



Recent advances in industrial CO₂ electroreduction

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Abstract

In light of the energy transition, electrochemical CO₂ reduction (CO₂R) has commonly been postulated as a favorable strategy for renewable energy storage and electrification of the chemical industry. However, for an effective impact of CO₂R, large-scale implementation of this technology is required. The majority of research in this field has focused on fundamental and mechanistic understanding of the CO₂R reaction and on the development of highly active and selective catalytic materials. Herein, we review the current status of the technology and discuss very recent developments and remaining challenges from an industrial perspective. We underscore the importance of system-level investigation and optimization of CO₂R aimed at industrialization of the technology.

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Introduction

Carbon capture and utilization (CCU) technologies have been proposed as an attractive way to alleviate CO₂ accumulation in the atmosphere and, consequently, positively impact the global climate change. As part of these CCU technologies, (bio)electroconversion of CO₂ has received increased interest in the past couple of decades, especially in view of favorable prospects related to renewable electricity production [1–3]. Research in this field has mainly focused on fundamental and mechanistic aspects of the electrocatalytic CO₂ reduction (CO₂R) [4,5]. Although significant progress is experienced in this field, there are still major challenges, which hinder the understanding of the electrocatalysis

of CO₂R [6]. Attractive benefits of CO₂R, such as a CO₂ neutral economy, a positive influence on the climate change, storage of renewable electricity in fuels, and decarbonization or defossilization of the chemical industry, are mentioned in the literature. However, these advantages are only in place when CO₂R is carried out on industrial scale, using renewable energy. Large-scale implementation of CO₂R technology is still at an infant stage because, in contrast to fundamental CO₂R studies, research to understand CO₂R from an industrial perspective and efforts to develop an industrial/commercial CO₂ electrolyzer is scarce.

It is well known that the selectivity, activity, and stability are key parameters, which impede the implementation of CO₂R in industry [7]. Each of these parameters has been investigated and are being improved by focusing on the nature of the electrocatalyst, the morphology of the electrocatalyst, the electrolyte composition, and process conditions [6,8]. From an industrial point of view, a techno-economic analysis (TEA) plays an important role as well, which indicates favorable output products, specific industrial routes, or specific requirements of the reactor [3,9–13]. Based on these recent TEA studies, the electrosynthesis of the 2-electron transfer products, formic acid and carbon monoxide, as preferred products could be competitive with current (nonelectrochemical) production methods, whereas electrosynthesis of higher order products is usually not economically viable. Although electrification of the chemical industry may be challenging to compete economically with the non-electrochemical routes or fossil fuel-based industry, we believe that the development of large-scale electrochemical technologies (e.g. for CO₂R) powered by zero-emission electricity is necessary in view of the enormous environmental impact and unavoidable CO₂ emission costs in the future. The economic viability of CO₂R processes depends not only on its technology readiness but also on future decision-making, incentives for green production routes, and carbon tax policies.

In this review, we cover advances toward industrial applications of CO₂R technologies. Very recent (2016–2018) literature and examples of (pre)commercial CO₂R industries are reviewed and discussed from an integrated and future industrial perspective to point out important breakthroughs and hurdles. Compared with the majority of available review articles in the field of CO₂R, looking from an industrial perspective to the CO₂R highlights

different aspects and explores different routes for research and development of this technology. We mainly focus on direct electrochemical CO₂R technologies where special attention is given to the reactor design, electrode structure, membranes, and anode reaction, while we avoid in-depth discussion of catalyst-related or mechanistic aspects and techno-economic analyses. Preconversion and postconversion technologies such as CO₂ capture, product separation, and purification are not covered in this review. Unless mentioned explicitly, we discuss CO₂R in aqueous electrolytes, which is more favorable in terms of large-scale application compared with nonaqueous electrolytes.

Status quo of industrial CO₂R technologies

Commercially available CO₂R technologies are almost nonexistent. The main challenge for the industrial electroconversion of CO₂ to chemicals lies in upscaling, which is related to optimization of the process to make it profitable and competitive. The few existing large-scale demonstrators of CO₂R are mainly in the precommercial stage. In 2011, Det Norske Veritas assembled a demonstration reactor (ECFORM) for the electrochemical reduction of 1 kg CO₂/day to formate/formic acid [14]. The device consisted of 600 cm² of electrodes with electrodeposited Sn as electrocatalyst and was powered by photovoltaics. Around the same time, Mantra Energy (currently not in existence) developed a pilot plant with 100 kg CO₂/day capacity by a similar process with the reactor on the basis of prototypes and patents by Oloman and Li [15]. Nowadays, other companies are developing technologies for CO₂R aimed at upscaling to a pilot plant. Carbon Recycling International and Mitsui Chemical Inc. are mature industries converting captured CO₂ to methanol. However, these processes do not electrochemically reduce CO₂ but use electrochemically produced H₂ for CO₂ hydrogenation on a ZnO-Cu/alumina catalyst. Dioxide Materials developed a commercial laboratory-scale electrolyzer (an integrated lab-scale process) that converts CO₂ to formic acid in the cathodic compartment using a nanostructured Sn catalyst on a gas diffusion electrode (GDE), and H₂O to O₂ in the anodic compartment containing an IrO₂ catalyst [16]. Siemens and Evonik have launched the Rheticus project in 2018, which aims at technology development for electrochemical reduction of CO₂ and H₂O to syngas, followed by fermentation and upscaling to the pilot level [17]. Carbon Electrocatalytic Recycling Toronto is another company working on upscaling their technology, which has reached a micropilot scale for the production of CO for syngas applications [18,19]. Because of the importance of this topic, many projects have been initiated recently, involving institutes, universities and companies from different countries aiming at developing an efficient and optimized process for CO₂ capture and (bio)electroconversion. Some of the relevant projects in Europe, recently finished or still on-going, are shown in Table 1.

The main approach of the industries discussed before and most of the projects shown in Table 1 is to scale-up an efficient reactor or process, working under environmentally relevant conditions, to realize a meaningful productivity. This step is the key factor to upgrade the electrocatalytic manufacturing into one of the top technologies in chemical and process CCU industries. On the other hand, these technologies are contributing directly to the objective of environmental decarbonization (through atmospheric CO₂ consumption) while at the same time, the rate of carbon resources used in chemical industries is getting reduced, making them sustainable and high valued nowadays and in close/midterm future.

In the following paragraphs, we zoom in on individual components which play an important role in the upscaling and commercialization of the CO₂R technology.

Reactor configuration

Fundamental research on CO₂R has mainly been carried out in batch-type, two-compartment electrochemical cells (H-cells), whereas for industrial application, these cells are not convenient because of mass transport limitations, high IR losses, and low current densities. Continuous-flow reactors have potential for the electrochemical CO₂R on industrial scale [20–22]. The reactors in use for low-temperature CO₂R can be categorized in membrane reactors or microfluidic reactors. At high temperatures (500–1000 °C), a solid oxide electrolyzer (SOE) can be used. The typical configurations of the various reactors are depicted in Figure 1.

Membrane reactors are the most used electrochemical cells in CO₂R research and show great potential for industrialization purposes. Recently, Merino-Garcia et al. [23] reviewed electrochemical membrane reactors for CO₂ utilization. This reactor type consists of an ion-exchange membrane which separates the anode and cathode compartment, leading to improved product separation and avoiding reoxidation of reaction products. The catalyst is usually incorporated in a gas diffusion layer (GDL) to enhance mass transport and increase the electrochemical active surface area. Another possibility is to coat the catalyst directly on the membrane (catalyst-coated membrane). These two reactor components, (gas diffusion) electrode and membrane, will be discussed in sections 4 and 6, respectively. A subdivision into gas–gas, gas–liquid, or liquid–liquid membrane reactors can be made on the basis the electrolyte state (Figure 1B–D) [24]. Introducing CO₂ as (humidified) gas is attractive because it allows to circumvent the solubility issues, to avoid the hydrogen evolution reaction by controlling the water content and to suppress CO₂ transport limitations. Masel et al. [25] introduced a novel three-compartment reactor for CO₂R to formic

Table 1

Some representative electrochemical CO₂ reduction projects.

Project name	Project lead (Country)	Target product	Description of the technology and achievements/objectives	Project's website
CHOCHCO	The French National Research Agency (France)	Methane via H ₂ and CO	Aims to develop a methane production plant on the basis of catalytic methanation of syngas (CO + H ₂) obtained from coelectrolysis of CO ₂ and H ₂ O. The technology has been demonstrated on laboratory scale.	https://chochco.fr/http://www.agence-nationale-recherche.fr/Project-ANR-13-SEED-0002
enCO2re	Covestro (Germany)	CO	Target technology includes the electrocatalytic conversion of CO ₂ to CO using renewable electricity as energy supply, coupling the electrolytic splitting of water into H ₂ and O ₂ with reuse of CO ₂ , and the implementation of gas diffusion electrode devices. The coupling of the two reactions forms the basis for a promising future one-step process technology for reducing/reuse CO ₂ emissions in waste gas streams, while delivering valuable chemical products.	http://enco2re.climate-kic.org/
VALCO2 II	Solvay (Belgium)	Obtained electrochemically: formic acid, methanol Via other routes: hydrogen carbonates, alkyl carbonates	Aims to develop large-scale CO ₂ conversion processes for various chemical and energy markets and to set up an observatory to identify available sources of industrial CO ₂ in France.	https://www.axelera.org/uploads/2015/07/AXELERA-RA-2013-GB-VF.pdf
BioRECO2VER	VITO (Belgium)	Lactate and isobutene	Aims to develop a process that includes enzymatic CO ₂ capture and bioelectrochemical systems using microbial platforms, in-situ generated H ₂ , and renewable energy for CO ₂ conversion. Along with a high-efficient novel fermentation design, it validates the most promising isobutene and lactate sustainable production route.	http://bioreco2ver.eu/
Kopernikus Power-to-X	Forschungszentrum Jülich (Germany)	Liquid fuels, H ₂ , syngas, and CO ₂ -based polymers	Electricity from renewable sources is first converted electrochemically into H ₂ , CO, and syngas. These resources are efficiently stored, distributed, and converted into the end product. The project consists of six research clusters, three of them related to electrolysis and three related to the conversion of syngas from electrolysis into fuels and chemicals via nonelectrochemical processes (heterogeneous catalytic synthesis).	https://www.kopernikus-projekte.de/projekte/power-to-x
Rheticus project	Siemens and Evonik (Germany)	Butanol and hexanol. Potentially other C ₂ , C ₄ , and C ₆ compounds	Aims to develop a technology able to electrochemically reduce CO ₂ and H ₂ O to syngas, followed by its fermentation toward high-value alcohols. They demonstrate the feasibility of 'technical photosynthesis,' proven successful in laboratory conditions. Aims to scale up to 20,000 tonnes per year by 2021.	https://www.siemens.com/press/en/pressrelease/?press=/en/pressrelease/2018/corporate/pr2018010135coen.htm&content[] = Corp https://www.creavis.com/sites/creavis/en/activities/current-projects/rheticus/pages/default.aspx
CO2perate	Ghent University (Belgium)	Formic acid	Conversion of CO ₂ to value-added chemicals using renewable energy on the basis of four catalytic routes (homogeneous and heterogeneous, photochemical plasma, electrochemical, and bio-based).	http://catalisti.be/project/co2perate/

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Table 1 (continued)

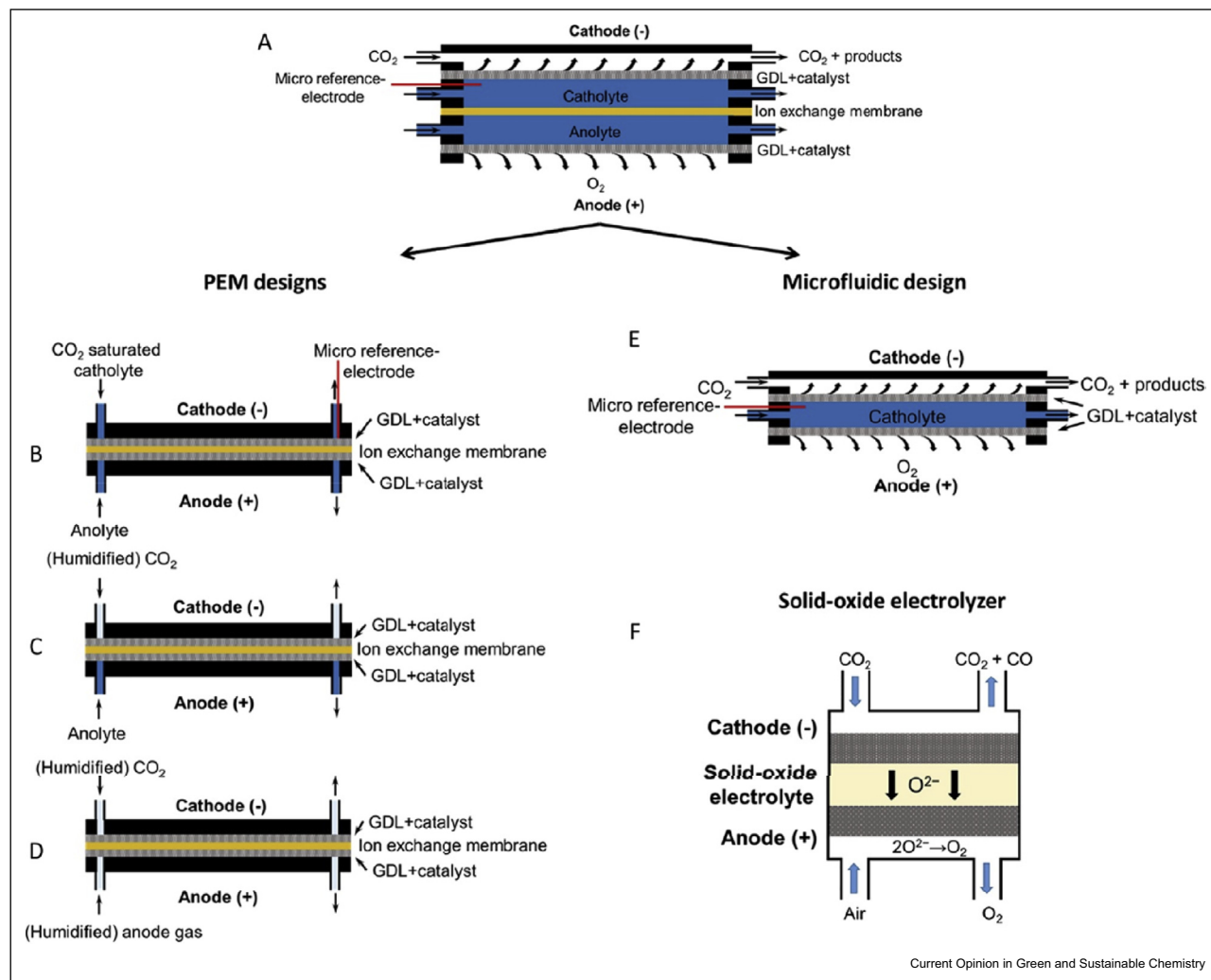
Project name	Project lead (Country)	Target product	Description of the technology and achievements/objectives	Project's website
eForFuel	Max Planck Institute of Molecular Plant Biology (Germany)	Propane and isobutene	Earth-abundant metals will be used as catalysts (except in bio-based catalysis). Produced formic acid will be used as a building block for the biocatalytic production of value-added chemicals, such as single-cell proteins, or as a H ₂ carrier. Aims to develop an integrated electrobioreactor to produce hydrocarbons. Includes the electrocatalytic conversion of CO ₂ to formic acid and the bacterial conversion of formate toward hydrocarbons.	https://www.eforfuel.eu/
OCEAN	European Research Institute of Catalysis (Belgium)	Formic acid and oxalic acid Potentially other high-value C2 compounds and polymers.	Aims to develop an integrated process for the production of oxalic acid from formate, previously obtained electrocatalytically from CO ₂ . Claims to bring this technology one step away from commercialization, converting 250 g of CO ₂ per hour at 1.5 kA/m ² . The energy efficiency will be improved by coupling the cathodic reaction to the oxidation of glucose at the anode.	https://www.spire2030.eu/ocean
Recode	Fondazione Istituto Italiano di Tecnologia (Italy)	Formic acid, oxalic acid, and glycine	CO ₂ from the flue gases produced by the cement industry is reused partly within the plant itself to produce cement-related products in a circular economy approach technology. Meaningful CO ₂ emission reduction (20%) and mass production of high-value products would be some of the features achieved on scaling up the process.	https://www.recodeh2020.eu/project
ENGICOIN	Fondazione Istituto Italiano di Tecnologia (Italy)	Lactic acid, PHA bioplastics, and acetone	Development of three microbial factories (from TRL 3 to 5) exploiting CO ₂ sources and renewable solar radiation or H ₂ for the production of value-added chemicals. To achieve competitive selling prices for the key target products, high process integration will be guaranteed.	https://www.engico.in.eu/
TERRA	European Research Institute of Catalysis (Belgium)	Polyethylene furanoate	Aims to develop a tandem electrocatalytic reactor from TRL 3 to 5. Objectives include the operation at higher pressures and temperatures than conventional electrochemical devices, the use of noble metal-free and 3D electrocatalysts and electrodes with modulation of activity.	http://www.terraproject.it/
E2C	TNO (Netherlands)	Fuel and platform chemical	Conversion of CO ₂ into chemicals and fuels using renewable electricity in a demonstrator (up to TRL 6-7)	https://www.interreg2seas.eu/en/E2C

PHA, poly hydroxy butyrate; TRL, technology readiness level.

acid and reported improved CO₂R performance (stability of 500 h, cell voltage of 3.5 V, current density of 140 mA cm⁻², and faradaic efficiency up to 94%). In this configuration, a center compartment separated by a cation-exchange membrane and anion-exchange

membrane (AEM) at, respectively, the anode and cathode side has the ability to use protons produced at the anode to acidify formate ions produced at the cathode to obtain the more valuable formic acid. Such a configuration can circumvent expensive separation/

Figure 1



Various configurations for electrochemical flow reactors. (A) General design; (B–D) membrane reactors depending on the state of catholyte and anolyte; (E) classical microfluidic reactor; and (F) solid oxide electrolyzer. GDL, gas diffusion layer. This figure is reproduced with permission from Ref. [20].

purification downstream processes. In terms of upscaling, inspiration can be sought from the state-of-the-art large-scale membrane reactors such as chlor-alkali and hydrogen electrolyzers. A possible configuration for a future CO₂ electrorefinery, which aims to create an industrial (bio)electrochemical production platform to convert waste CO₂ to building block chemicals and higher organic compounds, was proposed recently². To reach this level, VITO targets to improve the overall energy efficiency by developing high selective CO₂ capture and conversion processes, more efficient purification technologies, and robust catalyst systems.

Microfluidic reactors for CO₂ electroreduction were introduced by Whipple *et al.* [26]. In this configuration, a membrane is not needed to separate anode and

cathode, and the separation is established by the flowing electrolyte within a <1 mm channel. Better control of flooding and dry-out phenomena at the electrodes (electrode wetting) and mixed-media operation are reported to be the advantages of this configuration [26,27]. However, pressurization and scale-up is generally more difficult compared with a membrane reactor. CO₂R studies in microfluidic reactors have been limited to the screening of different electrocatalysts and operating conditions.

CO₂R in an SOE has been studied since the previous decade [28]. Recently, more attention has been given to this type of reactor for CO₂R due to its operation under high temperature, longer operation times, and coelectrolysis of CO₂ and H₂O for the production of syngas

[29,30]. However, because a TEA has not been reported for CO₂R in an SOE, it is difficult to assess the economic viability of industrial CO₂R in an SOE. In addition, the flexibility of the process in terms of components using an SOE is relatively poor because the electrode has to be very specialized (usually Ni-yttria stabilized zirconia (YSZ), lanthanum strontium manganite-YSZ electrodes), leading to a specific product distribution besides the intrinsic weaknesses of high T operation (thermal stress, diffusion, nonequilibrated anion-conducting membrane). We, therefore, believe that the membrane and microfluidic reactors have a higher potential to be used in large-scale CO₂R processes compared with an SOE.

The main advantages and disadvantages of the various reactor designs are shown in Table 2.

Electrode structure

In this section, we focus on the configuration and composition of the cathode and highlight recent advances leading to the improvement of CO₂R performance. Aiming at a CO₂ electrolyzer operating at industrial scale, GDEs have been suggested because of lower mass transfer resistance and larger availability of active sites per unit area compared with planar electrode

systems [31]. GDEs have been used for a variety of catalysts, ranging from metals, metal-free catalysts, molecular catalysts, enzymes, and microbes [32–34]. As shown in Figure 2, a GDE is generally composed of a catalyst layer (CL), GDL, and current collector. The GDL is a porous medium that facilitates transport of reactants and products to and from the CL and consists of a macroporous layer either with or without a microporous layer (MPL). A wide variety of GDL parameters have been investigated to enhance electrolyzer or fuel cell performance [33]. However, optimization of GDEs for CO₂R has been given little attention.

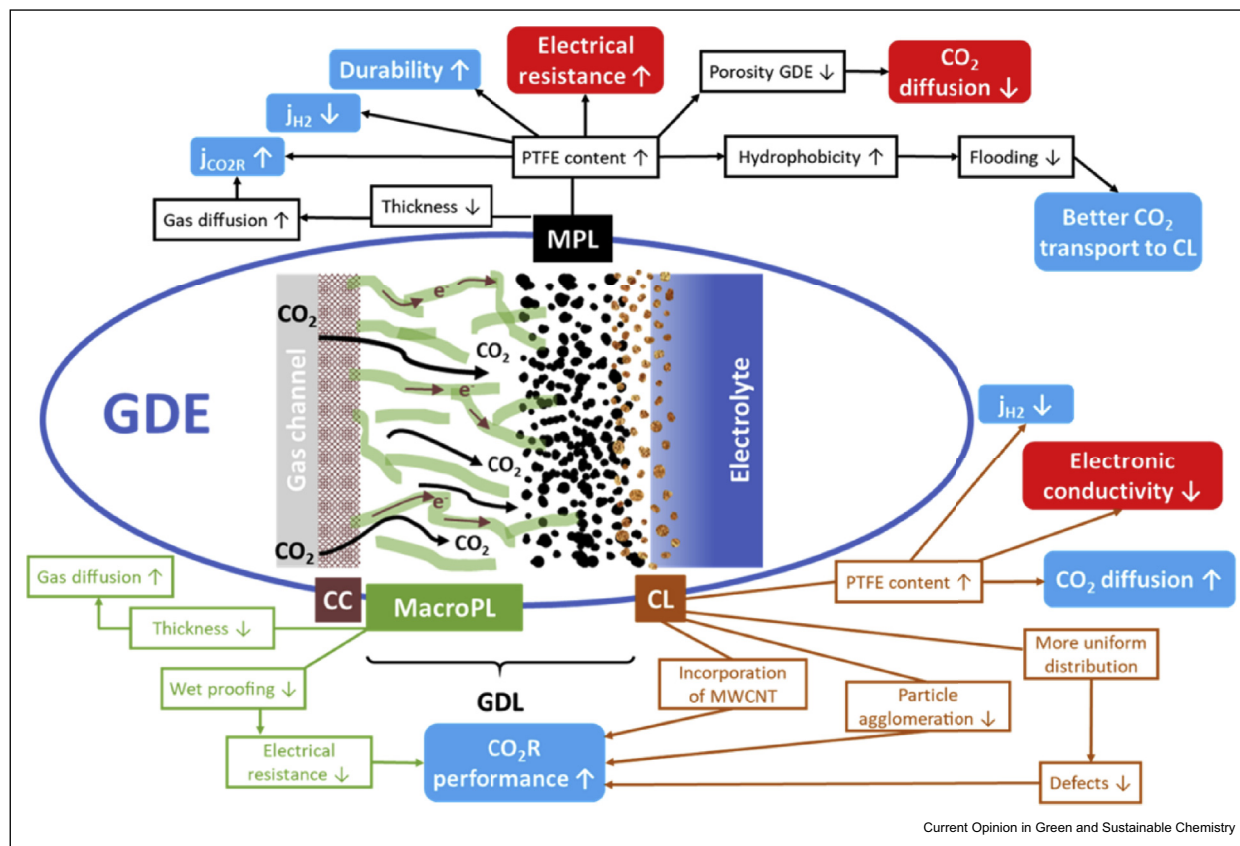
Weng et al. [31] developed a model of a GDE consisting of a Ag catalyst for CO₂R to CO, which provides a quantitative basis for the effects of different parameters. They showed that the performance strongly depends on the local environment of the CL and interaction between reaction kinetics and transport phenomena. The influence of wettability, catalyst loading, flow rate, and porosity on the local CO₂ concentration was discussed quantitatively, and it was concluded that flooding of the CL leads to an inhomogeneous CO₂ distribution and poor catalyst utilization. Such a model can provide guidelines on how to tune design parameters of GDEs for improved performance of CO₂R. Han et al. [35]

Table 2

Main advantages and drawbacks of CO₂R reactor configurations.

Reactor configuration		Advantages	Drawbacks
Batch reactors	One-compartment cells	<ul style="list-style-type: none"> Simple design Convenient for small-scale experiments 	<ul style="list-style-type: none"> Poor mass transfer Poor mixing Reoxidation of reaction products at the anode Contamination of working electrode more likely
	Two-compartment cells (H-cell)	<ul style="list-style-type: none"> Convenient to study half-cell reactions Convenient for small-scale experiments Separated compartments avoid product crossover and reoxidation 	<ul style="list-style-type: none"> Poor mass transfer Poor mixing Additional losses due to membrane resistance
Continuous-flow reactors	Membrane reactor	<ul style="list-style-type: none"> Relatively easy to upscale Different configurations possible Pressurization relatively easy Existing know-how, due to similarities with water electrolyzers Straightforward stack construction 	<ul style="list-style-type: none"> Little knowledge on effects of various types of membranes Membrane may lead to additional resistance or product crossover Membrane cost and stability issues
	Microfluidic reactor	<ul style="list-style-type: none"> No membrane included Fast screening of catalysts under various operating conditions Better control of flooding/dry-out phenomena at electrodes 	<ul style="list-style-type: none"> Less effective separation of reaction products from electrodes Difficult to pressurize compared with the membrane reactor Scale-up more difficult compared with the membrane reactor
	Solid oxide electrolyzer	<ul style="list-style-type: none"> Decrease in overpotentials Increase in charge transfer Long-term CO₂ electrolysis feasible (~500 h) 	<ul style="list-style-type: none"> Extreme conditions required Impurities in the gas stream may lead to electrode passivation Techno-economic feasibility for CO₂ reduction unknown Specialized electrode needed

Figure 2



Schematic of a gas diffusion electrode including interrelated effects of the GDL and CL design parameters. Parameters shown in the black, brown, and green boxes refer to the microporous layer, catalyst layer, and macroporous layer, respectively. Positive effects are shown in blue, and negative effects, in red colored boxes. GDL, gas diffusion layer; CL, catalyst layer; PTFE, polytetrafluoroethylene; MPL, microporous layer; CC, current collector; GDE, gas diffusion electrode.

demonstrated the important role of the flow configuration on the CO₂R performance. They reported enhanced activity and selectivity of CO reduction to C₂H₄ on a Cu GDE in a flow-through configuration of GDE compared with a flow-by configuration. The differences are explained by a low diffusion constant and solubility in the latter configuration and are expected to play a role in CO₂R as well.

There are several technologies for the preparation of GDEs. Wet deposition methods, where a catalyst ink is coated on a support, are time-consuming, whereas a dry pressing method is relatively simple and easily upscalable [36]. Focusing on CO₂R, the deposition methodology of the CL has been reported to ultimately affect the CO₂R performance. Jhong *et al.* [37] showed that a fully automated air-brushing method of CL deposition leads to significant higher partial current density for CO on silver GDEs compared with hand-painting and screen-printing techniques. This enhancement is attributed to an increase in homogeneity and a decrease of agglomeration in the CL. Another strategy to enhance the performance of the

silver-based CL for CO₂R to CO is the incorporation of multiwalled carbon nanotubes (MWCNTs), leading to enhanced current densities, which is partly due to a decreased charge-transfer resistance [38]. Moreover, uniform mixing of Ag nanoparticles with MWCNTs shows better results compared with a Ag layer on top of an MWCNT layer. Recently, Dinh *et al.* [39] reported on the increased stability and selectivity of CO₂R to C₂H₄ on an ‘abrupt reaction interface’ in highly alkaline media. In this configuration, the Cu catalyst was embedded between a hydrophobic polytetrafluoroethylene (PTFE or teflon) layer and conductive carbon nanoparticles, which maintains the hydrophobicity of the GDL and consequently prevents flooding.

The GDL may contain an MPL, which improves electrical conductivity and water management. The Kenis group investigated several properties of the MPL with respect to CO₂R performance in a microfluidic flow cell. They found that the presence of an MPL enhances CO₂R toward CO with tenfold higher activity, due to the increased electronic conductivity, the ability to prevent

flooding of the CL, and catalyst loss from the CL [40]. Another parameter that is investigated is the amount of PTFE binder in the MPL. The PTFE content determines the hydrophobicity of the MPL, which ideally prevents the electrolyte flow from CL through the MPL, but decreases the electronic conductivity. Owing to counteracting influences of these parameters, there is usually an optimum of PTFE content for the MPL [40] and CL [41]. A qualitative overview of the effects of different parameters is summarized in Figure 2.

Wang et al. [42] reported a membrane that functions as a GDE without the need of a binder, exhibiting less ohmic losses, increased stability, large amount of active sites, and hence enhanced CO₂R activity. Such catalyst-coated membranes have been observed before with a molecular catalyst for CO₂R and for the oxygen evolution reaction (OER) [43,44]. We believe that the optimization of this type of catalyst configuration can play an important role in the industrialization of the CO₂R process.

Anode reaction

For the operation of a CO₂ electrolyzer, an electro-oxidation process at the anode must occur simultaneously with CO₂R at the cathode. Because the majority of CO₂R research has focused solely on the cathode reaction, the anode reaction is often not closely looked into as part of the complete system. The OER as half reaction has been under study for a century and has been optimized over the last few decades. It is important to improve the anode reaction as part of the complete CO₂R system because it has been shown that lowering the overpotential of the anode reaction significantly benefits the total cell energy efficiency and, consequently, the electrical requirements of a CO₂ electrolyzer [45]. Usually, water splitting (OER) is the reaction taking place at the anode, producing O₂ from H₂O at high overpotentials. Here, we highlight CO₂R studies that take into account the anode reaction, instead of research on the OER as half reaction. Luc et al. [44] reported that titanium-based materials are ideal catalyst supports for OER catalysts compatible with near-neutral operation conditions of CO₂R in aqueous media. Moreover, Ti coated with Ir has shown excellent stability and OER activity. Other Ir-based anode materials have been reported to have a beneficial effect on the overall performance of the integrated system [46,47]. From an economical perspective, the use of Ir-based catalysts is undoubtedly less attractive [10]. However, it is still the catalyst of choice because of stability/performance. Cheaper alternatives (lower loading and effect of support) are also being sought after including non-PGM materials, but there is a lack of upscaling strategies. Another strategy to improve the anode reaction is to step away from the OER. Other anode reactions, such as the oxidation of chloride ions to

Cl₂ and the oxidation of alcohols to ketones/aldehydes/carboxylic acids, leading to an additional benefit of producing value-added products at both electrodes, have been studied [45,48,49]. For a large-scale operation, the anode reactions apart from OER still need to be optimized for continuous operation and included in techno-economic analyses.

Membranes

Apart from the cathode and anode which can positively impact the energetic efficiency of a CO₂ electrolyzer by decreasing the respective overpotential, another measure to obtain lower energy requirements is to lower the IR drop between anode and cathode. The majority of CO₂R research used cation- or proton-exchange membranes, viz., Nafion™ [20,23]. However, recently, AEMs and bipolar membranes (BPMs) have received increased interest for CO₂R [20,50–52]. The difference of using these membranes lies in the transport of ionic species from anode to cathode and vice versa. In case of a BPM, water is dissociated into H⁺ and OH[−], which is driven toward the cathode and anode, respectively, leading to similar pH on both sides of the membrane, allowing for different compositions of anolyte and catholyte. In all cases, thinner membranes are generally better performing because of a lower resistance but bring along sealing and cross-contamination issues.

Product crossover is an important aspect of membranes. Recently, this issue was investigated for AEMs and BPMs [53]. It was found that through AEMs, the rate of product crossover is proportional to the current density, and even neutral alcohols experience crossover, as is the case for AEM fuel cells. In addition, BPMs were found to inhibit charged and neutral product crossover owing to the outward fluxes of generated H⁺ and OH[−] species, leading to enhanced performance.

Dioxide Materials has developed ion exchange Sustainion® membranes that contain imidazolium functional groups, which were found to improve the performance and steer the selectivity toward CO₂R products [54,55]. Aeshala et al. [56] highlighted the improved CO₂R efficiency of quaternary ammonium groups in anionic solid polymer electrolytes. Recently, it was reported that encapsulation of the catalyst in different types of polymers may have a significant influence on the CO₂R selectivity and stability, depending on the nature of the polymer [57]. The design and tuning of the membranes can, therefore, be an attractive strategy toward enhancement of CO₂R performance in membrane-type reactors needed for large-scale implementation.

Conclusions and future perspectives

Industrial CO₂R may not be economically competitive compared with fossil fuel-based alternatives for the

chemical industry and energy storage. However, from an environmental and sustainability perspective, it is needed to realize this technology on large scale via pilot plants or demonstrator electrolyzers. Prospected carbon taxes in the future for CO₂ emissions, together with the need for intrinsically flexible production methods using renewable power as energy input, will also pave the way for this approach, especially when imposed on a global scale. Despite breakthroughs in the individual components on small scale, the key bottleneck toward industrialization of the electrochemical CO₂R process is system integration and system-level optimization. Solely focusing on either high selectivity, activity, stability, cost, or scalability would not be effective; a trade-off between all the parameters is ultimately required. Hence, research and demonstration activities are needed, studying the interactions between the individual technological aspects to come to the optimization of a CO₂R electrolyzer as a complete system. The next steps would be to emphasize on the reactor design for enhanced mass transport, as well as on the robustness of the catalysts and electrode structures under various operational regimes.

Conflict of interest statement

Nothing declared.

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