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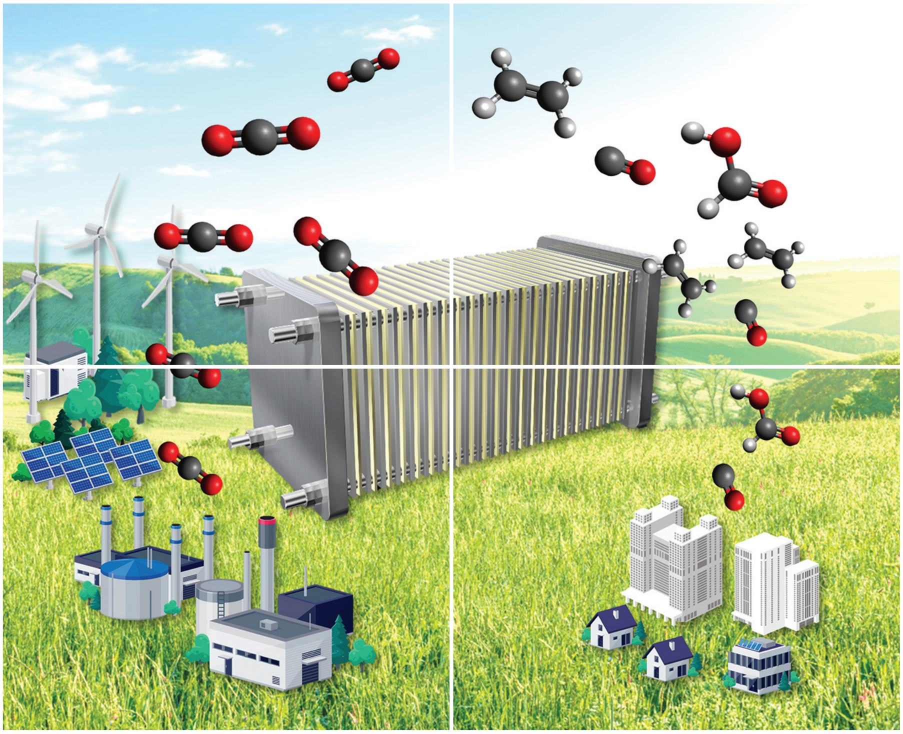

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REVIEW

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Recent advances in electrocatalytic reduction of ambient CO_2 toward high-value feedstock

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The effects of climate change have arisen due to greenhouse gases emitted into the atmosphere, and the finite supply of fossil fuels will eventually be unable to support the needs of the petrochemical industry. Solutions to these two complex problems will have to be multipronged, but the industrial implementation of the electrocatalytic reduction of CO_2 can help with both issues. Importantly, the demand for multi-carbon feedstock offers immediate financial incentives, accelerating the search for solutions to the climate problem. However, the technology for the electrocatalytic reduction of CO_2 is still in the process of being commercialised, and the use of ambient CO_2 is a prerequisite for widescale adoption. Here we discuss the progress in this area and the remaining barriers to realizing its potential.

1. Introduction

Nature has a rich history of converting CO_2 into valuable resources driven by the abundant renewable energy from the sun. Carbon monoxide dehydrogenase/acetyl–CoA synthase, the main enzymatic complex in thousands of types of bacteria, has been remarkably effective in microorganisms for more than 3.5 billion years, fixing CO_2 as a carbon resource.[1] In contrast, human beings have only enjoyed highly energy-intensive modern life since the industrial revolution, powered by oxidising energetically compressed fossil fuels. This process results in the reverse carbon flow from underground to the atmosphere. This anthropogenic oxidative carbon consumption accounts for the rise of atmospheric CO_2 levels, as illustrated by the Keeling Curve.[2] Consequently, the United Nations has declared "a code red for humanity", warning that the concentration of atmospheric greenhouse gases poses a threat to lives, economies, health and food security.

A desired pathway is to aggressively implement renewable energies, which would consequently lead to a dramatic shift in the material production scheme from the fossil-fuel dependent supply chain to one that relies on more sustainable resources. The CO_2 reduction reaction (CO_2RR) has the potential to play a pivotal role in accelerating such a material evolution due to its attractive natural features: it occurs under atmospheric reaction conditions, does not require any side reactants such as hydrogen, is compatible with renewable energy resources, and offers a wide range of potential products.

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A literature search shows that the CO_2RR study dates back as far as the 1950s as a way to produce chemicals.[3,4] In the 1980s and 90s, comprehensive research was conducted on a variety of metal or molecular catalysts and electrolytes to discuss the selectivity of CO_2RR.[5–7] As predicted by Hori,[7] there has been a significant resurgence in the use of CO_2RR within the research community in recent years, resulting in an increasing number of publications equivalent to Moore's law (Fig. 1). Despite its long history and the renewed focus on developing efficient and selective electrocatalysts, CO_2RR has not been adopted by conventional chemical industries as a replacement for fossil fuels. This is in contrast to lithium-ion battery technology, which was discovered later but has been widely commercialised with an even steeper rise in the publication rate.

Why has nature successfully implemented ambient CO_2 reduction, while the same achievement has thus far eluded

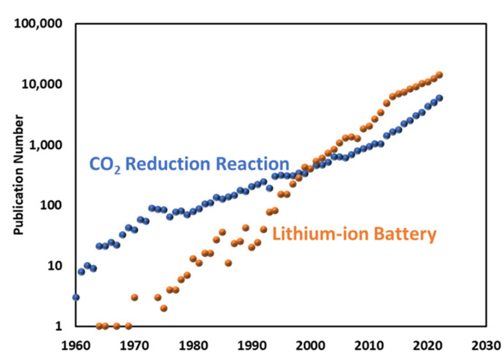

Fig. 1 Annual publications for an electrocatalytic CO_2 reduction reaction and lithium-ion battery research.

human ingenuity? With this question in mind, we will discuss several important aspects of CO_2RR. However, given the breadth of research in this field, this review does not seek to be exhaustive; rather, it aims to provide insight into the economic viability and future of CO_2RR. First, we introduce the potential products of CO_2RR, followed by a techno-economic analysis to shed light on the current barriers towards the successful commercialization of CO_2RR. Finally, we will review a few studies dealing with the less-discussed but significant properties for successful CO_2RR implementation.

2. Basic principles and catalyst science for CO_2RR

One of the attractive but complicating features of CO_2RR is that it has a variety of possible products along with competing hydrogen evolution reaction (HER), all of which have similar standard redox potentials *vs.* reversible hydrogen electrode derived from the Gibbs energy and physicochemical constant.[8] Due to the close thermodynamic characteristics of CO_2RR, the selectivity of the expected CO_2RR is dependent on both the modulation of electrochemical activation energy toward a specific route and the availability of the corresponding reactants. An electrochemical catalyst is needed to lower the activation energy of a specific target by stabilising an intermediate for the reaction. CO_2RR is an inner-sphere reaction involving multiple electron- and proton-transfer processes. In contrast to an outer-sphere reaction, in which the electron transfer occurs through tunnelling across a monolayer of solvents, the heterogeneous inner-sphere reaction is based on the interaction of a reactant, a product, or an intermediate with the catalyst surface. These interactions enable a critical intermediate species more likely to be structurally changed in subsequent steps.

As a principle, the rate of the multi-step reaction is determined by the slowest step, *i.e.*, the rate-determining step (RDS). It has been proposed that two-electron transfer reactions of CO_2RR into CO or HCOOH may possess different types of RDS.[9–11]

As for CO_2RR into CO and HCOOH (Fig. 2), steps 1 and 5 represent the CO_2 adsorption process which triggers the CO_2RR pathway. A recent study indicates that this process can be dependent on the applied potential because of the interaction between the dipoles of the participating reaction intermediates with the interfacial field.[10,11] Both field-dependent density functional theory and pH-dependent activity measurements concluded that the ideal catalyst should possess large adsorbate dipoles on CO_2*.[10] Steps 2 and 6 are concerted proton–electron transfer steps, and the configuration of CO_2* seems to determine the selectivity with transition metal surfaces.[12] One computational study[13] suggests that the C-atom bonding structure leads to the CO production pathway while an O-atom mediated bond is more likely to induce formate/formic acid production. Experimental studies such as *in situ* surface Raman scattering confirm that such a configurational change determines the selectivity of the CO_2RR product.[14,15] Steps 1′ and 5′ are proton-decoupled electron-transfer steps whose kinetics are independent of the number of local protons in the vicinity of the catalytic site, followed by the protonation to form COOH or OCOH [steps 2′ and 6′]. The final step of CO_2RR is the desorption of a product from the catalytic site [steps 4 and 8]. Since the electrochemical activation energy expectedly correlates with the adsorption energy between the intermediate species of the rate determining step and the catalytic sites, the free energy of the adsorption of the intermediate is usually discussed to elucidate the catalyst selectivity.

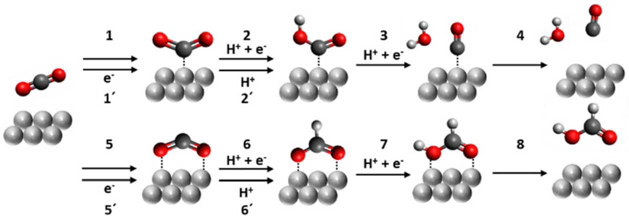

Fig. 2 Reaction schemes for the CO_2 reduction reaction into CO or HCOO.

3. Techno-economic analysis of CO_2RR in the context of performance matrices

Since CO_2RR is an alternative way to produce existing fossil fuel-derived catalysts, the electro-synthesized product needs to compete economically with the widely-established market products. In this context, a techno-economic analysis (TEA) should be considered and included in the discussion of studies which investigate the application of CO_2RR. One of the simplest ways to approximate the economic validity of CO_2RR products is to plot the relationship between the minimum energy requirement for the targeted product and the corresponding market price. Here the minimum energy consumption per unit mass E_{min} is defined by

$$E_{min} = n(E^{\circ}_{red} - E^{\circ}_{min})F/\mathrm{MW} \tag{1}$$

where n is the electron number for a specific reaction, E°_{red} is the standard redox potential for CO_2RR, E°_{ox} is the standard redox potential for the counter reaction, F is the faradaic constant, and MW is the molar mass of the product.

The thermodynamic cell potential serves as an indicator of the minimum energy requirement for a given product and thus, given the energy costs, provides a means to estimate the economic viability of a product. Fig. 3 shows the possible CO_2RR products plotted as a function of E_{min} and market price as of 2023. One notices that CO and formic acid are well positioned in this proximity of economic analysis due to its two-electron transfer characteristics. Some oxygenates such as acetic acid and acetaldehyde also possess a relatively high

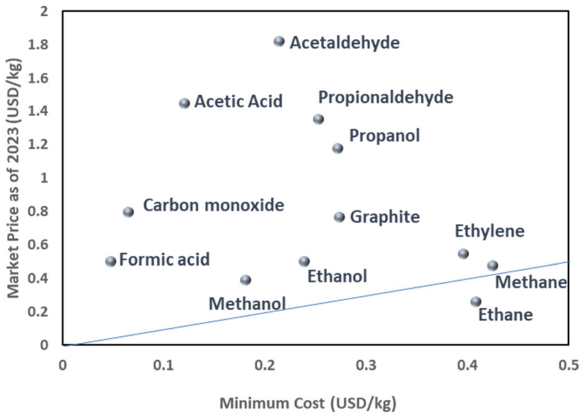

Fig. 3 Possible electrocatalytic CO_2 reduction reaction products plotted as a function of minimum energy consumption per unit mass and market price as of 2023. The line represents the break-even point assuming no additional financial incentives.

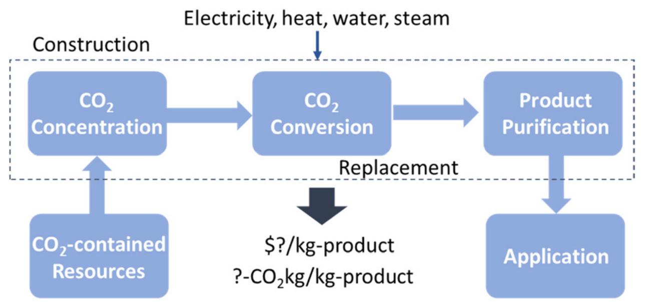

Fig. 4 Basic processes for a scaled-up electrocatalytic CO_2 reduction reaction: CO_2 purification, CO_2 conversion, and product purification.

market value compared to the required minimum cost. Alcohol derivatives and graphite materials are in the middle group because of the moderate minimum costs and current economic value. As the carbon number in the alcohol increases, the minimum cost and current market price increase concomitantly, indicating that the market price reflects the energy required for the chemical supply. The graph also highlights the challenges of synthesizing hydrocarbon products such as ethylene, methane, and ethane. The discrepancy between the low market price and the high-cost characteristics of these derivatives is attributed to the fundamental differences between the processes in the existing petrochemical infrastructure and in a future CO_2-based electrochemical supply. Specifically, hydrocarbons can be extracted from fossil fuels without additional energy to convert chemical structures since nature has already converted CO_2 into hydrocarbons over a long period of time. By contrast, CO_2RR needs additional energy to convert CO_2 into hydrocarbons, which inevitably adds costs relative to fossil-fuel-derived hydrocarbons. Since hydrocarbons are a fundamental commodity for the chemical industry, subsidies are likely needed for the timely implementation of CO_2RR to support the hydrocarbon chemical chain.

Note that recent electrocatalyst and photocatalyst studies have demonstrated the combination of CO_2RR and an unconventional anode reaction to either reduce the cell voltage[16] or directly synthesize more complex chemicals,[17,18] which may pave the way toward an efficient CO_2RR production system.

While the minimum cost approximation is helpful to identify the economic potential of CO_2RR targets, the actual TEA should be more in-depth. There are three basic process steps for CO_2RR: CO_2 purification, CO_2 conversion, and product purification (Fig. 4). The TEA of the overall chemical process reminds us of what we need to rapidly scale up the CO_2RR and, in turn, provides key insights for essential future studies.

The cost associated with CO_2 purification depends on the CO_2 ratio of the initial gas mixture and a capture method. CO_2 captured from concentrated CO_2 sources, such as power and chemical plants or from amine technology, has the lowest price of \$50–70 t^{-1} with a US Department of Energy target of \$40 t^{-1}.[19] On the contrary, capturing CO_2 from the air is more expensive than from flue gas because of its low concentration: one study estimated that the cost for CO_2 capture from the air could potentially reach ≈\$100–200 t^{-1} in the future.[20] The cost of CO_2 purification in a typical carbon conversion unit provides an opportunity to pursue new technology to simplify or eliminate CO_2 purification. If effluent gas is converted in the CO_2 conversion unit on site in places such as fired power plants or incineration plants, the cost for the CO_2 purification step decreases. In addition, the degree of required CO_2 purification depends on how sensitive the CO_2 conversion is to the impurities in the gas stream entering the CO_2 conversion. For instance, NO_x and SO_x are usually present in exhaust gas and the effects of these oxide impurities on the selectivity and durability of the CO_2RR catalyst are still largely unexplored.

The CO_2RR product purification process includes gas and/or liquid separation, depending on the physicochemical properties of the production. Gas separation is usually required because of the presence of unconverted CO_2 and unintended side products such as H_2 in the product effluent. Liquid product separation is often required to extract products in the liquid catholyte. Pressure swing adsorption (PSA) and membrane technologies are currently used in other industrial processes with similar gas compositions.[21] It appears that PSA is generally preferred because of its relatively low operating costs and high efficiency with an estimated cost of around \$10 t^{-1} based on CO_2RR TEA[22] and the Sherwood plot for the separation of dilute streams.[23] Liquid product separation can be executed through distillation, extraction, precipitation, and pervaporation.[21] Among these, distillation is widely used but it is expected to have a much higher operational cost than gas separation with PSA.

The operational cost of the CO_2RR product depends on the purity of the target and chemical composition in the product stream from the electrochemical conversion unit. Thus, both the selectivity and conversion ratio of CO_2RR are imperative to determine the energy required for the purification process. In addition, the additives for the electrochemical reaction, such as electrolyte salts and co-catalysts, should be considered in the cost analysis for the product separation process.

The CO_2 conversion unit operates predominantly with electricity as input energy and CO_2 as feedstock. Therefore, the energy efficiency in converting CO_2 into target chemicals, defined as the ratio of thermodynamic energy to input energy, affects the operational cost of CO_2RR. Energy efficiency is a function of the sum of the overpotential of cathodic and anodic reactions along with other voltage drops in an electrolyser and FE for the specific product. CO_2RR into hydrocarbon such as ethylene usually requires prominent overpotential to kinetically drive the reaction, which may push up the operational costs. As for the CO_2 feedstock, the conversion ratio of CO_2 as a system affects the operational cost as the unconverted CO_2 is either wasted or requires more energy to be recycled. The CO_2RR cell is preferably designed to minimize CO_2 loss. For instance, when an alkaline electrolyte is used on the cathode side, CO_2 loss likely occurs as a dissolved carbonate, preventing the efficient utilization of CO_2. One strategy is to utilize a fully carbonated system with an anion exchange membrane, which leads to the consumption of CO_2 at the cathode and the re-emission of CO_2 with oxygen at a locally acidic anode. However, an additional separation step is required to recover CO_2 from the anode vapours.

As for the capital cost, the partial current density, the observed current for the relevant reaction per geometric area, is important to determine the total electrode size of the electrolyser for the CO_2RR. Given that the number of electrons to be transferred varies depending on the CO_2RR reaction, a more practical manner to evaluate the productivity of CO_2RR may be to convert current density into the production rate of the targeted product per geometric area.

The durability of the CO_2 converting unit or electrochemical cell is also an important factor in affecting the frequency of cell replacement and the operational cost. TEA studies often use a lifecycle of 5–30 years.[22,24,25] However, conventional CO_2RR studies usually report durability results for times of 10–100 h, and there is a gap between the current testing period and the prolonged durability test required before building the actual plant. Moreover, an accelerated testing protocol needs to be designed to speed up the durability development, which is also currently not well addressed. The definition of the reduction in performance at which the CO_2RR cell should be replaced will remain an open question until key stability/durability relationships are experimentally established.

One should note that the CO_2RR process can reduce or increase CO_2 emissions depending on the energy required for the total production process and the carbon intensity of the electricity and utilization. The carbon intensity of renewable energy is significantly lower than that of fossil fuel-derived electricity, suggesting the combination of the CO_2RR process and such renewable energy can be a more carbon-neutral scheme. In this case, integrating the CO_2RR process into the off-grid renewable energy should be discussed since the plant system requires additional electric equipment, such as energy storage systems and converters. A hydrogen production electrolyser plant powered by renewable energy can be a good model for estimating the cost impact of electricity management in a CO_2RR plant.

The source of CO_2 and electricity significantly affects the cost of the CO_2RR process and the benefit of CO_2 emission reduction. The CO_2RR process prefers more concentrated CO_2 sources in the fluent gas. However, we should envision the long-term viability of CO_2 emitters since the social system will require a change toward more carbon–neutral structures. The electricity price changes significantly depending on the region, the electricity resources, and geopolitical environments. Since the CO_2RR plant is an electricity-demanding process, one needs to choose the place to develop the plant carefully. Usually, TEA applies an electricity cost of 0.02–0.03 USD per kW per h,[22,24,25] which still limits the actual short-term option to scale up the CO_2RR process, which can reflect the cost simulation of the TEA.

After providing an overview of TEA, we propose emphasizing the following domains in the plant flow (CO_2 concentration, conversion, and the production purification step) for scaling up CO_2RR deployment (Fig. 5): (1) the effect of chemical composition of the feed gas, (2) the industrially relevant productivity and durability of CO_2RR, and (3) maximizing the CO_2 conversion ratio and optimizing selectivity to minimize the need for purification processes.

4. Noteworthy CO_2RR research toward economically valuable feedstock

4.1. Effect of the chemical composition of feed gas

Most CO_2RR research has been carried out with concentrated CO_2, which helps increase the reaction rate and selectivity of CO_2RR due to the high availability of CO_2 at catalytic sites and avoids undesirable side reactions stemming from impurities. As mentioned in section 3, the CO_2 concentration process, while relatively mature, introduces additional energy consumption and costs to implement CO_2RR, which may induce unfavourable CO_2 emissions. Therefore, it is desirable that the CO_2RR is compatible with direct effluents from CO_2 sources. The CO_2 concentration of fired power plants is around 15% (v/v), depending on the type of fossil fuels and combustion

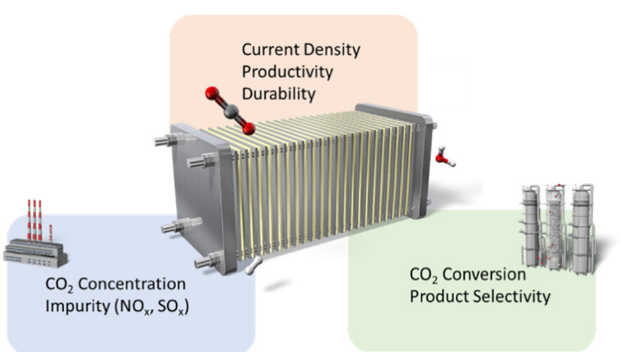

Fig. 5 The highlighted research domain in the process flow of the electrocatalytic CO_2 reduction reaction.

system. Also, industry exhaust streams often contain other gaseous species such as N_2, O_2, H_2O, NO_x, SO_x, and volatile organic compounds. The oxidized components of flue gas, such as SO_x and NO_x, may influence CO_2RR catalysts, although their concentrations are low (typically in the order of hundreds of ppm). Therefore, deviating from pure CO_2 gas could impact the CO_2RR catalytic activity and durability.

The decrease in CO_2 partial pressure is expected to decrease the reaction rate of CO_2RR when CO_2 diffusion is a rate-limiting step. This is the case for electrolysis under the practical conditions of operating close to the maximum partial current density regardless of the structure of the electrolyser cell. Additionally, the decreased CO_2 partial pressure creates a reaction environment preferable to the competing HER since the number of protons for the reaction is independent of the gas component. Moreover, the adverse effect of limited CO_2 in the incoming gas may become more severe as the size of the electrolyser increases because the consumption of CO_2 in the gas or electrolyte occurs along with the plane of the electrode, and the gas/liquid stream close to the outlet of the flow cell has the lowest amount of CO_2. Therefore, the influence of CO_2 partial pressure is a vital factor in determining the compatibility of CO_2RR with the exhaust gas.

There have been some studies on the effect of CO_2 partial pressure and presenting engineering-based strategies to tackle limitations. Among the pioneering studies in the 1990s,[26,27] Komatsu observed that the current density and FE for CO_2RR decreased as CO_2 concentration decreased from 100 to 14% with the copper composite electrode for the gas-phase CO_2RR.[28] Consistent with that work, Kenis *et al.*[29] reported that the partial current density noticeably decreased with the decrease in the CO_2 concentration with Ag nanoparticle catalysts on the gas diffusion electrode in the CO_2/N_2 mixture feed in 1 M KCl electrolyte media. The authors also observed the decrease in the FE for CO_2RR to CO by using phosphate buffer as the electrolyte to distinguish between the effect of CO_2 partial pressure and pH in the electrolyte. The pH dependency study showed that the FE for CO_2RR to CO decreased more severely with the decrease in pH, suggesting that the number of local protons initiates the HER, diminishing CO_2RR more easily as either the CO_2 concentration in the feed or the pH in the electrolyte decreased.

A straightforward way to address the diluted CO_2 concentration is to elevate the pressure of the electrolyser system, which increases CO_2 availability at the catalyst. Xu *et al.*[30] demonstrated that the pressurization of the feed gas at 15 bar successfully maintained a 91% FE for CO_2RR to CO with 15% (v/v) CO_2, which is similar to or higher than that of the performance with pure CO_2 at 1 bar, depending on the applied potential. While pressurization requires some additional energy input, they calculated that the energy required to pressurize to 10 bar represents only ~3% of the energy required to perform efficient CO_2RR to C_2 products. These results indicate that pressurization helps enable the direct conversion of streams with CO_2 concentrations characteristic of major flue gas sources at industrially relevant current densities.

O_2 is the highest concentration reactive impurity in flue gas and is challenging to remove. The oxygen reduction reaction has a more favourable thermodynamic potential and kinetics compared to CO_2RR, which significantly impedes the target selectivity. As an initial study, Morikawa *et al.*[31] confirmed that the inclusion of O_2 significantly reduces the FE for CO_2RR to formate with a porous ruthenium complex polymer catalyst on a photocathode from 93% (at 0% O_2) to 6% (at 7% O_2) due to the selective O_2 reduction competing with CO_2 reduction. They demonstrated that the combination of the catalyst with carbon papers mitigated the drop of FE to 75% at 7% O_2, which is attributed to the affinity of the carbon materials to gaseous CO_2 in aqueous solution, resulting in the relatively concentrated CO_2 in the vicinity of the catalytic sites. However, the measurement of local CO_2 should be carried out for further discussion.

Exploiting the difference in solubility between CO_2 and O_2 in the electrolyte media is one way of mitigating the parasitic effect of O_2. Sinton *et al.*[30] exploited an ionomer and TiO_2 coating to create a hydrophilic environment around the Cu catalysts so that CO_2 can predominantly dissolve and reach the catalytic sites over O_2. They observed a FE towards C_2 products of 68% and energy efficiency of 26% over 10 h of stable operation (at 10 bar), a performance competitive with some of the best results previously reported on reactors using pure CO_2.

Another methodology to circumvent the oxygen reduction reaction is to implement an additional layer to selectively transport or adsorb CO_2 over O_2. Wang *et al.*[32] demonstrated that a polymer of intrinsic microporosity serves a role in selectively permitting CO_2 to permeate while preventing O_2 from reaching the catalytic sites. They coated the gas separation polymer on the opposite side of the carbon paper of the cobalt phthalocyanine catalyst and observed FE for CO of 75.9% in a gas with 5% O_2 in contrast to the catalyst without the gas separation layer performing no observable FE with the same O_2 concentration. Subsequently,[33] the authors applied aniline molecules to enhance the ability of the permeable ionic membrane (PIM) to separate CO_2 from O_2 using chemical interactions between the acidic CO_2 and the basic amino group of aniline. In an electrolytic flow cell with a cobalt phthalocyanine/carbon nanotube catalyst, they observed a FE for CO of 71% in the presence of 10% O_2 in CO_2 using the PIM/aniline membrane, therefore outperforming the pure PIM with a FE for CO of 63% under the same conditions. While these studies highlight the effectiveness of structurally or chemically engineering the microstructure, further research regarding the physicochemical properties of CO_2 and O combined with kinetic modelling will lead to clearer design principles for selective CO_2 supply in a microenvironment.

NO_x is among the major contaminants present in industrial CO_2 point sources with a typical concentration of 10–500 ppm depending on the regional regulation and combustion system.[34] NO_x usually consists of 90–95% NO and 5–10% NO_2, N_2O being a common by-product formed in the NO_x removal process. All of these NO_x gases can compete with CO_2 for electrons through the corresponding reduction reaction, which has a more favourable standard redox potential than CO_2RR. Therefore, the kinetics of the NO_x reduction reaction, along with the concentration of NO_x, could be crucial factors to be investigated. Moreover, NO_2 can also react with water to produce various acidic products, including nitric and nitrous acids.

Komatsu *et al.*[28] found no effect of 200 ppm NO on the catalytic activity of gas-phase CO_2RR with a copper-deposited electrode. The author argued that the amount of NO was about two times higher than that of the exhaust gas from a typical coal-fired power plant. Jiao *et al.*[35] demonstrated that the presence of much higher amounts of NO, NO_2, and N_2O (8300 ppm) in the CO_2 feed leads to a considerable FE loss in CO_2RR with Cu, Ag, and Sn catalyst-loaded gas diffusion electrodes. Notably, they observed the recovery of the FE for CO_2RR after switching the feed gas without NO_x, suggesting that NO_x is involved in the electroreduction process but does not affect the structure of the catalysts in these conditions. In addition, they evaluated the effect of 830 ppm and 83 ppm NO, showing less severe (less than 5%) and negligible losses in FE, respectively, highlighting that CO_2RR can be compatible with typical concentrations of NO_x in flue gases. Note that the parasitic effect of NO_x is dependent on the nature of the catalyst and an electrochemical setup. Oh *et al.*[36] reported a decrease in FE for HCOO− from 69.4% to 37.7% using SnS_x as the catalyst in the presence of 90 ppm NO. Sridhar *et al.*[37] observed a loss in FE for ethylene of 22.9% after exposing the copper catalyst to 1% NO_2 and a change in the surface colour of the copper catalyst, showing that excessive NO_2 may contribute to the oxidation of the catalysts.

SO_x is another possible chemical component in the gas feed. Typical power plants emit exhaust containing 10–300 ppm SO_2. Komatsu *et al.*[28] found that 170 ppm SO_2 in the feed noticeably changed the distribution of the products with a copper catalyst. Jiao *et al.* observed a general decrease in the FE for total CO_2 reduction after copper, silver, and tin catalysts were exposed to a gas stream of 1% SO_2 in CO_2, which is attributed to the preferential reduction of SO_2. Silver and tin catalysts showed less change in the product distribution and the recovery of FE for each product was attained after stopping the feed of SO_2. However, the catalyst characterization shows the sulfurization and desulfurization reaction of Ag and Sn after the SO_2 and pure CO_2 feed, respectively, inferring that these materials are relatively durable against the sulfur-derived structural change. On the contrary, the exposure of SO_2 causes the product distribution with Cu catalysts toward formate, which is irreversible even after switching back to a pure CO_2 stream. The authors attributed the change to residual Cu_2S formed on the surface.

One finds that there is a sizeable difference between the amount of impurities used for the CO_2RR studies mentioned above and the actual content found in the exhaust from specific CO_2 sources. This is because the emitters have often already modified the fraction of impurities to prevent air pollution. Therefore, in more practical scenarios, the tested chemical composition for CO_2RR needs to match the actual composition for a true feasibility study. Investigations into the effects of impurities on the durability of the CO_2RR catalyst should also be conducted. Since the existing CO_2 purification process, such as the amine adsorption method, already works to reduce the impurities, the total design of combining the CO_2 purification and conversion relies on the efficiency and durability of the CO_2RR process.

Current CO_2RR demands a high CO_2 partial pressure compared to nature, which converts 440 ppm CO_2 with highly diluted solar energy. While direct air capture is in the pilot phase of plant testing, the general cost for concentrating CO_2 from a level of a few hundred ppm to nearly 100% is unacceptably high due to the intensive energy required for the process. One option would be combining the CO_2 concentrator and a converter compatible with significantly diluted CO_2 sources, but resolving the issues surrounding gas impurities needs to be addressed first.

4.2. Industrially relevant productivity and durability of CO_2RR

While the FE and energy efficiency for a specific product affect the operational cost of electrolysis, the current density or productivity per geometric surface area of the electrode is essential in determining the capital cost since as the productivity increases, the size of the electrolyser decreases. The current density is typically one of the matrices used to evaluate CO_2RR research. A practical measure is the productivity of the specific product per specific time and the electrode geometric area.

Fig. 6a shows the reported partial current density and expected production rate per day for various products.[33–126] HCOOH/HOO$^-$ has the highest value of production rate per partial current density due to its 2-electron transfer characteristics and relatively high molecular weight, followed by CO production. CO_2 to ethanol or ethylene has a lower production rate per partial current density because these products require 12 electrons to be transferred to the reactant but have a similar molecular weight.

Significant efforts to improve the partial current density have been made in the last few years, mainly focusing on the catalyst design to increase the catalytic site density and electrochemical cell engineering to achieve gas-phase reactions to cir-

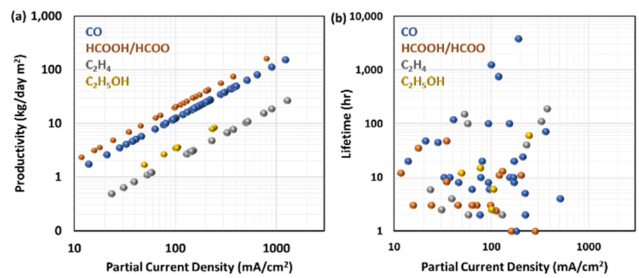

Fig. 6 (a) The expected production rate per day as a function of the partial current density for each CO_2RR product with the experimental data according to the literature survey. (b) Reported lifetime of CO_2RR as a function of the partial current density for each CO_2RR product with the experimental data according to the literature survey.

cumvent the limitations of CO_2 solubility in the electrolyte. The flow or membrane electrode assembly (MEA) cell configuration with a gas diffusion electrode especially has played a central role in creating a three-phase boundary environment where CO_2 can encounter the catalytic sites and ions as a counterpart for the CO_2RR reaction. In addition, recent studies[127] have introduced micropores or a hydrophobic environment in the catalytic layer to accumulate CO_2 near the catalytic sites.

Sun *et al.*[128] demonstrated a hierarchical nanoporous catalyst by retaining the micropores of a metal–organic framework precursor to enhance CO_2 concentration in the gas-diffusion electrode, achieving 645 mA cm^{-2} CO partial current density at −0.53 V *vs.* RHE with 86% FE for CO under ambient conditions, which is equivalent to a production rate of 80 kg d^{-1} m^{-2}. Chen *et al.*[78] developed a cell with 450 mA cm^{-2} partial current density with 90% FE for formate with a SnO_2 electrocatalyst. This corresponds to an impressive production rate of 88 kg d^{-1} m^{-2}. Liao *et al.*[129] implemented a Ni–N5–C single atom catalyst in a flow cell configuration, achieving industrial-scale performance for CO_2RR to CO a FE of 97% at a current density reaching a maximum of 1.23 A cm^{-2} with an FE of 99.6%, the highest production rate of CO_2RR to CO of 154 kg d^{-1} m^{-2} to date. The authors attributed the high performance to the Ni–N_5 catalytic site, which is superior in activating CO_2 molecules and reducing the energy barriers for the intermediate binding energy for boosting the kinetic activation process and catalytic activity. Endrődi *et al.* employed a PiperION membrane for electrocatalytic CO_2 reduction to CO in a tailored zero-gap electrolyser.[130] This membrane possesses high carbonate-ion conductivity, leading to a high CO current density (over 1 A cm^{-2}) with commercial Ag nanoparticles while maintaining a high FE for CO (up to 90%).

In contrast to the recent rapid advancement of the productivity of CO_2RR, industrially relevant durability has not been achieved yet. Many durability tests (Fig. 6b), including the aforementioned industrially viable production rates, are in the range of 10–100 h. There are only a few studies on CO_2RR to CO that report durability test results over 1000 h long. Notably, one case[44] involves a commercially available anion–exchange membrane (Sustainion) incorporated in MEAs, which illustrated at least 3800 hours of activity at 190 mA cm^{-2} with FE for CO_2RR to CO of 95% with a silver nanoparticle cathode and an IrO_x anode. The authors implemented two strategies to keep the membrane hydrated: (1) humidifying CO_2 and (2) circulating deionized water or diluted $KHCO_3$ solution in the anode.

In general, more thorough durability testing is required. So far, only *ex situ* and after-use characterization has been carried out for the CO_2RR electrolyser. There is an urgent need to develop conditions for accelerated testing and then correlating the results between accelerated aging and actual performance.

4.3. Minimizing the purification process

Here we suggest distinguishing between two performance metrics regarding the CO_2RR conversion. One is the CO_2 conversion efficiency (CE_{CO_2}) defined as the ratio of the amount of CO_2 converted into a target to the amount of CO_2 fed into the system. Another important but less discussed factor is product selectivity, defined as the fractional amount of the target product within the total stream. The former is relevant to the cost of CO_2 consumption and recovery if necessary, and there are some recent studies focused on CE_{CO_2}. The latter is important to determine how much energy is needed to purify the product in the following chemical process. The electrochemical cell can be divided into the cathode and anode compartments, and a path for the product stream is not always the same as the CO_2 flow pathway since the CO_2 can cross the membrane; CE_{CO_2} is often independent of the product selectivity.

Most CO_2RR studies have been carried out in neutral and alkaline electrolytes to impede HER, in which the high current density often creates a strongly alkaline microenvironment at the cathodic interface. This consumes some CO_2 in the feed through sequential chemical reactions of CO_2 driven by the pH gradient in the cell.[66,132,133] Specifically, an unfavourable reaction between CO_2 and OH^- produces carbonate or bicarbonate, which subsequently crosses the anion exchange membrane to the anode, reacts with H^+ from the oxygen evolution reaction, and is converted to CO_2 in the anode tail gas, giving rise to a low theoretical single pass conversion rate of 50%. Moreover, bicarbonates precipitate with alkaline metals at the cathode once their local solubility hits the limit, which closes microchannels for CO_2 and ion for the CO_2RR and causes a degradation mode.[134] It is expected that regenerating lost CO_2 demands additional energy and operating costs.

One adopted strategy for overcoming the CO_2 carbonation problem is to provide CO_2 regeneration space between the catalytic layer and an ion exchange membrane while maintaining the anionic micro-environment in the vicinity of the catalytic site. This methodology has been implemented by including additives in the catalyst layer or inserting an additional buffer layer.[124,135,136]

O'Brien *et al.*[135] developed a permeable CO_2 regeneration layer, which provides an alkaline environment at the CO_2RR catalyst surface and enables local CO_2 regeneration concomitantly. They coated the copper cathode layer with the functional groups of the anion exchange polymer (Aemion AP1-CNN5-00-X) to create a positive space charge, enabling the transport of anions and impeding the cations. The polymer coating on the cathode allows for CO_2 transport to the catalyst *via* diffusion through the water-filled hydrated ionic domains in the polymer matrix. With the careful tuning of the thickness of the regeneration layer of ∼10 μm to minimize impedance to CO_2 and water, they attained 85% CE_{CO_2} with a cation exchange membrane (Nafion 117) and deionized water. The authors proposed that the positively charged functional groups in the polymer structure act as a positive charge as an alternative to alkali metal cations, which can stabilize CO_2RR intermediates to promote C–C coupling on copper catalysts.

Li *et al.*[136] demonstrated that an acid-fed MEA for CO_2 electroreduction to CO with an H^+ to Cs^+ satisfies both the FE and conversion efficiency of CO_2. Essentially, an anion–exchange ionomer with quaternary ammonium side chains was incorporated into the Ag catalyst layer to shield the Ag surface from a high proton flux and provide diffusion pathways for dissolved CO_2 and water. After optimizing ion concentrations and operation parameters, they observed a single-pass conversion efficiency of ~90% and long-term stability of 50 h.

While such device and process engineering is an attractive approach, the carbonation of CO_2 at a microscopic level, which seems inevitable as long as the local environment is basic, and the subsequent regeneration process across the two components raise concerns about the long-term durability of the cycle. Moreover, the use of alkaline metals raises another issue of metal precipitation.[137,138] Therefore, designing a catalyst to accomplish acidic CO_2RR without alkaline metals is an imperative subject for tackling both the CO_2 conversion ratio and precipitation problem. One alternative is a metal-heteroatom-involved polymer catalyst, which is compatible with zero-gap CEM cells with deionized water.[131] Such a configuration may contribute to increasing the CO_2 conversion efficiency.

The product selectivity of CO_2RR is less discussed in most CO_2RR studies, though the plant process design requires the specification of the product component from the conversion unit to access the cost of the following purification. Krause *et al.*[139] reported the product gas composition in an effort to scale up the CO_2RR to CO. The ratio of CO_2 in the product gas was 10–50% which significantly depends on the CO_2 flow rate and current density. Since product selectivity is closely linked to operation and structural parameters, it is important to clarify both CO_2 conversion efficiency and product concentration, especially when the CO_2RR is scaled up.

There have been several recent approaches to engineer selectivity. Rather than a constant potential for electrosynthesis, Timoshenko and colleagues[140] have used electrical pulses to tune the products. This presumably protects the catalyst from poisoning. Liu *et al.*[141] developed pyramidal catalysts, the shape of which presumably controlled the selectivity. While such effects, such as confinement, have long been known, Zhu *et al.*[142] used multilayer pyramids to optimize selectivity by combining geometrical effects with layer sequencing to accelerate the reaction. To reach the requisite selectivity, such synergies in the catalyst (and even electrolyser) design must be exploited.

5. Conclusions

For CO_2RR to be rapidly implemented, it must be scalable and profitable, providing the means and incentive for the procedure. Scalability requires readily available catalysts, electrolytes, and devices that can safely operate with ambient CO_2. On the other hand, profitability necessitates affordable and durable electrolysers that synthesize value-added products with energy efficient processes at a sufficiently high rate and purity. While nature has had billions of years to perfect photosynthesis, our first intentional use of catalysts for any type of synthesis can be traced back to just over a century ago, and our efforts on CO_2RR are even more recent. Nevertheless, our knowledge has grown rapidly. This acceleration can be attributed to continued progress in experimental techniques with the advent of *in operando* measurements to verify the reaction mechanisms, the understanding and development of quantum chemistry to provide the theoretical framework, and now the use of artificial intelligence to examine trends to fill the gaps between experimental results and computational predictions in this multi-dimensional space. Discovery has been advanced by high throughput investigations, yet the promise of CO_2RR has yet to be realized on an industrial scale especially with perhaps the most important outstanding issues – purity and durability. Given the progress that humanity has made in the exceedingly short time spent investigating viable CO_2RR, in comparison to the eons nature has had to perfect the process, it is not a question of if we succeed in its realization but when.

Author contributions

Naohiro Fujinuma: Writing – original draft, writing – review & editing; Samuel Lofland: Conceptualization, writing – review & editing, funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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