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Review Article

Developments on carbon dioxide reduction: Their promise, achievements, and challenges

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Abstract

CO_2 reduction processes continue to be developed for electrosynthesis, energy storage applications, and environmental remediation. A number of promising materials have shown high activity and selectivity to target reduction products. However, the progress has been mainly at a small laboratory scale, and the technical challenges of large scale CO_2 reduction have not been considered adequately. This review covers recent advancements in catalyst materials and cell designs. The leading materials for CO_2 reduction to a number of useful products are presented with their corresponding cell and reactor designs. The latest efforts to progress to industrially relevant scales are discussed, along with the challenges that must be met for carbon dioxide reduction to be a viable route for mass scale production.

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Carbon dioxide reduction, Electrosynthesis, Energy storage.

Abbreviations

CO_2RR, carbon dioxide reduction reaction; HER, hydrogen evolution reaction; FE, Faradaic efficiency; GDE, gas diffusion electrode; MEA, membrane electrode assembly; PEM, proton exchange membrane; SEM, scanning electron microscope.

Introduction

CO_2 reduction is a key component in the global plan to offset carbon emissions and reduce human impact on the environment. The CO_2 reduction reaction (CO_2RR) offers a viable synthetic route to a number of industrially important materials that are usually sourced from fossil fuels, such as methane, ethylene, formate, and CO [1]. Feedstock CO_2 could be captured from industrial processes that would otherwise release CO_2 into the atmosphere, reducing total CO_2 emissions and fossil fuel dependence in one process. Additionally, CO_2 reduction reactors can be integrated into intermittent green power sources such as wind or solar, where CO_2 is converted into a fuel such as methanol during peak energy production, which can then supplement energy production during periods of low energy generation.

The feasibility of CO_2RR as a long-term solution to the synthesis of useful materials or in fuel production requires the optimization of both the catalyst materials and the reactor design to maximize the product production with minimal energy input. This is especially complex for the CO_2RR, as the wide range of potential products means that even the most selective systems currently produce a mixture of multiple products. Such mixtures are costly to separate, and so achieving a system that is selective to a single CO_2RR reduction product is a vital step for this to be economically viable.

This review will discuss the latest developments in catalyst and reactor design for the CO_2RR. We will cover the challenges faced when trying to drive CO_2RR to a specific product and look forward to where the next developments are needed to make CO_2RR a more widespread means of environmentally friendly chemical synthesis and energy storage technology.

Fundamentals and mechanisms of the CO_2RR

The reduction of CO_2 at a heterogeneous catalyst surface can afford a number of different products. The most commonly reported are given below: [2].

$$CO_2 + 2e^- + H^+ \rightarrow HCO_2^- \quad E^0 = -0.02\,V\,vs.\,RHE \quad (1)$$

$$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O \; E^0 = -0.10\,V\,vs.\,RHE \quad (2)$$

$$CO_2 + 6e^- + 6H^+ \rightarrow CH_3OH + H_2O \; E^0 = 0.10\,V\,vs.\,RHE \quad (3)$$

$$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O\ E^0 = 0.03\ V\ vs.\ RHE \quad (4)$$

$$2CO_2 + 8e^- + 7H^+ \rightarrow CH_3COO^- + 2H_2O\ E^0 = -0.26\ V\ vs.\ RHE \quad (5)$$

$$2CO_2 + 10e^- + 10H^+ \rightarrow CH_3COH + 3H_2O\ E^0 = 0.05\ V\ vs.\ RHE \quad (6)$$

$$2CO_2 + 12e^- + 12H^+ \rightarrow CH_3CH_2OH + 3H_2O\ E^0 = 0.09\ V\ vs.\ RHE \quad (7)$$

$$2CO_2 + 12e^- + 12H^+ \rightarrow C_2H_4 + 4H_2O\ E^0 = 0.08\ V\ vs.\ RHE \quad (8)$$

$$3CO_2 + 16e^- + 16H^+ \rightarrow CH_2CHCH_2OH + 5H_2O\ E^0 = 0.11\ V\ vs.\ RHE \quad (9)$$

$$3CO_2 + 18e^- + 18H^+ \rightarrow CH_3CH_2CH_2OH + 5H_2O\ E^0 = 0.21\ V\ vs.\ RHE \quad (10)$$

Equations (1)–(10) highlight the challenge facing systems for selectively producing one CO_2RR product, as there is significant overlap between the standard potentials for all of these products. This is further complicated by the hydrogen evolution reaction (HER), which is present over this same potential range.

$$2H^+ + 2e^- \rightarrow H_2\ E^0 = 0.00\ V\ vs.\ RHE \quad (11)$$

The CO_2RR begins with an initial adsorption of CO_2 onto a vacant catalyst site and subsequent electron transfer [3]. The CO_2RR then proceeds via a series of intermediates that determine the product [4]. Proposed routes to a number of CO_2RR products are given in Figure 1.

The selection of the correct catalyst material allows for reasonable selectivity to a specific product, by favoring certain reaction intermediates or by hindering or facilitating the formation of carbon–carbon bonds to give C_1 or C_2 products, respectively. A number of pure metals catalysts show selectivity toward specific CO_2RR products. In aqueous electrolytes, Pb, Hg, In, Tl, Cd, and Sn catalysts favor formate, whereas Au, Ag, Pd, and Zn catalysts favor CO [5].

Cu is unique in that it is capable of producing substantial amounts of multiple products; predominantly CO, methane, formate, and ethylene [6]. All of the products in Equations (1)–(10) have been detected under certain conditions, although some featured with Faradaic efficiencies < 1% [2]. Only Cu-based catalysts give C_{2+} species in significant amounts because of the favorable formation of C–C bonds [7,8]; some alloys such as Ni_3Al [9] and PdAu [10] have produced detectable C_{2+} products, but Faradaic efficiencies have thus far been limited to < 2%.

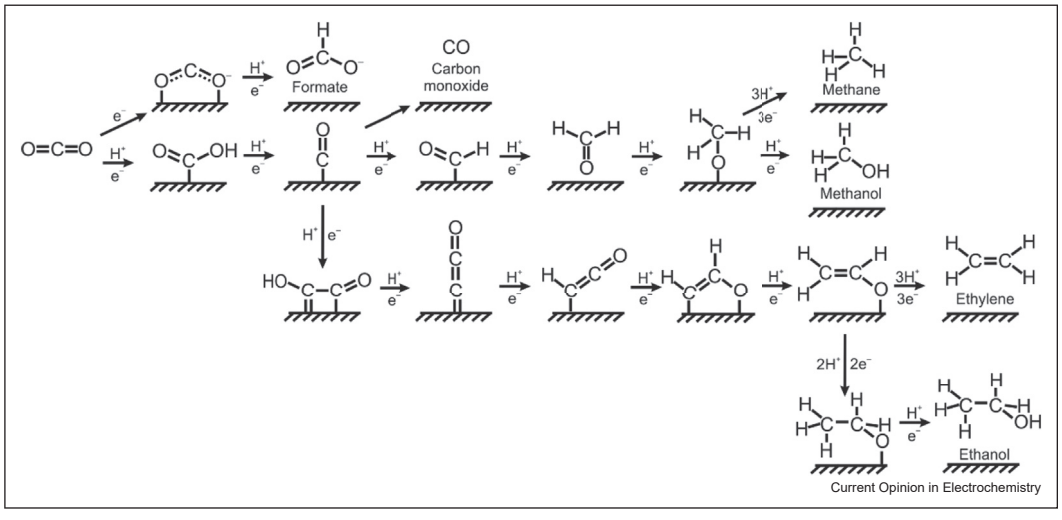
Catalyst designs

A number of metal alloys [11] and doped carbon materials [12] have been investigated for CO_2 reduction, giving reasonable selectivity for a range of C_1 and C_2 products. Some of the leading materials are given in Table 1.

Catalyst micro-structuring and nanostructuring

Modifications to the CO_2RR catalyst structure may impact the overall activity or selectivity toward a certain product. Simple materials are enhanced by maximizing the electrochemically active surface area via

Figure 1



Proposed reaction mechanism for CO_2RR. Routes are shown for producing formate, CO, methane, methanol ethylene, and ethanol, based on the lowest energy pathways from computational studies [4].

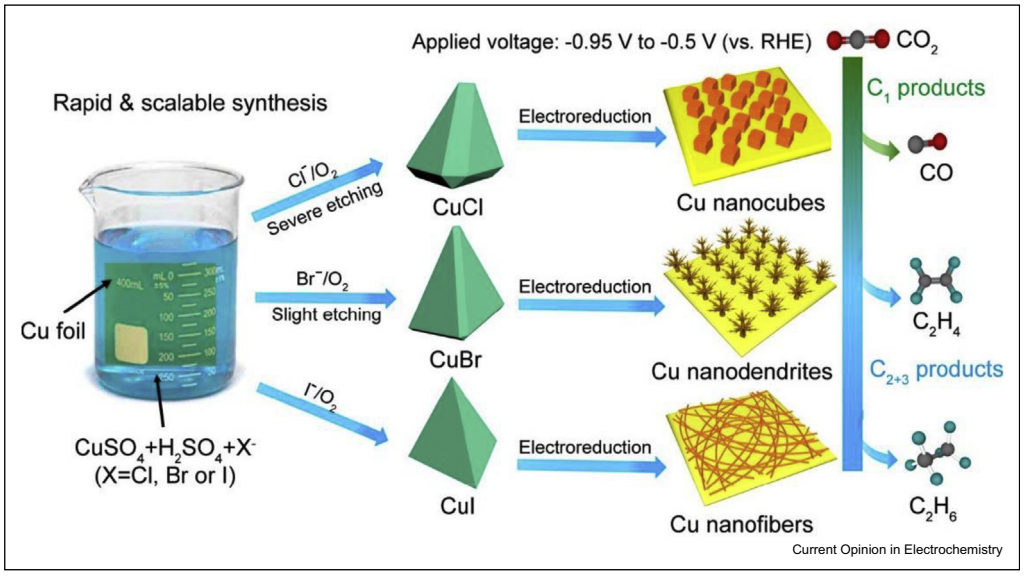
Table 1

A sample of the leading catalysts for CO_2RR published in the last 2 years for a number of CO_2RR products, with the corresponding Faradaic efficiencies (FE), current densities (*j*), and cell designs.

Product	Metal	Electrode	Cell	Electrolyte	*j*/mA cm^{-2}	FE/ %	Ref.
CO							
	Fe–N–C	Nanoparticles	H-cell	0.5 M $NaHCO_3$	7.5	91	[13]
	PdNi	Nanoparticles	H-cell	0.5 M $KHCO_3$	4.68	85.1	[14]
	Co (phthalocyanine)	Carbon ink on GDL	Flow electrolyser	1 M KOH	165	94	[15]
Formate							
	S–In	Nanoparticles	H-cell	0.5 M $CsHCO_3$	84	93	[16]
	SnPbSb	Oxide derived foil	H-cell	0.1 M $KHCO_3$	8.3	91	[17]
	Bi	Porous dendrites	PEM electrolyser	1 M $KHCO_3$ + 0.1 M $CsHCO_3$	17	95	[18]
Methane							
	Cu_2O@Cu-MOF	Carbon ink on glassy carbon	H-cell	0.1 M $KHCO_3$	13.3	63.2	[19]
	AgCu	Foil	H-cell	0.1 M $NaHCO_3$	9	55	[20]
	FeCu@GaN	Nanowires	H-cell	0.5 M $KHCO_3$	38.3	51	[21]
Methanol							
	CuSe	Nanoparticles	H-cell	[Bmim]PF_6 (30 wt%)/CH_3CN/H_2O (5 wt%)	41.5	77.6	[22]
	$PdSnO_2$	Nanoparticles	H-cell	0.1 M $NaHCO_3$	1.5	54.8	[23]
Ethylene							
	Cu	Nanoparticles	Flow electrolyser	3.5 M KOH/5 M KI	750	63	[24]
	CuAg	Nanoparticles	Flow electrolyser	1 M KOH	300	60	[25]
	Cu/*N*-arylpyridinium	Nanoparticles	MEA	1 M $KHCO_3$	600	64	[26]
Ethanol							
	CuAg	Nanoparticles	Flow electrolyser	1 M KOH	300	25	[25]
	$Ce(OH)_x$/Cu	Nanoparticles	Flow electrolyser	1 M KOH	300	43	[27]
	$Cu_{0.5}$-N-C	Carbon ink on GDL	H-Cell	0.1 M $CsHCO_3$	16.2	43	[28]

CO_2RR, CO_2reduction reaction; MEA, membrane electrode assembly; PEM, proton exchange membrane.

Figure 2



Schematic synthesis route to a number of copper microstructures via selective etching in different acidic halide media. Electrochemical reduction of the resultant copper halide gives varying microstructures, each with selectivity to a different CO_2RR product. Reprinted with permission from H. Wang et al., Nano Lett 2019, 19, 3925–3932. Copyright 2019 American Chemical Society.

microstructuring and nanostructuring techniques [29–31]. These can be engineering through electrodeposition, de-alloying, or templates, giving access to a range of surface structures including nanorods, foams, corals, and inverse opals [32]. One method that has received increasing interest is to cycle metals in halide electrolytes, causing metal dissolution to leave a highly active microstructure [33,34]. Interestingly, the choice of halide impacts the microstructure and CO_2RR product, providing a simple route to product specificity (Figure 2) [35].

Porous structures also impact the local pH and mass transport of gases at the electrode surface [36]. Recent experimental and computational studies showed that dendritic metal surfaces favor C_2 products by optimizing both factors [37,38]. Similarly, foam electrodes give increased alkalinity with the porous structure, which simultaneously disfavors H_2 evolution while facilitating CO and ethylene production [39].

Nanoparticle catalysts exhibit size-dependent and shape-dependent performance; differently sized or shaped particles give different facets and defect sites [40], which results in product yield being directly affected by nanoparticle size [41]. Oxide-derived catalysts reduce metallic oxides to reveal a highly active surface [42,43]. These show increased selectivity toward C_2 over C_1 products [44] and can enhance nanoparticle and dendritic catalysts by providing additional defect sites [45,46].

The high activity of nanostructured surfaces give intrinsic challenges in stability because of high atom mobility and particle aggregation, resulting in the loss of catalyst mass and active structures [47]. A number of approaches have been taken to address this, such as using metallic supports [48], coating catalysts in carbon [49], and using zero-gap membrane configurations [50], though further developments are still needed to reach selectivity, activity, and stability targets with a single material.

Alloyed materials

The range of alloyed materials used for CO_2RR is incredibly broad and has been the subject of a number of extensive reviews [6,11,51]. Introducing alloying elements can tune the adsorption strength of certain intermediates to drive CO_2RR toward a specific product. Owing to the wide range of potential products, copper catalysts are subject to a broad range of alloying studies. Doping copper with Fe [21], Ni [52], S [53,54] or Bi [55], and $Ce(OH)_2$ [27] have been shown to increase selectivity toward methane, CO, formate, and ethanol respectively, by favoring specific intermediates in the CO_2RR pathway.

Similar effects have been shown with copper catalyst by producing materials that confine copper within multiple oxidation states. Recent works have highlighted a synergistic role of Cu(I) and Cu(0) in the crucial C–C bond formation step for ethylene formation [56]. Cu surface modifications that result in a mixed Cu(0) and Cu(I) surface component have therefore been used to enhance the ethylene yield [57,58]. One of the leading systems for ethylene production used this approach to achieve 40% ethylene at 400 mA cm^{-2} [59].

Catalyst coatings

The reaction environment at the catalyst surface has a sizeable impact on both the reactant rate and product selectivity for the CO_2RR. Often, works refer to the 'triphasic interface' meaning gaseous CO_2 at the interface between the solid catalyst and liquid electrolyte. Various coatings can trap CO_2 and facilitate reduction, such as polymers with intrinsic microporosity for ethylene [60], and metal organic frameworks (MOFs) for methane [19]. Others use the polymer layer to hinder hydrogen evolution, where hydrophobic coatings hinder water reduction to increase the CO_2RR yield for ethylene and ethanol [61]. Recent works have shown a new function of polymer coatings that can drive the formation of active nanostructures during CO_2RR itself. CO_2RR at Cu electrodes with an *N*-aryl pyrdinium drove the formation of Cu nanocubes, leading to enhanced ethanol and ethylene production [26,62].

Catalyst supports

Gas diffusion electrodes (GDEs) provide a rapid rate of CO_2 mass transport and negate poor CO_2 solubility in aqueous electrolytes [63]. Carbon GDEs can enhance the HER, so choosing a material that is less active toward HER gives an increased Faradaic efficiency toward CO_2RR products [64]. One of the leading GDEs for ethylene production replaced the carbon GDE with a hydrophobic polymer, giving Faradaic efficiencies exceeding 60% up to 750 mA cm^{-2}, with consistent performance over 150 h [24].

Carbon-based materials can still be useful for CO_2RR, particularly when surface and structural changes can be made to enhance the hydrophobicity [65]. Incorporating catalytic metal sites into the carbon structure gives promising catalysts for a number of CO_2RR products, such as Au/C for CO [66] or CuN_4/C for ethanol [28]. A further route is to start with materials that are known to have high CO_2 storage capacities, which enhances catalyst performance [67]. Catalytic sites have also been encapsulated in MOFs. Although MOF based catalysts themselves are limited by poor stability and selectivity [68], MOF-derived catalysts are an interesting route to catalytic sites in highly N-doped carbon environments, which have been achieved for formate [69] and CO [70] selective catalysts.

It is worth noting that removing the HER is not always desirable for the CO_2RR. Syn-gas in an industrially important mixture of CO and H_2, so a reactor capable of producing CO from the CO_2RR and H_2 from the HER is of interest [71]. In these cases, the ratio of CO to H_2 becomes important, because the HER tends to outpace the CO_2RR at larger current densities, although careful reactor design can give a fair degree of control over the ratio [72].

Electrolytes

Certain electrolytes can hinder the HER, improving the efficiency toward CO_2RR products. High pH electrolytes slow the kinetics of the first water reduction step and strongly adsorbing OH^- blocks H_2 evolution sites [73]. The same surface-blocking effect has been demonstrated with strongly adsorbing halide electrolytes [24]. Larger cations increase CO and formate yields on Ag, Sn, and Bi by stabilizing adsorbed CO_2 and increase formate, ethylene, and ethanol on Cu by stabilizing important precursors for C–C bond formation [18,74].

Other groups have moved to ionic liquids because of their wide solvent window and ability to stabilize charged CO_2 intermediates [75]. The protons required for the CO_2RR have been supplied through humidifying the CO_2 [76], diluting the ionic liquid with water [77], or attaching functionalized ionic liquid components to the catalyst surface [78]. It is worth noting that, thus far, all published examples of the CO_2RR in ionic liquids have produced C_1 products [75].

Reactor designs

Cathodic compartment

Most CO_2RR reactors are based on an electrolyser or fuel cell designs with a GDE cathode and oxygen evolving anode separated by an ionic membrane. CO_2 feed can be either in the gas or liquid phase [79]. Most high-throughput systems use gas phase supply, as aqueous-fed systems are restricted to $\sim$35 mA cm^{-2} because of low solubility of CO_2, [80] whereas GDEs enable current densities of two orders of magnitude higher by facilitating the transport of CO_2 to the catalyst [81]. Products can be collected in the gas or liquid phase, or both can be done simultaneously as has been achieved for the production of ethanol and ethylene [82]. The total concentration of liquid products can be increased by continually cycling the catholyte via a peristaltic pump [83]. Careful controls are needed over the gas and liquid phase flows as these can influence product selectivity, reaction rate, and lifetime. Using CO_2/N_2 mixtures can impact C_1 vs C_{2+} selectivity, where lower CO_2 ratios decrease C–C bond formation to favor C_1 products [84] and increased gas phase pressure increases CO selectivity [85].

Membrane

Most reactors use a membrane between anodic and cathodic compartments to prevent product crossover [86]. Typically, the membrane can separate liquid catholyte and anolyte (Fig 3c). Fewer works have reported zero-gap electrolysers using membrane electrode assemblies (MEAs), where the catalyst is in direct contact with the membrane (Fig 3b). MEA systems have no liquid catholyte and bring the cathode and anode into close proximity to minimize the *iR* drop.

CO_2RR studies at MEAs have been limited to formate and carbon monoxide [87,88], with anion exchange membranes outperforming proton exchange membranes (PEMs) by increasing the local pH at the catalyst surface to suppress the HER [89–91]. Further advancements have been made by taking ionic liquid components that enhance the CO_2RR, such as imidazole, and incorporating them into the membrane structure [92].

Accessing higher order CO_2RR products like methanol or ethylene requires a liquid catholyte, so zero-gap MEAs are not feasible. Steps can be taken to keep the *iR* drop low, such as having a zero-gap anodic chamber and minimizing the catholyte channel depth [93]. These designs have allowed the production of ethylene with Faradaic efficiencies up to 25% at 1.3 A cm^{-2} [94].

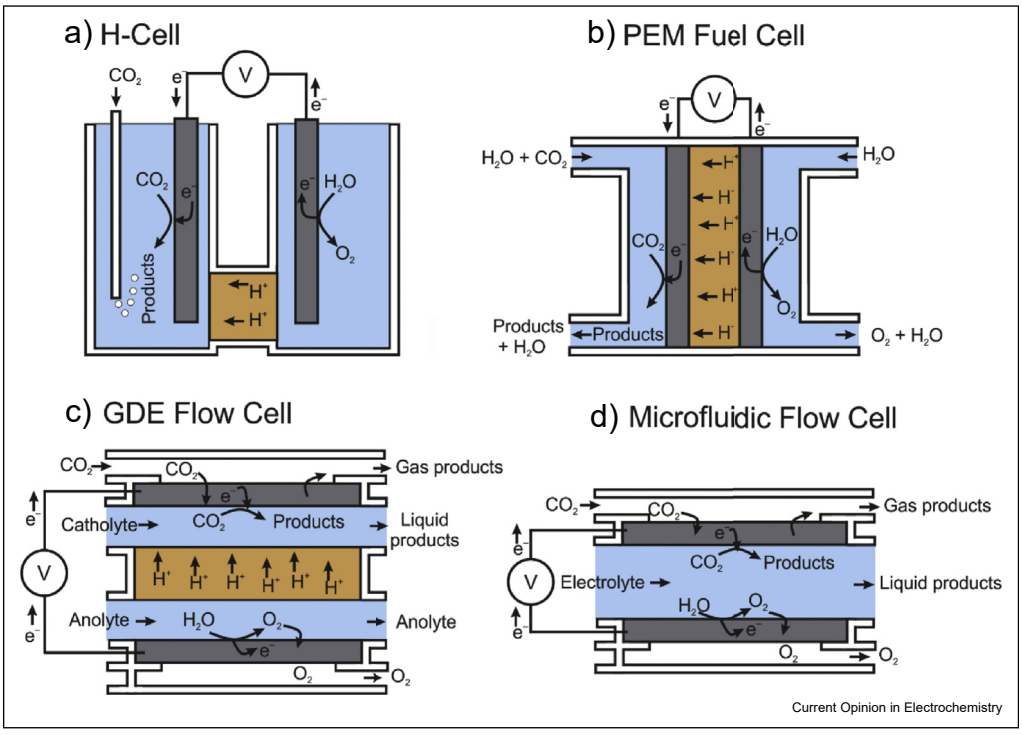
One popular alternative to membrane-separated reactors are microfluidic CO_2RR reactors (Fig 3d), where the laminar flow profile can separate anolyte and catholyte without a membrane [95]. This has been exploited to introduce different pH electrolytes to enhance the anode and cathode separately, giving an overall improvement in cell performance [96]. Turnover rates can be increased by increasing the path length or incorporating multiple channels in parallel, providing a viable means to up-scaling [97].

Anodic compartment

Most published CO_2RR reactors use IrO_2 or Pt-based anodes to facilitate the oxygen evolution reaction in the anodic compartment. There exists a wealth of published catalysts for the oxygen evolution reaction [98,99], yet novel anodic materials are rarely incorporated into CO_2RR reactor reports. This becomes increasingly important for up-scaling, where the high current densities can cause delamination at the anode or O_2 bubbles may block active sites if they are not removed by anolyte flow [93]. Realizing the industrial potential of the CO_2RR will require a unified optimization of the anode, cathode, membrane, and reactor design.

Some investigations suggest the use of the hydrogen oxidation reaction to decrease the cell potential during the CO_2RR and allow the use of GDEs on both sides of

Figure 3



Schematic reactor designs commonly used for the CO_2RR. Blue indicates electrolyte, grey indicates catalyst (a) or catalyst loaded GDE (b–d), orange indicates an ion exchange membrane, and white indicates gas phase flow. (a) H-cell with the anode and cathode compartments separated by a conductive membrane. (b) PEM fuel cell with a GDE in a MEA. CO_2 can be flowed into the cathodic compartment dissolved in electrolyte or as humidified gas. (c) GDE flow cell with the catholyte and anolyte separated via an ion exchange membrane. (d) Microfluidic flow cell with a single electrolyte flowing between anode and cathode.

the cell [100]. Another strategy is to use the oxidation of organic materials at the anode to give additional value-added products for the same charge passed [101]. In either case, a successful CO_2RR reactor must consider the anodic environment as carefully as that of the cathode.

Materials manufacturing scale research

Compared with batch-type or static electrolysers, continuous-flow reactors are more suitable for scale-up applications, because of their improved CO_2 mass transport, product removal, electrolyte mixing, and temperature control [102]. The development of large or multiple-stack electrolysers have been limited, although a few start-ups (OPUS12, CERT, Dioxide Materials) and established companies (Siemens) have evidenced ongoing up-scaling activities [80].

A few research groups have demonstrated up-scaled systems using continuous flow reactors. Cycling CO_2-saturated electrolyte through a flow cell achieved 63–91% formate selectivity in a 300 cm^2 single cell without using a GDE [103]. A semipilot scale reactor capable of converting 1 kg CO_2 per day to formate at 78% efficiency is one of the largest scale designs reported thus far [87].

Up-scaling GDEs and MEAs requires regulation of the CO_2 back-pressure to prevent GDE flooding while permitting electrolyte contact with the catalyst [104]. It also becomes increasingly important to consider non-catalytic limitations to the GDE design, such as in-plane resistance and local pH changes [105]. Recent up-scaled GDEs have been reported, including a 250 cm^2 silver/imidazolium GDE, which gave 95–99% carbon monoxide over a 200–600 mA cm^{-2} range [106].

Most up-scaling reports have used MEAs in zero-gap electrolysers, as they can be readily integrated into existing PEM fuel cell and electrolyser technologies, giving reactors with low cell resistance and a straightforward approach to raising the pressure in the reaction chamber [102]. Careful consideration is needed regarding the catholyte, anolyte, and membrane because ion crossover can significantly alter the pH and ionic strength after extended operations [107,108]. In particular, PEMs give poor stability at high reaction rates because of cation depletion [109]. Anion exchange membranes offer improved stability, though suffer from bicarbonate crossover, which can lead to substantial CO_2 evolution at the anode [50]. Bipolar membranes are

promising route to improve stability at high CO_2RR rates, hindering ionic crossover maintaining a high cathodic pH [110].

Further enhanced outputs have been demonstrated through a stacked zero-gap electrolyser, where multiple 61 cm^2 silver cells gave 95% carbon monoxide at 300 mA cm^{-2} [111]. Importantly, when connecting the cells in parallel, the operation of the stack was identical to the sum of each single-cell, whereas connecting the cells in series significantly increased the conversion rate. It is worth mentioning that there is still interest in efficient materials that operate in the 10–50 mA cm^{-2} range, because this corresponds to the photocurrent density of a solar CO_2RR reactor operating without solar concentration [109].

Looking at long-term viability, it is also important to consider separation and purification alongside operating costs. This is particularly pertinent to formic acid/formate production; formate production in alkali media proceeds with higher Faradaic efficiency than formic acid production acidic media but increased separation costs for formate separation make formic acid the more economically desirable option, despite the lower efficiency [112]. Some technologies have been developed to mitigate this, where the liquid formate phase passes into an electrolytic acidification reactor to facilitate separation [113].

Other works aim to mitigate costs by introducing additional value added components into their designs. Electrolysis in a membrane-free cell in bromide electrolyte has been shown to produce 2-bromoethanol, which presents a route to higher order value-added products [114]. Alternatively, CO_2RR reactors can be hyphenated with secondary reactors, as has been achieved for a formate feed into a thermal reactor to produce oxalic acid [115].

There is little information regarding large CO_2RR systems and the challenges and technical difficulties associated with up-scaling. Catalytic performances are sensitive toward operating conditions and surface impurities and tend to change drastically when operated in less ideal conditions. In up-scaled devices, deactivation, transport, resistance, and stability losses can result in reduced performances over prolonged operations [116]. Furthermore, managing the gas–liquid interface within the GDE, that is, avoiding flooding with electrolyte, is often crucial to maintaining product selectivity [117]. It appears that up-scaled CO_2 electrolysers have been unable to address all of these issues and delivered either low energy efficiencies and/or poor activities [111]. Regardless of the size, continued CO_2 reduction longer than several days are rarely reported in the literature possibly because of catalyst and system degradations.

Conclusions

The CO_2RR community have produced a number of high-quality catalyst materials and reactor designs to drive the production of value-added chemicals from a CO_2 feedstock. Initial selectivity toward a specific product is achieved through the selection of an appropriate catalyst material, with further enhancements made possible by engineering the catalyst surface through alloying and micro-structuring or nanostructuring.

The next advancements in CO_2RR field will come from meeting the requirements to up-scale the reactor operations to industrially relevant standards. Faradaic efficiencies toward a specific product tend to fall as the current density increases because of the increased HER at larger current densities. Designing catalyst materials, innovative supports and reactor designs that disfavor water reduction and enhance the CO_2RR will facilitate improved operations on larger scales.

In addition to cathode materials, further developments of anode catalysts, cell configurations, membranes, and other interfacial contacts (i.e. within the GDE) are also necessary. Reactors need to be optimized for cathodic and anodic efficiencies, energy requirements, and stability to catalyst loss/deactivation and gas phase flooding. There is a need for computational simulations for parameters that are typically used for electrochemical reactors, including current and potential distribution, fluid flow, pressure drop, and mechanical integrity of GDEs.

Typical figures of merit for electrochemical reactors, such as mass transport, space-time velocity, or pressure drop suitable for up-scaling, have not been reported in larger systems. Technoeconomic feasibility models for CO_2 electrolysers for different conversion products will be useful for identifying the technical feasibility and financial viability of processes using particular reactions, catalysts, and cell designs.

Conflicts of interest

The authors declare that there is no conflict of interests.

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