Developments on carbon dioxide reduction: Their promise, achievements, and challenges
Samuel C. Perry¹, Pui-ki Leung¹, Ling Wang¹,² and Carlos Ponce de León¹,²

Abstract
CO₂ reduction processes continue to be developed for electro-synthesis, 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 advances 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.

Addresses
¹ Electrochemical Engineering Laboratory, Energy Technology Research Group, Faculty of Engineering and Physical Sciences, University of Southampton, Highfield, Southampton, SO17 1BJ, UK
² National Centre of Advanced Tribology at Southampton (NCATS), Faculty of Engineering and Physical Sciences, University of Southampton, University Rd., Southampton, SO17 1BJ, UK

Corresponding author: Ponce de León, Carlos (capla@soton.ac.uk)

Current Opinion in Electrochemistry 2020, 20:88–98
This review comes from a themed issue on Electrochemical Engineering
Edited by Mark E. Orazem
For a complete overview see the Issue and the Editorial
Available online 6 May 2020
https://doi.org/10.1016/j.coelec.2020.04.014
2451-9103/© 2020 Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

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.

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 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 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 to make CO₂RR a more widespread means of environmentally friendly chemical synthesis and energy storage technology.

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].

\[ \text{CO}_2 + 2e^- + H^+ \rightarrow \text{HCO}_2^- \quad E^0 = -0.02 \text{ V vs. RHE} \quad (1) \]

\[ \text{CO}_2 + 2e^- + 2H^+ \rightarrow \text{CO} + \text{H}_2\text{O} \quad E^0 = -0.10 \text{ V vs. RHE} \quad (2) \]

\[ \text{CO}_2 + 6e^- + 6H^+ \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad E^0 = 0.10 \text{ V vs. RHE} \quad (3) \]
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\textsubscript{1} or C\textsubscript{2} products, respectively. A number of pure metals catalysts show selectivity toward specific CO\textsubscript{2}RR 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\textsubscript{2}+ species in significant amounts because of the favorable formation of C–C bonds [7,8]; some alloys such as Ni\textsubscript{3}Al [9] and PdAu [10] have produced detectable C\textsubscript{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\textsubscript{2} reduction, giving reasonable selectivity for a range of C\textsubscript{1} and C\textsubscript{2} products. Some of the leading materials are given in Table 1.

**Catalyst micro-structuring and nanostructuring**

Modifications to the CO\textsubscript{2}RR 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
**Table 1**

| Product | Metal          | Electrode | Cell     | Electrolyte                  | \(j/\text{mA}\) 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\(_2\)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/N-arylpyridinium | Nanoparticles | MEA  | 1 M KHCO\(_3\)        | 600  | 64   | [26] |
| Ethanol | CuAg           | Nanoparticles | Flow electrolyser 1 M KOH | 300 | 25   | [25] |
|         | Ce(OH)\(_2\)/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] |

\(\text{CO}_2\text{RR}, \text{CO}_2\text{reduction reaction}; \text{MEA}, \text{membrane electrode assembly}; \text{PEM}, \text{proton exchange membrane.}\)

**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 \(\text{CO}_2\text{RR}\) 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 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 favor C2 products by optimizing both factors [37,38]. Similarly, foam electrodes give increased alkalinity with the porous structure, which simultaneously disfavors H2 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 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 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 CO2RR 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 CO2RR 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 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 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 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 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 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].

**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 toward HER gives an increased Faradaic efficiency toward 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 h [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 CO$_2$RR. Syn-gas in an industrially important mixture of CO and H$_2$, so a reactor capable of producing CO from the CO$_2$RR 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$_2$RR 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$_2$RR 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$_2$RR have been supplied through humidifying the CO$_2$ [76], diluting the ionic liquid with water [77], or attaching functionalized ionic liquid components to their wide solvent window and ability to stabilize important precursors for C–C bond formation [18,74].

Reactors designs

Cathodic compartment

Most CO$_2$RR 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 ~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 recycling 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$_2$RR 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 advances have been made by taking ionic liquid components that enhance the CO$_2$RR, such as imidazole, and incorporating them into the membrane structure [92].

Accessing higher order CO$_2$RR 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$_2$RR 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$_2$RR 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$_2$RR 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$_2$RR 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$_2$RR 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.

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 CO₂ 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 CO₂-saturated electrolyte through a flow cell achieved 63–91% formate selectivity in a 300 cm² single cell without using a GDE [103]. A semipilot 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 while permitting electrolyte contact with the catalyst [104]. It also becomes increasingly important to consider noncatalytic 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 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 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, because 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 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 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 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 because of catalyst and system degradations.

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 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 CO2RR 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 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 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. 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.

Conflicts of interest

The authors declare that there is no conflict of interests.

Acknowledgements

This work is supported as part of the CO2-based electro-synthesis of ethylene oxide (CO2EXIDE) project, which receives funding from the European Union’s Horizon 2020 research and innovation program in cooperation with the sustainable process industry through resource and energy efficiency (SPIRE) initiative under grant agreement no. 768789.

References

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest

1. Fletcher D: The cathodic reduction of carbon dioxide—what can it realistically achieve? A mini review. Electrocem Commun 2015, 61:97–101.
A detailed summary of the latest mechanistic understandings of the CO2RR with direct implications on catalyst design for favouring specific products.

4. Kortlever R, Shen J, Schouten KJP, Calle-Vallée F, Koper MTM: Catalysts and reaction pathways for the electrochemical reduction of carbon dioxide. J Phys Chem Lett 2015, 6: 4073–4082.

10. Kortlever R, Andre P, Balemans C, Kas R, Kwon Y, Mul G, Huang-fu Z-C, Song Q-T, He Y-H, Wang J-J, Ye J-Y, Zhou Z-Y, Lee JH, Kattel S, Jiang Z, Xie Z, Yao S, Tackett BM, Xu W: A comprehensive study into the surface functionalisation of catalysts from CO2 reduction. The novel polymer GDE gives both high selectivity and stability, and is arguably the most promising GDE design for the future up-scaling efforts.

19. Tan X, Yu C, Zhao C, Huang H, Yao X, Han X, Guo W, Cui S, Huang H, Qiu J: Restructuring of Cu2O to Cu2O@Cu-metal–organic frameworks for selective electrochemical reduction of CO2. ACS Appl Mater Interfaces 2019, 11:9904–9910.

20. Zhang H, Chang X, Chen JG, Goddard WA, Xu B, Cheng M-J, Lu Q: Computational and experimental demonstrations of one-pot tandem catalysis for electrochemical carbon dioxide reduction to methane. Nat Commun 2019, 10:3340.

21. Zhou B, Ou P, Pant N, Cheng S, Vanka S, Chu S, Rashid RT, Bolton G, Song J, Mil M Z: Highly efficient binary copper–iron catalyst for photoelectrochemical carbon dioxide reduction toward methane. Proc Natl Acad Sci USA 2020, 117: 1330–1338.

24. Dinh C-T, Boudry T, Kibria MG, Sefi-takaldani A, Gabardo CM, Garcia de Arquer FP, Kiani A, Edwards JP, De Luna P, Bushuyev OS, Zou C, Quintero-Bermudez R, Pang Y, Sinton D, Sargent EH: CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. Science 2018, 360:783–787.

One of the leading catalyst architectures to date for ethylene synthesis from CO2 reduction. The novel polymer GDE gives both high selectivity and stability, and is arguably the most promising GDE design for the future up-scaling efforts.

25. Hoang TTH, Verma S, Ma S, Fister TT, Timoshenko J, Frenkel AI, Kenis PJA, Gewirth AA: Nanoporous copper–silver alloys by additive-controlled electrodeposition for the selective electroreduction of CO2 to ethylene and ethanol. J Am Chem Soc 2018, 140:5791–5797.

26. Li F, Thevenon A, Rosas-Hernández A, Wang Z, Li Y, Gabardo CM, Ozden A, Dinh CT, Li J, Wang Y, Edwards JP, Xu Y, McCullum G, Tao L, Liang Z-Q, Luo M, Wang X, Li H, O’Brien CP, Tan C-S, Nam D-H, Quintero-Bermudez R, Zhuang T-T, Li YC, Han Z, Britt RD, Sinton D, Agapie T, Peters JC, Sargent EH: Molecular tuning of CO2-to-ethylene conversion. Nature 2020, 577:509–513.

A comprehensive study into the surface functionalisation of catalysts for ethylene formation, giving a sizeable improvement to ethylene selectivity in neutral media.

27. Luo M, Wang Z, Li YC, Li J, Li F, Lui M, Nam D-H, Chen B, Wicks J, Xu A, Zhuang T, Leow WR, Wang X, Dinh C-T, Wang Y, Vank J, Sinton D, Sargent EH: Hydroxide promotes carbon dioxide electroreduction to ethanol on copper via tuning of adsorbed hydrogen. Nat Commun 2019, 10:5814.

28. Karapinar D, Huan NT, Ranjbar Sahraie N, Li J, Wakerley D, Touati N, Zanna S, Taverna D, Galvão Tizei LH, Zitolo A, Jaouen F, Mougel V, Fontecave M: Electroreduction of CO2 to C3 hydrocarbons using bimetallic Cu–Pd catalysts with different mixing patterns. J Am Chem Soc 2017, 139:47–50.

29. Hou L, Yan J, Takele L, Wang Y, Yan X, Gao Y: Current progress of metallic and carbon-based nanostructure catalysts towards the electrochemical reduction of CO2. Inorg Chem Front 2019, 6:3363–3380.

An important aspect of this area is the development of new catalysts for the electroreduction of CO2 to C3 hydrocarbons, which has been achieved through the use of bimetallic Cu–Pd catalysts with different mixing patterns.

30. Hahn C, Hatsukade T, Kim Y-G, Vailionis A, Baricuatro JH, Karapinar D, Huan NT, Ranjbar Sahraie N, Li J, Wakerley D, Touati N, Zanna S, Taverna D, Galvão Tizei LH, Zitolo A, Jaouen F, Mougel V, Fontecave M: Electroreduction of CO2 to C3 hydrocarbons using bimetallic Cu–Pd catalysts with different mixing patterns. J Am Chem Soc 2017, 139:47–50.

A comprehensive study into the surface functionalisation of catalysts for ethylene formation, giving a sizeable improvement to ethylene selectivity in neutral media.

31. Li YH, Liu PF, Li C, Yang HG: Sharp-tipped zinc nanowires as an efficient electrocatalyst for carbon dioxide reduction. Chem Eur J 2018, 24:15486–15490.

32. Zhou H, Liu K, Li H, Cao M, Fu J, Gao X, Hu J, Li W, Pan H, Zhao J, Li Q, Qiu X, Liu M: Recent advances in different-dimension electrocatalysts for carbon dioxide reduction. J Colloid Interface Sci 2019, 556:17–47.

10.1016/j.elecchem.2020.03.029.
This work demonstrates the impact of oxide derived copper catalysts and larger cations in the electrolyte on product selectivity, with techniques for enhancing catalyst activity promoting CO2 reduction on CuS catalysts. ACS Appl Mater Interfaces 2018, 10: 29872–29881.

Deng Y, Huang Y, Ren D, Handoko AD, Seh ZW, Hirunpit S, Yeo BS: On the role of sulfur for the selective electrochemical reduction of CO2 to formate on CuS catalysts. ACS Appl Mater Interfaces 2018, 10:28572–28581.

Huang Y, Deng Y, Handoko AD, Goh GKL, Yeo BS: Rational design of sulfur-doped copper catalysts for the selective electroreduction of carbon dioxide to formate. ChemSusChem 2019, 11:320–326.

Hoffman ZB, Gray TS, Yu X, Lin Q, Gunnese TB, Zangari G: High selectivity towards formate production by electrochemical reduction of carbon dioxide at copper–bismuth dendrites. ChemSusChem 2019, 12:231–239.

Shang L, Lv X, Shen H, Shao Z, Zheng G: Selective carbon dioxide electroreduction to ethylene and ethanol by core-shell copper/cuprous oxide. J Colloid Interface Sci 2019, 552: 426–431.

Klibria MG, Dinh C-T, Seifitokalani A, De Luna P, Burdny T, Quintero-Bermudez R, Ross MB, Bushuyev OS, Garcia de Arquer FP, Yang P, Sinton D, Sargent EH: A surface reconstruction route to high productivity and selectivity in CO2 electroreduction toward C2x hydrocarbons. Adv Mater 2018, 30:1804867.

Chou T-C, Chang C-C, Yu H-L, Yu W-Y, Dong C-L, Velasco-Vélez J-J, Chuang C-H, Chen L-C, Lee J-F, Chen J-M, Wu H-L: Controlling the oxidation state of the Cu electrode and reaction intermediates for CO2 reduction to ethylene. J Am Chem Soc 2020, 142:2867–2868.

Martic N, Reiler C, Macauley C, Löffler M, Reinisch D, Volkova E, Maltenberger A, Rucki A, Mayrhofer KJJ, Schmid G: Paramelaconite-enriched copper-based material as an efficient and robust catalyst for electrochemical carbon dioxide reduction. Adv Energy Mater 2019, 9:1901228.

Perry SC, Gateman SM, Malpass-Evans R, McKeeown N, Wegener M, Nazarovs P, Mauzeroll J, Wang L, Ponce de Leon C: Polymers with intrinsic microporosity (PIMs) for targeted CO2 reduction to ethylene. Chemosphere 2020, 248:125093.

The first example of polymers with intrinsic microporosity applied to CO2RR. This work highlights both the positive and negative impacts of using organic polymer layers to modify catalyst surfaces for CO2RR to ethylene.

Wakerley D, Lamaison S, Ozanam F, Mengay N, Mercier D, Marcus P, Fontecave M, Mougel V: Controlling the oxidation state of the Cu electrode and reaction intermediates for CO2 reduction to ethylene. Angew Chem Int Ed 2019, 58: 16952–16958.

Durst J, Rudnev A, Dutta A, Fu Y, Herranz J, Kalginedi V, Kuzure A, Pernyakova AA, Paratcha Y, Broekmann P, Schmidt TJ: Electrochemical CO2 reduction - a critical view on fundamentals, materials and applications. CHEMIA 2015, 69: 769–778.

Baturina O, Lu Q, Xu F, Purdy A, Dytkin B, Sang X, Unocic R, Br Hillinger T, Gogotsi Y: Effect of nanostructured carbon support on copper electrocatalytic activity toward CO2
An important discussion of the limitations of analysing carbon dioxide reduction GDEs on a laboratory scale, and the impact of moving towards higher current densities

81. Weng L-C, Bell AT, Weber AZ: Modeling gas-diffusion electrodes for CO2 reduction. Phys Chem Phys 2018, 20: 16973–16984.

82. Ma S, Sadakiyo M, Luo R, Heima M, Yamauchi M, Kenis PJA: One-step electrosynthesis of ethylene and ethanol from CO2 in an alkaline electrolyzer. J Power Sources 2016, 301: 219–228.

83. Proietto F, Schiavo B, Galia A, Scaldone O: Electrochemical conversion of CO2 to HCOOH at tin cathode in a pressurized undivided filter-press cell. Electrochim Acta 2018, 277: 30–40.

84. Wang X, Xu A, Li F, Hung S-F, Nam D-H, Gabardo CM, Wang Z, Xu Y, Ozden A, Rasouli AS, Ip AH, Sinton D, Sargent EH: Efficient methane electrosynthesis enabled by tuning local CO2 availability. J Am Chem Soc 2020, 142:3525–3531.

85. Edwards JP, Xu Y, Gabardo CM, Dinh C-T, Li J, Qi Z, Ozden A, Sargent EH, Sinton D: Efficient electrocatalytic conversion of carbon dioxide in a low-resistance pressurized alkaline electrolyzer. Appl Energy 2020, 261:114305.

86. Lu Q, Jiao F: Electrochemical CO2 reduction: electrocatalyst, reaction mechanism, and process engineering. Nanomater Energy 2016, 29:430–456.

87. Ju H, Kaur G, Kulkarni AP, Giddey S: Challenges and trends in developing technology for electrochemically reducing CO2 in solid polymer electrolyte membrane reactors. J CO2 Util 2019, 32:179–186.

88. Díaz-Sainz G, Alvarez-Guerra M, Solla-Gullón J, García-Cruz L, Montiel V, Ibrahim A: Catalyst coated membrane electrodes for the gas phase CO2 electroreduction to formate. Catal Today 2018.

89. Wang G, Pan J, Jiang SP, Yang H: Gas phase electrochemical conversion of humidified CO2 to CO and H2 on proton-exchange and alkaline anion-exchange membrane fuel cell reactors. J CO2 Util 2018, 23:152–158.

90. Lee J, Lim J, Roh C-W, Whang HS, Lee H: Electrochemical CO2 reduction using alkaline membrane electrode assembly on various metal electrodes. J CO2 Util 2019, 31:244–250.

91. Hou P, Wang X, Wang Z, Kang P: Gas phase electrolysis of carbon dioxide to carbon monoxide using nickel nitride as the carbon enrichment catalyst. ACS Appl Mater Interfaces 2018, 10:38024–38031.

92. Yang H, Kaczur JJ, Sajjad SD, Masel RI: Electrochemical conversion of CO2 to formic acid utilizing Sustain™ membranes. J CO2 Util 2017, 20:208–217.

93. Vennekotter J-B, Sengpiel R, Wessling M: Beyond the catalyst: how electrode and reactor design determine the product spectrum during electrochemical CO2 reduction. Chem Eng J 2019, 364:89–101.

94. García de Arquer FP, Dinh C-T, Ozden A, Wicks J, McCallum C, Kimani AR, Nam D-H, Gabardo C, Seifitokhtari A, Wang X, Li YC, Li P, Edwards J, Richter LJ, Thorpe SJ, Sinton D, Sargent EH: CO2 electrolysis to multivariant products at activities greater than 1 A cm−2. Science 2020, 367:661–666.

95. Monroe MM, Lobaccaro P, Lum Y, Ager JW: Membraneless laminar flow cell for electrocatalytic CO2 reduction with liquid product separation. J Phys D Appl Phys 2017, 50.
96. Lu X, Leung DYC, Wang H, Maroto-Valer MM, Xuan J: A pH-differential dual-electrolyte microfluidic electrochemical cells for CO2 utilization. Renew Energy 2016, 95:277–285.

97. Zhang F, Jin Z, Chen C, Tang Y, Mahyoub SA, Yan S, Cheng Z-M: Electrochemical conversion of CO2 to CO in a micro-channel reactor system in the case of aqueous electrolyte. Ind Eng Chem Res 2020.

98. Jameh M-I, Sun X: Recent progress on earth abundant electrocatalysts for oxygen evolution reaction (OER) in alkaline medium to achieve efficient water splitting – a review. J Power Sources 2018, 400:31–68.

99. Shi Q, Zhu C, Du D, Lin Y: Robust noble metal-based electrocatalysts for oxygen evolution reaction. Chem Soc Rev 2019, 48:3181–3192.

100. Pérez-Rodríguez S, Barreras F, Pastor E, Lázaro MJ: Electrochemical reactors for CO2 reduction: from acid media to gas phase. Int J Hydrogen Energy 2016, 41:19756–19765.

101. Na J, Seo B, Kim J, Lee CW, Lee H, Hwang YJ, Min BK, Lee DK, Oh H-S, Lee J: General technoeconomic analysis for electrochemical coproduction coupling carbon dioxide reduction with organic oxidation. Nat Commun 2019, 10:5193.

102. Endrödi B, Bencsik G, Darvas F, Jones R, Rajeshwar K, JANÁKY C: Continuous-flow electroreduction of carbon dioxide. Prog Energy Combust Sci 2017, 62:133–154.

103. Li H, Oloman C: Development of a continuous reactor for the electro-reduction of carbon dioxide to formate – part 2: scale-up. J Appl Electrochem 2007, 37:1107–1117.

104. Jeanty P, Scherer C, Magori E, Wiesner-Fleischer K, Hinrichsen O, Fleischer M: Upscaling and continuous operation of electrochemical CO2 to CO conversion in aqueous solutions on silver gas diffusion electrodes. J CO2 Util 2018, 24:454–462.

105. Liu K, Smith WA, Burdyny T: Introductory guide to assembling and operating gas diffusion electrodes for electrochemical CO2 reduction. ACS Energy Lett 2019, 4:639–643.

106. Kaczur JJ, Yang H, Liu Z, Sajjad SD, Masel RI: Carbon dioxide and water electrolysis using new alkaline stable anion membranes. Front Chem 2018, 6:263.

107. Vennekötter J-B, Scheuermann T, Sengpiel R, Wessling M: The electrolyte matters: stable systems for high rate electrochemical CO2 reduction. J CO2 Util 2019, 32:202–213.

108. Blom MJW, van Swaaij WPM, Mul G, Kersten SRA: Overall mass balance evaluation of electrochemical reactors: the case of CO2 reduction. Electrochim Acta 2020, 333:135460.

An important discussion on the side reactions that must be considered when operating CO2RR reactors, discussing membrane crossover in the context of industrial feasibility.

109. Lin M, Han L, Singh MR, Xiang C: An experimental- and simulation-based evaluation of the CO2 utilization efficiency of aqueous-based electrochemical CO2 reduction reactors with ion-selective membranes. ACS Appl Energy Mater 2019, 2:5843–5850.

110. Liang S, Altaf N, Huang L, Gao Y, Wang Q: Electrolytic cell design for electrochemical CO2 reduction. J CO2 Util 2020, 35:90–105.

111. Endrödi B, Kecsenovity E, Samu A, Darvas F, Jones RV, Tórók V, Danyi A, Janáky C: Multilayer electrolyzer stack converts carbon dioxide to gas products at high pressure with high efficiency. ACS Energy Lett 2019, 4:1770–1777.

112. Ramdin M, Morrison ART, de Groen M, van Haperen R, de Klerk R, Intem E, Laitinen AT, van den Broeke LJ, Breugelmans T, Trusler JPM, Jong WD, Vlugt TJH: High-pressure electrochemical reduction of CO2 to formic acid/formate: effect of pH on the downstream separation process and economics. Ind Eng Chem Res 2019, 58:22718–22740.

The authors highlight the importance for choosing CO2RR products not just in terms of their charge efficiency but also for their separation costs in the context of formic acid vs formate production.

113. J.J.N.M.B. Kaczur, (FL, US), Kramer, Theodore J. (New York, NY, US), Keyshar, Kunttai (Houston, TX, US), Majsztrik, Paul (Cranbury, NJ, US), Twardowski, Zbigniew (Burnaby, CA), Process and high surface area electrodes for the electrochemical reduction of carbon dioxide, Liquid Light, Inc. (Monmouth Junction, NJ, US), Patent No. US 10,287,696 B2, United States, 2019.

114. Zhong S, Cao Z, Yang X, Kozlov SM, Huang K-W, Tung V, Cavallo L, Li L-J, Han Y: Electrochemical conversion of CO2 to 2-bromoethanol in a membraneless cell. ACS Energy Lett 2019, 4:600–605.

115. J.J.N.M.B. Kaczur, (FL, US), Lakkaraju, Prasad (East Brunswick, NJ, US), Teamey, Kyle (Washington, DC, US), Method and system for electrochemical reduction of carbon dioxide employing a gas diffusion electrode, LIQUID LIGHT, INC., Patent No. US 10,329,676 B2, United States, 2016.

116. Reiler C, Krause R, Volkova E, Schmid B, Neubauer S, Rucki A, Schuster M, Schmid G: Selective electroreduction of CO2 toward ethylene on nano dendritic copper catalysts at high current density. Adv Energy Mater 2017, 7:1602114.

117. Rivera FF, Ponce de León C, Nava JL, Walsh FC: The filter-press FM01-LC laboratory flow reactor and its applications. Electrochim Acta 2015, 163:338–354.