

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

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Highlights

- Catalyst materials and cell designs for carbon dioxide reduction are briefly reviewed
- Pure metals, alloys and micro-/nano-structured catalysts are discussed
- The activity and selectivity of catalyst to a specific reduction product are discussed
- Challenges to up-scaling from the lab scale cells are highlighted
- Industrially relevant production rates are presented, along with the latest innovations

Abstract

CO₂ 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 CO₂ reduction have not been considered adequately. This review covers recent advancements in catalyst materials and cell designs. The leading materials for CO₂ 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.

Keywords: carbon dioxide reduction, electrosynthesis, energy storage,

Abbreviations: CO₂RR, 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.

1. Introduction

CO₂ reduction is a key component in the global plan to offset carbon emissions and reduce human impact on the environment. The CO₂ reduction reaction (CO₂RR) 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 CO₂ could be captured from industrial processes that would otherwise release CO₂ into the atmosphere, reducing total CO₂ emissions and fossil fuel dependence in one process.

Additionally, CO₂ reduction reactors can be integrated into intermittent green power sources such as wind or solar, where CO₂ is converted into a fuel such as methanol during peak energy production, which can then supplement energy production during periods of low energy generation.

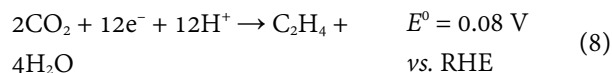
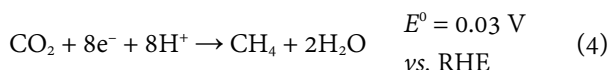
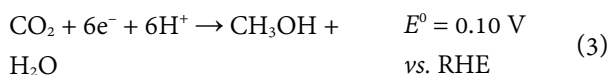
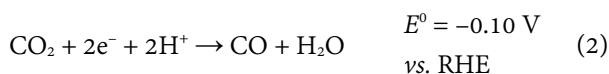
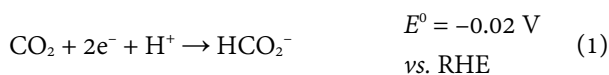
The feasibility of CO₂RR as a long-term solution to the synthesis of useful materials or in fuel production requires the optimisation of both the catalyst materials and the reactor design in order to maximise the product production with minimal energy input. This is especially complex for the

CO₂RR, 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 CO₂RR 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 CO₂RR. We will cover the challenges faced when trying to drive CO₂RR to a specific product, and look forward to where the next developments are needed in order to make CO₂RR a more widespread means of environmentally friendly chemical synthesis and energy storage technology.

2. Fundamentals and mechanisms of the CO₂RR

The reduction of CO₂ at a heterogeneous catalyst surface can afford a number of different products. The most commonly reported are given below:[2]



Equations 1 – 10 highlight the challenge facing systems for selectively producing one CO₂RR 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.



The CO₂RR begins with an initial adsorption of CO₂ onto a vacant catalyst site and subsequent electron transfer.[3] The CO₂RR then proceeds via a series of intermediates that determine the product.[4] Proposed routes to a number of CO₂RR products are given in Figure 1.

The selection of the correct catalyst material allows for reasonable selectivity to a specific product, by favouring

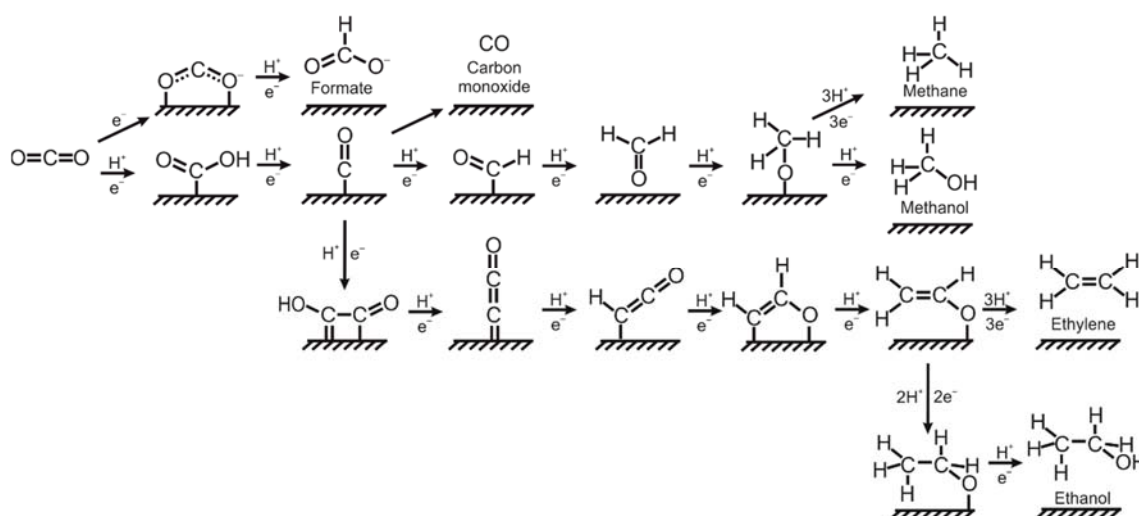


Figure 1. Proposed reaction mechanism for CO₂RR. Routes are shown for producing formate, CO, methane, methanol ethylene and ethanol, based on the lowest energy pathways from computational studies.[4]

certain reaction intermediates or by hindering or facilitating the formation of carbon – carbon bonds to give C₁ or C₂ products respectively. A number of pure metals catalysts show selectivity towards specific CO₂RR products. In aqueous electrolytes, Pb, Hg, In, Tl, Cd and Sn catalysts favour formate, whereas Au, Ag, Pd and Zn catalysts favour 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 C₂₊ species in significant amounts due to the favourable formation of C-C bonds[7, 8]; some alloys such as Ni₃Al[9] and PdAu[10] have produced detectable C₂₊ products, but Faradaic efficiencies have thus far been limited to < 2%.

3. Catalyst designs

A number of metal alloys[11] and doped carbon materials[12] have been investigated for CO₂ reduction, giving reasonable selectivity for a range of C₁ and C₂ products. Some of the leading materials are given in Table 1.

Table 1. A sample of the leading catalysts for CO₂RR published in the last two years for a number of CO₂RR products, with the corresponding Faradaic efficiencies (FE), current densities (*j*) and cell designs.

Product	Metal	Electrode	Cell	Electrolyte	<i>j</i> / 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-doped 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	1M KHCO ₃ + 0.1 M CsHCO ₃	17	95	[18]
Methane							
	Cu ₂ O@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 ₃ CN/ H ₂ O (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/ <i>N</i> -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]

3.1 Catalyst micro- and nano-structuring

Modifications to the CO₂RR catalyst structure may impact the overall activity or selectivity towards a certain product. Simple materials are enhanced by maximising the electrochemically active surface area via micro- and nano-structuring techniques.[29-31] These can be engineered 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 CO₂RR 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 favour C₂ products by optimising both factors.[37, 38] Similarly, foam electrodes give increased alkalinity with the porous structure, which simultaneously disfavours H₂ evolution whilst facilitating CO and ethylene production.[39]

Nanoparticle catalysts exhibit size- 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

towards C₂ over C₁ 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 due to 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.

3.2 Alloyed materials

The range of alloyed materials used for CO₂RR is incredible 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 CO₂RR towards a specific product. Due 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 towards methane, CO, formate and ethanol respectively, by favouring specific intermediates in the CO₂RR 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

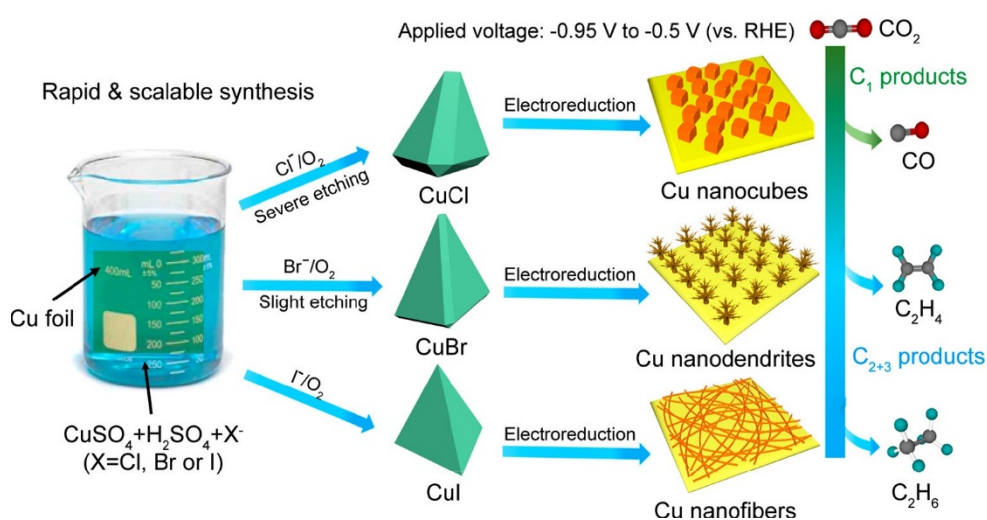


Figure 2. Schematic synthesis route to a number of copper microstructures via selective etching in different acidic halide media. Electrochemical reduction of the resultant copper halide gives varying microstructures, each with selectivity to a different CO₂RR product. Reprinted with permission from H. Wang, *et al.*, Nano Lett 2019, 19, 3925-3932. Copyright 2019 American Chemical Society.

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]

3.3 Catalyst coatings

The reaction environment at the catalyst surface has a sizeable impact on both the reactant rate and product selectivity for the CO₂RR. Often, works refer to the ‘triphasic interface’ meaning gaseous CO₂ at the interface between the solid catalyst and liquid electrolyte. Various coatings can trap CO₂ 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 CO₂RR 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 CO₂RR itself. CO₂RR at Cu electrodes with an *N*-aryl pyridinium drove the formation of Cu nanocubes, leading to enhanced ethanol and ethylene production.[26, 62]

3.4 Catalyst supports

Gas diffusion electrodes (GDEs) provide a rapid rate of CO₂ mass transport and negate poor CO₂ solubility in aqueous electrolytes.[63] Carbon GDEs can enhance the HER, so choosing a material that is less active towards HER gives an increased Faradaic efficiency towards CO₂RR 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 hours.[24]

Carbon-based materials can still be useful for CO₂RR, 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 CO₂RR products, such as Au/C for CO [66] or CuN₄/C for ethanol. [28] A further route is to start with materials that are known to have high CO₂ 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 CO₂RR. Syn-gas in an industrially important mixture of CO and H₂, so a reactor capable of producing CO from the CO₂RR and H₂ from the HER is of interest.[71]. In these cases, the ratio of CO to H₂ becomes important, since the HER tends to outpace the CO₂RR at larger current densities, although careful reactor design can give a fair degree of control over the ratio.[72]

3.5 Electrolytes

Certain electrolytes can hinder the HER, improving the efficiency towards CO₂RR products. High pH electrolytes slow the kinetics of the first water reduction step, and strongly adsorbing OH⁻ blocks H₂ 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 stabilising adsorbed CO₂, and increase formate, ethylene and ethanol on Cu but stabilising important precursors for C-C bond formation.[18, 74]

Other groups have moved to ionic liquids, due to their wide solvent window and ability to stabilise charged CO₂ intermediates.[75] The protons required for the CO₂RR have been supplied through humidifying the CO₂, [76] diluting the ionic liquid with water,[77] or attaching functionalised ionic liquid components to the catalyst surface.[78] It is worth noting that, thus far, all published examples of the CO₂RR in ionic liquids have produced C₁ products.[75]

4. Reactor designs

4.1 Cathodic compartment

Most CO₂RR reactors are based on an electrolyser or fuel cell designs with a GDE cathode and oxygen evolving anode separated by an ionic membrane. CO₂ 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 ~35 mA cm⁻² due to low solubility of CO₂. [80] whereas GDEs enable current densities of two orders of magnitude higher by facilitating the transport of CO₂ 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 favour C_1 products,[84] and increased gas phase pressure increases CO selectivity.[85]

4.2 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 electrolyzers 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 minimise the iR drop.

CO_2RR studies at MEAs have been limited to formate and carbon monoxide,[87, 88] with anion exchange membranes (AEMs) 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 minimising 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]

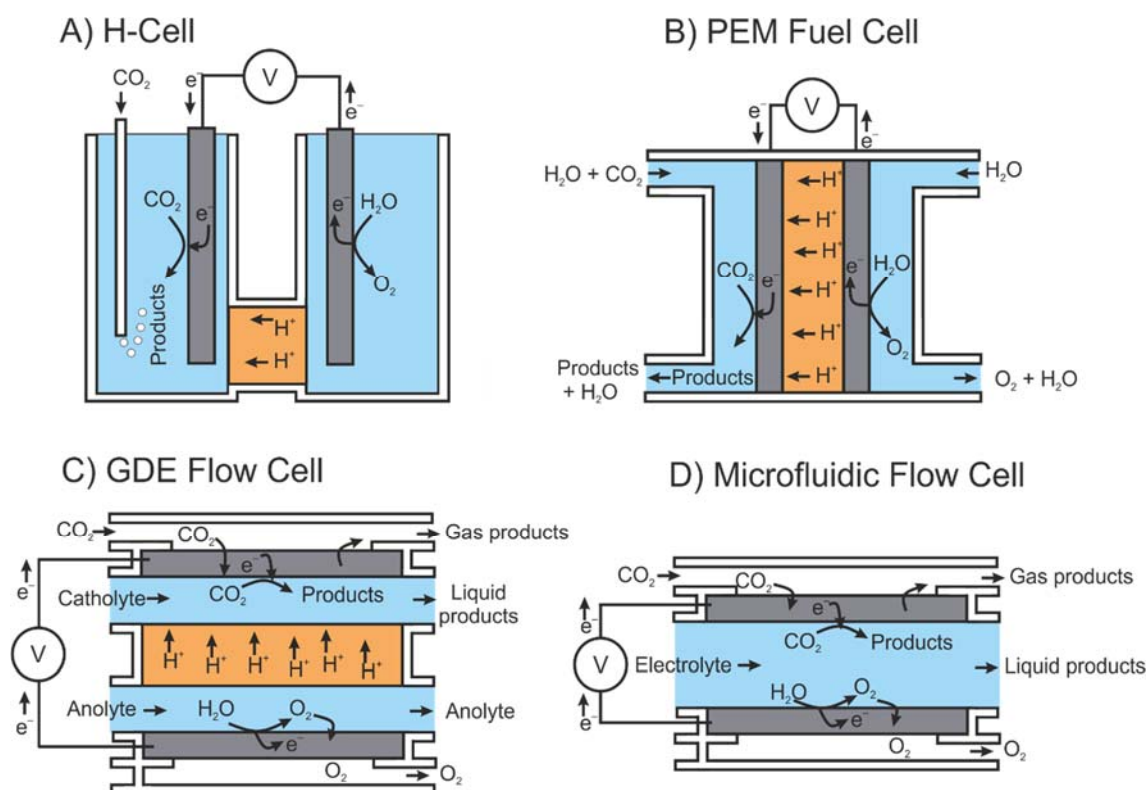


Figure 3. Schematic reactor designs commonly used for the CO_2RR . Blue indicates electrolyte, grey indicates catalyst (A) or catalyst loaded GDE (B-D), orange indicates an ion exchange membrane, white indicates gas phase flow. A) H-cell with the anode and cathode compartments separated by a conductive 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.

4.3 Anodic compartment

Most published CO₂RR reactors use IrO₂ or Pt based anodes to facilitate the oxygen evolution reaction (OER) in the anodic compartment. There exists a wealth of published catalysts for the OER,[98, 99] yet novel anodic materials are rarely incorporated into CO₂RR reactor reports. This becomes increasingly important for up-scaling, where the high current densities can cause delamination at the anode, or O₂ bubbles may block active sites if they are not removed by anolyte flow.[93] Realising the industrial potential of the CO₂RR will require a unified optimisation of the anode, cathode, membrane, and reactor design.

Some investigations suggest the use of the hydrogen oxidation reaction in order to decrease the cell potential of the cell during the CO₂RR and allow the use of GDEs on both sides of 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 CO₂RR reactor must consider the anodic environment as carefully as that of the cathode.

5. Materials manufacturing scale research

Compared to batch-type or static electrolyzers, continuous-flow reactors are more suitable for scale-up applications, due to their improved CO₂ mass transport, product removal, electrolyte mixing and temperature control.[102] The development of large or multiple-stack electrolyzers 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 CO₂-saturated electrolyte through a flow cell achieved 63 – 91% formate selectivity in a 300 cm² single cell without using a GDE.[103] A semi-pilot scale reactor capable of converting 1 kg CO₂ 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 CO₂ back-pressure to prevent GDE flooding whilst 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 cm² 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 electrolyzers, 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, since 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 due to cation depletion.[109] AEMs offer improved stability, though suffer from bicarbonate crossover, which can lead to substantial CO₂ evolution at the anode.[50] Bipolar membranes are promising route to improve stability at high CO₂RR 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 cm² 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, since this corresponds to the photocurrent density of a solar CO₂RR 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 in 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, CO₂RR 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 CO₂RR systems and the challenges and technical difficulties associated with up-scaling. Catalytic performances are sensitive towards 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, i.e. avoiding flooding with electrolyte, is often crucial to maintaining product selectivity.[117] It appears that up-scaled CO₂ electrolyzers 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 CO₂ reduction longer than several days are rarely reported in the literature possibly due to catalyst and system degradations.

5. Conclusions

The CO₂RR community have produced a number of high quality catalyst materials and reactor designs to drive the production of value-added chemicals from a CO₂ feedstock. Initial selectivity towards 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- or nano-structuring.

The next advancements in CO₂RR field will come from meeting the requirements to up-scale the reactor operations to industrially relevant standards. Faradaic efficiencies towards a specific product tend to fall as the current density increases, due to the increased HER at larger current densities. Designing catalyst materials, innovative supports and reactor designs that disfavour water reduction and enhance the CO₂RR 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 optimised 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 gas diffusion electrodes.

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. Techno-economic feasibility models for CO₂ electrolyzers for different conversion products will be useful for identifying the technical feasibility and financial viability of processes using particular reactions, catalysts and cell designs.

6. Conflict of interest statement

The authors declare that there is no conflict of interests.

7. Acknowledgements

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