

# Cathodes for Electrochemical Carbon Dioxide Reduction to Multi-Carbon Products: Part I

A focused review of recent highlights

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## PEER REVIEWED

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This is a focused review of recent highlights in the literature in cathode development for low temperature electrochemical carbon dioxide and carbon monoxide reduction to multi-carbon ( $C_{2+}$ ) products. The major goals for the field are to increase Faradaic efficiency (FE) for specific  $C_{2+}$  products, lower cell voltage for industrially relevant current densities and increase cell lifetime. A key to achieving these goals is the rational design of cathodes through increased understanding of structure-selectivity and structure-activity relationships for catalysts and the influence of catalyst binders and gas diffusion layers (GDLs) on the catalyst microenvironment and subsequent performance.

## 1. Introduction

Decarbonising the chemical industry will be a significant step towards reaching net zero greenhouse gas emissions. Simple  $C_{2+}$  products such as ethylene and propylene are among the chemicals whose production emits the most  $CO_2$  (1), making them prime targets. Decarbonisation can be achieved by using renewable electricity instead of heat from the combustion of fossil fuels as the energy input for production. This approach can be taken one step further by using  $CO_2$  instead of fossil sources as the carbon source. A promising embodiment of this idea is direct electrochemical reduction of  $CO_2$  to  $C_{2+}$  products like ethylene, in which renewable energy can be used directly as electricity rather than *via* heat or the production of hydrogen (2).

Despite significant efforts, developing efficient electrochemical reactors to convert  $CO_2$  into

value-added products at competitive cost and scale continues to be a technical and scientific challenge. A CO<sub>2</sub> electrolyser is a complex multi-component device. The electrochemical CO<sub>2</sub> reduction reaction takes place on the cathode, while the coupled oxidation reaction occurs at the anode (commonly oxygen evolution reaction). In addition to the kinetics of both electrode reactions, mass transport of the reactants and products to and from the electrodes also determines on the overall performance. A sufficient flux of CO<sub>2</sub> to the cathode is required for relevant conversion rates, while at the same time water is needed as the source of protons. An ionically conductive membrane separates the cathode and the anode reactions, and at the same time enables exchange of charge carriers, such as H<sup>+</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>.

Two types of cells have emerged as having promising performance for CO<sub>2</sub> electrolysis: a gas diffusion electrode (GDE) flow-cell type and a membrane electrode assembly (MEA) type (3), schematically represented on **Figure 1**. A GDE-type reactor employs a GDL, which is a porous or fibrous mat that allows permeation of CO<sub>2</sub> gas to a catalyst layer (CL). The CL is deposited on the other side of the GDL, often on an additional microporous support layer. CO<sub>2</sub> gas is fed on one side of the GDE and a constant flow of liquid electrolyte (catholyte) is fed on the other side. An ion-exchange membrane is separating the catholyte from a flow of anolyte over the anode. This design is also referred to as a two-gap cell, since there are two electrolyte 'gaps' between the electrodes. The two-gap design

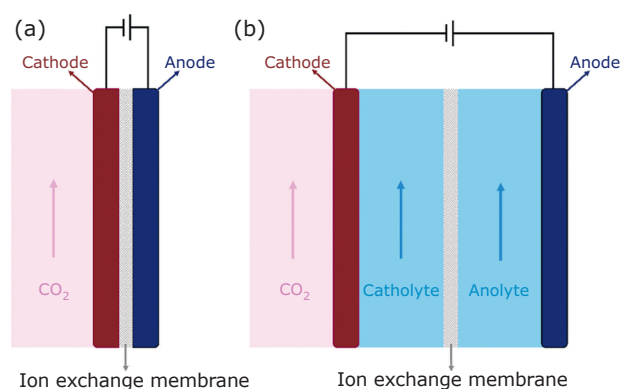


Fig. 1. Schematic depictions of two distinct electrolyser designs: (a) a MEA flow-cell design; (b) a GDE flow-cell design. Note that the schematics are simplified and do not include other auxiliary reactor components (for example, flow fields and external electrolyte layers in MEA design)

contributes to a higher Ohmic resistance, which raises the operating cell voltage and thus lowers the energy efficiency of the cell (4). This inspired the adoption of MEA-type reactors, well-known in the water proton exchange membrane electrolyser (5). In a MEA cell, the CLs are pressed directly onto the ion exchange membrane. Avoiding layers of liquid electrolyte separating the cathode and the anode can reduce the cell resistance and bring the operating voltage down. However, the MEA reactors tend to suffer from poor stability, since they are more prone to accumulation of water in the pores of the catalyst, which blocks CO<sub>2</sub> mass transport to the catalyst surface area and causes water reduction to become the dominating cathode reaction. Cathode flooding is also an issue in the GDE design with flowing electrolytes, however the problem can be partially managed with the electrolyte flow.

Advances in electrolyser design and development of components, such as ion exchange membranes, anode catalyst and integration with up and downstream processes will play significant roles in efforts towards commercialisation. The most pressing problem to resolve is maintaining high product selectivity for a reasonable operation lifetime while keeping the production rate high and cell voltage low. To a large extent, this will be achieved by improving the performance of the cathode.

Cathode development is a multidisciplinary endeavour in itself. To develop an optimally performing cathode, firstly an active, selective and stable catalyst is required. In addition to experimental screening, theoretical approaches can be valuable when trying to predict the activity and selectivity of various catalysts, such as copper alloys. Modelling using density functional theory (DFT) can predict binding energies of reactants, products and intermediates and support the experimental endeavours by predicting likely mechanistic pathways for the reactions. While *ex situ* material characterisation is necessary, it does not give the insight into the properties of the material when low potentials are applied under reaction conditions. Post-mortem analyses suffer from the structural and chemical changes occurring in the material when the cell is disassembled and the catalyst exposed to open circuit potential and air. *In situ* or *operando* characterisation methods are thus invaluable when trying to build understanding of the catalyst behaviour and properties under operating conditions. A high intrinsic CO<sub>2</sub> conversion activity of a given catalyst does not automatically ensure

a good performance of the cathode. The catalyst must first be incorporated into a homogeneous and stable CL, which often contains ionomers and other additives to give it the necessary mechanical stability and improve its flooding resistance. The GDL properties also contribute to the flooding resistance of the electrode. Not only the stability, but also the activity and selectivity of the cathode depend on the selection of the right GDL and the CL properties. Through influencing the mass flow of CO<sub>2</sub>, as well as the mass flows of intermediates and products, the GDL and GDE properties directly affect the local environment near the catalyst surface, which in turn influences the catalysis process. Rational design of the parts and the whole of the electrode can be achieved by understanding the relationships between structure, activity and selectivity.

This literature review summarises cathode catalyst developments, challenges, improvements and discusses the complex interplay between the cathode components and the observed C<sub>2+</sub> selectivity, focusing on a GDE cell design. While it has a significant effect on the overall performance, the design of the electrolyser is beyond the scope of this review.

## 2. Catalysts

As early as the 1980s, copper has been widely explored for its unique ability to reduce CO<sub>2</sub> to C<sub>2+</sub> products electrochemically. Ever since this discovery by Hori *et al.* (6), the development of a highly efficient and selective catalyst for the production of valuable carbon products has been the focus of much research in the field. Thus far, a range of different copper materials have been

developed and tested in the literature, including metallic nanoparticles, bimetallic composites and alloys, oxide-derived copper (OD-Cu) and many more (Figure 2). While there are examples of each of these catalysts performing well in testing, understanding the reaction mechanisms and catalyst structure are key to designing better materials in the future.

In this pursuit, significant effort has been put into developing mechanistic models for the reduction of CO<sub>2</sub> to common products. Unfortunately, this is highly complicated, often results are contradictory and there is little consensus on the various reaction pathways involved. A detailed compilation of mechanistic research has been published in a review by Nitopi *et al.* (7). Modelling does generally agree that different mechanisms for C–C coupling are favoured depending on reaction conditions such as pH, surface structure and overpotential. For example, the C–C coupling step, which is key for C<sub>2</sub> products, is thought to proceed through three different pathways. Firstly, dimerisation of \*CO is thought to occur at low overpotentials on Cu(100) surfaces. At higher overpotentials, the formation of \*CHO on Cu(111), a key intermediate for C<sub>1</sub> products, becomes more favourable, which can couple with \*CO to form \*C<sub>2</sub> species. A third set of mechanisms involving \*CH<sub>2</sub> species are thermodynamically feasible. However, it is thought that the surface concentration of these species is insignificant at reasonable overpotentials.

Keeping these mechanistic conclusions in mind, it should be possible to see a difference in product distribution on different crystal facet surfaces. Experimental studies on various copper crystal facets have been completed by many research groups (8), including Hori and coworkers (9, 10).

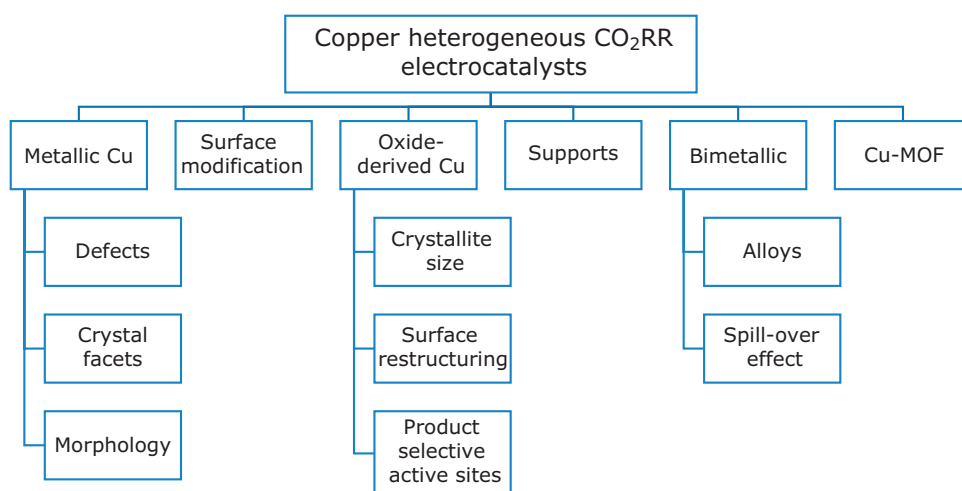


Fig. 2. Overview of heterogeneous CO<sub>2</sub> reduction reactions (CO<sub>2</sub>RR) copper catalysts research observed in the literature

These all show that reduction on Cu(100) yields primarily ethylene,  $C_2H_4$ , with smaller yields of other products like carbon monoxide, methane and hydrogen (a byproduct from the hydrogen evolution reaction (HER)). Reduction on Cu(111) produces high yields of methane and significantly lower yields of ethylene. De Gregorio *et al.* (11) take this further by synthesising and testing highly engineered, single-facet copper nanoparticles, which take the form of cubes (Cu(100) faceted), octahedra (Cu(111) faceted) and spheres (not mono-faceted) (Figure 3). These nanoparticles have a much higher surface area than electropolished single crystals studied previously, allowing them to reach higher current densities. As before, the same trend in results was observed, with the cubes producing mostly ethylene and octahedra producing mostly methane and hydrogen. The spherical particles were less specific in their product distribution, with a lower overall FE. The catalyst loading was also found to have some impact on product distribution.

Single crystal-facet studies are very useful for corroborating theoretical mechanistic work. However, it is well known that metallic copper materials are highly susceptible to surface oxidation. Subsequent re-reduction during electrolyser operation causes surface restructuring and, as a result, a decrease in product selectivity (10). Maintaining structural integrity from catalyst synthesis to catalytic testing

is a significant task in practice and makes the scale up of these materials very challenging. In addition, *in situ* surface reconstruction of metallic copper electrodes has been observed under typical reduction conditions (12).

Changing the structural properties, for example by facet engineering, is just one way to influence catalyst activity. Ever since the pioneering work done by Hori (6), it has been known that using different metals can give control over the mechanism and resultant product molecules. While copper was the only metal found to produce  $C_{2+}$  products in appreciable amounts, the other metals can be grouped by their major reduction products, which is found to correlate with  $*CO$ ,  $*COOH$  and  $*H$  intermediate binding energies (13). If these binding energies are significant for determining product selectivity, then doping copper with small amounts of other metals will have an influence on the product distribution. In addition, doping a metallic copper surface will also introduce lattice strain, new defects sites and bifunctional active sites, all of which could influence activity (14, 15).

Indeed, bimetallics have been a major focus of catalyst research. For example, copper-palladium alloys have been explored in detail both in theoretical modelling (15) and experimental testing (16). Ma *et al.* (17) studied the effect of different copper-palladium mixing patterns in

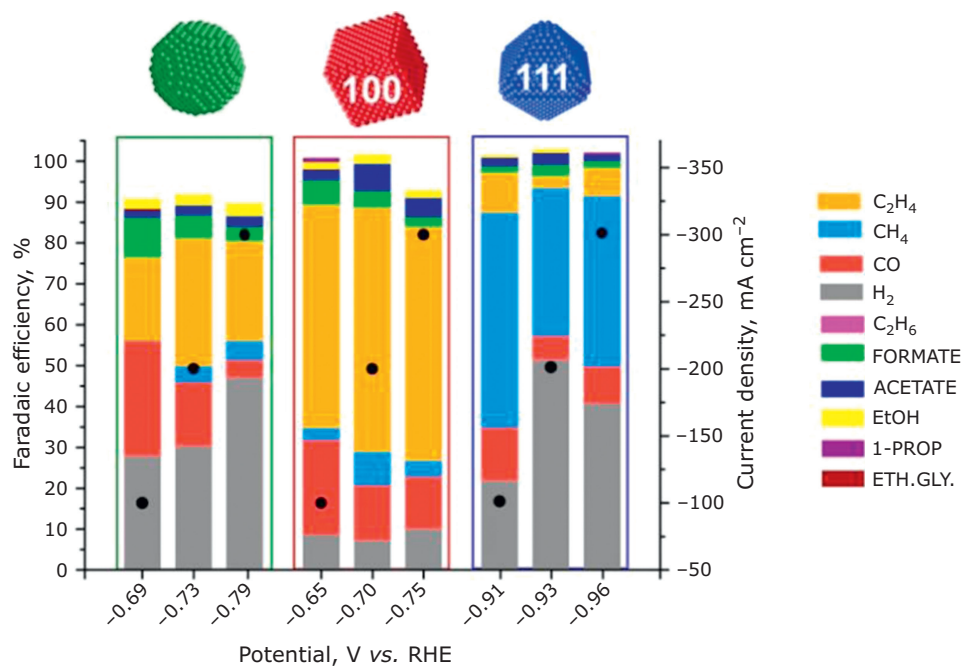


Fig. 3. Illustration of facet-engineered copper nanoparticle structures and their respective product selectivities for  $CO_2$  electrochemical reduction. Reproduced from De Gregorio *et al.* (11), Copyright 2020 American Chemical Society

bimetallic nanoparticles. Firstly, bimetallic catalysts with ordered, disordered and phase-separated atomic arrangements were synthesised with copper:palladium = 1:1. Two additional disordered arrangements were made with copper:palladium = 3:1 and 1:3. It was found that a highly ordered distribution of copper and palladium severely suppressed the formation of  $C_{2+}$  products, producing mainly CO. Selectivity for  $C_{2+}$  products increased with atomic disorder, with the phase-separated particles producing >60% selectivity for  $C_{2+}$  products (Figure 4). Furthermore, increasing the ratio of copper in these nanoparticles had a direct correlation to  $C_{2+}$  product selectivity, with the most  $C_{2+}$  selective catalyst being undoped copper. These results suggest that the C–C coupling ability of copper and the theorised beneficial \*H adsorption qualities of palladium were both diminished upon metal alloying, producing a weaker catalyst overall.

Another motivation for making bimetallic catalysts is the CO spill-over effect. By co-locating copper sites next to CO-producing metal sites (such as gold, silver or zinc), additional CO can be supplied to the copper for C–C coupling by increasing the local CO concentration and \*CO surface coverage. Morales-Guio *et al.* (18) demonstrate this effect experimentally using gold-copper polycrystalline alloys and justify the proposed synergistic mechanism through transport modelling. These gold-copper alloys were found to have a significantly increased selectivity for  $C_{2+}$  alcohols. Exploring the spill-over effect with novel metals and varying atomic ratios may offer a route to

further increasing catalyst activity and selectivity. In a similar way to the spill-over effect, the idea of tandem catalysis refers to the incorporation and mixing of two catalyst materials into a single CL of an electrode, where one catalyst selectively reduces  $CO_2$  to CO, and the other subsequently reduces CO to  $C_{2+}$  (or other) products. Optimising a tandem catalysis electrode presents the unique challenge of needing to balance the catalytic activity and turnover rate of each catalyst to prevent either the accumulation of CO, or the under-utilisation of the CO to  $C_{2+}$  catalyst. In addition, the different catalysts must be chemically compatible to prevent catalyst degradation. Lin *et al.* (19) demonstrate a successful tandem system using nickel-incorporated nitrogen-doped carbon as a CO evolution catalyst and  $Cu_2O$  nano-cubes as the CO reduction catalyst. In the most optimised system, 40% FE was achieved towards ethylene at  $150\text{ mA cm}^{-2}$  and 3.2 V in a MEA setup.

OD-Cu is a convenient means to produce copper nanostructured materials with high electrochemical active surface area (ECSA). Copper oxides, both (II) and (I), are reduced *in situ* during  $CO_2$  reduction reactions ( $CO_2RR$ ) to form metallic copper. The resulting materials are generally highly porous, high surface area and tend to exhibit strong activity for  $CO_2RR$ . Li *et al.* (20) reported that copper electrodes with various morphologies, including nanowires, can be made by thermal annealing of a metallic copper electrode. Subsequent electrochemical reduction of the oxidised electrodes exhibited an enhanced catalytic activity at low overpotentials and greater stability over 7 h vs. an untreated electrode. While the increase in achievable current density was ascribed to the surface area, the electrodes were found to be more selective for CO. Other groups have shown an increase in FE for  $C_{2+}$  products using OD-Cu, but this was generally rationalised by local pH effects (21).

The outstanding catalytic performance for  $C_{2+}$  products over OD-Cu and the nature of the active sites is a contentious topic that holds great importance for improving catalyst design in the future. Features such as subsurface oxygen (22), grain boundaries (23, 24), exposed facets (25) and local pH (21) are among the most common theories and findings. Cheng and coworkers (26) modelled the structure of over 150 potential active site structures and used DFT mechanistic modelling to show that some sites, such as grain boundary planar-square sites and convex-square sites, are selective for ethylene evolution, while other sites,

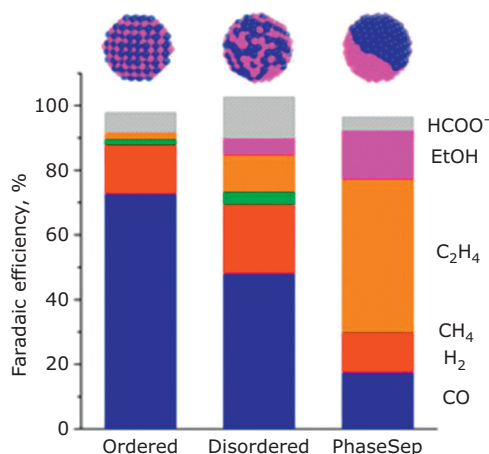


Fig. 4. Illustration of copper-palladium nanoparticle alloys with different structures and their corresponding product selectivities for  $CO_2$  reduction. Reprinted with permission from Ma *et al.* (17), Copyright 2016 American Chemical Society

such as step-square sites, are selective for alcohol generation. In the case of the alcohol evolving sites, the geometric shape of the site is thought to stabilise acetaldehyde intermediates and destabilise the copper-oxygen interaction. A report by Lum *et al.* (27) details experimental evidence of product selective active sites using isotopic labelling. By reducing mixtures of  $^{13}\text{CO}$  and  $^{12}\text{CO}_2$  and analysing the products, any difference in the carbon isotopic ratio between products indicates they have been produced by different active sites. At least three active sites were discovered which selectively produce ethylene, ethanol/acetate and 1-propanol, respectively. Interestingly, the isotopic ratios of ethanol and acetate were identical across all applied potentials, which strongly suggests that these products are generated from the same site. Lum *et al.* (27) also showed that the isotopic ratios of each product were different for four different OD-Cu catalysts, showing how catalysts with different physical characteristics (i.e. morphology, surface area) can have different product selectivities. In addition, no evidence for product specific active sites was observed for a metallic copper polycrystalline electrode.

Lastly, metal organic frameworks present a unique opportunity not only as catalyst materials for  $\text{CO}_2$  reduction, but also as a way of increasing  $\text{CO}_2$  gas concentration near the catalyst. Nam *et al.* (28) achieved 45% FE for ethylene using a HKUST-1 structure copper metal-organic framework (copper-MOF) by distorting the structure of the MOF to promote undercoordination of the copper sites. Yao *et al.* (29) report the use of HKUST-1 copper-MOF as a precursor to the synthesis of a porous  $\text{CuO}/\text{Cu}_2\text{O}/\text{Cu}$  material with residual carbon. This catalyst exhibited poor phase crystallinity and reached 51%  $\text{FE}_{\text{C}_2\text{H}_4}$  and 70%  $\text{FE}_{\text{C}_2+}$  with an operational stability of 20 h in an H-cell configuration. In a GDE flow cell configuration, a partial ethylene current density of  $150 \text{ mA cm}^{-2}$  was achieved with a 49.8%  $\text{FE}_{\text{C}_2\text{H}_4}$ . In addition to acting as a catalyst material, copper-MOFs have been studied for their ability to store  $\text{CO}_2$ . Qui *et al.* (30) report that an addition of 7.5–10 wt% HKUST-1 copper-MOF in the CL can increase the FE for methane by up to three times on a carbon-supported metallic copper catalyst. This was attributed to the ability of the MOF to store and supply  $\text{CO}_2$  to the catalyst surface.

Tuning product selectivity, decreasing product overpotentials, increasing the achievable current density and catalyst stability will continue to be the main goals of catalyst research going forwards. Both *in situ* characterisation and theoretical

modelling are powerful tools to help solve these problems but translating theoretical mechanisms and atomic surface structuring into a scalable catalyst synthesis route is likely to be a significant challenge for the future.

### 3. Modelling

#### 3.1 Reaction Thermodynamics

Experiments have been used for decades to study  $\text{CO}_2$  and  $\text{CO}$  reduction reactions (31, 32). Looking at the list of metal electrodes tested so far, copper has been identified as the promising candidate for these reactions (33–35). The use of theoretical studies provides a quicker way to make estimations and give an insight on catalyst materials. Although the developed models may not provide the exact mechanisms, they may suggest the important parameters to consider during experiments.

It is generally accepted that  $\text{CO}_2$  reduction reaction goes through the  $^*\text{COOH}$  to form  $^*\text{CO}$  (34, 36). This step may be followed-up by the reduction of  $^*\text{CO}$  to either  $^*\text{COH}$  or  $^*\text{CHO}$  species. By making use of computational hydrogen electrode model coupled with DFT calculations, Peterson *et al.* (37) proposed the hydrogenation of  $^*\text{CO}$  to form  $^*\text{CHO}$  intermediate species to be the key step in the formation of methane and ethylene over copper electrode.

Nie and coworkers (38), presented a different reaction pathway which goes through a  $^*\text{COH}$  intermediate species. They claim that the water bilayer solvation facilitates reduction of  $\text{CO}_2$  to  $^*\text{COOH}$  species, leading to the formation of  $^*\text{COH}$  intermediate. This shows how the various parameters, such as surface structure and solvation inclusion may affect the rate of formation of  $^*\text{COH}$  vs.  $^*\text{CHO}$  intermediates.

To date, several reaction mechanisms have been identified. A detailed review has been published by Mota and colleagues (39), highlighting strategies that have been used to suggest pathways in the conversion of  $\text{CO}_2$  to hydrocarbons. **Figure 5** maps out several possible reaction pathways for  $\text{CO}_2$  and  $\text{CO}$  reduction to form  $\text{C}_1$  and various  $\text{C}_2$  species respectively.

#### 3.2 Catalyst Structure and Reaction Condition Effects

To improve the accuracy of the computational models for  $\text{CO}_2\text{RR}$ , various factors have been incorporated and extensively studied to determine

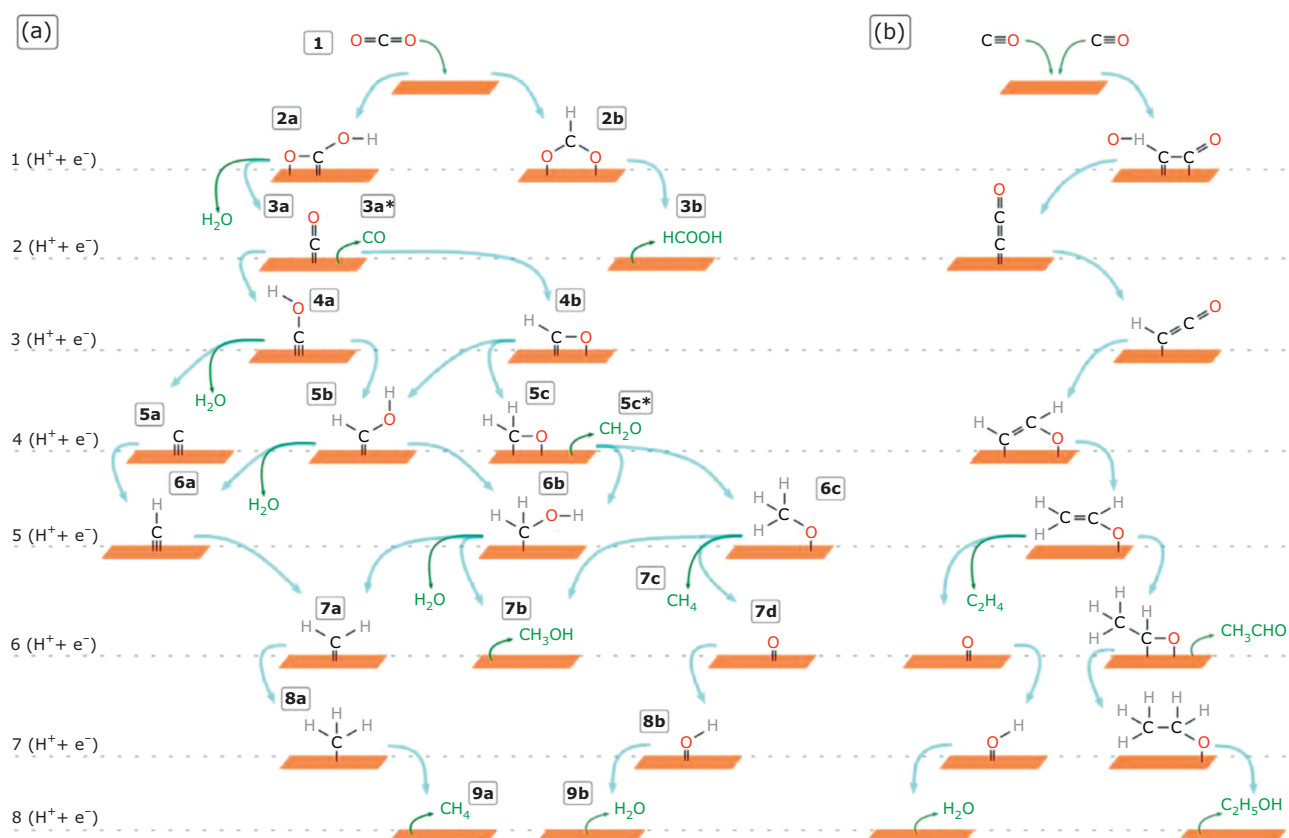


Fig. 5. (a) Full reaction network for CO<sub>2</sub>RR to C<sub>1</sub> species; (b) lowest-overpotential pathway for CO reduction to various C<sub>2</sub> species. Reprinted from (40), Copyright (2018), with permission from Elsevier. Carbon, oxygen and hydrogen atoms in CO<sub>2</sub> and adsorbed species are shown in black, red and grey respectively. Arrows and species in green denote the desorbed products. Blue arrows connect adsorbates in the reaction network separated by a single proton-electron transfer

their effect on both activity and selectivity on the copper catalyst. Over the years, several studies of the reduction of CO<sub>2</sub> and CO to C<sub>2+</sub> products have been published (39, 41, 42). Popular topics include the incorporation of various effects such as particle size and catalyst structure. While little has been done using theoretical studies to investigate the influence of support materials.

Using static energy calculations and dynamic simulations, Li *et al.* (43) presented the effect of particle size and dynamic structure change on activity and selectivity towards methane and C<sub>2+</sub> products of the copper clusters for CO<sub>2</sub>RR. They claim that the copper clusters with a large ratio of undercoordinated sites enhance activity. Furthermore, the selectivity towards C<sub>2+</sub> products has been associated with structural change of copper clusters induced by carbon supports.

Mangione and coworkers (44) conducted a study on electrochemical CO<sub>2</sub> reduction into methane over copper nanocubes. The used model has not been sufficient to explain the selectivity nor product distribution on this shape-controlled catalyst.

However, the study reveals that although the \*CO dimerisation mechanism may not take place on the {100} surface of the nanocubes, C–C coupling step utilises the interface between the {100} terraces and {110} edges, giving preference to \*CO–COH coupling. This demonstrated that shape-controlled catalysts surpassed the facet selectivity in single crystals.

Tuning the morphology of metallic catalysts alone is not sufficient to direct the selectivity towards desired products. In addition to the factors associated with the catalyst structure, in recent years an interest to consider the effect of reaction conditions such as potential, pH and the presence of cations on CO<sub>2</sub>RR has rapidly started to grow.

The effect of applied potential for CO<sub>2</sub>RR on various copper facets has been extensively studied (45, 46). Hussain and coworkers (35) studied the effect of applied potential on the activation energy barriers of various elementary steps to predict product selectivity. Over a range of applied potential, the activation energy has been found to be lower for the CO<sub>2</sub>RR rather than the HER on

Cu(111) surface. In comparison to other metals studied, this reveals why copper is considered the most promising candidate for CO<sub>2</sub>RR.

Montoya *et al.* (45) provided an explanation behind the low overpotential for the C–C coupling over Cu(100) surfaces. They proposed that the combined effect of solvation and local electric field enhance the reduction of the activation energy barrier for CO dimerisation. Where the presence of Li<sup>+</sup> and Na<sup>+</sup> seemed to have a better effect than H<sup>+</sup>.

The effect of solvated cations has been also presented by Resasco and colleagues (47). Their study focused on the investigation of alkali metal cations size effect on the activity and selectivity of several metal catalysts for the CO<sub>2</sub>RR. They showed that the distribution of products formed are influenced by the alkali metal cation, resulting from the interaction of the solvated cation and the adsorbed species.

Monteiro *et al.* (48) recently confirmed the claims made previously on the effect of alkali metals. They showed that the primary role of cations is making use of the electric field effect to stabilise the negatively charged intermediates in CO<sub>2</sub> reduction. In addition, they highlighted how the increase in concentration of the cation, such as Cs<sup>+</sup>, promote an increase in selected products formation on copper electrode.

### 3.3 Scaling Relationships and Volcano Plots

Incorporating both structural and reaction condition factors into computational models involves large sets of computational data. Hence, there is still a need to devise simpler predictive and descriptive CO<sub>2</sub>RR models to reduce computational costs. Scaling relationships and volcano plots are some of the commonly used tools to understand the reactivity and predict the optimal catalyst for both CO<sub>2</sub> and CO reduction reactions. An overview of the development of scaling relationships and how they are associated with surface science and catalysis has been recently published by Greeley (49).

Making use of the scaling relationships, Peterson and coworkers (36) compared trends of adsorption energies of \*COOH, \*CH<sub>2</sub>O, \*CHO, \*COH, \*CHOH, \*CH and \*CH<sub>2</sub> correlated against \*CO over transition metal catalyst in CO<sub>2</sub>RR. This study added an insight towards the reactivity of the metal catalyst for the reduction reactions for CO<sub>2</sub>. These relationships were used to build volcano plots to predict potential catalyst for a given chemical reaction. This is shown in **Figure 6**,

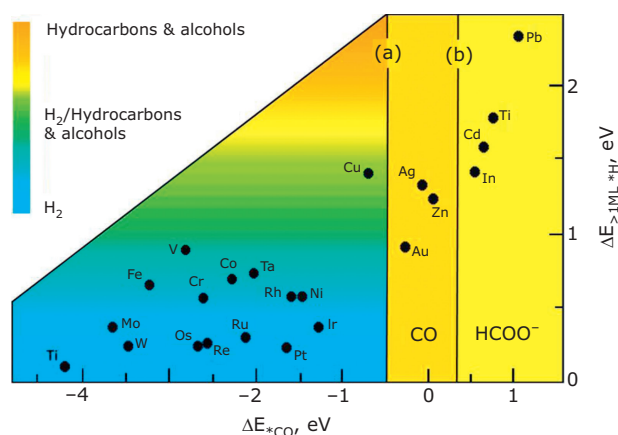


Fig. 6. Two-parameter descriptor of the electrocatalytic activity of metal electrode. Relative rate of CO<sub>2</sub> reduction and H<sub>2</sub> formation is shown as a function of the adsorption energy of an isolated CO molecule and differential adsorption energy of H-atom at the on-top site. Reproduced from Hussain *et al.* (35), Copyright (2018) American Chemical Society

where screening of various metal electrode has been performed using a similar technique.

By making use of a two-parameter descriptor, Hussain *et al.* (35) predicted the formation of electroreduction products such as hydrocarbons, alcohols, hydrogen, CO and HCOO<sup>-</sup> over various metal electrode surfaces. Using this tool, the studied metal electrodes have been classified into four categories: (a) copper being the only metal promoting hydrocarbons and alcohols formation; (b) metals promoting hydrogen evolution (titanium, iron, cobalt, platinum, nickel and iridium); (c) metals promoting CO formation (gold, silver and zinc); and (d) formate forming metals (indium, cadmium and thallium).

Rendón-Calle and coworkers (40) published a review of computational modelling studies of the electrochemical reduction of CO<sub>2</sub> on copper electrodes. The use of these tools to predict activity and screen for the optimal catalyst has been highlighted, where the use of scaling relationships has been noted to be useful for the classification of materials.

### 3.4 Theoretical Methods

The use of first-principles methods play an important role in providing insight in the electrochemical interface chemistry. However, it remains a challenge to capture all relevant effects such as interfacial fields and solvation using one approach.



Thermal fluctuations description of solvent molecules and ions remains one of the main issues when using DFT method (50, 51). *Ab initio* molecular dynamics (AIMD) simulation is potentially the direct and accurate approach to address these challenges (52, 53). However, this approach requires substantial computational cost.

Schwarz *et al.* (54) described a variety of electrochemical modelling methods used in *ab initio*. They presented the relation between the major electrochemistry techniques including simple methods with no solvents, continuum, as well as AIMD of solvents and electrolyte. In addition, the review lays out the main challenges of electrochemical modelling at atomic scale and highlights the limitation of each method in term of accuracy, efficiency and computational cost.

The implicit solvent theory (IST) is an alternative method to reduce the computational cost. Nishihara and Otani (55) developed a hybrid solvation method called effective screening medium-reference interaction site method (ESM-RISM) based on one of the ISTs. The method is a combination of the modified three-dimensional reference interaction site method (3D-RISM) with effective screening medium method (ESM). The technique opens the possibility to calculate and model thin film immersed into a solvent with acceptable computational cost.

Fernandez-Alvarez *et al.* (56) adopted the hybrid DFT-solvation model to study the partially oxidised Pt(111) surface in aqueous electrolyte solution. This work also serves as a case study for the description of interface properties in regions under conditions of the oxygen reduction reaction (ORR) using ESM-RISM method. Although there are limitations in the applicability of DFT/ESM-RISM for studying electrochemical processes, the insight obtained from this work may assist in the improvement of the existing techniques or development of new hybrid methods.

Weitzner and coworkers (57) recently modelled the electrolyte composite effect on CO adsorption energies over various copper surfaces using ESM-RISM based DFT-continuum approach. The study focuses on determining the influence of solution pH and applied voltage in potassium-containing electrolytes on the binding energies of CO. In addition, the study highlights the importance of electrical double-layer structure for predicting catalyst operation.

ESM-RISM is known to underestimate the dielectric constant of a solution with dipolar solvent molecules. However, dielectrically consistent RISM (DRISM) is one of the methods used to

overcome the challenge. Recently, Hagiwara and coworkers (58) combined DRISM with ESM-RISM to improve the accuracy of electrochemical interface simulations. The new developed method has been benchmarked and applied on Pt(111)/1M-HCl(aq) interface. The obtained results are in reasonable agreement with experiments.

Over the past decade, huge progress has been made on the development of techniques and approaches to simulate catalyst-electrolyte interface and incorporate the reaction conditions for the electrochemical catalytic processes. Few extensive reviews have been recently published (7, 59) and the main approaches used in CO<sub>2</sub> and CO electrochemical reduction reaction on copper-based catalysts are summarised by Todorova and colleagues (60).

Incorporating various factors improves the accuracy of computational models to describe the electrochemical reduction reaction of both CO<sub>2</sub> and CO. Although there is a growing interest around this topic, the effect of the support material and the use of metal alloys electrodes have not yet been extensively explored.

So far, scaling relationships and volcano plots are the most useful tools in computational electrochemistry for understanding the reactivity of materials and screening. However, usually these tools assume a single mechanism for various facets and materials which is not necessarily true. Therefore, there is still a need to develop simple and convenient models with various factors considered, to improve accuracy and provide an in-depth understanding of the reduction reaction.

Although a perfect technique has not yet been discovered, notable progress has been made recently towards describing the electrochemical interface. The development of hybrid models provides us a possibility to model these systems with better accuracy and lower computational cost.

Part II (61) will explore *in situ* characterisation, the catalyst layer and the gas diffusion layer.

## Authors Contributions

Harry Macpherson wrote the 'Catalyst Layer' section and created the layout of the review; Toby Hodges wrote the 'Catalysts' section; Moyahabo H. Chuma wrote the 'Modelling' section; Connor Sherwin wrote the 'In Situ Characterisation' section; Urša Podbevšek wrote the 'Gas Diffusion Layer' section; Katie Rigg, Veronica Celorrio and Andrea Russell contributed to the 'In Situ Characterisation'

section; Elena C. Corbos proofread the manuscript and gave overall advice.

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