% increase in cell voltage can increase the cost of ethylene by more than 75%,[61] substantially reducing the economic

performance of CO_2 electrolysis. Therefore, the choice of membrane for CO_2 electrolyzers should be carefully considered in concert with the overall desired reaction product and durability of components to their preferred microenvironment. A more detailed discussion regarding stability and scalability of membranes for CO_2 electrolysis is provided in the literature.[20,54]

Reactors for CO_2 electrolysis

Several designs of electrochemical reactors can be used to assess components such as catalysts and membranes, whereas others can be considered for scaling up this technology to industrially relevant operational conditions. In general, CO_2 electrolyzers should be designed to reduce the electrical resistance, which reduces the energy consumption, and to maintain long-term stability/operation.[29] Pioneering work on CO_2 electrolysis was carried out in aqueous H cells, where catalysts were assessed to determine their product selectivity under well-defined conditions.[28,66] The utility of these studies was enormous in helping to develop the interest and foundational knowledge in this field; however, this reactor configuration is limited by poor mass transport and low CO_2 solubility. Flow reactors that incorporate GDEs can overcome the poor mass transport issues associated with gaseous reactants, e.g., the solubility of CO_2 and CO in aqueous electrolytes is limited.[23,73] The utilization of GDEs as supports for catalysts has shown the ability to increase reaction rates from mA/cm^2 to A/cm^2.[20,21] Reactors that use GDEs can have a flowing liquid electrolyte to aid liquid transport and separations, MEAs that use a membrane to directly connect the anode and cathode have shown the most promise for scalable reactor architectures.[20,25] Note that there is a breadth of reactor architectures/configurations that may affect the overall performance just as much as a catalyst, e.g., zero gap MEA and systems with flowing electrolyte.[60,74] Moreover, the experimental CO_2 electrolysis data obtained at laboratory scale cannot be safely extrapolated to industrial scale electrolyzers.[29] Thus, testing and validation at large scale is critical to obtain more reliable industrial CO_2 electrolysis data, which is very scarce in the CO_2 electrolysis literature.

In addition to the choice of reactor architecture, the operational conditions must be considered, not only in the context of improving CO_2 electrolysis[75] but also in allowing for (1) the most direct integration with up- and downstream processes,[28,43] (2) process scalability in the context of CO_2 utilization,[25] and (3) cost effectiveness.[9] From the technology standpoint, there is a need to develop CO_2 electrolysis systems that simultaneously achieve cell voltages lower than 3 V, current densities greater than 1 A/cm^2, Faradaic efficiencies greater than 80%, single-pass conversion greater than 30% for C_1 products (or 15% for C_2 products), and demonstrate long-term stability, e.g., lifetime of 5 years or more. Additionally, future development of CO_2 electrolyzers should consider the temperature and pressure needed in up-/downstream processes to reduce compression/expansion energetic costs.

INTEGRATION OF CO_2 ELECTROLYSIS WITH CO_2 CAPTURE

The integration of CO_2 electrolysis with upstream processes requires the simultaneous process design of both CO_2 electrolysis and capture systems. For instance, some flue gas streams include sulfur oxides (SO_x) and nitrogen oxides (NO_x) impurities[76–79] that need to be either separated from captured CO_2 during the capture step or tolerated by the CO_2 electrolyzer in the conversion step. Indeed, although CO_2 electroreduction to C_{2+} products is desired, the use of CO_2 captured from point sources may not be possible due to the detrimental effect of SO_2 on Cu.[23] On the other hand, CO_2 captured from air has fewer impurities, which can make it more

attractive to the currently commercially available CO_2 electrolyzers that are intolerant to such impurities. In this section, we discuss the opportunities and challenges of the upstream integration of CO_2 capture and electrolysis from a futuristic (i.e., 2050) viewpoint. We focus on the initial concentration of CO_2 because it is a main driver in reducing the minimum work required for the separation process, and thus its cost per tonne of CO_2. For instance, the minimum work required for a point-source carbon capture from a coal-fired power plant is estimated to be 5.87 kJ per mol of CO_2, whereas the same metric for DAC is estimated to be 20.48 kJ per mol of CO_2.[80]

CO_2 capture from point sources

High concentration streams

The most mature CO_2 capture processes (TRLs 9–11) use physical separation (e.g., Rectisol and Selexol) and chemical absorption (e.g., monoethanolamine) methods to capture CO_2 from highly concentrated streams (e.g., in ammonia and ethanol productions).[76,79,81,82] Physical separation methods require the use of weak physical forces to capture the otherwise-emitted CO_2, whereas chemical separation methods demand stronger forces that can separate CO_2 from other impurities, especially at lower CO_2 concentrations. Such methods have already been integrated in the chemicals industry, which makes them the most mature, and thus the cheapest, options for mitigating CO_2 emissions. Indeed, the levelized cost of capturing CO_2 from highly concentrated streams (i.e., $\geq$90 vol %) can range anywhere from $13 to $35 per tonne of captured CO_2,[81] which is a very attractive cost, especially with existing carbon taxation,[83,84] because it can generate an additional revenue stream for chemical companies. In fact, several companies have already adopted these methods.[81,85–87]

The cost advantage of capturing CO_2 on-site from highly concentrated streams is appealing; however, the amount of CO_2 produced and its availability are vital metrics to be considered for supply chain purposes. The global CO_2 emissions from ammonia production in 2020, for instance, are estimated to be 450 Mt CO_2, which accounts for only 1.3% of the global energy-related CO_2 emissions in that year.[88] Capturing 90% of this amount, a reasonable assumption with current point-source CO_2 capture technologies,[81] will allow 405 Mt CO_2 to be supplied from ammonia production throughout the year. Moreover, the typical capacity factor (CF) for ammonia plants is 90%,[89] indicating the high availability of CO_2 when captured from these plants. Similarly, estimating CO_2 emissions from ethanol 2019 production gives a value of 190 Mt CO_2,[6] only 0.55% of the global energy-related CO_2 emissions in 2019. With a capture fraction of 90%, CO_2 from ethanol plants can supply only approximately 171 Mt CO_2 per year, which is not sufficient to supply the total potential use of CO_2 for CO, ethanol, or ethylene productions (Figure 1B). In addition, the operating days of hydrous ethanol plants is estimated to be 185 per year, an approximately 50% plant CF, which reduces the availability of ethanol without storage throughout the year. Moreover, CO_2 is emitted from natural gas processing at very high concentrations[76,90] and is captured using acid gas removal technologies.[76] In the United States alone, CO_2 emissions from natural gas processing were estimated to be 26.4 Mt CO_2[91] from 656 Mt of processed natural gas in 2019. With the 2019 world consumption of natural gas equivalent to 2.17 Gt,[92] we can estimate global CO_2 emissions from natural gas processing in the same year to be approximately 86.33 Mt CO_2. Even with a 100% capture fraction, this amount would not provide enough raw material for the potential use of CO_2 for the production of the previously considered hydrocarbons (Figure 1B). On the other hand, cement plants emitted roughly 1.5 Gt CO_2 in 2019 as CO_2 process emissions.[93] With a CF of 80%,[94] the cement industry could be a key player in terms of supplying

high-purity CO_2 steadily for electrolysis in 2050. To put this into perspective, consider a cement plant with a production capacity of about 1 Mt cement per year, typical for a cement plant in Europe.[94] With a CO_2 process emissions factor of 0.52 tonne of CO_2 per tonne of cement,[95] one can calculate the production and power capacity of a CO_2 electrolysis facility to be 520 kt of CO_2 per year (1,425 tonne of CO_2 per day) and 303 MW, respectively, assuming a plant utilization of 90% and a typical power consumption of 5.68 kWh per kg of CO produced using a low-temperature CO_2-to-CO electrolyzer.[37]

Low-concentration streams

Although physical and chemical separation methods are attractive for point-source CO_2 capture from highly concentrated streams, they might not be suitable for processes that have less than 50 vol %CO_2 in their waste streams. For example, energy-related CO_2 emissions from the cement, iron, and steel industries, as well as CO_2 emissions from coal and natural gas power plants, are usually produced with other byproducts, reducing the CO_2 concentration to 3–33 vol %, depending on the process.[76,81] This low concentration requires stronger chemical forces to capture a high percentage of the emitted CO_2. Such stronger forces will require high energy consumption to regenerate the captured CO_2, which will increase the cost range of CO_2 captured per tonne to between $50 and $125.[81]

Even when capturing 90% of the emitted CO_2 from low-concentration (3–33 vol %) CO_2 streams, the captured solution will still contain some harmful impurities to CO_2 electrolysis, especially if captured from the flue gases of power plants. Thus, further separation or tolerance of the CO_2 electrolyzer will be needed to efficiently convert CO_2 to the desired hydrocarbon products. For instance, electrochemical CO_2 reduction in a three-compartment flow cell in the presence of merely 0.83% nitric oxide (NO) has been tested, and at least 20% loss in the Faradaic efficiency of the desired products was found as a result of the strong competition of the electroreduction of NO over the tested electrocatalysts (i.e., Cu, Ag, and Sn).[96] A similar test was performed in the presence of 1% SO_2, and similar effects were observed over Cu, Ag, and Sn electrocatalysts.[97] This study found that the selectivity over Cu was not recovered by merely flowing pure CO_2. In fact, it was found that the dominant products were shifted from C_{2+} hydrocarbons to H_2 and formate at approximately 40% and 30% Faradaic efficiencies, respectively.[97] The study concluded that CO_2 supplied from the flue gases of power plants would not be suitable for electrochemical CO_2 reduction over Cu because it will not produce the desired C_{2+} hydrocarbons (e.g., ethanol and ethylene).[97] Similarly, the presence of O_2 has also been tested in the context of CO_2 electrolysis,[98] and it was found that the electroreduction of O_2 is preferred at lower voltages, which diminished the selectivity of electrochemical CO_2 reduction products.[98] Such studies highlight the impact of the presence of impurities in the captured solution that will be fed to CO_2 electrolyzers, stressing the need for the simultaneous design of both CO_2 capture and conversion processes to avoid such detrimental effects during operation.

Regarding the availability of captured CO_2 from cement, iron, steel, and power plants, one needs to look at both the CFs, as well as the amount of CO_2 that can be supplied by each industry. Cement plants have a high CF of 80%,[94] as well as high CO_2 emissions of approximately 2.3 Gt CO_2 in 2019,[93] making it a great source of CO_2 for CO_2 electrolysis; however, we expect at least some of this high CO_2 amount to be difficult to purchase because some cement plants have already chosen to inject their captured CO_2 into concrete.[99] Iron and steel plants also possess high CFs, ranging from 85% to 90%,[100] as well as high CO_2 emissions of approximately

2.6 Gt CO_2 in 2019.[93] Such emissions result mainly from energy consumption, raising the concern of impurity in the supplied CO_2 from the iron and steel industry. Coal and natural gas-fired combined-cycle plants, on the other hand, have a limited CF of approximately 55%,[101] implying their inability to supply continuous CO_2 streams to electrolyzers for conversion to valuable chemicals and fuels; however, coal and natural gas power plants emitted 10.2 and 3.1 Gt CO_2 in 2019, respectively,[102] sufficient to produce 13 times higher supply than the combined formic acid, CO, ethanol, and ethylene demands in 2019. Although some of this amount would likely be used in enhanced oil recovery, there will still be enough to supply the CO_2 electrolysis processes, especially if CO_2 storage and transportation is an available option. Similar to the iron and steel industries, however, the captured CO_2 from power plants will contain other impurities, which will require either difficult separations before feeding the captured CO_2 to the electrolyzer or tolerance of such impurities by the electrolyzers.

In terms of maturity, point-source CO_2 capture technologies are quickly climbing the TRL ladder because of the large effort applied in this field during the previous decades, which translated to their easy retrofitting to current infrastructures and/or their relatively low costs that compare well with governmental incentives.[83,103,104] The major downside of these technologies, however, is the restriction of their location because they can be placed only inside industrial plants to capture the emitted CO_2 from gas streams. An alternative process that overcomes this challenge is DAC, which captures CO_2 directly from air.

Direct CO_2 capture from air

Unlike point-source CO_2 capture, DAC is a relatively immature technology that is mostly still in an early development phase.[105] There are currently three major DAC technologies, led by three companies, based on hydroxides solvents (carbon engineering)[106] and solid amine sorbents (Climeworks and Global Thermostat).[107,108] In 2021, Climeworks introduced the Orca plant,[109] a first-of-a-kind commercial plant in Hellisheiði, Iceland, that captures 4 kt CO_2 per year; however, the realized cost of approximately \$600/t CO_2[110] underscores the need for further development and scale-up. In 2022, the company announced their plan for a second commercial plant, the Mammoth plant,[111] which is set to capture 9 times of the amount captured by the Orca plant (36 kt CO_2 per year). Such scaling up is expected to reduce the levelized cost of CO_2 captured per tonne according to economies of scale; however, it is yet to be proven when the plant is operational. Further, innovative developments are still needed in terms of the sorbent choice and process design that will allow the process to become economically suitable. The Global Thermostat process, uses the same principles as the solid-amine technology but with a more complex design that is engineered to reduce the estimated overall cost of CO_2 capture to \$50/t CO_2.[112] This optimistic cost projection has not yet been investigated by a thorough and public techno-economic assessment, as far as the authors are aware. On the other hand, the solvent-based DAC, as commercialized by Carbon Engineering, has been developed in a more transparent fashion.[106] In addition, the process leverages materials that are manufactured at a large scale and integrates commercialized processes to allow for a reduced cost of CO_2 capture from air. Indeed, CO_2 capture costs are projected to be between \$94 and \$232/t CO_2 for a planned scaled-up process that captures approximately 1 Mt CO_2 per year in Texas.[106] Such a low cost is highly attractive, especially after the plant becomes operational, because it will create a valuable feedback loop, e.g., learning by doing, which will help further reduce the cost of CO_2 captured by future DAC plants.

The advantages of using DAC include its modular designs,[113] ability to capture emitted CO_2 by the transportation sector,[114] high availability throughout the year because its main feed to the contactor is air, ability to be located almost anywhere,[115,116] low competition with food lands,[115] and high CO_2 purities[115,116] that avoid detrimental effects from NO_x, SO_x, and O_2 impurities during electrolysis. DAC is currently limited, however, by its high and uncertain cost estimates ($100–$1,690/t CO_2),[116–119] as well as its relatively low levels of maturity. Future efforts in this field should focus on minimizing the solvent/sorbent regeneration energy and capital costs of major equipment, in an attempt to lower the cost of CO_2 capture from the atmosphere. The US Department of Energy (DOE) recently announced the Carbon Negative Shot, aiming to reduce the price of CO_2 capture from air, coupled with underground storage, to less than $100 per tonne by 2050.[120] This incentivizing effort, as well as similar ones elsewhere,[121–123] will aid CO_2 removal technologies to be quickly commercialized, potentially providing a stable source of CO_2 for CO_2 electrolysis in 2050. Until then, point-source CO_2 capture remains the most cost-appropriate technology to supply CO_2 for electrolysis.

Integration pathways for CO_2 capture and electrolysis

The capture and conversion of CO_2 can be integrated in multiple ways, depending on the demand location, capture and conversion process conditions, and availability of CO_2. The integration pathways can be classified into three types: independent, subsequent, and fully integrated capture and conversion.[64] This categorization will help us assess the three integration routes while considering CO_2 electrolysis in the 2050 net-zero energy system.

After CO_2 is captured, it can be either regenerated or directly converted to valuable products from its captured form. The regeneration of CO_2 alone, however, does not allow it to be transported to CO_2 electrolysis facilities, requiring it to be compressed to a high pressure before storage and transportation. This process consists of two independent capture and conversion steps, hence called the independent integration type. For CO_2 electrolysis, this route is not competitive because it would add to the cost of the main feedstock (i.e., CO_2) for compression and transportation. Therefore, if the captured CO_2 is meant to be used in CO_2 electrolysis, it would be more appropriate to choose the subsequent integration type because it should exclude any storage and long-distance transportation costs. Regarding the source of the CO_2 feedstock, we consider either CO_2 captured from point sources or directly from air. Although the capture of CO_2 from point sources is cost effective, it is not necessarily the most reasonable choice because it would restrict the placement of electrolyzers to be very close to emitting sources, which would also require facing challenges with integrating electrochemical processes with thermochemical ones. In addition, if CO_2 electrolyzers are placed without consideration of distance to emitting sources, they will require the transportation and storage of CO_2, which will increase its cost by $1.5–51.7/t CO_2, depending on the amount needed, distance, region of the world, and transportation type.[124,125] Adding this number to the capture cost from point sources[81] gives an overall CO_2 cost between $14.5/t CO_2 and $171.7/t CO_2. On the other hand, it is expected that the cost of CO_2 capture and storage by DAC will be less than $100/t CO_2 by 2050 because this effort is being pushed for by both governments and companies (e.g., Carbon Negative Shot by the DOE[120]). Other advantages of DAC for CO_2 electrolysis include the absence of SO_x and NO_x contaminants,[96,97] low to no transportation and storage costs, and high modularity in contactor designs.[113] Therefore, sourcing CO_2 from DAC can be a cost-competitive option compared with point-source CO_2 capture in the

context of 2050 net-zero energy systems because it has high locational flexibility and low SO_x and NO_x contamination levels.

The third type, referred to as the fully integrated type, directly converts the captured solution to the desired product. This pathway is attractive because it omits the regeneration energy costs, thus reducing the overall cost of the capture and conversion of CO_2. For instance, the integration of the alkaline CO_2 capture process with a downstream (bi)carbonate utilization has been proposed,[126] reporting favorable energetic arguments for this route compared with conventional ones for forming syngas at an H_2:CO molar ratio between 2:1 and 3:1. Other potential routes using amine-based capture solutions have been proposed.[127] However, depending on the CO_2 source, low CO_2 concentration, the presence of reactive O_2, and the presence of potentially toxic impurities could limit the performance of the fully integrated CO_2 capture and conversion pathway.[27,29] Note that carbon enrichment catalyst with high O_2 tolerance could facilitate the direct conversion of CO_2 sources, e.g., fuel gas, into desired products.[29] The direct conversion pathway creates a promising yet immature process that requires further research in terms of optimizing conditions and reducing costs. Omitting the regeneration step has already been proven to be energetically favorable compared with conventional routes,[126] but further techno-economic and optimization research needs to be pursued for the fully integrated route to become more attractive. Indeed, an integrated system needs to fulfill additional criteria compared with separate subsystems, which could be a challenge for fully integrated CO_2 capture and electrolysis processes.

INTEGRATION WITH RENEWABLE POWER AND ELECTRICITY MARKETS

As mentioned in the introduction, electricity is a key cost driver for CO_2 electrolysis. Additionally, CO_2 electrolysis should be powered by low-carbon or renewable power sources to make the corresponding product carbon neutral or carbon negative.[9,10] Thus, the integration with renewable power sources and electricity markets is a critical step toward low-carbon and cost-effective CO_2 electrolysis products. To this end, different integration pathways can be explored, including: (1) integration with on-site solar photovoltaics (PV) and/or wind power sources; (2) integration with electricity markets, e.g., wholesale or retail electricity markets; and (3) fully integrated systems, which include both on-site solar PV and/or wind power sources and integration with electricity markets,[128,129] as shown in Figure 2.

Integration with on-site solar PV and/or wind power sources

Integration with on-site variable and uncertain solar PV and/or wind power sources implies that the CO_2 electrolyzers should operate in a flexible manner or that energy storage systems should be used to ensure baseload operation despite the variability of the power source.[130,131] For example, solar PV has diurnal cycles and no power output during nighttime, which constrains the maximum CF of the electrolyzer to approximately 50% (see Figure 5A), and likely much less in practice. Wind can also exhibit diurnal patterns, but power output tends to be more consistent across the day, and the maximum electrolyzer CF tends to be higher than that of electrolyzers co-located with solar PV (see Figure 5A). Note that energy storage technologies, e.g., a battery, could be used to increase the CF of the electrolyzer; however, this does add extra capital costs, lowering the overall system efficiency.[131]

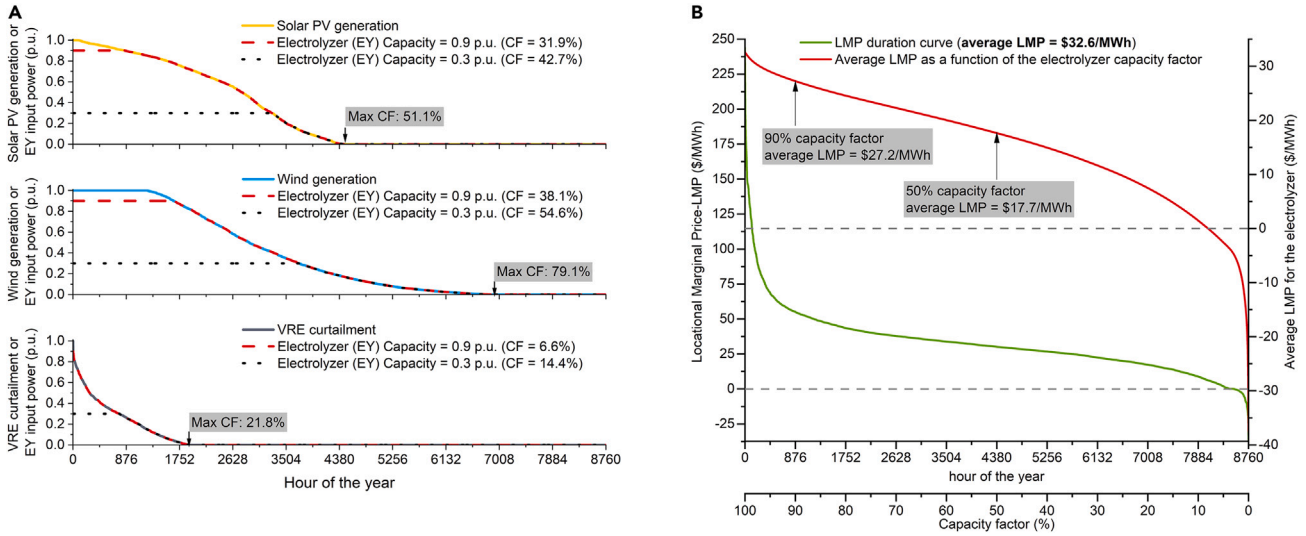

Figure 5. Variable renewable energy (VRE) generation, VRE curtailment, locational marginal prices (LMPs), and electrolyzer capacity factor

(A) Normalized VRE generation duration curve (for given solar PV and wind locations in California),[152] normalized VRE curtailment duration curve (for a 100% renewable California power system by 2050),[152] and equivalent maximum electrolyzer (EY) capacity factor (CF). Electrolyzer capacity is expressed as a fraction of the maximum VRE hourly generation or curtailment. For example, for electrolyzer (EY) capacity = 0.3 p.u., the capacity of the electrolyzer is equivalent to 30%, e.g., 0.3 MW, the capacity of the wind or solar PV facility, e.g., 1 MW. Note that the electrolyzer capacity factor increases as the electrolyzer relative capacity decreases, but there is a limit, e.g., maximum capacity factor, depending on the # of hours with available VRE generation or curtailment, e.g., 51.1%, 79.1%, and 21.8% for solar PV, wind, and VRE curtailment cases presented in this figure.

(B) LMP duration curve for a given location in California[153] and the average LMP, energy price, for the electrolyzer as a function of the capacity factor. This plot illustrates the value of flexibility for a grid-driven electrolysis system. For example, a grid-connected electrolyzer with 90% capacity factor will pay $27.2/MWh versus an electrolyzer with 50% capacity factor that would pay just $17.7/MWh.

Integration with electricity markets

The power system is rapidly changing as a result of the addition of large amounts of variable and uncertain renewable energy generation sources.[132] In particular, the addition of these zero-marginal-cost-generating technologies is reducing the average cost of wholesale electricity while also increasing the price volatility.[133,134] This presents opportunities for electrolysis technologies that provide even small amounts of flexibility in their operations to reduce the overall cost of producing their products through selective scheduling, if connected to the power grid at the multimegawatt scale to take advantage of wholesale electricity markets (see Figure 5B). Also, grid-driven CO_2 electrolyzers could achieve higher CFs when compared with on-site solar PV and/or wind-driven systems (reducing production costs), while relaxing the strict location requirement for the electrolysis system and the renewable power generator (co-location requirement). There are significant economic advantages to participating in wholesale electricity markets instead of accepting retail rates or building plant-specific generation capacity,[129] although there might be particular applications in which other concerns make these other routes for electricity supply more favorable. If operational flexibility is built into the design of large-scale electrolysis systems and is seen as an economic opportunity, rather than as an economic loss because of reductions in the CF, there are additional potential improvements to be gained in other design factors, e.g., equipment lifetime and maintenance costs. Because electricity costs are still expected to comprise a significant portion of total electrolyzer system costs, note that lower future electricity costs does not mean free electricity. Moreover, although there might be times of increased wind and solar PV curtailment in the future electricity system, there are also many other uses for electricity that make sustained zero-cost electricity prices unlikely. Given the current high capital costs

associated with electrolyzers, it is unlikely that they would be able to economically sustain the extremely low CFs that relying only on curtailed renewable generation would require (see Figure 5A). This is true even without considering the downstream supply chain issues that such a production schedule would be likely to create. One potential issue of the electricity market integration is the carbon intensity of the electricity from the grid if the power system is not 100% carbon-free or renewable.[9] For instance, the electrolyzer could use fossil-based electricity during some time periods, which could significantly increase the carbon footprint of the CO_2 electrolysis-based product. One alternative to address this issue is to constrain the electrolyzer operation to time periods when the power system is not using any fossil-based power generation, but this would likely have a negative economic impact because of the lower utilization rate. Alternatively, the carbon intensity issue could be addressed by ensuring the following: (1) additionality of renewable power generation e.g., renewable power to drive electrolysis must be procured from new renewable generators (generators that are not in operation), (2) locational matching, e.g., the electrolysis system and the new renewable generator should be located in the same region or electricity market bidding zone (ensuring the deliverability of the renewable electrons by avoiding transmission/congestion constraints), and (3) temporal matching, e.g., the electricity demand for electrolysis over a given time period matches the electricity generation from the new renewable generator (sub-hourly matching, hourly matching, weekly matching, etc.).[135,136]

Fully integrated CO_2 electrolysis systems: On-site solar PV and/or wind power sources plus electricity market participation

Fully integrated systems could be more cost effective given the variety of value and cost-savings opportunities contemplated in this integration pathway. For example, the electrolyzer could use power from the on-site solar PV or wind facility supplemented with electricity from the grid during time periods with low electricity prices, which could increase the CF of the electrolyzer and reduce the total electricity costs. Additionally, the on-site solar PV or wind facility could sell power to the grid during time periods with extremely high electricity prices, which represents an additional potential revenue stream. Note that CO_2 electrolysis products with higher electron demand, e.g., ethylene (12 electrons), could benefit the most from flexible operation compared with products with lower electron demand, e.g., CO (two electrons).[9] Moreover, despite the potential economic benefits of operational flexibility, the stability and degradation of CO_2 electrolyzers over extended time periods, e.g., >1,000 h, and variable operation require a better understanding.[21] At these timescales, side reactions and system-level deactivation become more outstanding.[137] Thus, standards for testing and validation of CO_2 electrolysis scalability could be useful.[137] On the other hand, frequent cycling could reduce the lifetime of the electrolyzer (degradation of components), which could reduce the economic benefits of operational flexibility, e.g., in single-gap electrolyzers, fast increase/decrease in the production rate could lead to fluctuations in the local pressure, which might lead to flooding in the cathode GDE, negatively affecting the stability of the electrolyzer cell.[138] Note that this issue is not present in zero-gap electrolyzers, which have demonstrated efficient intermittent operation (emulating a solar PV power output profile) for a week without significant performance degradation.[138] With respect to integration with renewable energy inputs, low-temperature electrolysis might have a higher degree of flexibility than high-temperature electrolysis, which relies on heat from burning fossil fuels and typically operates within a narrower operating window because of poor material durability.

SUMMARY AND OUTLOOK

Achieving net-zero emissions energy systems requires the decarbonization of hard-to-decarbonize sectors, e.g., industrial and transportation. The deployment of CO_2 electrolysis, i.e., powered by renewable or low-carbon energy sources, could help to achieve this goal by (1) replacing carbon-intensive petrochemical and fuel production and (2) using otherwise emitted CO_2 from industrial processes or CO_2 from the atmosphere. For example, based on 2019 global consumption, the production of CO, formic acid, ethylene, and ethanol via CO_2 electrolysis requires approximately 1 Gt of CO_2 per year (100% of the projected required CO_2 capture from air or 19% of the projected required CO_2 capture from point sources by 2050). Despite recent advances toward scale-up and commercialization, however, the industrial deployment of CO_2 electrolysis technology is yet to be seen. Indeed, large-scale industrial deployment of CO_2 electrolysis poses technical and economic challenges associated not only with the technology itself but also with the integration with CO_2 capture processes and renewable power/electricity markets. For instance, although significant advances have been achieved in the selectivity, i.e., Faradaic efficiency, and production rate, i.e., current density, of both low- and high-temperature CO_2 electrolysis, more efforts are required to improve the performance of this technology. In particular, the energy efficiency (i.e., cell voltage), carbon efficiency (i.e., single-pass conversion), and durability (i.e., long-term stability), of CO_2 electrolysis need to be improved, particularly for C_{2+} products. To this end, catalysts with improved activity, selectivity, and stability/durability, as well as membranes and reactors that prevent carbonate formation or crossover, achieve higher reaction rates, e.g., >1 A/cm^2, and demonstrate long-term stability, e.g., >5 years should be developed. In addition, the integration of CO_2 electrolysis with CO_2 capture processes requires significant further investigation. For instance, supplying pure CO_2 at the industrial scale would be very expensive. Thus, impurity-tolerant CO_2 electrolysis systems need to be developed and tested under relevant conditions, e.g., CO_2 streams with traces of impurities (NO_x, SO_x, O_2, N_2, H_2S, etc.). Indeed, the effects of impurities on the performance of CO_2 electrolysis systems have thus far been mostly overlooked by both the low-temperature and high-temperature CO_2 electrolysis communities. Moreover, because electricity is a key cost driver for CO_2 electrolysis, the integration with renewable power sources and/or electricity markets could play a critical role in achieving cost effectiveness. Yet, most existing techno-economic studies on CO_2 electrolysis assume continuous renewable power supply at a constant electricity price; however, wind and solar PV power sources exhibit diurnal patterns; therefore, the assumption of continuous renewable power supply is questionable. Additionally, if renewable power is provided by the grid, the electricity prices will be subject to the dynamics of the electricity markets. Indeed, CO_2 electrolysis systems could take advantage of these dynamics to reduce the electricity cost by reducing the capacity factor, e.g., shutting down the electrolyzer during periods with high electricity prices. Nevertheless, the operational flexibility of CO_2 electrolysis is not well understood (specially for low-temperature electrolysis). For example, the effects of frequent cycling on the performance and degradation of CO_2 electrolysis require more attention. In summary, CO_2 electrolysis presents a promising avenue to help decarbonize the industrial and transportation sectors, but research attention must now be paid to engineering conditions that will be relevant to its economic viability and deployment, such as catalyst and membrane durability, process flexibility, and integration with electricity systems. Note that availability and costs of CO_2 sources, availability and costs of renewable power sources, and electricity prices depend on the location; thus, the specific quantitative targets and optimal system design and integration for CO_2 electrolysis depend on

the specific case, e.g., solar PV- or wind-driven versus grid-integrated CO_2 electrolysis. However, in any case, the use of renewable power for CO_2 electrolysis, e.g., 100% renewable-driven CO_2 electrolysis, is critical to achieve climate and environmental benefits from the large-scale deployment of CO_2 electrolysis.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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