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Total number of authors:
13

Published in:
Chemical Reviews

Link to article, DOI:
[10.1021/acs.chemrev.8b00705](https://doi.org/10.1021/acs.chemrev.8b00705)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Nitopi, S. A., Bertheussen, E., Scott, S. B., Liu, X., Engstfeld, A. K., Horch, S., Seger, B., Stephens, I., Chan, K., Hahn, C., Nørskov, J. K., Jaramillo, T., & Chorkendorff, I. (2019). Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte. *Chemical Reviews*, 119(12), 7610-7672.
<https://doi.org/10.1021/acs.chemrev.8b00705>

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Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte

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Abstract

To date, copper is the only heterogeneous catalyst that has shown a propensity to produce valuable hydrocarbons and alcohols, such as ethylene and ethanol, from electrochemical CO₂ reduction (CO₂R). There are variety of factors that impact CO₂R activity and selectivity, including the catalyst surface structure, morphology, composition, the choice of electrolyte ions and pH, the electrochemical cell design, etc. Many of these factors are often intertwined, which can complicate catalyst discovery and design efforts. Here we take a broad and historical view of these different aspects and their complex interplay in CO₂R catalysis on Cu, with the purpose of providing new insights, critical evaluations, and guidance to the field with regards to research directions and best practices. First, we describe the various experimental probes and complementary theoretical methods that have been used to discern the mechanisms by which products are formed, and next we present our current understanding of the complex reaction networks for CO₂R on Cu. Then we analyze two key methods that have been used in attempts to alter the activity and selectivity of Cu: nanostructuring and the formation of bimetallic electrodes. Finally, we offer some perspectives on the future outlook for electrochemical CO₂R.

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1. Introduction

There is a pressing need to advance the development of CO₂ utilization technologies such as electrochemical CO₂ reduction (CO₂R); as a result, this has been a rapidly expanding field of research in recent years. In particular, there is a large body of work on copper (Cu) materials for this reaction, since Cu is, as of yet, unique in its ability to catalyze the electrochemical conversion of CO₂ to valuable fuels and chemicals. While many great review and perspective articles have been published in this area, they have typically had a more narrow focus either in terms of timespan or topics covered.^{1–21} Here we aim to provide an organized and comprehensive review of CO₂R on copper and the multitude of approaches that have been used to tune its catalytic activity and selectivity. The scope strives to include all studies of electrochemical CO₂R in aqueous electrolytes on Cu-based catalysts, beginning with many of the early works in the 1980s-90s through those published in 2018, and takes into consideration both experimental and theoretical methods, planar and nanostructured Cu, and Cu modified with other elements. This work is also a perspective, in which we critically analyze the literature in attempts to normalize/compare the various results and show general trends throughout the field. Additionally, we suggest several techniques and protocols that can allow for more reliable comparisons, enable a more fundamental understanding of the catalysis, and help drive this technology towards commercialization. This chapter first provides a broad context by summarizing anthropogenic carbon streams, comparing different strategies to recycle CO₂, and touching upon the economics of electrochemical CO₂ conversion. Then, planar polycrystalline copper is introduced as a unique electrocatalyst for this reaction, which will serve as the basis for all the discussions that follow.

1.1 Motivation for CO₂ Recycling

At the core of biological metabolism is the ability to convert carbon between different oxidation states in order to store and release energy, as well as to synthesize functional molecules. Likewise, the oxidation of carbon is at the center of human civilization's collective "industrial metabolism" consisting of our energy infrastructure and chemical industry. Whereas in biological metabolism, reduction of CO₂

in photosynthesis balances the oxidation of carbon in cellular respiration, carbon reduction is as of yet a missing piece of humanity's industrial metabolism. This imbalance has become a significant perturbation to Earth's natural carbon cycle, as indicated in the top two sections of **Table 1**. The resulting accumulation of the greenhouse gas CO₂ in the atmosphere is the primary driver of today's climate change.²² While the Paris Climate Accord commits signatories to the goal of achieving "a balance between anthropogenic emissions by sources and removals by sinks of greenhouse gases in the second half of this century,"²³ it leaves it to individual nations to volunteer the specifics of how to achieve this goal. The problem is urgent: net CO₂ emissions need to decrease rapidly and cross zero around the year 2050 if global warming is to be limited to the relatively safe level of 1.5 °C above pre-industrial levels.²⁴ Strategies to reduce net CO₂ emissions fall under three categories: decarbonization, carbon sequestration, and carbon recycling, all three of which will most likely need to play a role. This review will focus in-depth on the scientific progress and challenges of carbon recycling based on electrochemical CO₂ reduction on Cu catalysts. For context, we will first briefly comment on decarbonization and carbon sequestration, as well as the other major CO₂ recycling strategies.

1.1.1 Closing the Carbon Cycle

Significant progress is presently being made in decarbonization. Economic growth is increasingly decoupled from energy consumption and from CO₂ emissions (**Figure 1**),^{25–27} electricity from renewable sources such as wind turbines and photovoltaics is increasing in volume and decreasing in price,²⁸ private investment in renewable energy is outpacing investment in fossil fuels,²⁹ and global annual CO₂ emissions are plateauing.²⁵ However, significant challenges remain for full decarbonization.³⁰ Firstly, renewable energy sources such as wind and solar are variable and produce electrical power, which has to be utilized immediately or stored. While a number of energy storage technologies exist, including pumped hydro, compressed air, batteries, redox flow batteries, and flywheels, they all have limitations in terms of scalability, versatility, and/or maximum storage time.^{31,32} As of yet there is no technology in use that could feasibly store enough renewable electricity to power society through a cloudy and windless day. Secondly, not all energy is easily electrifiable. In transport,

especially, which accounts for 14% of global CO₂ emissions²² (middle portion of **Table 1**), there are clear advantages to energy in the form of liquid fuel. Finally, not all CO₂ emissions are due to energy use. The bottom section of **Table 1** shows a lower-bound estimation to the direct non-energy carbon use in industry, calculated as the stoichiometric amount of carbon used or released globally in the production of several key products: cement,³³ steel,³⁴ plastic,³⁵ ammonia,³⁶ and aluminum.³⁷ Together, these products involve as much carbon as 12% of global carbon emissions. Increased recycling can help to lower this number, and decarbonization may be possible, if difficult, in some of these industries.³⁰ However, it is clear that industry would continue to have an appetite for carbon even if energy were to be fully decarbonized.

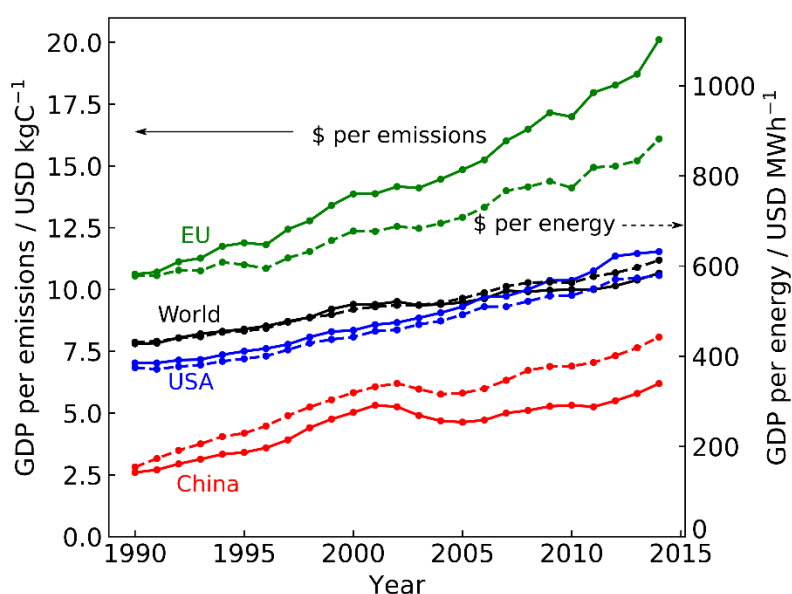


Figure 1: World GDP (purchasing power parity, 2011 dollars) is growing relative to energy consumption and CO₂ emissions. Data obtained from The World Bank.²⁷

Table 1: Global carbon fluxes

Carbon flux	Amount / [GtC/yr]	Year ^{citation}
<i>Carbon cycle overview</i>		
Air-land natural exchange	120	2007 ³⁸
Air-ocean natural exchange	90	2007 ³⁸
Anthropogenic carbon emissions	11	2014 ³⁹
Total anthropogenic GHG emissions by CO ₂ equivalent	13	2010 ²²
<i>Fate of anthropogenic emissions</i>		
Net ocean uptake	4	2014 ³⁹
Net land uptake	3	2014 ³⁹

Accumulated in atmosphere	4	2014 ³⁹
<i>Anthropogenic emissions by sector (100%=13 GtC/yr)</i>		
Electricity generation	3.3 (25%)	2010 ²²
Agriculture and land-use change (deforestation)	3.2 (24%)	2010 ²²
Industry (excluding electricity)	2.8 (21%)	2010 ²²
Transportation	1.9 (14%)	2010 ²²
Buildings	0.9 (6%)	2010 ²²
Other	1.4 (10%)	2010 ²²
<i>Carbon in industrial reactions, CO₂ as ultimate biproduct</i>		
Cement (calcination): $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	0.59	2017 ³³
Steel (via CO): $2 \text{Fe}_2\text{O}_3 + 6 \text{C} + 3 \text{O}_2 \rightarrow 4 \text{Fe} + 6 \text{CO}_2$	0.38	2017 ³⁴
Plastic (disposal): $(\text{CH}_2)_{2n} + 3n \text{O}_2 \rightarrow 2n \text{H}_2\text{O} + 2n \text{CO}_2$	0.26	2015 ³⁵
Ammonia (via H ₂): $3 \text{CH}_4 + 6 \text{H}_2\text{O} + 4 \text{N}_2 \rightarrow 8 \text{NH}_3 + 3 \text{CO}_2$	0.045	2016 ³⁶
Aluminum (carbon anode): $2 \text{Al}_2\text{O}_3 + 3 \text{C} \rightarrow 4 \text{Al} + 3 \text{CO}_2$	0.019	2016 ³⁷
Total non-fuel carbon as industrial reactant	1.28	
<p>Some of the carbon fluxes have been converted from carbon dioxide fluxes emissions to molecular mass (1 GtC/yr is equivalent to 3.66 GtCO₂/yr). The data from Reference 1 are reported, not in terms of carbon or carbon dioxide flux, but by total greenhouse gas emissions converted to the equivalent mass of CO₂ emissions based on the greenhouse gas's global warming potential. These data were converted to carbon flux as if they were CO₂ emissions.</p> <p>The bottom section of the table shows the minimum non-energy carbon usage of the most important carbon-using industrial processes, calculated based on global production and the stoichiometry of the simplified reaction shown. Figures for steel and plastic exclude recycling. For plastic, we write the combustion reaction to represent the stoichiometric amount of CO₂, even though most plastic today is not incinerated but ends up in landfills or the environment after use.³⁵</p> <p>For more details, see Section 2 of the Supporting Information (SI).</p>		

In contrast to decarbonization, carbon sequestration is a strategy that accepts some continued net production of CO₂ but aims to prevent its release to the atmosphere.^{40,41} There are at present 18 large-scale carbon capture and storage (CCS) projects in operation worldwide, separating about 40 megatonnes of CO₂ per year (9.6 MtC/yr), from industrial point sources and storing it underground.⁴² This is just under 0.1% of global carbon emissions, but this could in principle be scaled up indefinitely as there are suitable geological formations for the storage of hundreds of years of CO₂ at the present emissions rate.⁴³ In particular, if the carbon stored underground originates from the atmosphere rather than from fossil fuels, as the case when CO₂ resulting from the combustion of biomass is stored, the result is net-negative emissions. This strategy, bio-energy with carbon capture and storage (BECCS), can provide electricity at the same time as net-negative emissions, and will be necessary for stabilizing the climate in all but the most optimistic projections, but is as of yet largely unused.²⁴ Unfortunately for net CO₂ emissions, most existing and planned projects for CCS fall under the category of enhanced oil

recovery (EOR), whereby CO₂ is pumped underground to aid in the extraction of additional fossil fuels.⁴² This highlights one of the main challenges with carbon sequestration: the lack of a viable business case. CO₂ separation from a power plant, for example, costs on the order of \$60 to \$100 USD per ton CO₂ (approximately \$200 to \$350 USD/tC),⁴⁰ and together with transportation and storage costs, this results in a total increase of more than 25% in the cost of the electricity generated by a power plant utilizing CCS.⁴⁴ Under existing policies and economics, carbon sequestration is thus rarely economically viable without EOR, which in effect adds value to the CO₂ by using it to facilitate the extraction of additional fossil fuels. The immense potential of CCS, and in particular BECCS, for reducing net carbon emissions will only be realized once regulations make the cost of emitting CO₂ higher than the costs of separation and storage.⁴⁰

The limitations to full implementation of decarbonization and carbon sequestration outlined above all point to a common missing piece of human civilization's collective "industrial metabolism," namely carbon recycling based on the conversion of CO₂ to more reduced products. CO₂ recycling can enable the storage of renewable electricity from intermittent sources in a dense and versatile form, provide a renewable carbon feedstock to chemical industries, and add value to CO₂ captured at industrial point sources or directly from the air.

1.1.2 Strategies for CO₂ Recycling

CO₂ is the most oxidized form of carbon, together with carbonate minerals, with a formal oxidation state of +4. As a result, conversion of CO₂ into a more energetic product involves transfer of electrons to carbon, reducing its oxidation state. The family of reactions by which CO₂ is converted to a more reduced product is most often called *CO₂ reduction*. These reactions are also often referred to as *CO₂ hydrogenation* for thermally-driven processes involving reaction with hydrogen (H₂) or *CO₂ fixation* in natural photosynthesis and bio-inspired catalysis.⁴⁵

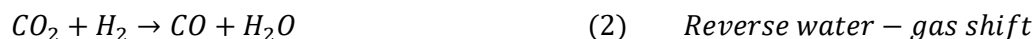
In order for the production and ultimate combustion of CO₂ reduction/hydrogenation products to represent a closed cycle, the ultimate source of electrons and protons for the reduction of CO₂ must be water (H₂O), as combustion of a hydrogenated carbon product releases H₂O. CO₂ reduction /

hydrogenation / fixation thus follows the overall formula:

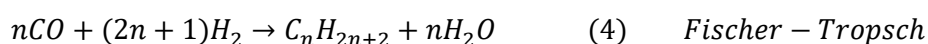


Natural photosynthesis by plants and other phototrophs fixates a much larger amount of carbon globally than human activity releases (**Table 1**),^{38,39} so using biomass as a carbon source is an obvious carbon recycling strategy. However, the utility of bio-based carbon is limited by the amount of land required. Well-intended markets for transportation biofuels such as ethanol and biodiesel need energy-intensive care (*e.g.* fertilizers, pesticides, etc.) and have led to deforestation in some cases, thus greatly mitigating or even eliminating any potential CO₂ emission savings.^{46,47} As mentioned above, biomass energy with carbon capture and storage (BECCS), has the potential of achieving net negative emissions, however the land requirement is immense. Near-term availability of biomass for BECCS in the US, for example, corresponds at most to about 370 MtCO₂/yr (0.1 GtC/yr), less than 10% of US emissions.⁴⁸ The picture is similar on a global scale.⁴⁹ High-yield biomass such as short-rotation forestry can yield up to about 800 tC/km²/yr,⁵⁰ meaning that it would require about 14 million square kilometers to offset the present global carbon emissions of 11 GtC/yr. Repurposing this amount of land, about the same area as is used globally for food crop production,²² is clearly not feasible. Thus, while important, harnessing the power of natural photosynthesis can only play a limited role in reaching net-zero emissions, leaving room for other CO₂ recycling strategies.

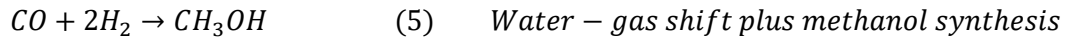
There are pathways in the traditional chemical industry, all thermally activated, that could be used for CO₂ hydrogenation, using H₂ as the reductant.^{51,52} CO₂ can be reduced to carbon monoxide (CO) by the reverse water gas shift reaction:



If an excess of H₂ is used and the water is condensed out, the product gas is a mixture of H₂ and CO, which is called synthesis gas or syngas. Syngas can be used as the precursor to methane on a Ni catalyst,⁵³ to multi-carbon hydrocarbons on an Fe or Co catalyst,⁵⁴ or to methanol on a Cu/ZnO catalyst.^{55,56} These reactions are called methanation, the Fischer-Tropsch reaction, and methanol synthesis, respectively.



In methanol synthesis, some CO₂ is required in the syngas stream because CO₂ is actually the immediate reactant.⁵⁷ The role of CO is to react with the water released by CO₂ hydrogenation and generate more CO₂ via the water-gas shift (reverse of Reaction 2). The net reaction is:

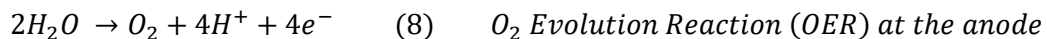
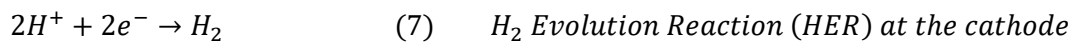


All of these processes run at high pressures and temperatures; for example, ~100 bar and 250 °C are typical conditions for methanol synthesis, the mildest of the three reactions.⁵²

In order for CO₂ hydrogenation by the above reactions to be a renewable process, the hydrogen must come from water splitting using renewable energy:

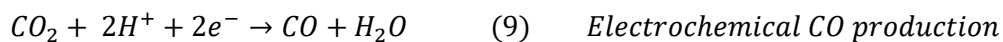


such that the combined reaction is on the form of Reaction 1 above. The water splitting would be driven electrochemically using electrical energy from renewable sources such as wind and solar,^{30,58,59} according to the half-reactions:



Compared to hydrogen, carbon-based fuels have the advantages of higher volumetric energy density and greater ease of integration in the present infrastructure (drop-in fuels). Furthermore, carbon-based chemicals will still be needed regardless of energy decarbonization.⁶⁰

An alternative to CO production by the reverse water-gas shift (Reaction 2) is electrochemical reduction of CO₂ to CO:



balanced by the OER (reaction 8). The electrochemically produced CO can then be reacted further as described above to form hydrocarbons or alcohols from CO₂. This combined approach using electroreduction of CO₂ in a high-temperature solid-oxide electrolysis cell and subsequent thermal hydrogenation proved especially promising in an analysis of CO₂ recycling strategies.⁶¹

However, direct electrochemical reduction of CO₂ can have a number of advantages compared to hydrogenation of CO₂ or CO by electrochemically produced H₂.^{2,62} it (1) combines the electrochemical water splitting and subsequent thermal hydrogenation into a single electrochemical

process, (2) enables products that cannot easily be prepared by thermally driven processes, and (3) can often run at or near room temperature and ambient pressure. These features imply that processes based on electrochemical CO₂ reduction are more suitable to decentralization than the thermal counterparts, and that electrochemical CO₂ reduction processes can be designed to enable relatively quick adjustment of production in order to match the overproduction of electricity from intermittent renewable sources.⁶³

1.2 Electrochemical CO₂ Reduction

In electrochemical CO₂ reduction, the cathodic reaction is of the general form:



Like in water splitting, the anodic reaction in electrochemical CO₂R must be the oxygen evolution reaction (OER, Reaction 8) in order to sum to the overall reaction given by Reaction 1 above. In other words, water is the only renewable and scalable source of electrons and protons.⁶⁴ In this section, we first discuss the carbon dioxide reduction reaction in general, with a focus on the thermodynamics and economics of reducing CO₂ to various products. We then summarize the actual CO₂R activity and selectivity of metal electrodes, highlighting the unique ability of copper to reduce CO₂ to hydrocarbons and alcohols.

1.2.1 Desired Products: Thermodynamics and Economics

Table 2 lists the equilibrium potentials for CO₂R to commonly reported electrochemical products. All of the CO₂R standard potentials here are calculated via the Gibbs free energy of reaction using gas-phase thermochemistry data and, for aqueous products, Henry's Law data, from NIST.⁶⁵ CO₂ is always considered a gas, water a liquid, and the state of the product is gas or aqueous as indicated. Regardless of which CO₂R product is formed at the cathode, the fact that the CO₂R reaction together with OER (Reaction 8) must add to an overall reaction of the form of Reaction 1 means that the stoichiometric coefficients for electrons and protons in a sustained CO₂ reduction reaction must be equal. Acidic products are therefore considered in the fully protonated form. Similar tables and lists provided

in previous CO₂R reviews,^{1,2,15,16,45} studies of CO₂R electrocatalysis,⁶⁶ and process/economic analyses for electrochemical CO₂ conversion^{67–70} all show some variation due to the use of different potential scales, deprotonated products, and/or different standard states (for instance liquid instead of aqueous).

As described in detail in subsequent sections of this review, CO is an important intermediate in CO₂R to hydrocarbons, aldehydes, and alcohols on Cu, and a promising approach to CO₂R is a stepwise one via CO, in which CO reduction (COR) is an important reaction in its own right.⁷¹ The equilibrium potential for CO reduction to a few products is therefore also included in this table, and an equation relating CO reduction equilibrium potential to CO₂ reduction equilibrium potential is given in Section 1 of the Supporting Information (SI).

Table 2: Electrochemical reactions with equilibrium potentials

Reaction	E ⁰ / [V vs. RHE]	(Product) Name, abbreviation
2H ₂ O → O ₂ + 4 H ⁺ + 4 e ⁻	1.23	Oxygen Evolution Reaction, OER
2 H ⁺ + 2 e ⁻ → H ₂	0	Hydrogen Evolution Reaction, HER
$x \text{ CO}_2 + n \text{ H}^+ + n \text{ e}^- \rightarrow \text{Product} + y \text{ H}_2\text{O}$		CO ₂ Reduction, CO ₂ R
CO ₂ + 2 H ⁺ + 2 e ⁻ → HCOOH _(aq)	-0.12	Formic acid
CO ₂ + 2 H ⁺ + 2 e ⁻ → CO _(g) + H ₂ O	-0.10	Carbon monoxide
CO ₂ + 6 H ⁺ + 6 e ⁻ → CH ₃ OH _(aq) + H ₂ O	0.03	Methanol, MeOH
CO ₂ + 4 H ⁺ + 4 e ⁻ → C _(s) + 2 H ₂ O	0.21	Graphite
CO ₂ + 8 H ⁺ + 8 e ⁻ → CH ₄ (g) + 2 H ₂ O	0.17	Methane
2 CO ₂ + 2 H ⁺ + 2 e ⁻ → (COOH) _{2(s)}	-0.47	Oxalic acid
2 CO ₂ + 8 H ⁺ + 8 e ⁻ → CH ₃ COOH _(aq) + 2 H ₂ O	0.11	Acetic acid
2 CO ₂ + 10 H ⁺ + 10 e ⁻ → CH ₃ CHO _(aq) + 3 H ₂ O	0.06	Acetaldehyde
2 CO ₂ + 12 H ⁺ + 12 e ⁻ → C ₂ H ₅ OH _(aq) + 3 H ₂ O	0.09	Ethanol, EtOH
2 CO ₂ + 12 H ⁺ + 12 e ⁻ → C ₂ H ₄ (g) + 4 H ₂ O	0.08	Ethylene
2 CO ₂ + 14 H ⁺ + 14 e ⁻ → C ₂ H ₆ (g) + 4 H ₂ O	0.14	Ethane
3 CO ₂ + 16 H ⁺ + 16 e ⁻ → C ₂ H ₅ CHO _(aq) + 5 H ₂ O	0.09	Propionaldehyde
3 CO ₂ + 18 H ⁺ + 18 e ⁻ → C ₃ H ₇ OH _(aq) + 5 H ₂ O	0.10	Propanol, PrOH
$x \text{ CO} + n \text{ H}^+ + n \text{ e}^- \rightarrow \text{Product} + y \text{ H}_2\text{O}$		CO Reduction, COR
CO + 6 H ⁺ + 6 e ⁻ → CH ₄ (g) + H ₂ O	0.26	Methane
2 CO + 8 H ⁺ + 8 e ⁻ → CH ₃ CH ₂ OH _(aq) + H ₂ O	0.19	Ethanol, EtOH
2 CO + 8 H ⁺ + 8 e ⁻ → C ₂ H ₄ (g) + 2 H ₂ O	0.17	Ethylene

We recommend reporting and using potentials on the thermodynamically relevant and pH-independent RHE scale for all calculations of overpotential and energetic efficiency. For more discussion of thermodynamics and equilibrium potentials, please see Section 1 of the SI.

While the equilibrium potential of CO₂ reduction to hydrocarbons, aldehydes, and alcohols is slightly positive of RHE, their direct electrochemical production still requires significant energy input, as the minimum possible potential to drive the overall reaction (*i.e.*, the difference between the CO₂R equilibrium potential and the equilibrium potential of OER) is larger than 1 V. Furthermore, both the OER and CO₂R currently require large overpotentials, meaning that a CO₂R device will run at a larger cell potential than this thermodynamic potential. Nonetheless, the thermodynamic cell potential indicates the minimum energy requirement for a given product, and thus, given a cost of energy, provides a means to estimate the economic viability of a product. More thorough techno-economic analyses have also been performed, which include capital and operational costs and assumptions about the overpotential and Faradaic efficiency of the desired CO₂ reduction reaction.^{67,69,70,72}

Figure 2 shows a simple mapping of the economics and energetics of possible CO₂ reduction products. The approximate market price of selected possible CO₂ reduction products are plotted against the minimum energy needed for their production by CO₂R balanced with OER. The marker size indicates the (logarithmic) size of the global market, which spans more than four orders of magnitude. All economic quantities are normalized to mass of carbon. The dashed and dotted lines indicate the minimum cost of production given a captured CO₂ price of \$200/tC and an electricity price of \$50/MWh, or \$20/MWh, respectively. \$200/tC is a representative price for carbon captured from a power plant.⁴⁰ \$50/MWh is representative of recent solar installations.²⁹ Current record lows for solar installation are around \$20/MWh, which will likely become more common in the future. Products above the line for a given CO₂ capture cost and electricity cost may be economically feasible depending on capital and other costs, which are not considered here, but are in other analyses. Products below the line are not economically feasible. Direct air capture is estimated to cost \$2000/tC with current technologies,⁴⁰ which would push the lines up above nearly all products, though this will likely come down in the future. Taxes on carbon emissions push the effective price of captured CO₂ down, since capturing CO₂ avoids the tax. The raw data, sources, and calculations are given in Section 2 of the SI. For a more full picture we refer the reader to techno-economic analyses of CO₂ reduction in the literature.^{67,69,70,72}

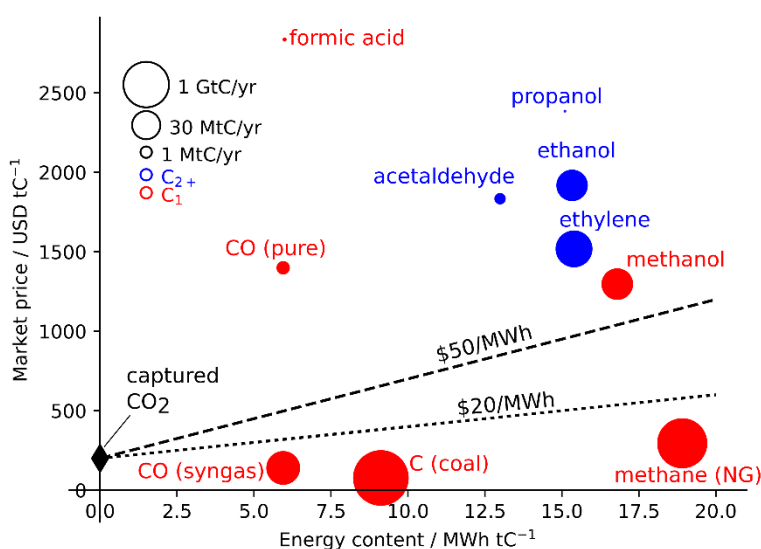


Figure 2: Market price of select CO₂ recycling products as a function of energy content. Lines represent minimum energy and CO₂ costs. Capital costs are not considered.

Despite its simplicity, **Figure 2** captures a widely shared conclusion.^{28,40,69,70,73,74} CO₂ reduction to specialty chemicals such as formic acid (0.2 MtC/yr⁷⁵) and propanol (0.1 MtC/yr⁷⁰) give a better chance of near-term economic feasibility, whereas making an impact on the GtC/year scale relevant for global climate change will likely require renewable production of fuels competitive with the likes of coal (4 GtC/yr²²) and natural gas (1.4 GtC/yr⁷⁶). This is not feasible in the near term, as coal and natural gas are cheaper than the minimum energy required to synthesize them from CO₂ even at \$20/MWh.

Ethylene (120 MtC/yr⁷⁷) and ethanol (40 MtC/yr⁷⁰) represent promising compromises between profitable niche market and impactful mass market for CO₂ reduction. Ethylene is produced at large scale as a precursor for plastics and ethylene glycol in a highly energy-demanding and unselective process involving repeated cycles of steam cracking at 750-950 °C followed by quenching, distillation, and recompression.^{78,79} At an electricity price of \$50 USD/MWh, it is worth about twice as much as the minimum energy input, with a global market about 100 times larger than the specialty chemicals. Ethanol is a fuel with high volumetric energy density that can be substituted for fossil fuels in the transport industry with minimal modifications, and thus represents a market with high growth potential.⁸⁰ Ethanol is produced primarily as a bio-fuel today, and is sold for a price much higher than

the minimum energy required for its production by CO₂R at \$50/MWh. Ethylene and ethanol are both major products in CO₂ and CO electroreduction on copper, as described below.

1.2.2 Copper as a Unique Electrocatalyst

Studies of electrochemical CO₂ reduction date back to at least the 1950's.⁸¹ The first study to quantify both gaseous and liquid products, and thus account for 100% of Faradaic efficiency, was reported by Yoshio Hori and coworkers in 1985.⁸² In this study, constant-current electrolysis of CO₂-saturated 0.5 M KHCO₃ at 5 mA cm⁻² (geometric) was performed for up to an hour as a batch experiment on a number of polycrystalline metal electrodes. This and subsequent studies utilizing basically the same methods⁸³⁻⁸⁶ led to a classification of metal electrodes into four groups:¹ Pb, Hg, Tl, In, Sn, Cd, and Bi produce primarily formate (HCOO⁻); Au, Ag, Zn, Pd, and Ga produce primarily carbon monoxide (CO); Ni, Fe, Pt, and Ti reduce very little CO₂ and instead almost exclusively reduce water to H₂; and Cu stands out in uniquely producing a number of hydrocarbons, aldehydes, and alcohols. Cu is thus the only pure metal that reduces CO₂ to products requiring more than two electrons transfers (collectively referred to as “further reduced products” or “>2e⁻ products”) with substantial Faradaic efficiencies. These results are summarized in **Table 3**, adapted from Hori’s 2008 review of CO₂ reduction on metal electrodes.¹

Table 3: Faradaic efficiencies of CO₂ reduction products on metal electrodes in CO₂-saturated 0.1 M K₂CO₃ (pH=6.8). The potential has been converted from the reported SHE potential to the RHE scale by adding RT/Fln(10)pH = 0.40 V. Adapted with permission from Hori.¹ Copyright © 2008, Springer Science Business Media, LLC.

Metal	<i>E</i> [V vs. RHE]	<i>J_{geo}</i> [mA/cm ²]	CH ₄ [%]	C ₂ H ₄ [%]	EtOH [%]	PrOH [%]	CO [%]	HCOO ⁻ [%]	H ₂ [%]	Total [%]
Pb	-1.23	-5.0	0	0	0	0	0	97.4	5.0	102.4
Hg	-1.11	-0.5	0	0	0	0	0	99.5	0	99.5
Tl	-1.20	-5.0	0	0	0	0	0	95.1	6.2	101.3
In	-1.15	-5.0	0	0	0	0	2.1	94.9	3.3	100.3
Sn	-1.08	-5.0	0	0	0	0	7.1	88.4	4.6	100.1
Cd	-1.23	-5.0	1.3	0	0	0	13.9	78.4	9.4	103.0
Au	-0.64	-5.0	0	0	0	0	87.1	0.7	10.2	98.0
Ag	-0.97	-5.0	0	0	0	0	81.5	0.6	12.4	94.6
Zn	-1.14	-5.0	0	0	0	0	79.4	6.1	9.9	95.4
Pd	-0.8	-5.0	2.9	0	0	0	28.3	2.8	26.2	60.2
Ga	-0.84	-5.0	0	0	0	0	23.2	0	79.0	102.0

Cu	-1.04	-5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5
Ni	-1.08	-5.0	1.8	0.1	0	0	0	1.4	88.9	92.4
Fe	-0.51	-5.0	0	0	0	0	0	0	94.8	94.8
Pt	-0.67	-5.0	0	0	0	0	0	0.1	95.7	95.8
Ti	-1.20	-5.0	0	0	0	0	tr.	0	99.7	99.7

Note that in all cases, a significant overpotential is required to reach the specified current density, usually -5 mA/cm^2 . The largest overpotentials are required by the formate-producing metals, which also typically show very high CO_2R Faradaic efficiencies (for example, 97% of -5 mA/cm^2 for Pb at -1.23 V vs. RHE , an overpotential of 1.1 V) due to very low HER activity. The smallest overpotential for CO_2R is achieved by Au, which produces CO with high Faradaic efficiency, 87% of -5 mA/cm^2 at -0.7 V vs. RHE , an overpotential of 0.6 V . Copper uniquely produces a variety of hydrocarbon and oxygenated products at an intermediate potential -1.04 V vs. RHE (*e.g.*, an overpotential of 0.9 V for CO_2R to CO and an overpotential of 1.2 V for CO_2R to methane). Note also that these results, by measuring CO_2 reduction selectivity for each electrode at only one current density, effectively provide only a snapshot, as CO_2 reduction selectivity can change with conditions and electrode potential.

The splitting of the metals into these four groups based on their selectivity has been explained as the result of their binding energy to key CO_2R and HER intermediates, including $^*\text{H}$, $^*\text{OCHO}$ (bound to the surface through O), $^*\text{COOH}$ (bound to the surface through C), and $^*\text{CO}$.⁸⁷ The unique ability of Cu to reduce CO_2 to $>2e^-$ products may be due to the fact that it is the only metal that has a negative adsorption energy for $^*\text{CO}$ but a positive adsorption energy for $^*\text{H}$, as shown in **Figure 3**.

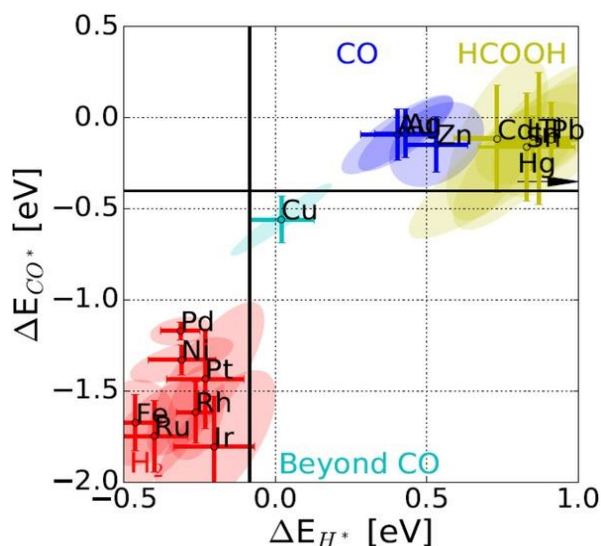


Figure 3: CO₂ reduction metal classification. Reproduced with permission from Bagger *et al.*⁸⁷ Copyright © 2017, John Wiley and Sons.

After the above-mentioned constant-current electrolysis experiments to compare different metal electrodes, Hori and coworkers also performed constant-potential electrolysis experiments on Cu in CO₂-saturated 0.1 M KHCO₃ (pH=6.8), the most common electrolyte for CO₂ reduction studies, to characterize the CO₂R product distribution as a function of potential.⁸⁶ The results, shown in **Figure 4** (hollow markers) span a potential range of -0.8 to -1.45 V *vs.* NHE, or approximately -0.4 to -1.05 V *vs.* RHE. In order of least cathodic to most cathodic onset potential (which loosely refers to the potential closest to the equilibrium potential at which a product is produced in detectable quantities), the major CO₂ reduction products are CO, HCOO⁻, C₂H₄, and CH₄. CO and HCOO⁻ pass through potentials of maximum Faradaic efficiency, and the Faradaic efficiency towards C₂H₄ reaches a plateau by about -1.0 V *vs.* RHE. Similar conclusions were reached years later by Kuhl *et al.*,⁶⁶ electrolysis experiments were performed at potentials between -0.6 and -1.2 V *vs.* RHE and, using more sensitive product detection techniques for liquid products, a total of 16 products were observed. These results are co-plotted with Hori's in **Figure 4** (filled markers).

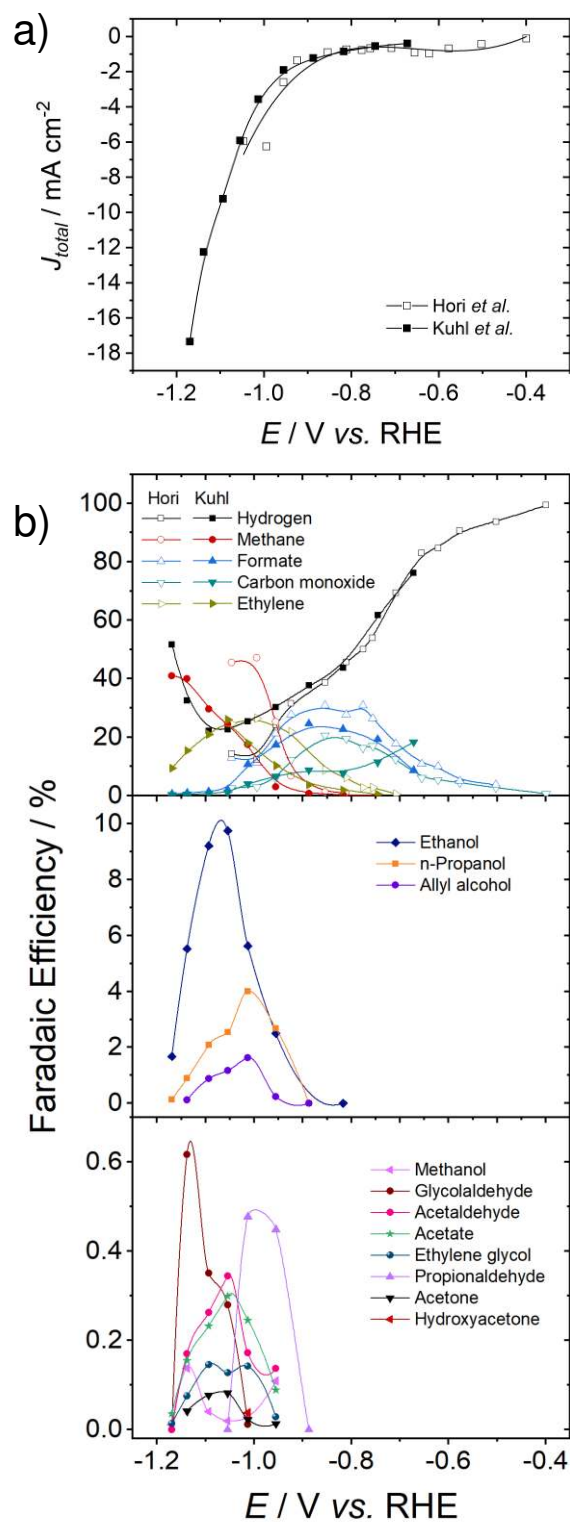


Figure 4: CO₂R activity and selectivity on polycrystalline copper in CO₂-saturated 0.1 M KHCO₃ (pH=6.8). **a)** total current density and **b)** product Faradaic efficiencies, data obtained from Hori *et al.*⁸⁶ (hollow) and Kuhl *et al.*⁶⁶ (filled).

The ability to reduce CO₂ to valuable hydrocarbons, aldehydes, and alcohols is of great interest; as a result, there has been much work done in the field to better understand the reactivity of Cu and how it can be tuned to achieve greater selectivity, stability, and efficiency. Thus, the remainder of this work will focus exclusively on Cu and Cu-based electrocatalysts. In the sections that follow, we will discuss experimental probes used to identify CO₂R reaction mechanisms on Cu and the complementary theoretical methods & descriptions of CO₂R. We will then discuss two materials classes that have been studied in attempts to alter the reactivity of planar polycrystalline Cu (nanostructured Cu and bimetallics with Cu). Finally, we will provide some overall perspectives and an outlook for the future of CO₂R.

2. Considerations for Conducting & Comparing Electrochemical CO₂

Reduction Experiments

Before diving into the results in subsequent sections, we would like to set the stage by discussing some of the difficulties encountered when trying to reliably compare the electrocatalytic behavior of Cu between different electrochemical cells and conditions. For more detailed discussions of these challenges in an objective evaluation of CO₂R performance, we direct the reader to recent perspective articles, which also provide recommendations to help standardize methods for measuring and reporting CO₂R data.^{88,89}

2.1 Reporting Data

First we would briefly like to discuss the metrics by which electrocatalytic activity and selectivity are reported. The selectivity is most often described in terms of *Faradaic efficiency*, which is the portion of the electrical current going to a specific product in steady-state electrolysis. The activity for CO₂R to a specific product is described in terms of the *overpotential*, which is the absolute difference between the actual potential needed to make a product and the thermodynamic potential, or in terms of the *partial current density* at a given potential, which is the total current times the Faradaic efficiency. A more active catalyst is one that achieves a given partial current density at a lower overpotential, and/or

provides a larger partial current density at a given overpotential. A major goal of applied electrocatalysis research is the development of electrode materials and conditions that are selective and active (as well as cheap and stable) for production of desired products. However, understanding the fundamentals of electrocatalysis on simple materials and model systems facilitates the design of better electrodes,⁵⁸ and the tradeoff between practical application and fundamental insight is important to keep in mind when comparing different works in the field.

An essential consideration is how the measured activity is normalized. The geometric area of the electrode is most commonly used to report the current density. While useful for assessing the overall electrode performance, this metric is inherently dependent on the catalyst loading or surface area. Thus, it is also important to consider the current normalized by the electrochemically active surface area (ECSA) of the electrode. This facilitates activity comparisons between catalysts with different roughness factors (RF, defined here as the ratio of ECSA/geometric electrode area), allowing one to determine if higher catalytic activity results from a higher average turnover frequency or simply from an increased number of active sites. There exist a variety of methods in electrocatalysis for determining the ECSA based on capacitance, under-potential deposition, CO stripping, and redox features that can be employed depending on the surface chemistry and morphology, and the best method varies based on the material studied. So far, only capacitance has found wide use for estimating the ECSA of nanostructured polycrystalline copper electrodes.^{90–96} We emphasize that on any non-planar surface, the measurement of the ECSA is at best an approximation; consequently, we recommend that researchers take the limitations of each method of determining the ECSA into account when analyzing their data. Furthermore, we would also like to highlight the need for all future work, particularly on nanostructured electrodes, to report the ECSA whenever possible. It is only possible to evaluate whether a novel catalyst represents an improvement in intrinsic activity compared to state-of-the-art materials if the ECSA-normalized activity can be compared with the literature. As will be shown in Subsection 6.2.4 and Section 7.4, much of the suggested activity improvements in the field can attributed to increased surface area.

2.2 Intrinsic Kinetics vs. Mass Transport Effects

As a consequence of the HER and CO₂R, which deplete protons or (equivalently) produce hydroxide ions, a pH gradient can develop at the electrode surface. This high local pH has several competing effects on these reactions due to a complicated interplay between mass transport, buffer equilibria, and pH, which will be discussed in more detail in Subsection 3.3.1. Notably, in the CO₂/bicarbonate system, CO₂ is both a reactant and a buffer, which means that changes in pH near the cathode surface can cause the concentration of dissolved CO₂ to deviate from the concentration in the bulk electrolyte. For planar polycrystalline Cu, it was found that the reported activity at potentials more cathodic than -1 V vs. RHE is strongly influenced by concentration polarization and thus does not represent its true intrinsic activity under bulk pH 6.8 conditions.⁹⁷ However, this cannot be used as a universal rule of thumb, as the hydrodynamics of the electrochemical cell and the morphology of the catalyst itself can both impact the extent of concentration polarization at a given potential.

Ultimately, since both the HER and CO₂R produce one equivalent of OH⁻ for each e⁻ transfer (with the exception of the organic anions formate and acetate, for which one less OH⁻ is released than electron transferred), changes in interfacial concentrations are primarily a function of the electrolyte and the total geometric current density,. This means that nanostructured catalysts with high surface areas will be more susceptible to concentration polarization at lower overpotentials due to the increased activity on a geometric area basis and increased transport requirements within a porous catalyst compared to a planar electrode.^{98,99} Therefore, caution must be taken when comparing CO₂R performance between catalysts with very different roughness factors since they will reach mass transport limitations at different rates.

In general, it is critical to ensure sufficient supply of CO₂ to the electrode surface. In aqueous systems, this is accomplished by diffusion of CO₂ through the electrolyte, so it is important that the electrochemical cell is well-mixed in order to maximize the potential window where the reaction is governed by intrinsic reaction kinetics. As one would expect for a diffusion-limited process, it has been shown that the maximum *rate* of CO₂R increases with increased mixing due to a decrease in the boundary layer thickness.^{100–103} Thus, the hydrodynamics of an electrochemical cell will also have a

direct effect on the local pH change at the electrode surface. We therefore recommend that researchers quantify the boundary layer thickness, for example, by measuring the diffusion-limited current density for a facile, outer sphere redox reaction such as ferricyanide reduction.⁸⁸ This will allow for better comparisons between different electrochemical cells and mass transport conditions. Still, as described further in Subsection 3.3.1, correcting for mass transport effects in aqueous systems is extremely difficult. As a result, we strongly recommend that conclusions about intrinsic activity and selectivity only be drawn from data that is not impacted by significant concentration polarization so as not to convolute effects of the catalyst properties and the effects of mass transport.

2.3 Deactivation of Cu Electrodes

It has been demonstrated that the activity and selectivity of polycrystalline and single crystalline Cu electrodes towards CO₂R and COR decays over time, although the details vary.^{104–118} The changes in activity can be tentatively attributed to (i) poisoning by impurities from the experimental setup, (ii) poisoning of the surface with reaction intermediates, and/or (iii) restructuring of the surface under reaction conditions. The latter will be discussed in Subsection 3.1.3, as it has been observed with *in-situ/operando* methods that the Cu surface structure is dynamic and can reconstruct under reaction conditions. More often, the deactivation is attributed either to deposition of metal contaminants from the electrolyte,^{112,114} CO₂ stream,¹¹³ glassware,¹¹⁵ or counter electrode,¹¹⁹ including Fe,^{112,113} Zn,^{112,114} Pb,¹¹⁴ Si,¹¹⁵ and Pt,¹¹⁹ or to poisoning or coking of the surface by (decomposition of) reaction intermediates.^{104–111,118} Authors have recommended using the highest-purity reagents,^{112,113} pre-electrolyzing the electrolyte solution,¹¹² and/or removing impurities from the electrolyte with a bed of chelating agent before use¹¹⁴ to minimize the impact of contaminants on the reaction. Additionally, in light of the observation that Pt from the counter electrode can deposit on the working electrode despite separation by an anion exchange membrane, the use of alternate counter electrodes has also been suggested.^{88,119} Deactivation does not seem to play as much of a role in high surface area electrodes (this has mechanistic implications that will be discussed in Chapter 5).^{88,110,115}

Finally, it is worth mentioning another technique that has been used to prevent deactivation and/or restore activity for CO₂R on Cu, namely, anodic pulses or sweeps.^{105,109,111,118,120} Pulsed electrolysis may allow for anodic stripping of poisoning species from the electrode surface.¹¹¹ Anodic pulses or sweeps will also likely cause roughening of the electrode and/or oxidation of the Cu surface.^{109,118,120,121} Gupta *et al.* modeled the effect of pulsed electroreduction and showed that pulsing causes corresponding swings in local pH and CO₂ concentrations.¹⁰⁰ While we cannot say with certainty which of these factors are responsible, it is clear that pulsing or sweeping to anodic potentials has a beneficial impact on maintaining and/or restoring CO₂R activity on Cu. There have also been several other interesting observations noted when using potential pulsing/sweeping techniques, such as the formation of methanol¹²² and increased selectivity for the production of C₂₊ compounds.^{101,120,123} These results have been attributed to transient changes in the local chemical conditions such as an increased coverage of *OH and an accumulation of CO near the Cu surface, respectively. On the other hand, studies using applied voltage pulses in the millisecond time regime demonstrated that the selectivity on polycrystalline Cu could be shifted entirely to syngas (H₂ and CO), with the ratio of these two products changing with the length of the pulses,¹²¹ or to strongly favor CO or CH₄ production.¹²⁴ Since these pulsed-bias methods have yielded increased selectivities for desirable products in addition to helping prevent deactivation, further work should be done to better understand the mechanisms at play and how they can best be utilized to enhance CO₂R catalysis.

2.4 Deconvolution of Various Effects in Complex Catalysts

In addition to the deactivation mechanisms just discussed, there are a number of other factors that can lead to discrepancies in the catalytic performance of Cu between electrochemical systems. For example, as we will discuss in Section 3.3, the choice of electrolyte anions, cations, and pH can have a significant influence on the catalyst performance, so ideally, direct comparisons should only be made between catalysts tested in the same electrolytes. Ultimately, the entire electrochemical system (including catalyst, electrolyte composition & concentration, electrochemical cell geometry & hydrodynamics, membrane composition, and operating conditions) needs to be considered in order to

determine if the measured activity and selectivity can be confidently attributed to the properties of the catalyst itself. To ensure that experimental conditions are satisfactory, researchers should benchmark their electrochemical set-up by making sure that literature results using a standard electrode material, such as planar polycrystalline Cu, can be reproduced (within the variation typical of the field, as indicated by **Figure 4**) If this is not the case, any results obtained from more advanced materials are not meaningful, as other factors could be impacting the catalysis.

As will be discussed further in Chapters 6 and 7, different preparation methods can also yield very different CO₂R performance for seemingly similar catalysts. Unfortunately, many advanced catalyst designs such as nanostructured and/or bimetallic electrodes are ill-defined, which can make it extremely challenging to deconvolute the influence of different morphological factors that can cause changes in behavior (such as surface faceting, composition, oxidation state, strain, grain boundaries, porosity, etc.). Complex catalysts should preferably be characterized to the greatest extent possible. In general, however, planar and/or well-defined electrodes are best for systematic studies that seek to draw fundamental relationships between activity/selectivity and structure/composition of catalysts. Furthermore, detailed studies as a function of voltage are needed to properly identify when novel catalysts are limited by their intrinsic kinetics rather than a convolution of kinetic and mass transport effects; only reporting data at one potential gives an incomplete picture of the catalyst behavior and can complicate comparisons between different catalysts and/or electrochemical systems.

Another key challenge in this area is the disconnect between *ex-situ* characterization and how catalysts function *in-situ*. This is especially challenging for a highly mobile and readily oxidized material such as Cu. We caution against drawing conclusions about the catalyst under reaction conditions using *ex-situ* measurements alone, since the electrolyte and negative polarization of the cathode can have a significant influence on the catalyst properties. We also urge the continued development of *in-situ/operando* spectroscopic techniques in order to elucidate the true chemical state and structure of active sites during electrochemical CO₂R. Not only will this aid in the search for more active and selective catalysts, but this can also provide more useful insights into the reaction mechanisms occurring on the surface on an atomic-scale level.

3. Experimental Probes of CO₂ Reduction Mechanisms

In Section 1.2 we discussed how a large number of $>2e^-$ products are formed during CO₂R on polycrystalline Cu electrodes. Steering selectivity towards certain products instead of others is therefore an important challenge, and could potentially be done by stabilizing/destabilizing key intermediates, making the pathway of the desired product(s) energetically more favorable. Thus, comprehensive mechanistic understanding of CO₂R is crucial in order to design more selective catalysts. In this chapter, various experimental studies aiming to provide mechanistic insight about CO₂R on Cu electrodes are presented. This includes measurements on single crystals, further reduction of possible intermediates, and measurements probing the impact of the electrolyte and electrochemical conditions. The key findings will furthermore be the basis of the theoretical descriptions of the processes occurring on Cu surfaces, which will be discussed in detail in Chapter 4. Then, Chapter 5 will bring together the key conclusions from these experimental and theoretical studies and present our current understanding of the complex reaction networks for electrochemical CO₂R on Cu.

We would first like to acknowledge a growing area of research that underpins much of the gains in mechanistic understanding: *in-situ/operando* spectroscopies. Development of spectroanalytic techniques, such as X-ray absorption spectroscopy (XAS),^{125–128} Raman spectroscopy^{96,129–137} and various forms of infrared (IR) spectroscopy,^{119,134,137–150} has become increasingly important for discerning the catalyst surface structure, composition, and oxidation state under *in-situ/operando* conditions, as well for detecting the presence of adsorbed intermediates. Therefore, we will highlight relevant studies where they have contributed to mechanistic understanding throughout the different sections of this work.

3.1 The Influence of Surface Facet on CO₂ and CO Reduction

It is complicated, if not impossible, to derive unambiguously which structural elements present on a polycrystalline catalyst surface are contributing to the observed catalytic activity, since the measured catalytic activity is always a sum of activities resulting from different structures. In a simplified picture, a catalyst surface can consist of planar areas with single crystal orientations and various step and kink sites with low coordination. Further, complex atomic structures could be present at the interface between different grains that are typically observed in polycrystalline materials and/or nanostructured surfaces. Cu single crystal electrodes with preferential orientation are possible model catalysts to investigate the first two of the mentioned structural properties. This includes planar surfaces, such as Cu(111), Cu(100) and Cu(110), as well as higher-index surfaces which can be described as a low-index surface with a certain density of step sites. Single crystal electrodes are ideal systems to draw comparisons with theoretical calculations because methods such as density functional theory (DFT) only probe local phenomena, which should be equally distributed on these atomically flat catalysts. Further, single crystals are also quite useful for studying the influence of other CO₂R rate-determining factors such as electrolyte pH, cations and anions since they provide a well-defined surface structure. Note, however, that single crystals themselves are not viable catalysts for practical applications, due to their low geometric surface area, and the resulting low geometric current densities. Therefore, several groups have synthesized nanostructured materials with preferential faceting and high dispersion, which will be discussed further in Chapter 6. In this section, we describe experimental findings obtained on single-crystal model systems, describe surface reconstructions on Cu, discuss the mechanistic interpretations, and suggest focus areas for future studies.

3.1.1 Influence of Various Cu(hkl) Surfaces on Product Distribution

The electrochemical reduction of CO₂ on Cu single crystals has been studied by a variety of methods, including voltammetry (linear potential sweeps),^{151–156} chronoamperometry (constant potential)^{155,157,158} and chronopotentiometry (constant current).^{151–154,159} The choice of electrochemical technique depends on the method employed to characterize liquid and gaseous products. For instance,

in-situ techniques that can monitor the evolution of products in real-time, such as differential electrochemical mass spectrometry (DEMS) can be coupled with cyclic voltammetry (CV) or other scanning techniques. However, *ex-situ* bulk product analysis, such as chromatography techniques and NMR spectroscopy, need to be coupled with chronoamperometry and/or chronopotentiometry. The choice of technique also depends on whether quantitative information, such as the concentrations of products formed, is of interest, or if it is sufficient to identify trends between electrodes.

Early chronopotentiometric measurements by Frese indicated that among the three low-index Cu single crystal facets, *i.e.*, Cu(111), Cu(110) and Cu(100), the Cu(111) surface yields the highest CH₄ rate and Cu(100) the lowest.¹⁵⁹ Further measurements by Hori *et al.* indicated that Cu(100) surfaces primarily form C₂H₄ and a somewhat smaller amount of CH₄, while Cu(110) and Cu(111) surfaces preferentially form CH₄ with very small amounts of C₂H₄.¹⁵¹ This was later confirmed in follow-up measurements by Hori *et al.*,^{152–154} as well as other research groups.^{155,156} In a study showing the product distribution over a range of potentials, C₂H₄ formation set in at a similar or lower overpotential than CH₄ formation for all investigated single crystal electrodes.¹⁵⁶ At higher overpotentials, the formation of CH₄ becomes the dominant process.¹⁵⁶ This is similar to the trend observed for polycrystalline Cu, as shown in **Figure 4** of Subsection 1.2.2, for which CH₄ formation reaches maximum selectivity at around -1.1 V to -1.2 V *vs.* RHE, where CO₂R activity starts becoming mass transport limited on planar electrodes.^{66,97,156}

Liquid, oxygenated compounds are interesting products as well, due to their aforementioned high energy density and moderate to high value. In the previously described studies by Hori *et al.*, several liquid compounds were detected, of which alcohols and carboxylates were the most significant, as shown in **Table 4**.^{152–154} Around -1.0 V *vs.* RHE, Cu(100) surfaces preferentially formed alcohols compared to formic acid, while the opposite could be observed for Cu(111). Cu(110) surfaces yielded similar selectivity towards alcohols and carboxylates. Huang *et al.* recently showed a similar trend as Hori *et al.* around -1.0 V *vs.* RHE, and less cathodic potentials, the main liquid product observed was formate.¹⁵⁶ At potentials cathodic of -1.0 V *vs.* RHE, where the formation of C₂H₄ reached a maximum on all single crystal surfaces, Huang *et al.* observed formation of ethanol with significant Faradaic

efficiency. A similar trend was observed on polycrystalline Cu, suggesting that the two products are formed through a partially shared pathway.

Table 4: Product distribution in CO₂ reduction at a series of copper single-crystal electrodes, Cu(S)-[n(100)x(111)] and Cu(S)-[n(100)x(110)]. The measurements were performed by chronopotentiometry at 5 mA cm⁻² in 0.1 M KHCO₃. The potentials *vs.* RHE were calculated from the potentials *vs.* SHE using the Nernst equation, assuming a pH of 6.8. Adapted with permission from Hori.¹ Copyright © 2008, Springer Science Business Media, LLC. The data for Cu(110) is from Hori, 1995.¹⁵¹

Crystal orientation	Potential / V vs. SHE	Potential / V vs. RHE	Faradaic efficiency / %							C ₂ H ₄ /CH ₄
			CH ₄	C ₂ H ₄	CO	Alc.	Ald.	HCOOH	H ₂	
Cu(S)-[n(100)×(111)]										
(100)	-1.40	-1.00	30.4	40.4	0.9	12.0	4.4	3.0	6.8	1.3
(11 1 1)	-1.37	-0.97	8.9	50.2	1.8	17.7	4.4	3.2	8.8	5.8
(711)	-1.34	-0.94	5.0	50.0	1.1	14.2	6.4	4.6	15.6	10.0
(311)	-1.37	-0.97	36.0	23.8	2.6	5.2	3.4	14.0	13.3	0.7
(111)	-1.55	-1.15	46.3	8.3	6.4	3.3	2.7	11.5	16.3	0.2
Cu(S)-[n(100)×(110)]										
(810)	-1.38	-0.98	6.4	45.1	1.4	28.8	2.0	1.5	8.7	7.0
(610)	-1.37	-0.97	7.6	44.7	0.9	29.3	2.7	1.4	9.0	5.9
(510)	-1.38	-0.98	8.1	42.3	2.1	29.5	5.6	2.9	10.5	5.2
(210)	-1.52	-1.12	64.0	13.4	2.2	7.3	1.5	5.5	7.0	0.2
(110)	-1.55	-1.15	49.5	15.1	0	7.4	3.1	6.6	18.8	0.3

In order to elucidate the influence of undercoordinated sites on the product distribution, Hori *et al.* also performed a series of CO₂ reduction studies on stepped Cu single crystal surfaces.^{152–154} The distribution of gaseous and liquid products is summarized in **Table 4**. The presence of (111) or (110) steps on Cu(100) surfaces led to significantly enhanced Faradaic efficiency toward alcohols. Their data also indicated that a number of stepped surfaces exist that yield higher C₂H₄/CH₄ ratios compared to the Cu(100) surface, which is the most selective low-index crystal facet for the formation of C₂H₄, as described above. In **Figure 5**, the C₂H₄/CH₄ ratio is plotted as a function of crystal orientation, clearly illustrating the notion that steps can further enhance the selectivity to C₂H₄ formation compared to the planar single crystals. Thus, it seems that one approach to improving the selectivity towards C₂H₄ is to engineer Cu electrodes with an increased occurrence of (100) surfaces and optimal occurrence of steps. Indeed, this has been seen in epitaxially-grown copper films with a high degree of preferential surface orientation, where films with a preferentially (751)-oriented surface rich in steps with highly

undercoordinated sites show high selectivity to C_{2+} products and especially oxygenated products.¹⁵⁸

Additional efforts following this direction will be discussed in more detail in Chapter 6.

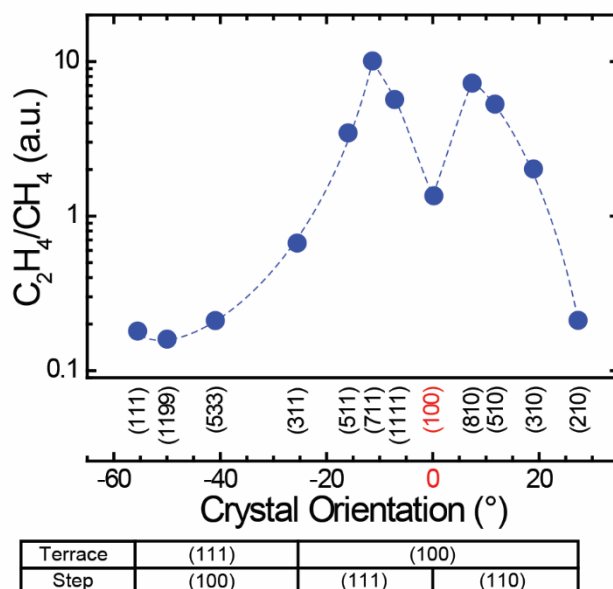


Figure 5: Variation of $\log(C_2H_4/CH_4)$ in terms of the current efficiency and the electrode potential with the angle of the crystal orientation with reference of Cu(100). The data for the figure were obtained from Hori *et al.*¹⁵⁴

As discussed later in Subsections 3.2.1 and 4.2.2, CO has been identified as a key intermediate in the reduction of CO_2 to $>2e^-$ products.^{86,104,160–162} Thus, to obtain further mechanistic insight about the formation of these compounds, COR has been studied on Cu single crystals.^{163–167} None of these studies quantified the various products formed, making it hard to draw conclusions about Faradaic efficiencies and partial current densities. However, studying the onset potentials for the various products can give an indication of the selectivity towards the different compounds in various potential ranges. In DEMS measurements of various single crystals in phosphate buffer at pH 7, Cu(100) exhibited an earlier onset than Cu(111) and Cu(110) for C_2H_4 .¹⁶⁷ Further, Cu(100) facilitated little to no CH_4 formation at the measured potentials, while Cu(111) gave a similar onset for C_2H_4 and CH_4 . Cu(911), which was shown by Hori *et al.* to be particularly selective towards C_2H_4 , behaves similarly to Cu(100) in this study. In order to gain more conclusive insights about COR on various single crystalline surfaces, further systematic investigations with complete product quantification are required, similar to what has been demonstrated by Hori *et al.* for CO_2 reduction.

Based on the discussion above, it is clear that CO₂R measurements on single crystals can yield important information about which surface sites are responsible for the formation of key products. Increasing our understanding of the active surface can aid in the development of highly selective catalyst materials. However, based on the measurements described in the previous paragraphs, it seems clear that more work performing thorough and complete product analysis is necessary before conclusions can be drawn about specific trends. In addition, the reports on non-planar surfaces indicate that engineering of materials to achieve presence of well-defined steps on the surface can be a valuable design principle for improving selectivity toward C₂₊ products such as C₂H₄ and alcohols.

3.1.2 Influence of Various Cu(hkl) Surfaces on Activity

As will be discussed in Chapter 4, theoretical studies predict vastly different *activity* for different crystal facets, rather than just the *selectivity* differences described so far. In order to be able to evaluate CO₂R activity experimentally, thorough, quantitative product analysis is needed. Additionally, the catalyst needs to be studied while under activation control, *i.e.*, not experiencing mass transport limitations, as discussed in detail in Section 2.2. As a result, only a few of the reports mentioned in the previous subsection can be used to draw conclusions about trends in activity. These studies^{154,156,158} do show slight variations in both overall and CO₂R activity depending on orientation, but nothing comparable to the magnitude expected based on computational studies. For example, the study on epitaxially grown Cu thin films reported ~1 order of magnitude higher activity towards C-C coupled products for the highly stepped Cu(751)-oriented surface as compared to the planar Cu(111)-oriented surface.¹⁵⁸ These results are illustrated in **Figure 6**. Note that while these electrodes exhibit preferential orientation, they are not truly single crystalline, meaning that they have a certain occurrence of grain boundaries and other undercoordinated defects on the surface. This could explain why the activity of these and other well-defined surfaces do not show as much difference as predicted by theory. Step sites have been identified as the main contributor to the activity of various catalytic systems. For instance, it has been seen in the field of thermally activated catalysis that blocking step sites can have a drastic impact; experiments where the steps of Ru single crystals (~1% of the surface) were blocked led to a reduction in N₂ dissociation activity by more than 9 orders of magnitude.¹⁶⁸ Similarly, a small

fraction of step sites have also been suggested to dominate the overall electrochemical CO₂/CO reduction activity.¹⁶⁹ Thus, even a small quantity of existing defects or step sites formed *in-situ* (*vide infra*) could be dominating the activity of these otherwise single crystalline electrodes.

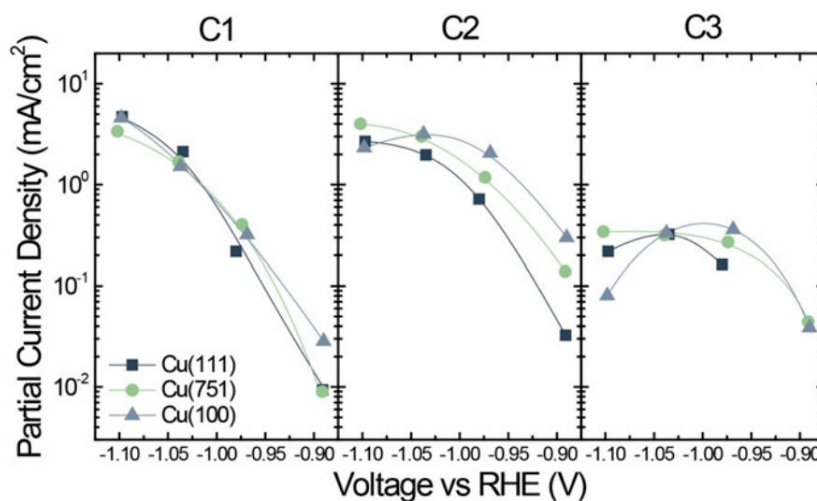


Figure 6: CO₂R on epitaxially grown Cu films oriented in the (111), (751) and (100) directions. The graphs show partial current density toward C₁ (left), C₂ (middle) and C₃ (right) products. Reprinted from Hahn *et al.*¹⁵⁸

3.1.3 Restructuring and Other Challenges Regarding Single Crystal Measurements

As described above, single crystal measurements can be highly useful to study the CO₂R activity and selectivity of various structures. However, one must be cautious because the quality and consistency of single crystal studies are sensitive to a number of factors, discussed herein. Hori *et al.* described in detail how the reproducibility of CO₂R measurements on Cu(110) and Cu(111) single crystals strongly depends on the pre-treatment of the electrodes.¹⁵³ Although the structural properties of the bulk are well-defined, the homogeneity of the surface can vary depending on the pre-treatment. One possible factor could be the formation of oxides during the preparation and transfer to the electrochemical cell. A partially oxidized surface, which is reduced in the actual electrochemical cell, could lead to an irreversible reconstruction of the Cu surface, a phenomenon that for example has been shown in detail for Pt electrodes.^{170,171} This effect has also been intentionally exploited to prepare nanostructured electrodes in a number of studies, as discussed in Subsection 6.2.1. As a result of the oxidation occurring upon exposure to ambient air, Hori and coworkers do not rule out that the final

electrodes might be textured with defect sites, which could have a large influence on the measured electrocatalytic activity of the electrodes, as we just discussed. However, they probed the surface structure only by the use of CV, which can give indicative but not conclusive evidence.

Surface probe techniques, such as scanning tunneling microscopy (STM), can image the surface with excellent resolution to evaluate whether defect sites are present. It is important to keep in mind that only small fractions of the electrode surface are probed with this type of technique, so the resulting image may therefore not provide a representative indication of the whole surface. Nonetheless, STM can give a good impression of the defect density for various types of electrodes. In **Figure 7**, STM images are shown from 4 different preferentially oriented electrodes, spanning 3 preparation procedures and 4 measurement conditions. **Figure 7a** shows an STM image of a Cu(100) single crystal that was prepared by annealing under ultra-high vacuum (UHV) and transferred to the characterization chamber without being exposed to oxygen. The crystal exhibits large terraces and a relatively small amount of defects on the surface. In comparison, *in-situ* STM images of electropolished Cu(111) (**Figure 7b**) and Cu(100) (**Figure 7c**) show significant occurrence of steps and other defects. An example of *in-situ* STM images from an epitaxially grown Cu(100)-oriented film are shown in **Figure 7d**, which also display a significant occurrence of defects since this preparation procedure does not lead to truly single crystalline electrodes.

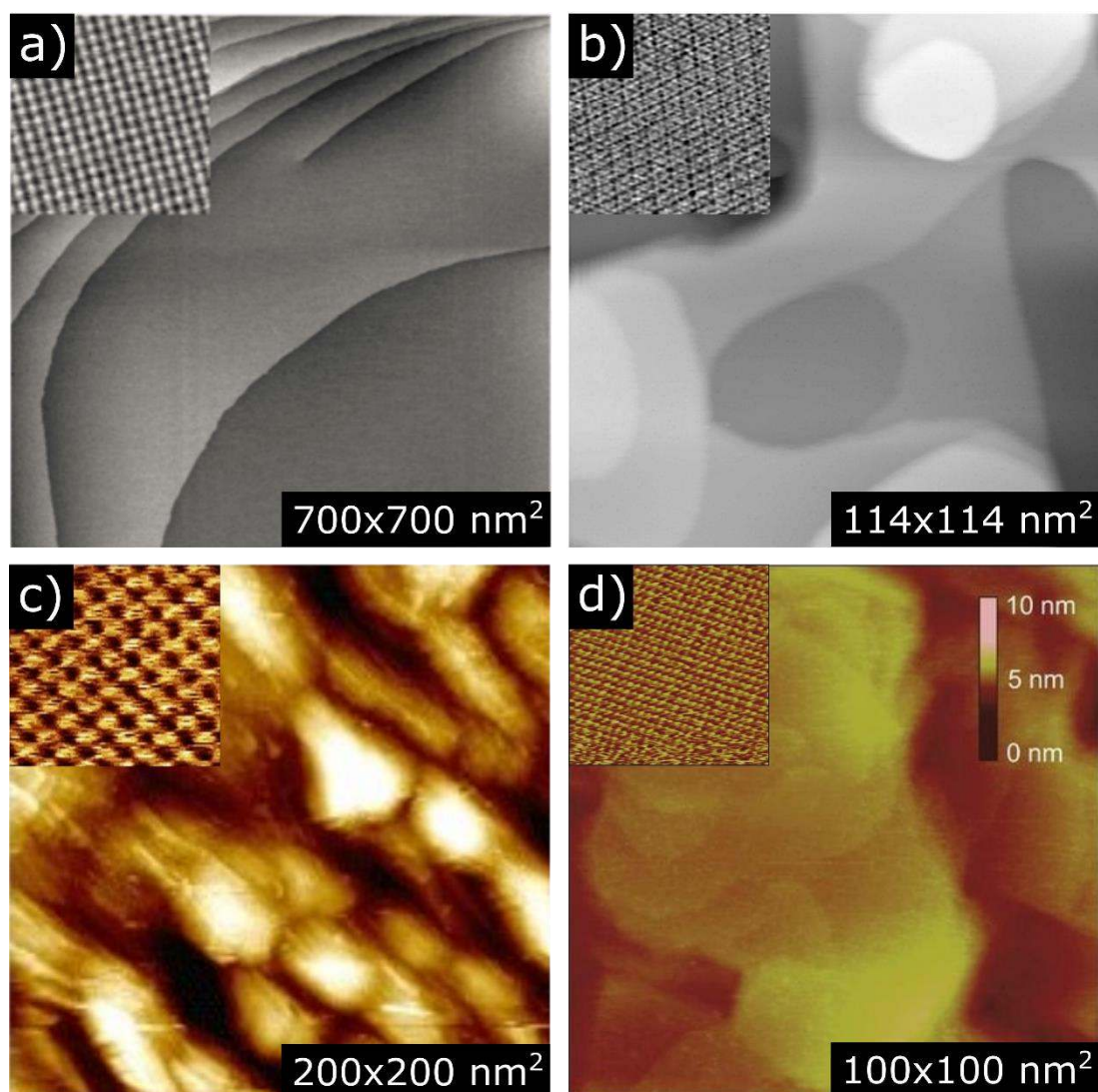


Figure 7: STM images of various oriented surfaces. **(a)** 700 nm x 700 nm STM image of ultra-high vacuum prepared Cu(100) single crystal. Inset: 4 nm x 4 nm image of the same surface. Reproduced with permission from Engstfeld *et al.*¹⁷² Copyright © 2018, John Wiley and Sons. **(b)** 114 nm x 114 nm *in-situ* STM image of electropolished Cu(111) single crystal at -0.6 V (vs. pseudo-reference) in PO₄ buffer. Inset: 9.5 nm x 9.5 nm image of the same surface. Reprinted with permission from Schlaup *et al.*¹⁷³ Copyright © 2012, Elsevier B.V. **(c)** 200 nm x 200 nm *in-situ* STM image of electropolished Cu(100) single crystal at -0.9 V vs. SHE. Inset: 2 nm x 2 nm image of the same surface. Adapted with permission from Kim *et al.*¹⁷⁴ Copyright © 2016, Springer Science Business Media New York. **(d)** 100 nm x 100 nm *in-situ* STM image of epitaxially grown Cu(100) film at -0.24 V vs. RHE in 0.1 M HClO₄. Inset: 5 nm x 5 nm image of the same surface. Reprinted from Hahn *et al.*¹⁵⁸

In addition to the influence of pre-treatment, there is the possibility that Cu surface restructuring under reaction conditions can lead to changes in activity and selectivity. Earlier reports indicated that Cu(111) restructures to a highly textured surface when exposed to even small CO partial pressures in vacuum,¹⁷⁵ and recent experimental spectroscopic¹³⁴ and computational¹⁷⁶ studies have also indicated that the presence of CO increases the density of highly active, undercoordinated step sites on

polycrystalline Cu. Furthermore, restructuring promoted by CO was also observed using *operando* grazing incidence X-ray diffraction (GIXRD) on polycrystalline copper thin films.¹⁷⁷ Thus, since there is typically a significant coverage of CO under CO₂R conditions,¹⁷⁸ it is possible that reconstruction and the formation of step sites on otherwise defect-free single crystalline surfaces during reaction could explain why there are only moderate differences in CO₂R activity on different facets, as mentioned above.

Various studies employing *in-situ* electrochemical scanning tunneling microscopy (ECSTM) have also reported reconstruction of Cu surfaces under applied potentials while not in the presence of CO₂/CO.^{173,174,179–182} For example, it has been demonstrated that at a potential of -0.9 V *vs.* SHE in both argon-purged 0.1 M KOH and 0.1 M KHCO₃, a polycrystalline Cu surface gradually forms Cu(111) facets on a timescale of 30 minutes, and subsequently transform into Cu(100) facets after another 30 minutes.^{179,182} The Cu(110) surface undergoes a similar restructuring compared to the polycrystalline Cu electrodes; the top-most planes of a Cu(110) surface transformed over time into a disordered Cu(110), then into a disordered mixed Cu(110)-Cu(111), and finally into an ordered Cu(110)-Cu(100) plane.¹⁸¹ In contrast, no reconstruction was observed on single crystal Cu(111) or Cu(100) surfaces under the same conditions,¹⁸¹ nor for epitaxially grown Cu(111) and Cu(100) films at -0.24 V *vs.* RHE in 0.1 M HClO₄.¹⁵⁸ While it is somewhat unclear what drives the (in)stability of these different systems, it is likely that it has to do with the comparative adhesions of various surfaces in contact with each other.¹⁸¹ Another possibility could be due to other factors from the local reaction environment (*i.e.*, electrolyte and/or potential-dependent effects). However, more work needs to be done to better understand how and why Cu restructuring occurs under reaction conditions.

Another important point for Cu is that, compared to other monometallic catalyst systems,¹⁷⁰ few thorough benchmarking studies on the electrochemical properties of Cu single crystal surfaces have been reported. Such data could be used to determine the properties of electrodes used for a particular study, which is standard practice for other electrode materials, such as Pt.¹⁸³ For example, CVs of single crystal electrodes recorded in alkaline solutions at potentials where only OH adsorption on the surface occurs (-0.2 V to 0.5 V *vs.* RHE) and no bulk oxide formation is expected, exhibit different redox features for different reports in the literature, which should not be the case for truly single crystal

electrodes.^{156,165,180,184–187} Further, a recent study on the electrochemical properties of polycrystalline Cu and Cu(100) electrodes, including samples prepared under UHV conditions to avoid surface contamination of oxygen, clearly suggests that the features observed in the CV strongly depend on the pre-treatment of the electrodes.¹⁷² This is illustrated in **Figure 8**, where the CV of a Cu electrode prepared under UHV conditions is plotted vs. the CVs obtained for samples exposed to different pre-treatments under laboratory conditions.¹⁷² The authors ascribed the features in the CV between 0.30 V and 0.45 V to different sites than the Cu(100) planes, indicating that all electrodes except for that prepared under UHV conditions contain a significant amount of defect sites on the surface. Other approaches to assess the consistency of Cu electrodes could include comparing key values for the HER, which so far has only been reported in a few studies on polycrystalline Cu electrodes in alkaline^{188–190} or acidic¹⁹¹ solutions, or investigating the distinct features obtained from lead^{191,192} or thallium¹⁹³ underpotential deposition (UPD) on single crystal electrodes.

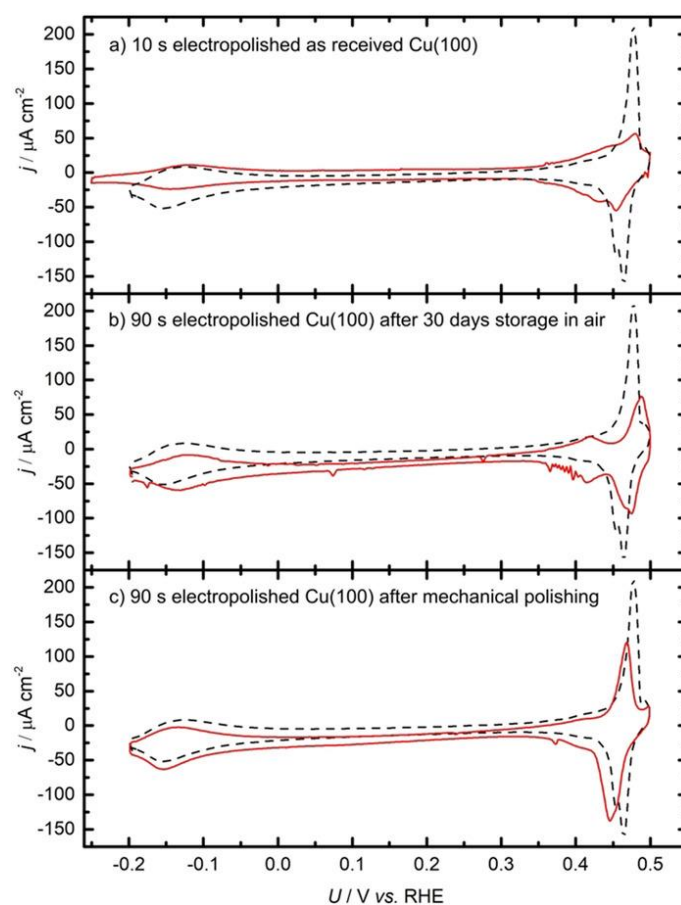


Figure 8: Comparison of the CV recorded on a Cu(100) electrode prepared under UHV conditions (dashed line) with **a)** an electropolished as received Cu(100) electrode from the supplier, **b)** 90 s electropolished Cu(100) electrode after storage in air for 30 days and **c)** an electropolished Cu(100)

electrode after mechanical polishing (0.1 μm Alumina powder for 10 minutes and further 10 minutes with 0.05 μm Alumina powder). All CVs were recorded in 0.1 M KOH and at a scan rate of 50 $\text{mV}\cdot\text{s}^{-1}$.¹ Reprinted with permission from Engstfeld *et al.*¹⁷² Copyright © 2018, John Wiley and Sons.

Better insight about the fundamental electrochemical properties of Cu single crystal electrodes would be valuable in order to better compare results among different research groups within the field of CO_2R . In addition, it would be useful to elucidate the influence of higher overpotentials and different electrolytes and pH ranges. For example, it was shown by CV that polycrystalline Cu electrodes exposed to -0.5 V or -0.6 V vs. RHE in 1 M NaOH at 60 °C for 3 hours that new sites are formed on the surface.¹⁹⁴ Cathodic corrosion, hydrogen embrittlement or hydride formation can also play a crucial role at such potentials.^{195,196} These effects have received little attention in relation to CO_2R as of yet, but could influence activity and stability. Furthermore, such insights could also be highly useful for other processes where the electro-chemical/-catalytic properties of Cu are important, such as nitrate reduction or studies related to the initial oxidation of Cu single crystal electrodes in aqueous environment.^{197–200}

3.2 Reduction of Possible Intermediates

In the previous section, we outlined the facet-dependent activity & selectivity of Cu and saw how tunable the reaction is on the atomic scale. Here we will discuss some of the key intermediate species and how probing their reactivity has helped shed light on CO_2 reduction pathways.

3.2.1 CO as a Crucial Intermediate

Carbon monoxide (CO) and formate (HCOO^-) are the 2e^- products formed from CO_2R , and as discussed in the Subsection 1.2.2, there are classes of metals that yield each of these products with high selectivity. Early experimental work found that the reduction of CO on Cu leads to a similar product distribution as CO_2R on Cu, suggesting that CO is a key reaction intermediate.^{86,104,160–162} Subsequent detailed studies of CO reduction (COR) on Cu have provided further support for this claim,^{115,160,201} in addition to the spectroscopic observation of surface adsorbed CO under CO_2R conditions.^{133–135,145–148} Consequently, several studies proposed that the binding energy of adsorbed CO ($^*\text{CO}$) is a key

descriptor for reduction activity to $>2e^-$ products.^{202–204} Metals that bind CO too strongly will be poisoned by this intermediate, whereas metals that bind CO too weakly will desorb it from the surface before it can react further. Thus, well-aligned with the Sabatier principle,²⁰⁵ the intermediate binding energy for CO on Cu is a key reason for its ability to catalyze CO₂R to products further reduced than CO. In addition, studies have shown that CO adsorption on Cu suppresses the competing hydrogen evolution reaction (HER) due to site blocking effects and/or changes in $*H$ binding energy.^{86,178,202,206} The coverage of CO on Cu is typically very high,¹⁷⁸ at least until there are mass transport limitations (*vide infra*). Thus, CO poisoning of the HER is an important mechanism by which Cu maintains a high Faradaic efficiency for CO₂R in aqueous electrolytes.²⁰⁶

Ever since the determination of CO as a key intermediate in the reduction of CO₂ to hydrocarbons and alcohols, there has been increasing interest in studying COR as a proxy for understanding trends in CO₂R. This has several advantages including fewer reaction steps/intermediates to consider and avoiding the complication of the reactant being part of the buffer (as is the case for CO₂R in bicarbonate solutions). The latter, in turn, allows for a wider range of pH conditions to be examined, in addition to allowing for direct comparison with blank measurements where the electrolyte is purged with an inert gas. Another motivation for better understanding COR catalysis is that this could provide an alternate route for CO₂R that can potentially overcome scaling relations by splitting the reaction into two separate steps: 1) CO₂ reduction to CO, then 2) CO reduction to the desired product(s). Thus, we will discuss insights gained from experimental and computational COR studies where appropriate in the sections that follow, and we also recommend continued development of viable COR catalysts for potential tandem systems.

3.2.2 Reduction of Oxygenated C₁ and C₂ Species

The discovery of at least 16 distinct products formed from CO₂R on Cu highlights the complexity of this reaction.⁶⁶ Besides the dominant hydrocarbons, methane and ethylene, this includes a broad mix of aldehydes, ketones, carboxylic acids, and alcohols, the majority of which are multi-carbon compounds. As a result, probing the reduction activity of small oxygenated species has been

used as a technique to help elucidate mechanistic pathways; here we will briefly describe the key findings from these studies.

Unlike CO, it has been shown that another $2e^-$ reduction product, formate/formic acid, does not typically undergo further reduction on Cu under reductive conditions;⁸⁶ however with very high concentrations, high cathodic bias, and highly acidic or basic electrolytes, trace amounts of methane have been reported.^{104,207} Formaldehyde (CH_2O) reduction has been shown to produce mainly methanol,^{108,113,160} although small amounts of methane have also been reported.^{104,108,113,160,207} Finally, reduction of methanol (or methoxide, which is methanol deprotonated under high pH) has been shown to yield no products.^{104,113,207} These results strongly suggest that formate and methanol are terminal products for electrochemical CO_2R , and intermediate(s) related to formaldehyde (such as adsorbed formyl $^*\text{CHO}$) may be on the pathway to methanol and methane.

The presence of hydroxyl and/or carbonyl moieties in many of the multi-carbon products suggests that the C-C bond is formed early in the reaction, at least before one of the two carbon-oxygen bonds in CO_2 is broken.⁶⁶ Accordingly, it has been suggested that enol-like species may be intermediates to multi-carbon products,⁶⁶ such as an enediol or enediolate.¹¹³ The observation that reduction of ethylene oxide produces ethylene indicates that a strongly adsorbed epoxide in the form of an oxametallacycle is another possible intermediate in ethylene formation.¹¹³ Ethylene glycol and oxalic acid reduction did not lead to any reduction products, suggesting that these are not intermediates in CO_2R .¹¹³ This is curious given that ethylene glycol has been detected as a minor product,⁶⁶ so a recent theoretical study suggested that the reason why this species is not further reduced is due to its OH groups being repelled by the surface, making its re-adsorption endergonic.²⁰⁸ Finally, both glyoxal^{113,209} and glycoaldehyde¹¹³ reduction have been shown to produce acetaldehyde and ethanol but not ethylene. This suggests that these minor products are intermediates on the pathway to acetaldehyde and ethanol.²⁰⁸

It has long been thought that aldehydes are key intermediates to alcohols after Hori and coworkers observed that acetaldehyde and propionaldehyde were easily reduced to ethanol and n-propanol, respectively.¹⁶⁰ Further support for this has been provided by several COR studies that have noted aldehyde production at lower overpotentials than alcohols that decreases with increasing

overpotential where alcohols become dominant,^{115,201} as well as recent demonstrations of direct acetaldehyde reduction to ethanol.^{91,210} Another study employed a DEMS set-up where the catalyst was coated directly onto the pervaporation membrane used to transfer volatile species into the mass spectrometer in order to detect species directly from the electrode-electrolyte interface.¹⁰¹ Through this method, it was observed that acetaldehyde and propionaldehyde are produced in 2-4 times higher abundance than ethanol or propanol compared to sampling from the bulk electrolyte, where they are typically only observed as minor products.¹⁰¹ Thus, the authors suggest that these aldehydes are transiently produced & relatively abundant within the local reaction environment, but are typically reduced further to the corresponding alcohols before diffusing into the bulk electrolyte. Interestingly, it was also found that ethanol production increased at the expense of propionaldehyde at more cathodic potentials, suggesting that ethanol and propionaldehyde may share a common intermediate such as acetaldehyde.¹⁰¹

Finally, it is worth highlighting a recent study that has led to significant new insights on the role of water in the formation of C₂₊ oxygenated products.²¹¹ By carrying out C¹⁶O reduction in H₂¹⁸O electrolyte and quantifying the isotopic composition of the products using gas chromatography–mass spectrometry (GC-MS), Lum *et al.* determined that the majority of ethanol, acetate, and 1-propanol formed were ¹⁸O enriched, meaning that they incorporated oxygen from the solvent water. Allyl alcohol and methanol were not enriched with ¹⁸O, which suggests different mechanisms for their formation. Importantly, water has not previously been considered as a dominant O source in the formation of oxygenated products, so the researchers then investigated how this could be the case using quantum mechanics-based metadynamics calculations. This led to the identification of a new mechanism for (¹⁸O)ethanol formation, which was termed as Grotthuss chain ethynyl concerted hydrolysis (GECH).²¹¹ The mechanistic pathways and intermediate branch points for formation of ethylene, (¹⁸O)ethanol, and (¹⁶O)ethanol were then elucidated; these C₂ reaction networks are shown in purple in **Figure 18**. It is important to keep in mind that Cannizzaro-type disproportionation reactions could also occur in the electrolyte, especially at high pH, converting an aldehyde (acetaldehyde) into the corresponding alcohol (ethanol) and carboxylate (acetate).²¹² Thus, this is another possible mechanism by which ¹⁸O could be

incorporated into the products. Lum *et al.* performed control experiments that indicate this is not the main mechanism by which these products are formed,²¹¹ but researchers should still keep the possibility of these reactions in mind when working under strongly alkaline conditions, especially when a high concentration of aldehydes are formed.

3.3 Electrolyte Effects

The choice of electrolyte can have a huge impact on CO₂R performance. There are a number of factors that have complex relations with the local reaction environment; the composition and concentration of anions & cations can cause changes in the electrostatic interactions, buffer capacity, pH, and availability of proton donors. These changes are not always straightforward to map due to intertwining effects. In this section we will discuss the major variables within the electrolyte (pH, cations, anions) and their impacts on CO₂R catalysis.

3.3.1 pH Effects

Studying the effect of pH on CO₂R comes with several challenges. Given that CO₂ forms bicarbonate and carbonate when it is purged through alkaline solutions, electrolytes for CO₂R are generally limited to neutral and acidic pH conditions. However, by using CO reduction (COR) as a proxy, mechanistic insights about the pathway to further reduced products can be obtained. Pioneering work of this nature by Hori *et al.* first revealed that the selectivity between CH₄ and C₂H₄ is impacted by pH.^{86,160,161} By studying COR on Cu, the production rates for each product could be compared in buffer solutions spanning a bulk pH of 6 to 12.¹⁶⁰ When the measurements of partial current density towards C₂H₄ (or C₂H₅OH) are included on a single Tafel plot on the SHE scale (**Figure 9a**), a straight line emerges. Thus, the rate-determining step on the pathway to C₂₊ products such as C₂H₄ is pH independent on an absolute potential scale (SHE), and thus will shift on the RHE scale to more positive potential (decreasing overpotential) by 59 mV per unit increase in pH. For CH₄, on the other hand, the Tafel plot was widely scattered unless only measurements at the same pH were included, indicating that

the rate-determining step for the C_1 pathway involves proton transfer and is thus dependent on pH. Hori *et al.* explained this pH dependence in terms of the Tafel equation where the partial current for CH_4 is proportional to the proton activity; indeed, by plotting the logarithm of the CH_4 partial current density plus pH (Figure 9b), a straight line emerges. From these plots, transfer coefficients of $\alpha = 0.35$ and $\alpha = 1.33$ were extracted for C_2H_4 and CH_4 , respectively.¹⁶⁰ This led Hori *et al.* to propose that the reaction paths for CH_4 and C_2H_4 formation do not share rate-determining steps and thus have mechanisms that are separated at early stages of CO reduction. Further evidence for this notion was provided in a series of studies on single crystal electrodes by the group of Marc Koper,^{164,166,167} which revealed that there are two possible pathways to C_2H_4 depending on the pH, surface structure and overpotential. These mechanisms will be discussed further in Chapters 4 and 5.

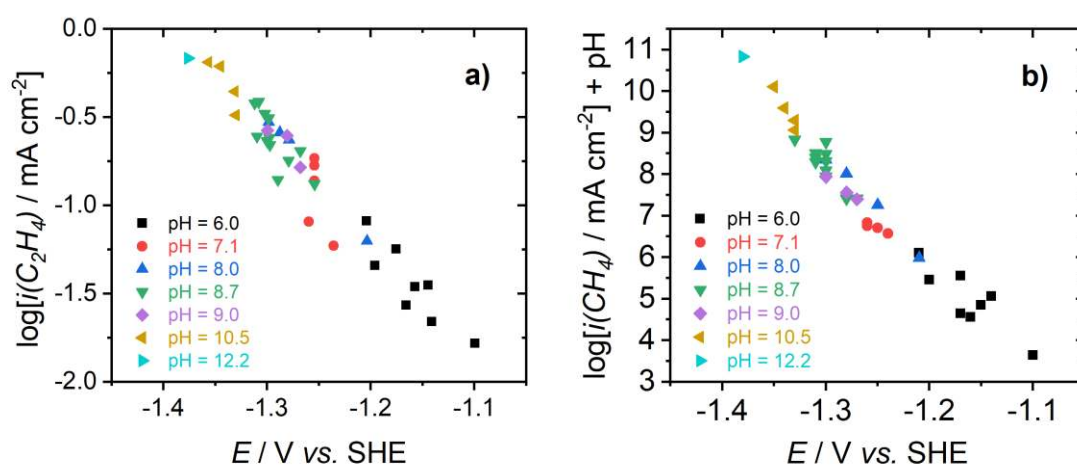


Figure 9: Tafel plots from COR measurements that were made over a pH range of 6 to 12. **a)** plots the logarithm of the partial current density going towards ethylene against applied potential on the SHE scale; **b)** plots the logarithm of the partial current density going towards methane, plus the pH, against applied potential on the SHE scale. Adapted from Hori *et al.*¹⁶⁰ Copyright © 1997, American Chemical Society.

Recent work comparing CO_2R and COR on planar polycrystalline Cu in pH 6.8 and 13, respectively, has led to increased mechanistic understanding of the role of pH.²⁰¹ The partial current densities for CO_2R and COR products plotted on both the RHE and SHE scale illustrates the overall effect of pH (Figure 10). The C_{2+} product overpotentials display a pH independence on the SHE scale, essentially overlapping for CO_2R and COR, which corresponds to a positive ~ 0.36 V shift on the RHE

scale from pH 6.8 to pH 13 (or ~59 mV per pH unit, as expected). On the other hand, the C₁ product (CH₄) overpotential shows a pH dependence on the SHE scale, leading to a much smaller shift on the RHE scale of ~0.15 V. It was concluded that both field stabilization of a rate-limiting chemical reaction (*i.e.* CO dimerization) or proton-electron transfer from water during the rate-limiting step are plausible explanations for the pH independence of the C₂₊ pathway on the SHE scale. Then, the complex pH dependence for CH₄ was rationalized by a kinetic analysis, which suggested that this pathway is limited by a later proton-electron transfer.^{201,213} These findings, which will be discussed in more detail in Section 4.2 and in the SI, are in good agreement with Hori's observations (see Section 1 of the SI for a derivation of the RHE-scale pH dependence from **Figure 9b**). Notably, because the overpotential for C₂₊ products is greatly reduced on the RHE scale, this means that operating in basic electrolytes can lead to a major improvement in energy efficiency for the production of multi-carbon compounds from CO₂R/COR. Consequently, KOH electrolytes are increasingly being explored as a means to achieve higher selectivity and energy efficiency for C₂₊ products, particularly in vapor-fed systems where CO₂ is directly delivered in the gas-phase rather than solubilized in the aqueous electrolyte and diffused to the cathode. These efforts are described in more detail in Section 6.3.

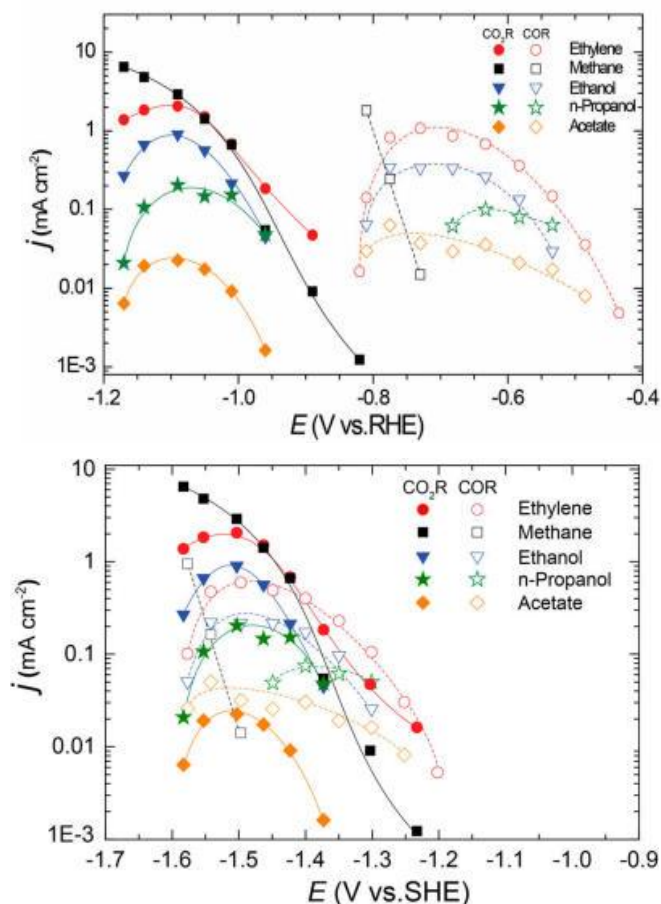
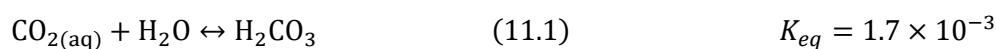
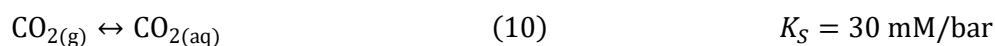
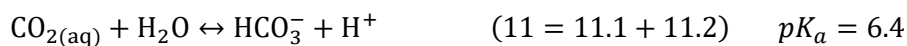


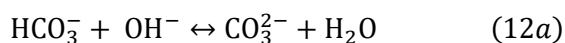
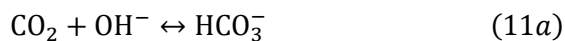
Figure 10: CO₂R (filled) and COR (hollow) partial current densities on the RHE scale (top) and the SHE scale (bottom). Reprinted from Wang *et al.*²⁰¹ Copyright © 2018, American Chemical Society

While CO₂R has not typically been conducted in aqueous electrolytes with high pH due to the buffering capacity of CO₂, understanding the impacts of pH has still been a major area of study due to the dynamic reaction environment at the electrode surface. As discussed in Section 2.2, a local pH gradient can develop at the cathode surface due to depletion of protons/production of hydroxide ions from the HER and CO₂R. In the CO₂/bicarbonate system, CO₂ is both a reactant and a buffer, so an increased pH near the cathode surface can cause the concentration of dissolved CO₂ to deviate (decrease) from that in the bulk electrolyte. The key equilibria reactions for this system are:^{2,100,214}





Or in alkaline solutions, these can be written as:



Reactions 10, 11, and 12 result in CO₂ saturated solutions having bulk pH values from around pH 6-8 for bicarbonate concentrations of 0.05 – 2 M, respectively.² The kinetics of CO₂ hydration (Reaction 11.1) are slow, and the equilibrium concentration of H₂CO₃ is very low.^{2,100} However, the nucleophilic attack of dissolved CO₂ by OH⁻ is faster, such that Reaction 11a dominates over Reaction 11 (11 = 11.1 + 11.2) when pH > 10.²¹⁴ The kinetics for the protonation/deprotonation reactions (11.2, 12, and 12a) are all quite fast, and it can be assumed that HCO₃⁻ is in equilibrium with CO₃²⁻ at all times.¹⁰⁰ Mathematical models have been used to solve the relevant diffusion equations, along with the reaction equations for CO₂ electroreduction with a given selectivity and geometric current density, to estimate the interfacial pH and concentrations, many of which are based on the seminal work by Gupta *et al.* (ref¹⁰⁰).^{86,97–100,110,215–218} It has been shown that even modest current densities can cause the interfacial pH to vary significantly from that in the bulk electrolyte, perturbing the reaction thermodynamics and kinetics in several ways.

First, it is worth taking a moment to briefly discuss the impact of pH on the HER. At higher pH where the proton concentration is low, water reduction is expected to dominate over proton reduction. From a thermodynamics standpoint, HER is pH-independent on the RHE scale and it is irrelevant whether the reaction proceeds via proton or water reduction; in principle, any Brønsted acid can act as a proton donor.²⁰⁶ However, this can have a huge impact on the kinetics of the HER, as demonstrated by Strmcnik *et al.* for noble-metal electrodes.^{219,220} Furthermore, Grozovski *et al.* distinguished H⁺ reduction from H₂O reduction and found their corresponding kinetic parameters using a combination of RDE experiments and modeling.²²¹ It is expected that the HER proceeds primarily via water reduction under CO₂R conditions.²⁰⁶ It is also possible that the electrolyte buffer can act as a proton donor,

depending on its pKa value, concentration, and mass transport/availability; this will be discussed in more detail in Subsection 3.3.3. While the explicit impact of pH on the HER is still an ongoing area of research, it has been thought that increasing local pH helps favor CO₂R over HER, mainly due to the decreasing overpotential for the formation of C₂₊ products, as discussed earlier. On the other hand, a high local pH shifts equilibria of the acid-base reactions towards (bi)carbonates, which can reduce the concentration of CO₂ near the surface, decreasing selectivity towards CO₂R and favoring the HER instead.^{97,215}

These contradictory consequences have led to some debate over whether a high local pH is beneficial or detrimental for CO₂R catalysis. Several researchers have proposed that CO₂ is still likely to be present under a non-equilibrium high pH owing to its slow hydration kinetics.^{86,139,150,222,223} This of course is very much dependent on the sufficient transport of CO₂ to the surface. However, with this in mind, it seems likely that there is an optimum pH that balances the benefits of increased pH with the slow, disadvantageous decline in CO₂ concentration. Indeed, recent modeling studies have found such a volcano-type dependence on pH for CO₂R selectivity (particularly to C₂₊ products) and proposed an optimal local pH range of 9-10.^{98,99} At higher pHs, the HER becomes dominant due to mass transport limitations of CO₂. Interestingly, in this mass transport limited regime, the activity and selectivity for C₂₊ products plateaus and eventually declines, while CH₄ production generally increases.^{66,97,201} Thus, one can identify when the reaction is limited by CO₂ mass transport by observing when the C₂₊ activity plateaus²⁰¹ or by increasing mixing at a given potential to see if the C₂₊ selectivity is altered.²⁰⁹ An example of the latter approach is shown in **Figure 11**. While it remains unclear how pH itself affects the adsorption energies and coverages of reaction intermediates, especially since these are all also a strong function of potential, it seems likely that *H coverage increases at the expense of *CO in this mass transport limited regime, providing a stronger driving force for hydrogenation of CO to CH₄ and a decreased probability of CO coupling to C₂₊ products.^{66,216} This hypothesis was further supported by a recent study incorporating microkinetic modeling, which revealed that *CO coverage is gradually depleted as its reduction becomes increasingly favorable with decreasing (more cathodic) potential, and

formation rates of C_{2+} products are more drastically impacted due to their second-order dependence on *CO coverage.²¹³

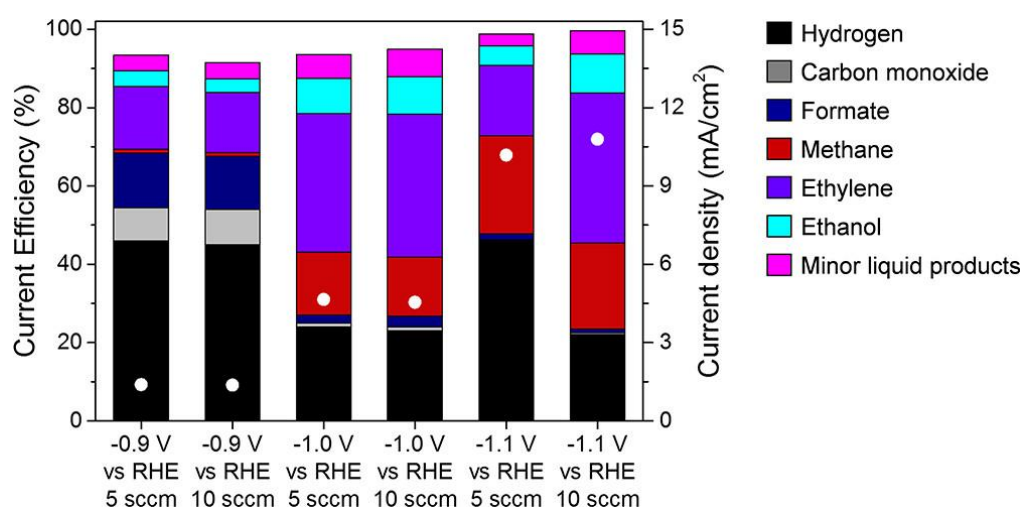


Figure 11: Current efficiency (bars) and total current density (dots) for CO_2 reduction over Cu(100) at different flow rates of CO_2 . Under mass transport limited conditions, increased reactant availability will affect the product distribution; thus, this was used to identify under what potentials the reaction is governed by the intrinsic kinetics. Reprinted from Resasco *et al.*²⁰⁹ Copyright © 2017, American Chemical Society.

Potential-dependent trends can be difficult to discuss in the context of the pH effect. First of all, it is important to realize that when the pH at the electrode surface significantly deviates from that in the bulk if the potential is compared to the (bulk) RHE equilibrium potential without accounting for local pH gradients, then the catalytic overpotential is overestimated, which can cause errors in mechanistic interpretations.^{110,150,206} This has led some researchers to report results on a “corrected RHE” scale that uses the local pH as estimated from mathematical modeling.²¹⁸ This has also motivated experimental measurement of the pH at the electrode/electrolyte interface under CO_2R conditions. While this has remained a difficult challenge, there are two recent reports that have attempted to do so using attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) to measure & correlate the relative intensities of species involved in the buffer equilibria reactions with the local pH near the electrode surface.^{149,150} There are a few discrepancies between these studies, as this is an active area of method development, and more work should be done to validate and further advance these techniques.

Secondly, as discussed in Section 2.2, it is also important to keep in mind that the extent of OH⁻ concentration polarization and thus local pH at a given applied potential will differ between catalysts and electrochemical cells. Catalysts with high surface areas will be more susceptible to OH⁻ concentration polarization at lower overpotentials. On the plus side, this likely explains the CH₄ suppression & enhanced selectivity to C₂₊ products typically observed on high surface area catalysts, which will be discussed in more detail in Chapter 6. This can also lead to HER suppression by local depletion of buffer species that act as competent proton donors,^{222,224} as discussed in Subsection 3.3.3. Unfortunately this also causes difficulties comparing potential-dependent CO₂R performance between catalysts with very different roughness factors. This is not only an issue for high surface area catalysts though; even planar catalysts can exhibit different activity and selectivity if evaluated in electrochemical cells with different hydrodynamic boundary layer thicknesses.¹⁰¹ Therefore, it is important to keep all of these factors in mind when drawing conclusions about potential-dependent activity and selectivity.

Finally, it is worth noting that a gas diffusion electrode (GDE), while not suited for fundamental studies due to a complex interface, can in principle combine the best of both worlds, enabling both high pH conditions and sufficient mass transport of CO₂ even with high surface area catalysts. See Section 6.3 for further discussion of these vapor-fed systems.

3.3.2 Cation Effects

It has been well documented in the literature that electrochemical CO₂R activity & selectivity is influenced by the alkali metal cation in the electrolyte. Initial work by Hori and Murata showed that the selectivity of CO₂ and CO reduction on polycrystalline Cu was strongly influenced by cation size, with larger cations increasing the selectivity towards formation of C₂₊ species and decreasing the selectivity for the HER.²²⁵ Since then, a number of reports have confirmed and expanded on these experimental observations.^{98,209,215,226,227} While the experimental trends are largely in agreement, there has been some disagreement over the explanation for this effect. Hori and Murata rationalized the change in selectivity with cation size by the difference of outer Helmholtz plane (OHP) potential, based

on Frumkin's theory,²²⁸ whereby the OHP potential will shift to more positive values with the degree of specific adsorption, which increases with cation size due to their lower hydration numbers.²²⁵ Recent theoretical work, however, has suggested that specific adsorption of alkali cations is not applicable to the conditions of CO₂R,²¹⁵ in part due to the very negative reduction potentials of alkali ions calculated on transition metal electrodes.²²⁹ In addition, oxygen reduction studies have shown that alkali cations primarily interact non-covalently, with surface X-ray scattering data suggesting that the cations are not adsorbed and remain partially solvated at the interface.^{230,231} DFT calculations demonstrate that solvation increases the favorability of specific adsorption and suggest a low coverage of partially hydrated K⁺ is thermodynamically favorable under high cathodic potentials and pH conditions.²³² Due to the complex nature of the electrochemical interface, it is difficult to say with certainty to what extent alkali cations interact with the electrode surface. Experimental identification of the mechanism(s) by which cations affect surface electrochemical processes (*i.e.*, via specific adsorption and/or non-specific interactions) is extremely challenging and remains an open question. We will not distinguish that here and instead simply focus on the potential impacts that cations on/near the surface could have on CO₂R.

Electrochemical CO₂ reduction potentials are typically more negative than the potential of zero charge (PZC) on low-index facets of Cu (~0.7 V *vs.* SHE),¹⁹¹ so solvated cations should accumulate on/near the surface of the electrode during reaction. This can block active sites on the surface, alter the binding energy or coverage of reaction intermediates, and/or influence the barriers of elementary steps.²³² The presence of the cation near the metal surface also gives rise to high electric fields of roughly -1 V/Å in the vicinity of the ion (within 5 Å).^{233,234} While cations in the bulk of the electrolyte are stable to hydrolysis, electrostatic interactions between the solvated cation and cathode lower the pK_a in the vicinity of the electrode; the magnitude of this decrease in pK_a increases with larger alkali cation size and larger cathodic potentials.²¹⁵ Thus, it was proposed that this allows larger cations to act as a pH buffer, offsetting the increase in local pH induced by concentration polarization and restoring the local CO₂ concentration closer to the bulk value.²¹⁵ This theoretical model matched their experimental measurements, but it must be noted that the experiments were performed under strong mass transport limitations. Thus, this model does not explain that fact that increasing activity and selectivity to C₂₊

products are observed both at lower overpotentials when not in a concentration polarized regime, as well as during COR, which does not have the same dependence of reactant concentration on pH.^{209,227}

Two recent studies have instead suggested that the primary role of the cation is to act as a promoter, stabilizing certain CO₂R/COR intermediates on the surface that have favorable electrostatic interactions with solvated cations.^{209,227} Specifically, cation-created electrostatic field stabilization decreases the energy for *CO₂ adsorption, the precursor to 2e⁻ products, and C-C coupling to form *OCCO or *OCCHO, possible precursors to C₂₊ products.²⁰⁹ This explains the trends observed not only for Cu, but is also consistent with CO₂R selectivity enhancements to 2e⁻ products observed on Ag^{209,215,235} and Sn.²⁰⁹ This alone, however, does not explain the observed trend with cation size. For that, DFT calculations by Resasco *et al.* revealed that larger hydrated cations are more energetically favored at the outer Helmholtz plane than smaller ones, which suggests that a higher concentration of cations will accumulate with increasing cation size leading to a larger local electric field.²⁰⁹ The same researchers then provided support for this hypothesis by conducting experiments in mixed electrolytes, which showed that only a small percentage of the larger cations is needed to observe their influence on the intrinsic rates of formation of certain reaction products (*e.g.*, ≤ 1 order of magnitude increase in partial current densities for C₂H₄, C₂H₅OH).²⁰⁹ A recent study using attenuated-total internal reflection Fourier-transform infrared (ATR-FTIR) spectroscopy has provided further evidence for this cation promotion effect, as it was found that with increasing cation size, surface-adsorbed CO molecules experience a greater interfacial electrostatic field that accelerates its reduction kinetics and acts to shift the C \equiv O stretch frequency to lower energies.¹³⁸

Future work in this area could expand on the findings for these monovalent alkali cations by investigating the impacts of divalent or trivalent cations. For example, CO₂R rate increases have been observed over a Cu-Sn-Pb alloy cathode as the size and surface charge of the cation in the supporting electrolyte increases from Na⁺ to La³⁺.²³⁶ There has also been some interest in the use of ionic liquids for CO₂R after initial reports showed increased selectivity to CO at low overpotentials on Ag, MoS₂ and Pt electrodes.^{237–239} It has been hypothesized that the presence of ionic liquids can stabilize reaction intermediates, help bind the CO₂ molecule, and/or suppress the HER by blocking active sites on the

surface. While this could be a promising avenue to explore, we offer a word of caution, as it has also been found that the ionic liquids break down during CO_2R ,^{240,241} which can cause difficulties with product detection and limit its practicality for (re)use at scale. Finally, in moving towards practical CO_2/CO electrolyzers, which will likely be vapor-fed reactors that employ GDEs, we will need to carefully consider how to engineer the ionomer/membrane moieties to promote stabilization of intermediates in a similar manner to the cation effects discussed here.

3.3.3 Anion Effects

The vast majority of CO_2 reduction catalysis has been studied in KHCO_3 electrolytes due to the CO_2 -(bi)carbonate-water equilibrium, which helps maintain a neutral bulk pH. As a result, the impacts of the electrolyte anion have been studied to a lesser extent. Hori and coworkers presented results for constant current electrolysis in various electrolyte solutions, which showed that hydrocarbons and alcohols are the preferred products in KCl , KClO_4 , K_2SO_4 , and dilute KHCO_3 solutions, while H_2 formation dominates in K_2HPO_4 solutions.^{84,86} These findings were explained in terms of a non-equilibrium local region of high pH close to the electrode. As discussed earlier, OH^- ions are released during electroreduction, which can be neutralized by HCO_3^- or H_2PO_4^- . Thus, in the non-buffering electrolytes or in dilute KHCO_3 , there is likely insufficient neutralization leading to a rise in pH, which favors CO_2R over HER and C_{2+} over C_1 products.^{84,86} Other studies on the impact of KHCO_3 concentration have mirrored these trends, showing that with increasing anion concentration the rates of hydrogen evolution and methane production increase, again pointing to local pH effects as the cause.^{110,242}

A recent report, however, found that the changes in pH near the electrode surface were insufficient to explain differences in activity and selectivity observed with changes in anion buffering capacity; instead, it was proposed that these differences result from the ability of buffering anions to donate hydrogen directly to the electrode surface.²¹⁸ While water is expected to be the proton source under CO_2R conditions, it is possible that buffering anions can serve as proton donors given the lower pKa values compared to water. Thus, products where the rate-limiting step involves a proton transfer

(H₂ and CH₄) will be impacted by changes in the hydrogen source. Accordingly, it was found that H₂ and CH₄ activity increased (≤ 1 order of magnitude) with decreasing pK_a of the buffering anion and were not impacted by non-buffering anions, while formation of CO, HCOO⁻, and C₂₊ products were insensitive to anion identity.²¹⁸ This suggests that the buffering anions can serve as competent proton donors, with their effectiveness increasing with decreasing pK_a. The impact was less pronounced once the local pH (as determined by mathematical modeling) was taken into account by plotting the activities on a calculated RHE scale; future studies should seek to test these effects over a wider range of potentials in case transport effects were also playing a role. Interestingly, this could still shed some light on one mechanism by which H₂ evolution may be suppressed during CO₂R; depletion of HCO₃⁻ under basic conditions could impose mass transport limitations for the HER and limit the ability for this buffer to serve as a proton donor.^{222,224} Especially for mesoporous electrodes with high RFs and inhibited diffusion, this could serve to slow the rate of HER until sufficient overpotential to drive the sluggish water reduction kinetics is achieved.

In addition to bicarbonate serving as a pH buffer and proton source, recent studies have also discussed the possibility of bicarbonate serving as a CO₂ source.^{119,139,140} Using a combination of *in-situ* spectroscopic analysis (ATR-SEIRAS) and isotopic labeling, along with mass spectroscopy (MS) or potential stepping techniques, two reports proposed that the CO₂ source during CO₂R is CO₂ in equilibrium with bicarbonate anions instead of free CO₂ molecules supplied to the solution.^{119,140} This hypothesis, however, relies on the critical assumption of fast equilibrium between CO₂ and bicarbonate, which may not be the case since rate constants for the other equilibrium reactions are several orders of magnitude larger.¹³⁹ With the increasing trend of *in-situ* spectroscopic analysis during CO₂R, the role of bicarbonate is an active area of research; thus, continued work should be done to further elucidate the CO₂R reaction mechanisms in bicarbonate electrolytes.

Finally, it is also worth noting that there have been various studies on the influence of halide ions on Cu electrochemistry.^{95,96,117,243–250} Some reports suggest that there will be specific adsorption of these anions on the Cu surface, which could alter the charge density and selectivity for CO₂R products, as well as aid in suppression of the HER.^{244–249} However, many studies show that the presence of halide

ions primarily leads to changes in the Cu surface structure & morphology; in particular, oxidation-reduction cycles in the presence of halide ions has been one strategy used to increase selectivity to C₂₊ products, such as C₂H₄ (see Chapter 6 for further discussion).^{95,96,117,243,244,249,250} Thus, it is currently unclear what the dominating effect(s) of employing halides are, so this represents another area for future studies aimed at better understanding ionic interactions during CO₂R catalysis.

3.4 Electrochemical Conditions

In addition to electrolyte effects, several studies outline the importance of the electrochemical cell design, components and operating conditions.^{88,97,251} While an in-depth discussion of these topics is outside the scope of this review, there are a few considerations and trends that we will touch upon here. Most CO₂R studies to date have been conducted under ambient temperature and pressure, but these factors have also been explored to manipulate the local reaction conditions. Here we will briefly discuss some of the trends observed under non-ambient environments.

3.4.1 Temperature & Pressure

From Henry's Law and the acid/base buffer equilibria (CO₂/HCO₃⁻/CO₃²⁻), it is understood that increasing the concentration of dissolved CO₂ in the electrolyte can be achieved by decreasing temperature or increasing pressure (**Figure 12**).^{2,102,103,110,252–255} As a result, several studies have looked at varying the temperature^{83,102,104,162,252–255} and pressure^{102,103,110,201,226} during CO₂R/COR. In general, it is difficult to draw direct comparisons between these limited studies due to the use of different electrolytes, applied voltages, techniques (galvanostatic vs. potentiostatic) and temperature/pressure ranges. However, a few high level trends can be extracted from their findings. Across the board, decreasing temperature was found to increase selectivity to CH₄.^{83,102,104,162,252–255} Trends for the other products are not as clear, although some results do show an increased production rate of C₂H₄^{83,104} and/or CO^{83,255} at higher temperatures. The rate of H₂ evolution was found to be suppressed at lower temperatures and greatly enhanced at higher temperatures.^{83,102,252,253,255} The overall rate of CO₂R was

impacted by temperature to a lesser degree,¹⁰² with some studies finding minimal changes in the total partial current density for CO₂R below room temperature^{4,104,105} and modest increases in reaction rate above room temperature.^{104,255} This leads to overall higher selectivity for CO₂R at lower temperatures, and lower selectivity at higher temperatures where the HER becomes dominant. The reasons for these temperature effects are not entirely clear; changes in temperature affect the CO₂ solubility, thermal diffusion rates, pH, solution resistance, and may also alter adsorption equilibria. More detailed studies are needed to better understand the impact of temperature on CO₂R product selectivity over a broader range of potentials.

As CO₂ or CO pressure decreases below 1 atm, the HER is dominant and minimal CO₂R/COR is detected.^{201,226} Meanwhile, with increased pressures, the total CO₂R current generally increases (with the exception of the highest pressures in Hara *et al.*,¹⁰³ where there is significant missing Faradaic efficiency in their galvanostatic experiments at 40 and 60 atm).^{102,103,110} These trends are likely due in large part to the changes in dissolved concentration of CO₂ with pressure. Interestingly, one study found that C₂H₄ selectivity increased with increased pressure, which was attributed to an increase in local CO concentration and surface coverage.¹¹⁰ Again, more systematic studies are needed to better understand the impact of pressure over a broader range of potentials and conditions. While operation of CO₂R under ambient temperature and pressure has been discussed as a potential advantage of electrochemical CO₂ recycling compared to other processes, we should not limit the scope of study to ambient conditions. Altering temperature and pressure remain areas ripe for further investigation, both to gain increased mechanistic understanding of electrochemical *vs.* chemical steps and for identifying operating conditions that achieve optimal activity and selectivity for CO₂R to desired product(s).

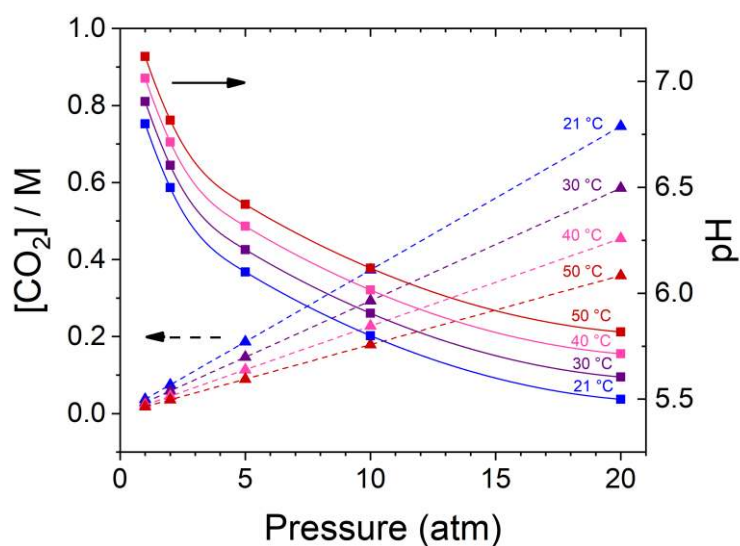


Figure 12: Effect of pressure and temperature on the concentration of dissolved CO₂ in the electrolyte, [CO₂], and pH. Adapted from T. Hatsukade.²⁵⁶ This work is licensed under a Creative Commons Attribution Noncommercial 3.0 United States License (<http://creativecommons.org/licenses/by-nc/3.0/us/>).

3.5 Summary

Electrochemical CO₂ reduction on copper is a complex reaction involving multiple steps, intermediates, and reaction pathways. It is also highly sensitive to many factors from the atomic scale to the reactor scale including the electrode surface structure and morphology, electrolyte pH and identity/quantity of ions present, degree of mass transport, temperature, pressure, etc.

Single crystals and oriented surfaces represent useful tools to study the impact of crystal facet on CO₂R performance of Cu electrodes. In particular, interesting trends in product distribution have been reported as a function of surface structure. Among the planar surfaces, Cu(100) was shown to yield a particularly high ethylene/methane ratio, and the selectivity toward ethylene could be further improved by adding steps to the surface.^{152–154,159} These findings can help provide design principles to steer the selectivity of catalyst materials towards important products. On the other hand, no significant trends in activity have been reported. This could be due to defects or step sites existing on the surface and/or formed *in-situ*, leading to similar overall activity on all the Cu single crystal surfaces investigated. We would like to emphasize the need for more quantitative data from oriented surfaces,

preferably of single crystal quality, as a function of potential. This is vital in order to obtain further mechanistic information, which can lead to identification of key parameters that can be optimized to steer selectivity and activity toward desired products.

At the same time, it is also important to keep in mind that the crystallographic orientation of the surface of single crystal electrodes can differ from their bulk orientation. Some reports indicated that the surface structure of the electrodes was strongly dependent on the choice of pre-treatment procedure,^{153,172} while others showed that certain electrodes tended to restructure under reaction conditions.^{173,174,179–182} While the causes for restructuring require further investigation, some likely reasons include effects from the presence of CO, the negative applied potentials, or other factors from the local reaction environment, such as electrolyte effects. We emphasize that phenomena exhibited by crystals or films oriented in a specific direction may not originate from the bulk orientation, but rather from the defects present at the surface, as illustrated in **Figure 7**; as such, scientists should be cautious in making direct comparisons between the results from experiments on single crystals to DFT-based models. In addition, due to the complications we discussed above, we strongly recommend that future studies of single crystals and other oriented systems investigate the structural properties the electrodes *in-situ/operando* whenever possible.

The electrolyte presents several variables that can be used to tune CO₂R activity and selectivity. In particular, the impact of pH is a complex subject that causes several competing effects on the local reaction environment. A high interfacial pH is beneficial for increasing selectivity towards CO₂R and reducing the overpotential required to form desirable C₂₊ products on an RHE scale; it becomes a detriment, however, when there is insufficient mass transport of CO₂, and the acid-base equilibria between CO₂, HCO₃⁻, CO₃²⁻ and OH⁻ causes a significant decrease in the local CO₂ concentration. The extent of concentration polarization is determined by the overall flux of species both to and from the electrode surface. This depends not only on the degree of mixing within an electrochemical cell, which impacts the hydrodynamic boundary layer thickness, but also the overall reaction rate (current density), which is impacted by the surface area of the catalyst. We strongly recommend that conclusions about intrinsic activity and selectivity only be drawn from data that is not significantly impacted by mass transport effects.

The electrolyte cation and anion also play important roles in the catalysis. Experimental trends for CO₂R on Cu have consistently demonstrated increased activity and selectivity for C₂₊ products with increasing alkali cation size, although the hypotheses behind these effects have evolved over time.^{98,209,215,225–227} By combining theoretical and experimental methods, greater mechanistic insights have been obtained. While the extent and mechanism of alkali cation interaction with the surface is still an open question, the localized electrostatic fields they create is proving to be a critical factor impacting CO₂R activity & selectivity. Indeed, DFT calculations reveal that cation-created field effects are crucial for CO₂ activation on weak binding surfaces²³³ and CO dimerization on Cu at room temperature.²³⁴ Anion effects have often been discussed in relation to the local pH at the electrode surface,^{84,86,110,242} but it also been proposed that buffering anions can donate hydrogen directly to the electrode surface, which increases the rates of H₂ and CH₄ formation.²¹⁸ Recent studies have additionally discussed the possibility of bicarbonate serving as a CO₂ source, but further work is needed to determine the extent to which this may occur. Finally, temperature and pressure represent additional levers by which to tune the catalysis since the concentration of CO₂ in the electrolyte can be increased via increasing pressure or decreasing temperature; in addition, these electrochemical conditions may also alter adsorption equilibria and diffusion rates. While some trends in product selectivity have been observed, this remains an area in need of further systematic investigations.

In summary, in this Chapter we discussed how a variety of different experimental factors can impact CO₂R on Cu, the mechanistic insights that have been gained from studying them, and how they can be tailored to optimize activity and selectivity to desired product(s), including areas for future study. In the next Chapter we will build upon these experimental findings and take a more in depth look at the complementary theoretical descriptions of CO₂R on Cu and how these methods have helped shape our mechanistic understanding of the factors governing CO₂R activity and selectivity.

4. Theoretical Studies on Copper

In recent years, developments in *ab initio* methods for the simulation of surface and

electrochemical reactions have enabled theoretical mechanistic investigations and theory-guided catalyst design.⁵⁸ Electrochemical CO₂ reduction is particularly challenging due to the complex reaction networks and the importance of activation energies and cation effects.^{169,233} In what follows, we provide an introduction to state-of-the-art modeling approaches for electrochemical processes and discuss the major conclusions, controversies, and open challenges in recent work.

4.1 Introduction to Theoretical Approaches

Modeling electrochemical interfaces from an atomistic perspective presents many open challenges. In general, the thermodynamics for electrochemical reactions are relatively simple to obtain with the computational hydrogen electrode model,²⁵⁷ which relies on calculations of adsorption energies and a H₂ gas reference to account for the free energy of proton-electron pairs, *i.e.* $\mu(\text{H}^+) + \mu(\text{e}) = \frac{1}{2}\mu(\text{H}_2) - eU$, where U is the potential vs. the reversible hydrogen electrode (RHE). For a proton-electron transfer to *CO to form *CHO, for instance, the corresponding free energy change is

$$\Delta G = \mu(\text{CHO}^*) - \mu(\text{CO}^*) - \left[\frac{1}{2}\mu(\text{H}_2) - eU \right] + \Delta G_{\text{solv}} + \Delta G_{\text{field}} \quad (13)$$

where ΔG_{solv} and ΔG_{field} refer to contributions of solvation and field.^{258,259} For a given reaction step, a thermodynamic limiting potential U_L can be determined, which is defined as the potential at which a reaction step becomes exergonic, where $\Delta G = 0$. For a reaction pathway, the corresponding limiting potential is given by that of the step with the highest reaction free energy. This approach has been applied to a mechanistic analysis of CO₂R pathways towards C₁ products on stepped Cu(211), and U_L for various products have been shown to be correlated with experimental onset potentials on polycrystalline copper.²⁰² Likewise, the onset potentials for CH₄ or CH₃OH across polycrystalline transition metals have been shown to follow trends in the corresponding U_L .⁵⁸

While a thermodynamic analysis using the limiting potential U_L as a key metric has shown mechanistic insight and correlation with experimental data on transition metals, this presents only a necessary but insufficient criterion for activity. Determination of activation energies allows for turnover frequencies to be evaluated as a function of potential. Surface hydrogenation barriers (*i.e.* Langmuir-

Hinshelwood type) through an adsorbed H^* , where electron transfer has already occurred, are easy to determine in vacuum, but electrochemical barriers (sometimes referred to as Eley-Rideal²⁶⁰ type) are considerably more challenging. In addition, as discussed in Section 3.3, ion and solvent effects have been shown to be important factors determining activity and selectivity towards various products. The investigation of electrochemical activation energies and the resultant kinetics and selectivities require models that explicitly account for the potential, solvent, and ions, where much method development is ongoing and where considerable variations exist in the energetics for similar processes determined using different approaches. In recent years, CO_2R energetics have been studied theoretically using implicit solvent models that include a continuum description of the ions,^{261,262} explicit solvent models where water and ions are considered atomistically,^{169,260} and also a H-shuttling approach^{262–264} where a water molecule shuttles protons from the surface and back. We will first briefly summarize these different theoretical approaches.

4.1.1 Implicit Models

In general, the inclusion of solvent molecules and ions adds many extra degrees of freedom and computational time relative to vacuum|metal calculations for activation barrier calculations. Implicit solvent models apply a continuum model of the electrolyte, which corresponds to a negligible increase in computational time. The charge at the interface can be varied continuously, such that the potential is easily tuned. While simple and computationally cheap, these models present several challenges. One of the most widely used implementations of the implicit method makes use of a simple linearized Poisson-Boltzmann distribution of the ions,²⁶⁵ which does not account for effects of finite ion size and has been suggested in classical models to lead to unphysical interfacial capacitances.²⁶⁶ The potential of zero charge (PZC) has been proposed as a benchmark for these methods;^{261,267} however, since PZCs and metal work functions are correlated,²⁶⁶ the agreement between experimental and theoretical PZC may reflect the accuracy of generalized gradient approximation (GGA) functionals in the determination of metal work functions more than the description of the solvent. Such a benchmark also does not evaluate the accuracy of the reaction energetics, where solvation or cation interactions can have a significant

effect. Finally, a fundamental challenge associated with implicit solvent simulations at constant potential is that the ions are modeled to adiabatically follow the shifts in dipoles associated with a reaction event. These two processes, however, occur on very different timescales.^{268,269} The effect of such an assumption on the energetics has not been evaluated against explicit models.

4.1.2 Explicit Models

Explicit solvent methods allow for an atomistic level picture of solvation and cation effects, but at the expense of significantly increased computational cost and the introduction of other challenges. Since ions are modeled explicitly and within finite-sized unit cells, the potential is not continuously variable. Proton-electron transfer processes modeled in finite-sized unit cells also give rise to significant shifts in the potential along the reaction pathway. These issues can be mitigated using a capacitor model of the interface, which allows for the extrapolation of calculated barriers to the limit of infinite cell sizes, corresponding to the constant-potential limit.^{270,271} State of the art GGA-level functionals predict a poor band alignment of solvent HOMO, LUMO with the metal Fermi level, which can give rise to artificial charge transfer across the interface and corresponding effects on the reaction energetics.²⁷² Unrelated to band alignment is the partial charge of hydronium ions at the Helmholtz plane arising from overlap of solvent and metal charge, which affect the reaction energetics.²⁷³ Transition states have been determined using either nudged elastic band (NEB)^{169,274} or metadynamics and potential of mean force,^{260,275} the latter method includes entropic contributions from solvent reorganization, but at an increased computational cost.

4.1.3 H-shuttling Model

An alternative to full explicit solvent models has been put forth by Janik *et al.*^{263,264,276} In this approach, a water molecule is used to shuttle an adsorbed H* from the surface to the adsorbate (**Figure 13**). This shuttling process is considered to provide an estimate of the associated proton-electron transfer barrier. The potential vs. RHE for the process is assumed to correspond to that where H* in the initial state is equilibrated with a proton-electron pair, as determined using the computational hydrogen

electrode. In contrast to explicit solvent calculations, potential shifts along the reaction pathway arising from shifts in charge are not considered. The transfer coefficient is assumed to be 0.5 plus a correction determined by shifts in the dipoles of the adsorbates. While the simplicity of this approach is compelling, the assumptions should be evaluated with more detailed models.

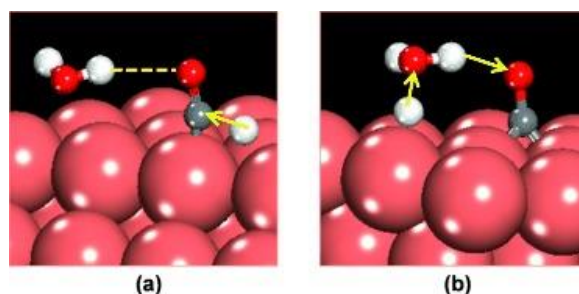


Figure 13: Water shuttling model for proton-electron transfer to *CO to form (a) *CHO and (b) *COH. A single water molecule is included to shuttle an adsorbed *H and mimic proton-electron transfer from solution. It was found that *CHO formation occurs through direct transfer of *H to the *CO. Reprinted with permission from Janik *et al.*²⁶⁴ Copyright © 2013, John Wiley and Sons.

4.2 Theoretical Insights

In general, thermodynamic analyses in the current literature have been performed using the computational hydrogen electrode model. The choice of functional, pseudopotentials, and the treatment of solvation should all affect the energies, but resultant trends and energies reported by different groups do not differ significantly (*e.g.* the similarity in trends in energetics of Cu(111) intermediates from Refs^{263,277}). Theoretical electrochemical activation energies, on the other hand, widely differ with approach, due to the differences in the simplifying assumptions made in modeling the electrochemical interface. **Tables S2, S3, S4** summarize, respectively, the activation energies for key CO₂R to CO, initial CO reduction, and C-C coupling steps determined using various methods, and, where available, their transfer coefficient β and the barrier for the corresponding surface hydrogenation process. These tables can be found in Section 3 of the Supporting Information (SI). In this review, we assume the criterion for facile kinetics to be a turnover frequency of 1/s per site, which corresponds to approximately a 0.75 eV barrier at room temperature,²⁷⁸ and we have reported the barriers at 0 V vs. RHE wherever possible. In reporting barriers determined with H-shuttling, we considered the transfer of H* through H₂O to be classified as electrochemical (*i.e.*, involving electron transfer) and a direct transfer of H* as a surface

hydrogenation. Overall, the differences in energetics and resultant mechanisms reported point to the importance of evaluating the assumptions made in the models of the electrochemical interface. In what follows, we discuss general insights and controversies in current theoretical investigations of CO₂R on Cu.

4.2.1 Trends in Electrochemical Barriers

One of the general insights from existing theoretical investigations is the trends in activation energies for proton-electron transfer towards different intermediates, which, given the complexity of CO₂R pathways towards the many possible products (as shown later in Chapter 5, **Figure 18**), provides some qualitative guidance in the search for rate-determining steps. Using an explicit solvent model and NEB barrier calculations on various transition metals, proton-electron transfers to oxygen ends of reaction intermediates were found to be in general facile, while those to carbon or those involving C-O bond scission are more difficult.²⁷⁴ Similarly, metadynamics²⁶⁰ with explicit solvent and H-shuttling^{264,276} barrier calculations found that oxygen are hydrogenated primarily through electrochemical vs. direct *H transfer steps.

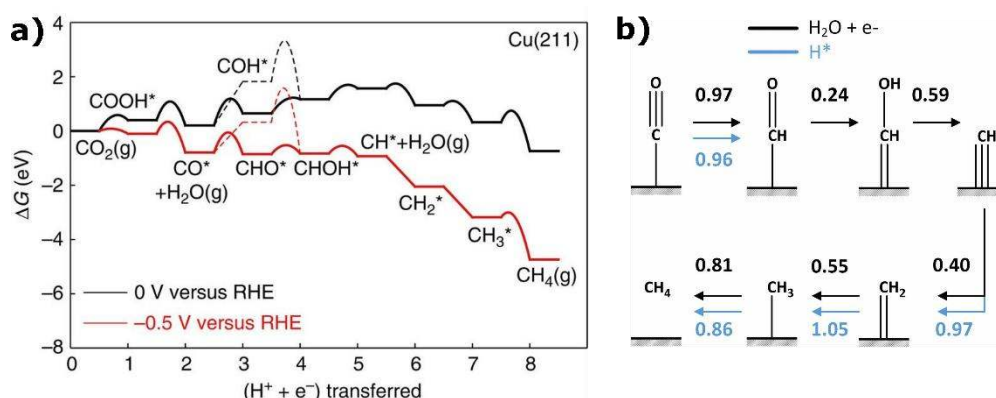
4.2.2 CO as a Crucial Intermediate

The pathway towards CO has been analyzed with several methods, as tabulated in **Table S2**. On Cu(111), both explicit solvent with NEB transition state search¹⁶⁹ and H-shuttling methods^{263,264} find the activation energies for CO₂ reduction to *CO to require low overpotentials to reach the 0.75 eV threshold for facile kinetics. On Cu(100), H-shuttling models²⁷⁶ report less surmountable barriers than explicit solvent with metadynamics,²⁷⁹ which give a net barrier of 0.8 eV for CO_{2(g)} to *COOH at -0.4 V vs. RHE; the reason for this discrepancy may be differences in solvation or the simplifying assumptions behind the H-shuttling model. Overall, a facile path towards CO is consistent with experimental reports that both CO and CO₂ reduction give similar product distributions, suggesting CO to be a key reaction intermediate in CO₂ reduction, as discussed earlier in Subsection 3.2.1. Formate, on the other hand, was shown to be a dead end, given that the free energy difference from *OCHO to

$^*\text{OCH}_2\text{O}$ is 1.6 eV.²⁰² This theoretical result is consistent with experiments using HCOO^- as a feedstock, which gave no detectable products.⁸⁶

4.2.3 Pathway Towards Methane

Using explicit water models, barriers determined using NEB and metadynamics suggest identical reaction intermediates from CO to CH_4 on stepped Cu(211)¹⁶⁹ and Cu(100)²⁶⁰ at pH 7, respectively. The free energy diagram for Cu(211) is shown in **Figure 14a**, and the reaction species determined on Cu(100) are shown in **Figure 14b**. In this pathway, $^*\text{CO}$ to $^*\text{CHO}$ is the rate-determining step, which is followed by a series of proton-electron transfers to form $^*\text{CHOH}$, $^*\text{CH}$, $^*\text{CH}_2$, $^*\text{CH}_3$, and CH_4 . In contrast to a purely thermochemical analysis,²⁰² $^*\text{CH}_3\text{O}$ is not found to be an intermediate towards CH_4 due to the insurmountable barrier for proton-electron transfer to $^*\text{CH}_3\text{O}$ to form $\text{CH}_4 + ^*\text{O}$.^{264,274} It must be noted that crucial differences exist between pathways determined by explicit and H-shuttling models. Whereas explicit methods^{169,260} suggest that all steps following $^*\text{CO}$ are proton-electron transfers on Cu(211) and Cu(100),^a H-shuttling calculations suggest that $^*\text{CHO}$ is formed through a direct transfer of $^*\text{H}$ on both Cu(100) and Cu(111).^{263,280} On Cu(111), H-shuttling in conjunction with implicit solvent²⁶² and explicit water¹⁶⁹ methods suggest a $^*\text{COH}$ and $^*\text{CHO}$ intermediate, respectively.



^a Goddard *et al.* consider the surface hydrogenation to $^*\text{CO}$ to form $^*\text{CHO}$ to be favored *vs.* the associated proton transfer, and report barriers of 0.96 and 0.97 eV (at -0.59 V *vs.* RHE) respectively. However, the latter electrochemical barrier would go down substantially with decreasing potential, assuming a usual $\beta \sim 0.5$.

Figure 14: a) Free energy diagram of CO₂R to CH₄ on Cu(211), model system for Cu steps. Reprinted from Liu *et al.*¹⁶⁹ This work is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>). **b)** Reaction intermediates towards CH₄ determined on Cu(100). Reprinted from Cheng *et al.*²⁶⁰

4.2.4 CO Dimerization

Pathways toward C₂₊ products are considerably more complex and present more controversy amongst theoretical studies. Adding to this complexity is that certain C₂₊ intermediates with large dipole moments are dramatically affected by the fields induced by cations at the interface, which add additional degrees of freedom affecting the energetics (see **Figure 15**). Both vibrational spectra^{134,145–148} and kinetic models^{169,261} suggest *CO to be present on Cu under CO₂ and CO reduction conditions, and the coupling of 2*CO to form a *OCCO dimer has been studied using several approaches. It was found that *OCCO on Cu(100), (111), and (211) have insurmountable dimerization barriers (>1 eV) in vacuum, but water solvation and cation effects together stabilize the *OCCO relative to 2*CO such that dimerization becomes facile.^{234,281–283} Further, it was found that Cu(100) and stepped (211) exhibit lower barriers than Cu(111).²⁸³ Implicit solvent models with a continuum ion distribution should also provide a field-induced stabilization, though the charge and field distribution would not be as localized as in the case of an explicit cation; Head-Gordon *et al.* report a dimerization barrier of only 0.53 eV at 0 V vs. RHE on Cu(100) in the presence of a continuum distribution of charge in the solvent.²⁶¹ Overall, the sensitivity of the energetics of this step to water solvation and cation-induced fields likely contributes to the tremendous variation in reported CO dimerization barriers on Cu facets: 0.53 to 1.3 eV on Cu(100), and 0.89 to 1.7 eV on Cu(111) (see **Table S3** in SI).

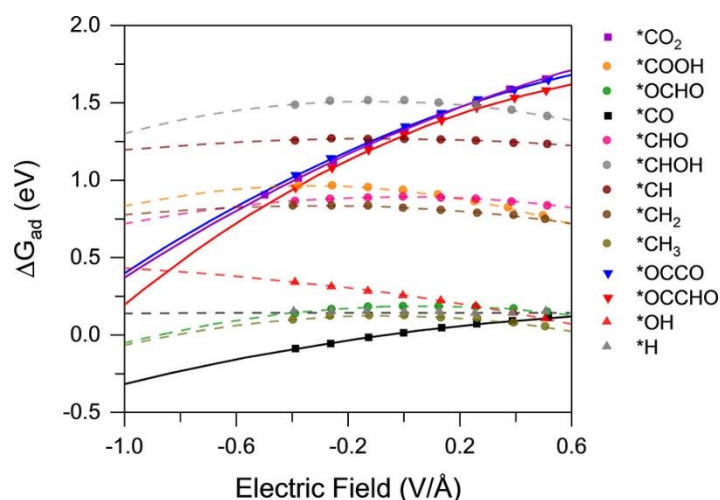


Figure 15: Field effects on various CO₂R intermediates on Cu(111). The energy of each adsorbate as a function of field strength is obtained by applying a uniform electric field oriented perpendicular to the slab. Adsorbates that are most stabilized by field are *CO₂, *OCCO, *OCCHO. Reprinted from Resasco *et al.*²⁰⁹ Copyright © 2017, American Chemical Society.

4.2.5 C₂ Pathways

Beyond *OCCO, the determination of C₂ mechanistic pathways and their facet dependence presents an open challenge, with different methods reporting different mechanisms. These differences point to the importance of method development and benchmarking efforts in *ab initio* simulations of the electrochemical interface. Vacuum calculations on Cu(211) suggest that coupling barriers tend to decrease with increasing hydrogenation of the coupling species,²⁸¹ and that the pathway to acetaldehyde and ethanol is thermodynamically downhill from *OCCHO.⁹¹ With vacuum|metal calculations on Cu(100), a *OCCOH to *OCC pathway was found to be thermodynamically favored after *CO dimerization.²⁸⁴ Likewise, this pathway was found to be dominant in an *ab initio*, explicit solvent study on Cu(211), despite the difference in the treatment of the interface and in the facet.²¹³ An analysis with the H-shuttling model suggests that pure Cu(100) facets do not have facile barriers to form C₂ products, and it is concluded that reconstruction of the surface is required for C-C coupling.²⁷⁶ However, these calculations were performed without cations and a full solvent layer, both of which can stabilize some crucial intermediates in the processes considered. An implicit solvent study on Cu(100) found *OCCHO to be a critical intermediate towards C₂₊ products, with *OCHCHO found to be the precursor to acetaldehyde and ethanol, and *COCHOH the precursor to ethylene.²⁰⁸ The former is in line with

experimental observation that OCHCHO (glyoxal) can be reduced to acetaldehyde and ethanol.^{113,209} Finally, explicit solvent simulations with metadynamics on Cu(100) suggest that, at low overpotentials, C₂₊ products are formed through CO dimerization and subsequent proton-electron transfers towards *HOCCOH²⁶⁰ (vs. the *OCC intermediate proposed by Ref.²⁸⁴). At high overpotentials, it is assumed that adsorbed *H saturates the surface such that *OCCHO is formed through 2 Eley-Rideal steps of CO_(g) + *H → *CHO, then *CHO + CO_(g) → *OCCHO.²⁶⁰ We note, however, that the barrier reported for the first Eley-Rideal step is insurmountable at room temperature at 1.01 eV. Microkinetic models also suggest that at steady state the *CO coverage continues to dominate over *H, even down to -1 V,^{169,261} and *CO has been observed with vibrational spectroscopy down to such potentials.¹⁴⁷

4.2.6 Kinetics

Given the challenge of determining electrochemical activation energies, few mean-field kinetic models of CO reduction have been reported in the literature.^{169,213,261} Kinetics provide insight into rates, selectivities, intermediate coverages and competition amongst different pathways, all as a function of reaction conditions. However, since rates depend exponentially on energies (*i.e.* $r \sim \exp(-E_a/kT)$), large uncertainties are expected in predicted rates. For example, only a 0.1 eV uncertainty in a barrier translates to over an order of magnitude uncertainty in rate at room temperature. Trends in general are therefore considered to be more reliable than absolute rates.

Recently, a kinetic model for CO reduction to CH₄ on transition metals was developed.¹⁶⁹ Based on the reaction pathway on Cu(211) (**Figure 14a**), it was assumed that the proton-electron transfer from *CO to *CHO is the limiting step for CO reduction on all transition metals. Scaling relations for the H-CO transition state and the corresponding kinetic activity volcano for CO reduction to CH₄ were determined on (111) and (211) surfaces, which is shown in **Figure 16**. Adsorbate-adsorbate interactions, which come into play on metals that bind as strongly as Cu or more, were included with a first-order adsorbate interaction model.²⁸⁵ The stepped facet was found to be considerably more favorable for *CO protonation than flat ones, owing to the ease of *CO rotation and also the accessibility of the C end to proton transfer from the solvent. Stepped facets were therefore predicted to give orders of magnitude

higher rates than flat ones.¹⁶⁹ In fact, it is suggested that only a small fraction of stepped sites can account for the experimentally determined activity of polycrystalline transition metals,²⁰⁴ which are overlaid in **Figure 16a**.¹⁶⁹ Cu already lies close to the peak of the activity volcano for materials that follow transition metal scaling, due to its intermediate *CO binding energy. Based on this analysis, two design criteria for active CO reduction catalysts were proposed: (i) stabilization of stepped sites and (ii) stabilization of the *H-CO intermediates for a given *CO binding energy.¹⁶⁹ The corresponding contour plot of activity based on *H-CO and *CO energies is given in **Figure 16b**. We note that the predicted significantly higher activity of steps has yet to be demonstrated experimentally, although studies of both single crystal¹ and epitaxial films¹⁵⁸ do suggest roughly an order of magnitude variation in activity amongst different facets. Step poisoning, undercoordinated surface defects, and/or surface reconstruction may contribute to this discrepancy between experimental and theoretical results, as discussed earlier in Section 3.1.

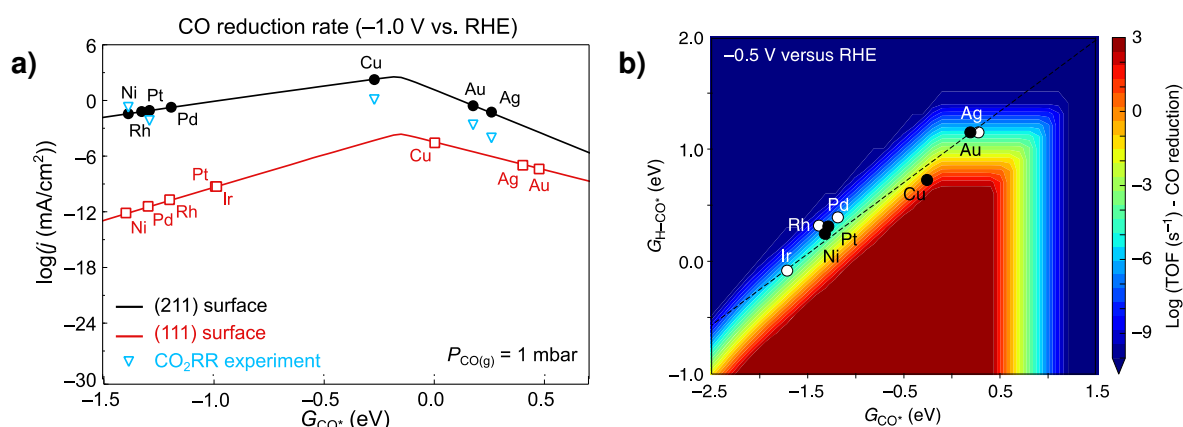


Figure 16: **a)** Kinetic volcano for CO reduction to CH₄ on transition metals. CO₂R Experiments from Kuhl *et al.*²⁰⁴ A 1 mbar CO pressure was assumed in the kinetic model to compare CO and CO₂R rates. **b)** 2D Volcano reflecting the dependence of activity on H-CO transition state and CO scaling. Both figures are reprinted from Liu *et al.*¹⁶⁹ This work is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>).

The C₂ kinetic model of Head-Gordon *et al.*²⁶¹ considers the initial C-C coupling steps, with energetics determined through an implicit solvent model. The coupling barriers for CO dimerization were found to slightly increase with more cathodic potential, such that the dimerization pathway shuts down in favor of CO-CHO coupling at high overpotential. The resultant kinetics suggested a decrease

in C₂₊ products at moderate overpotentials, consistent with DEMS experiments on Cu(100).¹⁶⁴ This picture is in contrast to an atomistic picture, where cation concentrations, and therefore CO dimerization rates, should increase with decreasing potential. The physical origin of these effects and the differences between conclusions obtained through implicit and explicit approaches requires further evaluation.

4.2.7 Rate-Limiting Electron Transfers

Rate-limiting electron transfers in CO₂ reduction has been a recurrent and contentious theme in the current theoretical literature. In particular, CO dimerization has been postulated to have a rate-limiting electron transfer decoupled from proton transfer.²⁸⁴ However, adsorbate states are strongly coupled to the metal surface, where electrons are readily available. Adsorbate-induced states have widths on the order of eV,^{169,277} and the corresponding rate of electron jumps is then of the order 10¹⁵/s; therefore the electrons respond adiabatically to the configurational changes of the reaction intermediates along the reaction pathway.²⁷⁸

One motivation for the hypothesis behind rate-limiting electron transfers is the experimental observation of a lower onset potential (*vs.* RHE) for C₂₊ products with increased pH,^{164,286} which is consistent with the analysis of the pH independence of ethylene formation on the SHE scale in the seminal work by Hori.¹⁶⁰ The idea is that a rate-limiting electron transfer decoupled from proton transfer would show an absolute potential (*e.g.*, *vs.* SHE) dependence, which is invariant with pH since the chemical potential of protons is not involved. Absolute potential dependence then translates to more positive onsets on an RHE scale, which accounts for pH. However, dependence on the absolute potential can also arise from either proton-electron transfer from H₂O, which is the proton source in neutral to basic solution, or through field-stabilization of chemical steps with large dipoles. Indeed, hydrogen evolution current densities from metal surfaces have been observed to depend only on SHE potential under a range of pH from neutral to very alkaline conditions,²¹⁹ which also translates to earlier onsets as pH is increased.

The effects of pH on C₂ *vs.* C₁ selectivity and activity for COR and CO₂R on Cu(211) was examined in a kinetic model that was based on *ab initio* activation energies and mean-field adsorbate-

adsorbate interactions.²¹³ In general, as discussed in Subsection 3.3.1, the C_{2+} activity is enhanced at high pH and only shows a dependence on the absolute potential, while the C_1 activity shows a lesser enhancement with increasing pH.^{160,201} H_2 formation was shown to exhibit a similar SHE dependence to C_2 activity.²⁰¹ The kinetic model suggested that the pure SHE dependence of C_2 and H_2 activities was due to an early rate-determining proton-electron transfer ($*OCCO$ to $*OCCOH$, and the Volmer step, respectively) while the mixed RHE/SHE dependence of C_1 activity was due to a later proton-electron transfer ($*CHOH$ to $*CH$). The latter is in line with the hypotheses from Hori's original study.¹⁶⁰ **Figure 17** shows the experimental²⁰¹ and theoretical²¹³ curves for CO reduction at pH 7 and 13.²¹³ Overall, the major qualitative features between experiment and theory are in agreement. The depletion of C_2 products at high overpotentials arises from a decreased CO coverage upon the onset of C_1 production; since C_2 production rates are 2nd order in CO coverage, C_2 activity is affected significantly more than C_1 products by decreases in coverage. This effect is worsened with mass transport limitations. The branching out of the C_1 activity at high overpotentials is due to a transition to a regime where the $*CO$ to $*CHO$ electrochemical step is rate limiting, in line with the conclusions from Liu *et al.*¹⁶⁹

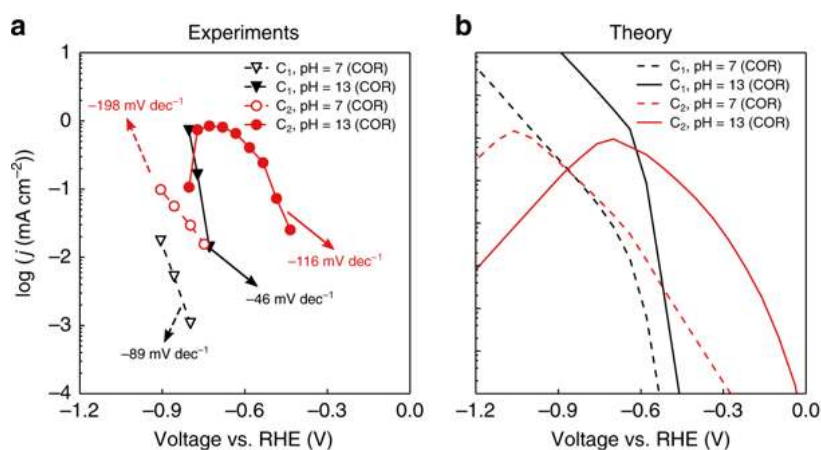


Figure 17: a) Measured COR activities towards C_1 and C_{2+} products on polycrystalline Cu at pH 7 and 13. Data from Ref. ²⁰¹ **b)** Predicted COR polarization curves from microkinetic model at pH=7 and pH=13. Reprinted from Liu *et al.*²¹³ This work is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>).

Xiao *et al.* also investigated the energetics of reaction pathways on Cu(111) as a function of pH, using a hybrid of H-shuttling and implicit solvent models.²⁶² A pH dependence was added by correcting proton-electron transfer barriers with the shift in the chemical potential of a proton with pH,

0.06eV/pH unit (some examples given in **Table S3** in SI). However, as discussed above, under neutral and alkaline conditions, the source of protons is water, such that the electrochemical barriers would show an absolute (SHE) potential dependence, translating to lower activation energies at higher pH. As a result of the model's pH correction, under alkaline conditions, all H transfers are less favored relative to C-C coupling. The main conclusion from this analysis was a higher C₂ selectivity at high pH, in accordance with experiment, but the assumptions behind the model applied require further examination.

4.3 Summary

In recent years, developments in atomistic modeling of the electrochemical interface have made the analysis of CO₂R pathways possible. Major advances in the field include the establishment of CO as a crucial reaction intermediate, investigations of cation promotion, the determination of the mechanism towards CH₄, where results from different explicit solvent methods appear to converge, and the establishment of design criteria for more active catalysts. On the other hand, there have thus far been little consensus in the theoretical literature regarding C₂ reaction pathways and their dependence on pH and facet termination, due to their inherent complexity, the sensitivity of the intermediates to the solvent and cation environment, and controversy regarding the origin of pH effects. Experimental evaluation of facet dependence is also challenging due to the possibility of surface reconstruction and defects in single crystal or epitaxial films, as discussed in Section 3.1. We suggest that, while the analysis of onset potentials from reaction energetics can offer significant insight, kinetic modeling is required to elucidate the interplay between coverage, potential dependence of activation energies, adsorbate-adsorbate interactions, and pH effects. Furthermore, we would like to highlight the need for development of multi-scale models²⁸⁷ that can help bridge quantum- and molecular-level dynamics with continuum models of reactant and product transport. Additional theoretical hurdles, not limited to investigations of CO₂R, are the reconciliation of differences in conclusions amongst existing theoretical approaches, the evaluation of the simplifying approximations made, and also development of new functionals for improved descriptions of charge at the interface, which would have major implications on the accuracy of the associated energetics.

5. Electrochemical CO₂ Reduction Pathways on Cu

Ever since Hori's discovery in 1985 that CO₂ is reduced to hydrocarbons on Cu electrodes with relatively large Faradaic efficiencies,⁸² many researchers have put a lot of effort into elucidating the reaction mechanisms of CO₂R on Cu. However, after three decades of work, there is still little consensus. Understanding the mechanisms by which products are formed during CO₂R is essential for the development of effective catalysts that can better meet our needs. Therefore, at this point, we would like to present our current state of understanding of the mechanistic pathways for CO₂R on Cu (**Figure 18**), which takes into account a variety of both experimental and theoretical studies described in the previous two chapters.

First we'll provide a few brief notes about the structure and flow of this figure. We have drawn the intermediates in a way that consistently gives each carbon atom a valency of 4, even though this sometimes differs slightly from the way the intermediate was drawn when proposed. The number on the horizontal axis is the number of carbons in an intermediate or product. The number on the vertical axis is the number of electrons transferred to the intermediate or product, which is four times the number of carbon atoms minus the total oxidation state of the species. The total oxidation state is taken to be the sum of the formal oxidation states of the carbon atoms plus the number of surface-oxygen bonds, representing the fact that bound oxygen has to be reductively cleared from the surface to complete a catalytic cycle.²⁰² The formal oxidation of each carbon atom is defined as the sum of the contributions from each of the four bonds: C-H bonds contribute -1 to the carbon atom's oxidation state, C-O bonds contribute +1, C-C bonds and C-surface bonds contribute 0, and an unbound electron pair contributes -1. A dotted bond contributes exactly half as much to the carbon atom's oxidation state as a full bond. Note that these rules are a formalism which actual charge distribution does not rigorously obey. When named, intermediates are generally referred to using the name of their desorbed state. For a bound intermediate to desorb, a pair of bonds to the surface are replaced by an additional bond in the molecule, enabling tautomerization if a C-C double bond is formed adjacent to an OH group.⁶⁶ If an intermediate with an odd total oxidation state were to desorb from the surface without an electron transfer, it would form a free radical.

Concerted proton-electron transfer (CPET) steps are represented by solid lines going down one level, while dashed lines involve no proton transfer, dash-dotted lines are coupling reactions involving neither proton nor electron transfer, and dotted lines involve multiple electron transfers. To simplify the figure, we have attempted to group mechanistic proposals that are consistent with each other, also considering which research groups have supported or contributed to each other's proposed mechanisms. The remainder of this chapter summarizes the key reasoning behind the proposed mechanisms based on the experimental and theoretical studies discussed in the previous two chapters. In short: the mechanism in black was proposed by Hori based on his own and other early research in the field.^{85,160} The mechanism in red includes a one-carbon (C_1) pathway²⁰² and initial C-C coupling mechanism²³⁴ proposed based on DFT calculations by the group of Jens Nørskov, and a C_2 pathway based on experimental work from Thomas Jaramillo's group.⁶⁶ The mechanism in blue was proposed by the group of Marc Koper¹⁶ based on a combination of their experimental observations¹¹³ and theoretical calculations,²⁸⁴ as well as much of the C_1 pathway suggested by the group of Michael Janik.²⁶⁴ The mechanisms in purple are works by the Goddard group.^{211,275} The orange lines represent a mechanism combining $2e^-$ product pathways from a combined theory-experiment study,²⁸⁸ and $>2e^-$ C_1 and C_2 pathways determined from microkinetic modeling.²¹³ Finally, the green lines depict recent reports on $2e^-$ pathways¹³⁵ and C_2 pathways.²⁰⁸ Keep in mind that the division of mechanistic proposals in **Figure 18** is not absolute or complete. For example, there are many individual theoretical studies described in Chapter 4 that only overlap with certain portions of more extensive mechanistic frameworks shown here. Furthermore, the field is developing quickly, with researchers often adding, removing, and adjusting proposed pathways. Thus, for clarity, the goal of this figure is not meant to be entirely exhaustive in representing *all* references and the divergences between them, but rather to show several schools of thought that have evolved over time. It is also worth noting that a few other reports have similarly provided mechanistic overviews in recent years.^{8,276,289,290}

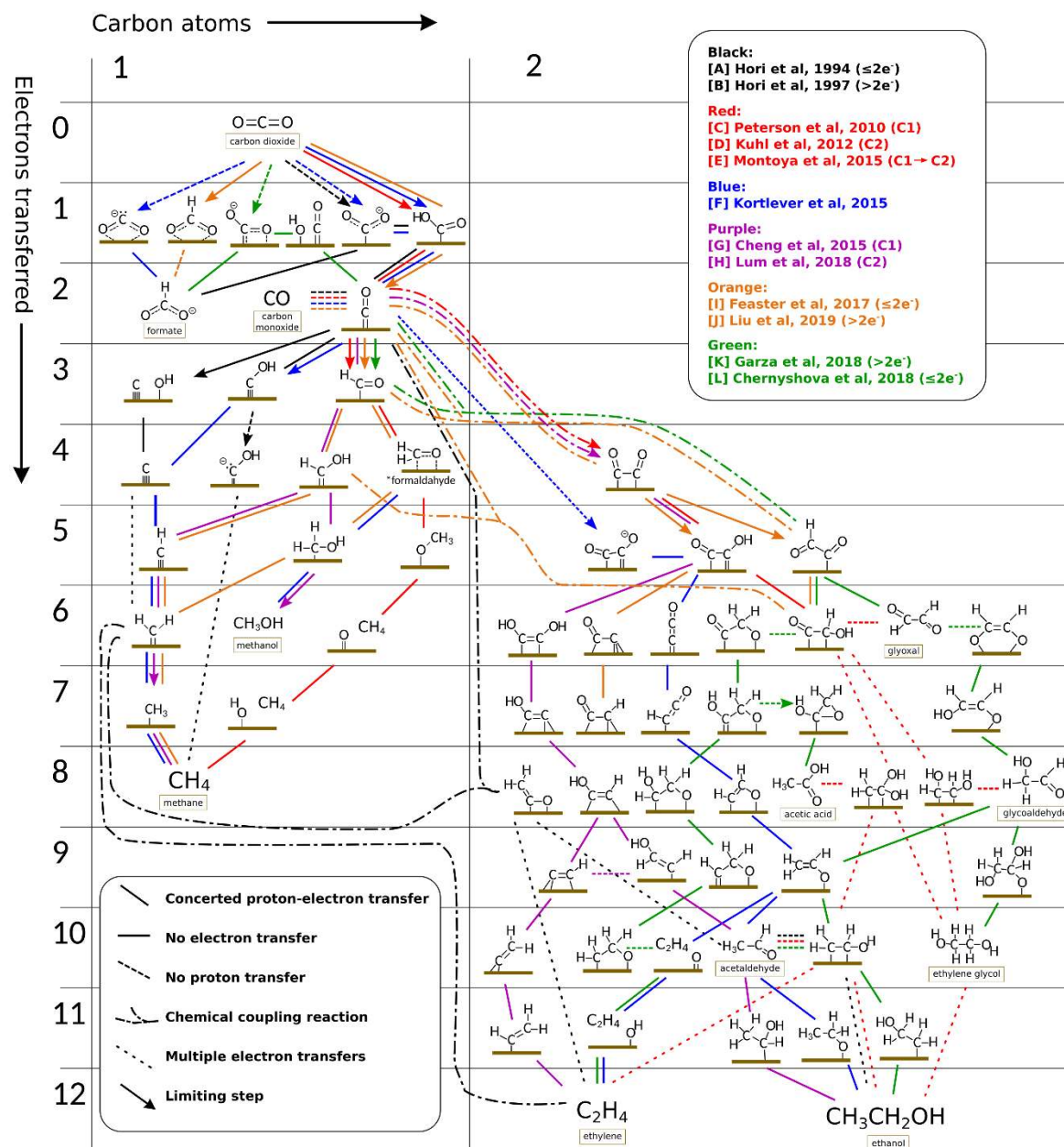


Figure 18: Possible mechanistic pathways of CO_2 reduction to C_1 and C_2 products on polycrystalline copper, grouped into different colored reaction schemes taken from the works in the top-right legend: [A] Hori et al.⁸⁵; [B] Hori et al.¹⁶⁰; [C] Peterson et al.²⁰²; [D] Kuhl et al.⁶⁶; [E] Montoya et al.²³⁴; [F] Kortlever et al.¹⁶; [G] Cheng et al.²⁷⁸; [H] Lum et al.²¹¹; [I] Feaster et al.²⁸⁸; [J] Liu et al.²¹³; [K] Garza et al.²⁰⁸; [L] Chernyshova et al.¹³⁵. The bottom-left legend states the meaning of the texture of the lines connecting intermediates. Expanded from the mechanistic compilation by S. Scott.²⁹¹

In general, most mechanisms agree that the step in which CO_2 is adsorbed is the limiting step in CO_2R to $2e^-$ products, but there is some uncertainty on whether this first intermediate is arrived at by CPET or a decoupled pathway through a charged intermediate.¹⁶ Then, whether this intermediate binds through the carbon atom or oxygen atom(s) is thought to be a key distinction between the formate and

CO pathways. A recent combined experimental and theoretical study found clear volcano trends for the $^*\text{COOH}$ binding energy and $^*\text{OCHO}$ binding energy for CO_2R to CO and HCOO^- , respectively, indicating that these are likely the main intermediates for these products.²⁸⁸ Alternatively, a recent report combining *operando* surface-enhanced Raman scattering (SERS), and DFT simulations provide evidence that the first intermediate to both HCOO^- and CO on Cu electrodes is a carboxylate anion $^*\text{CO}_2^-$.¹³⁵ However, rather than being bound through the carbon atom or the oxygen atoms, as shown above, the authors propose that carboxylate is coordinated to the surface through one of its C-O bonds, rigorously using isotope exchange and electrochemical Stark effects to verify the assignment of relevant SERS peaks. Then, DFT simulations suggest that this intermediate is converted into HCOO^- and CO via activation of the Cu-C and C-O bonds and stabilization of the Cu-O bond, respectively, with increasing negative potential.¹³⁵ Thus, while different intermediates are proposed, evidently both the Cu-C and Cu-O bond strengths may still serve as key descriptors governing the selectivity of Cu to both CO and HCOO^- .

As discussed earlier, it is widely accepted that CO is the key intermediate to $>2e^-$ products. Beyond $^*\text{CO}$, a significant distinguishing feature between the C_1 and C_{2+} pathways is the observed sensitivity to pH. It has been shown that the ethylene formation pathway is pH independent on the SHE scale, whereas the methane formation pathway is pH dependent on the SHE scale,^{160,201} which leads to the experimental observation of a lower onset potential (*vs.* RHE) for C_{2+} products with increased pH. Accordingly, the limiting step in C_1 formation has been thought to be CO protonation either through a $^*\text{COH}$ or $^*\text{CHO}$ intermediate,^{113,160,202,264,275,292} while the limiting step in C_{2+} formation has generally been thought to be CO dimerization that is decoupled from proton transfer.^{2,113,234,260,261,284} Theoretical calculations have differed in their view of $^*\text{COH}$ *vs.* $^*\text{CHO}$ depending on the computational techniques and assumptions. A recent microkinetic model has suggested that this C_1 rate-limiting step actually changes under different applied potentials, with $^*\text{CO} \rightarrow ^*\text{CHO}$ being limiting at high overpotentials and $^*\text{CHO} \rightarrow ^*\text{CHOH}$ being limiting at low overpotentials.²¹³ Furthermore, contrary to the above, this microkinetic model has also suggested that the C_{2+} pathway could indeed be limited by a CPET step, since the first proton-electron transfer from water to an adsorbate would yield a pure dependence on the

absolute potential (*i.e.*, it is pH independent on the SHE scale).²¹³ However, it is equally suggested that this pH independence could also arise from field-stabilization of a limiting chemical reaction with large dipoles (*i.e.*, CO dimerization), which is supported by studies investigating cation effects. This analysis highlights the need for future theoretical studies to consider not only thermodynamics but also reaction kinetics due to the complicated interplay between adsorbate coverages, adsorbate-adsorbate interactions, field effects, etc.

While CO dimerization has been widely suggested, there are many aspects to this step that are still up for debate, such as whether CO coupling is an electrochemical step (involving a rate-limiting electron transfer)^{2,113,234,261,284} or is purely a chemical step (not involving a rate-limiting electron transfer)^{234,261} and whether coupling occurs between two adsorbed CO molecules (*CO + *CO)^{2,113,234,260,261} and/or an adsorbed and a free CO molecule (*CO + CO_(g)).^{208,284} Additionally, some studies also include the possibility of coupling between species such as *CHO and *CO²⁶¹ or CO_(g),^{208,260} particularly at higher overpotentials. This partially stems from the notion that there are two possible pathways to ethylene depending on the surface structure and overpotential. A series of studies on Cu single crystals have noted a low overpotential pathway (CO dimerization) preferred on Cu(100) and a higher overpotential pathway shared with CH₄, likely through *CHO, that is preferred on Cu(111).^{164,166,167} This is consistent with the higher selectivity for C₂H₄ observed on Cu(100) compared to Cu(111), as discussed in Subsection 3.1.1. Furthermore, a recent study employing *in-situ* Fourier-transform infrared spectroscopy (FTIR) observed a hydrogenated CO dimer intermediate at low overpotentials on the Cu(100) surface but not Cu(111), providing strong support for this mechanism.¹⁴¹ While the authors assigned this species to be *COCOH based on their DFT calculations, another theoretical study²⁰⁸ suggested that, since the vibrational frequencies of adsorbates depend strongly on their adsorption mode, their calculated *COCHO structure could also have signals in the same range. Thus, discussions continue as to whether the CO dimerization pathway proceeds through a *COCHO^{208,234,261} or *COCOH^{141,260,284} intermediate.

Finally, it is also worth mentioning that alternate C₂₊ mechanisms have been proposed involving dimerization of CH₂ groups,^{104,160,276,293} dimerization of CH₃ groups,²⁹⁴ coupling of two hydrogenated

CO species,^{276,281} and a Fischer-Tropsch-like CO insertion mechanism of adsorbed CH₂ and CO.^{130,160,293}

While these may be thermodynamically feasible, it is suggested that the surface concentration of these intermediates is likely to be too low for them to be a major source of C-C bonds.²⁰⁸ However, this could be highly dependent on the reaction conditions, and thus, these possible mechanisms cannot be conclusively ruled out.

Within the C₁ pathway, the selectivity between methane and methanol is of particular interest, as methanol is by far the more valuable product (**Figure 2**), but has proven elusive. As discussed earlier in Subsection 3.2.2, species related to formaldehyde have been thought to serve as intermediates for methane and methanol formation. One plausible pathway is *CHO → *CH₂O → *CH₃O → CH₃OH or CH₄.²⁰² The lack of reduction of methanol to methane¹¹³ is one indicator that this may not be the most facile route to methane, although the reduction of formaldehyde primarily leads to methanol,^{108,113,160} suggesting that this may be an intermediate on the route to methanol formation. Still, Kuhl *et al.* observed methane and methanol formation on a number of transition metals and saw that the onset potentials for methane and methanol formation are closely correlated, indicating a mechanism in which these products share a common limiting step.²⁰⁴ Cheng *et al.* (purple C₁ lines in **Figure 18**) found that after subsequent protonation of *CHO, *CHOH is the likely branch point between methanol (*CHOH → *CH₂OH → CH₃OH) and methane (*CHOH → *CH → *CH₂ → *CH₃ → CH₄), with the latter pathway being more favorable.²⁷⁵ Thus, *CO protonation to *CHO could still apply to both pathways. Interestingly, Kuhl *et al.* found methanol but no detectable methane on Au (the least oxophilic metal studied) and methane but no detectable methanol on Fe (the most oxophilic metal studied), while the other 5 metals tested (Ag, Zn, Cu, Ni, Pt) produced both.²⁰⁴ Thus, the oxophilicity of the surface may play an important role in determining the selectivity between these two products.

Interestingly, when the selectivity towards methane is increased, a deactivation effect occurs that is not present when ethylene is the major product.¹¹⁰ This implies that large amounts of poisoning intermediates form on Cu in the C₁ pathway, and such intermediates may not take part in the C₂₊ pathway. A likely culprit in this regard is graphitic carbon. Some reports suggest that graphitic carbon can serve as an intermediate in CO₂R,^{107,264,295} and as shown above, a possible pathway to CH₄ could go

through $*\text{COH} \rightarrow *C \rightarrow$ subsequent hydrogenation to CH_4 .²⁶⁴ Buildup of graphitic carbon has been commonly suggested as a cause for deactivation though, so this could explain why deactivation is seen on Cu electrodes that more predominantly make CH_4 . This could also explain why nanostructured Cu electrodes, which typically exhibit suppression of the CH_4 pathway, have demonstrated increased stability with minimal or no deactivation observed over long term electrolysis.^{90,108,116,117} In addition, the increased surface area of nanostructured electrodes can itself be a cause for their increased stability since the higher ratio of ECSA to electrolyte volume can reduce the impact of poisoning via other mechanisms, such as deposition of trace metal impurities in the electrolyte.^{88,110,115} Furthermore, the surface area of Cu electrodes also plays a key role in determining selectivity, which will be addressed in the next chapter.

As can be seen in the right half of **Figure 18** above, the proposed mechanisms for C_2 products diverge completely after the C-C coupling step, and we refer the reader to the original studies for the detailed reasoning behind each proposed mechanism.^{16,66,160,208,211,213,234} In short, as discussed in Subsection 3.2.2, the reduction of oxygenated species such as glyoxal, glycoaldehyde, acetaldehyde, propionaldehyde, etc. have led to identification of possible intermediates and pathways to alcohols. In addition, water has recently been shown to play an important role in the formation of certain oxygenated products.²¹¹ Under strongly alkaline conditions, Cannizzaro-type disproportionation reactions in the electrolyte may also lead to the formation of alcohols and carboxylic acids from the corresponding aldehyde.²¹² In terms of potential-dependent trends, some studies have demonstrated that oxygenates are preferred over hydrocarbons at lower overpotentials.^{115,201} Overall, there is still much being learned about what dictates selectivity between the various C_{2+} oxygenates and hydrocarbons. Through future work developing *in-situ/operando* spectroscopies, isotope labeling experiments, and computational methods involving kinetic modeling, we may be able to ascertain the distinguishing features of the dominant pathway(s) in order to tailor CO_2R activity and selectivity towards the desired product(s).

This concludes our brief overview of reaction networks for CO_2R on Cu. In the chapters that follow, we will expand on this framework and discuss deeper insights on activity & selectivity trends that have been gained from studying more advanced (nanostructured and bimetallic) Cu catalysts.

6. Nanostructured Copper

Nanostructuring of Cu electrodes has been widely applied in attempts to improve selectivity and energy efficiency for CO₂R. Nanostructuring of electrocatalyst materials leads to improved geometric activity (current density normalized to the geometric surface area of the electrode) due to an increase in the electrochemically active surface area (ECSA) compared to planar electrodes. In addition, it can oftentimes lead to altered electrocatalytic properties compared to those of planar electrodes. These differences can be caused by a number of effects, including, but not limited to, a higher occurrence of undercoordinated sites, preferential faceting, changes in the local pH, and re-adsorption of products.^{296,297} In this work, we classify the Cu nanomaterials into two different types of systems: (supported) nanoparticles (Section 6.1) and (unsupported) three-dimensionally interconnected electrodes (Section 6.2). It is important to note that these two sections both address aqueous phase CO₂R, meaning that CO₂ is delivered to the electrode via diffusion through the aqueous electrolyte. Vapor-fed CO₂R systems, where the CO₂ is delivered directly to the electrode in the gas phase, will briefly be addressed in Section 6.3. In this chapter we will only discuss pure Cu systems, in some cases on a support material; nanostructured bimetallic systems with Cu are covered in Chapter 7.

6.1 Nanoparticles

Nanoparticles are individual particles with a diameter of 100 nm or less that are typically supported on a suitable material. Since all heterogeneous catalytic processes take place at the surface, the high surface area to volume ratio of nanoparticulate catalysts allows for greater utilization of a given material on a mass basis. This is an important concern for precious metal catalysts, but is less of an issue for Cu because of its natural abundance.²⁹⁸ An important motivating factor for studying nanoparticle catalysts is their high degree of compatibility to be incorporated into gas diffusion electrodes (GDEs) and membrane electrode assemblies (MEAs); these vapor-fed systems will be discussed in Section 6.3. Here we will detail work that has been done to study the fundamental effects of nanoparticle size, shape, and loading on CO₂R performance in aqueous-phase reactors.^{299–307}

6.1.1 Nanoparticle Size Effects

Particle size can have a direct influence on the reactivity of a catalyst material. This comes down to a number of possible effects, mainly related to a significant increase in the surface to bulk atom ratio as the size is decreased. Firstly, as the size of a particle decreases the curvature of its surface becomes larger and the average coordination of the surface atoms is lowered, due to a higher occurrence of undercoordinated sites.³⁰⁸ Decreasing the coordination number of catalytically active atoms leads to perturbed electronic structure and oftentimes increased reactivity. Furthermore, for very small particles, a significant amount of strain is induced on the surface atoms. This shifts the d-band and, again, influences reactivity.³⁰⁹ Depending on the catalytic process and material, increased reactivity may improve or deteriorate activity. For simple $2e^-$ processes, the effect of changes in reactivity can be predicted by determining the optimum binding energy of the key intermediate.²⁰⁵ However, CO_2R pathways to $>2e^-$ products are inherently much more complex (as was shown in **Figure 18**) and involve many more proton-electron transfers and intermediate species. Therefore, it is hard to predict the effect of changes in the electronic structure on the catalyst performance, and both theory and experimental work are needed.

Based on the concepts outlined above, a few different groups have investigated size effects of Cu nanoparticles for CO_2R .^{299–301} The results from various individual studies generally show different trends. Importantly, they all used different catalyst synthesis methods, which can lead to different nanoparticle size, morphology and stability. If ligands are used during synthesis, they can bind to active sites and alter the activity if not completely removed before electrochemical testing. Furthermore, Cu is inherently mobile, in particular in the presence of CO.¹⁷⁵ Thus, depending on the initial geometry, significant restructuring can take place under reaction conditions, which can cause changes in nanoparticle size, shape, and distribution.

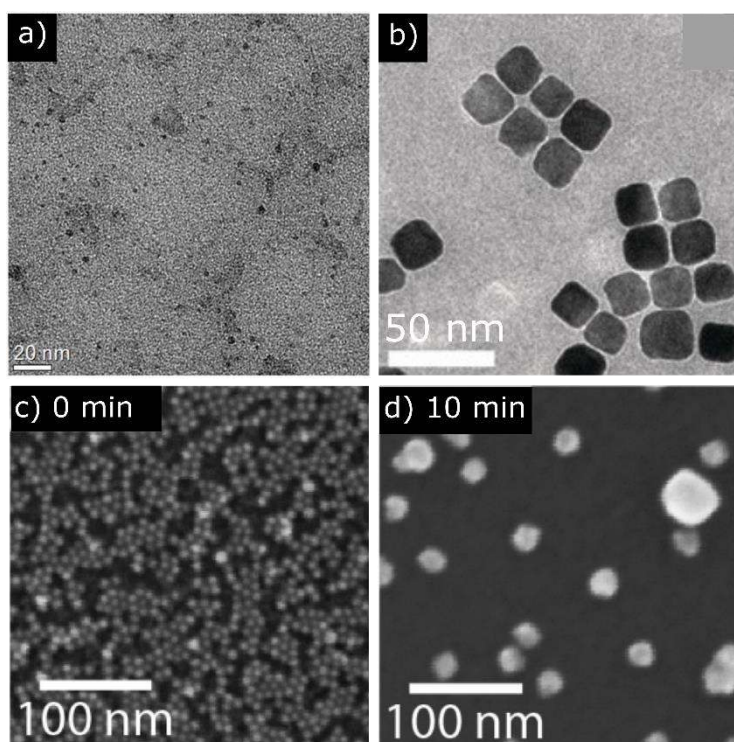


Figure 19: TEM images of Cu nanoparticles from various studies. **a)** Spherical particles, 2.4 nm average diameter. Reprinted from Reske *et al.*²⁹⁹ Copyright © 2014, American Chemical Society. **b)** Cubic particles, 24 nm average edge length, Reprinted with permission from Loiudice *et al.*³⁰¹ Copyright © 2016, John Wiley and Sons. **c)** and **d)** Spherical particles as-prepared and after 10 min CO₂R at -1.25 V vs. RHE, respectively. Reprinted from Manthiram *et al.*³⁰⁰ Copyright © 2014, American Chemical Society.

Reske *et al.* synthesized various Cu nanoparticle electrodes of diameter 15 nm and smaller. A TEM image of a representative sample is displayed in **Figure 19a**. When measuring CO₂R, the authors observed that the samples exhibited lower CO₂R Faradaic efficiency towards hydrocarbons and increased selectivity to the formation of CO and H₂ as compared to polycrystalline foils, as displayed in **Figure 20b**.²⁹⁹ Furthermore, they showed that particles smaller than 5 nm gave rise to significantly increased current density at a fixed potential, which led to increased production rates for the various products as displayed in **Figure 20a**. Surprisingly, no clear trend in product distribution could be observed with changing particle size in this study. Manthiram *et al.*, on the other hand, reported enhanced methane production between -0.95 and -1.45 V vs. RHE on Cu nanoparticles with an initial size of 7 nm, as compared to polycrystalline Cu.³⁰⁰ These nanoparticles quickly sintered, as illustrated by the transformation over 10 minutes of CO₂R shown in **Figures 19c** and **19d**. Loiudice *et al.*

synthesized larger, cube shaped nanocrystals of 24-63 nm, with a TEM image of a 24 nm particle sample displayed in **Figure 19b**.³⁰¹ They showed an optimal CO₂R Faradaic efficiency of around 80%, with high selectivity toward ethylene, for 44 nm particles at -1.1 V vs. RHE. As mentioned above, the divergence between these three studies can have different reasons. Manthiram *et al.* showed that their 7 nm particles aggregated to form larger clusters with an average size of 23 nm shortly after introduction to the catalytic environment.³⁰⁰ Furthermore, two of the studies used spherical particles,^{299,300} while the third mainly studied cube-shaped particles.³⁰¹ As discussed in Section 3.1, differences in surface structure can influence product distribution, and to some extent activity. Finally, different loadings were used, both between the different studies and within a single study. The effect of this will be discussed in the following subsection. Unfortunately, the diverging results make it difficult to draw clear conclusions about trends for different sizes of Cu nanoparticles.

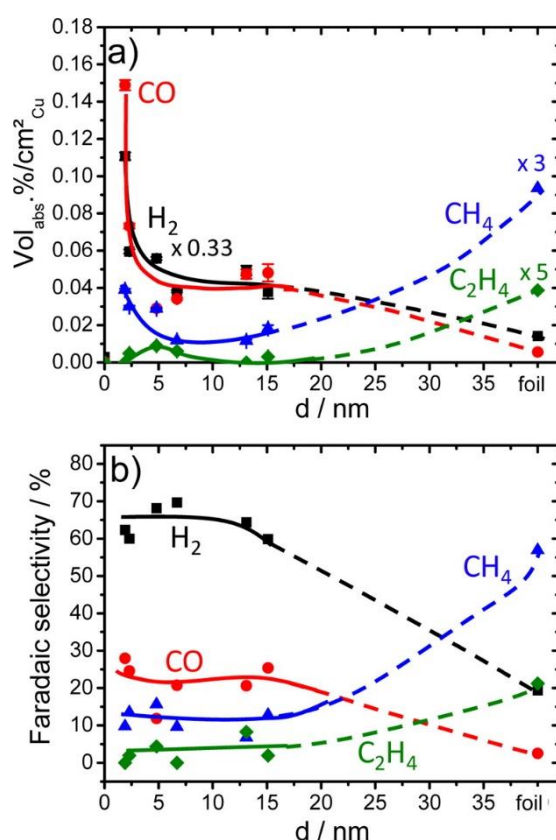


Figure 20: CO₂ reduction on Cu nanoparticles of different size at -1.1 V vs. RHE. (a) Production rate of individual products. (b) Faradaic efficiency to individual products. Reprinted from Reske *et al.*²⁹⁹ Copyright © 2014, American Chemical Society.

6.1.2 Loading/Interparticle Distance

Another parameter that can influence the CO₂R activity and selectivity of nanoparticles is the amount that is loaded onto the support.^{302,303} Mistry *et al.* used inverse micelle encapsulation to synthesize nanoparticles with well-defined size and interparticle distance.³⁰² They found some variation in the product distribution with loading, depending on particle size, but no clear trend, similarly to what was the case for the study of pure size effects, as discussed above. They attributed the effects to re-adsorption of products/intermediates and local pH effects. Kim *et al.* investigated three widely different loadings of 6.7 nm Cu particles on carbon paper.³⁰³ The highest loading was studied further, leading to observations of a structural transition of nanoparticle ensembles into cube-shaped structures. This coincided with a shift in product distribution towards more C₂₊ compounds and lower H₂ evolution, possibly caused by the exposure of different surface sites and/or local pH changes in the rough structure. The studies mentioned above should be followed up with further work regarding mass transport effects on CO₂R activity and selectivity for Cu nanoparticle systems. Additional well-controlled studies using alternative synthesis techniques and three-dimensional support materials will help to elucidate some of these phenomena.

6.1.3 Shape Effects

As discussed in Subsection 3.1.1, certain Cu single crystal facets exhibit improved selectivity to specific products. Cu(100) electrodes, and especially “miscut” Cu(100) electrodes with an optimal density of steps, have been shown to exhibit higher selectivity for C-C coupling than other planar surfaces.^{154,158,164,167} Reports also suggest that the production of oxygenates is enhanced on certain crystals, including single crystals with (100) and (110) terraces and varying step density, as well as epitaxially grown Cu films with (751) orientation.^{153,154,158} Motivated by the work on single crystals, some effort has gone into increasing the occurrence of certain facets by controlling nanoparticle shape. For instance, the surface of cubic structures should be dominated by (100) facets since Cu is a face-centered cubic (FCC) metal. In addition, unlike perfect single crystals, faceted nanoparticles also contain edge and corner sites, which could affect the resulting activity strongly. For instance, recent

DFT results suggest that Cu(211), which exhibits a high density of surface step sites, yields several orders of magnitude higher activity than (100) and (111) surfaces for CO reduction to CH₄.¹⁶⁹

Cubic Cu nanoparticles have been synthesized by different groups, as discussed in the previous two subsections.^{301,303,310} A representative TEM image is shown in **Figure 19b**. These particles exhibit enhanced C₂₊ product selectivity compared to polycrystalline Cu, possibly caused by increased occurrence of (100) facets. However, Grosse *et al.* reported drastic morphology changes undergoing during CO₂R, including loss of the cubic shape.³¹⁰ Li *et al.* produced thin nanowires with well-defined five-fold twinned edges, exhibiting high selectivity towards CO₂R, with CH₄ produced almost exclusively around -1.25 V *vs.* RHE.³⁰⁴ It is unclear, however, which facets are exposed on the terraces of the nanowires. It is also worth mentioning that -1.25 V is a large overpotential, where polycrystalline Cu also mainly produces methane from CO₂R.⁶⁶ Furthermore, at potentials more negative than -1.0 V *vs.* RHE, polarization effects begin to impact CO₂R catalysis on planar polycrystalline Cu,⁹⁷ meaning that these high surface area nanowire electrodes will likely experience mass transport limitations at even lower applied potentials. We would like to underline the importance of measuring novel catalyst materials at potentials where mass transport limitations are not prevalent in order to more directly investigate their intrinsic behavior; this issue was discussed in more detail in Section 2.2.

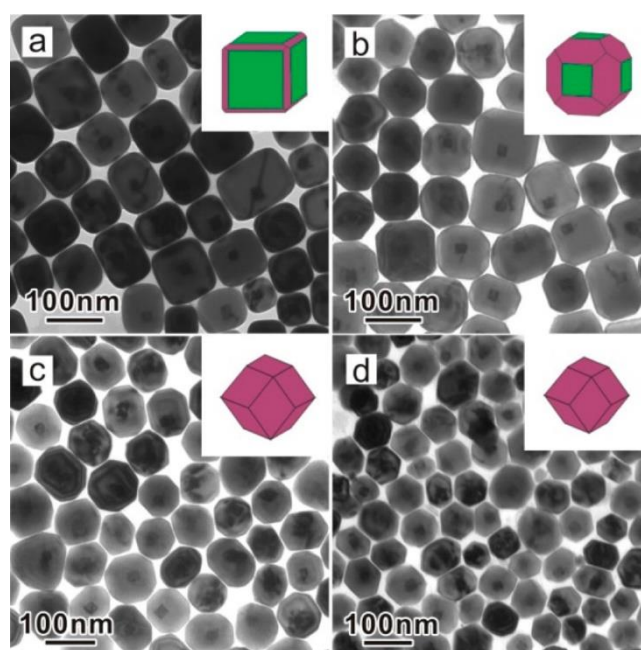


Figure 21: Cu nanoparticles prepared by etching cubic particles for different durations: **a)** 4 h, **b)** 8 h, **c)** 12 h, and **d)** 24 h. Reprinted from Wang *et al.*³⁰⁵ Copyright © 2016, American Chemical Society.

The studies mentioned in the previous paragraph utilized bottom-up methods to obtain faceting of their particles. With a different, top-down approach, Wang *et al.* used chemical etching of cubic Cu nanoparticles with varying duration to obtain different shapes, as shown in **Figure 21**.³⁰⁵ The nanocrystals that were etched for 12 hours or more (**Figures 21c** and **21d**) exhibited a rhombic dodecahedral shape with preferential exposure of (110) facets. These particles exhibited enhanced selectivity to hydrocarbons and reduced CO production at around -0.8 V *vs.* RHE. The authors did not, however, report any liquid products. As mentioned above, Hori *et al.* reported that single crystals with (110) orientation exhibit significantly enhanced production of oxygenates.¹⁵³ Therefore, it is likely that oxygenates were produced from these measurements as well. This emphasizes the importance of carrying out thorough product analysis, since this information can give significant fundamental insight. An important point to consider when investigating shape effects is stability, both in terms of activity and retaining the synthesized shape. This is particularly important for Cu, where structural transformations are likely due to its high mobility. In an attempt to address this issue, Huang *et al.* studied the development of shape and CO₂R activity of the cubic Cu nanoparticles shown in **Figure 19b** with electrolysis time. Using TEM, they performed *ex-situ* monitoring of changes to the morphology of the nanoparticles after various durations of electrolysis up to 12 h, while also tracking activity and product distribution. They saw some changes with time; H₂ evolution activity increased and CO₂R activity decreased with longer duration for most samples, and the nanoparticle shape became increasingly ill-defined. They attributed the changes to adsorbate-induced restructuring of the Cu catalyst, yielding useful information for further studies. However, they did not provide conclusive evidence that this is the only or main cause of the deactivation. Importantly, they did not provide evidence that their electrodes were not contaminated, which can be challenging to avoid for such long-term measurements due to the highly negative polarization of the electrode.^{112,114,115} Furthermore, they only reported CO₂R at -1.1 V *vs.* RHE, which is in a potential region where non-planar electrodes are likely to start reaching mass transport limited activity. Thus, any trends in activity that are observed here might not be valid at lower overpotentials.

In general, more work on nanoparticles with preferential faceting would be welcome, in particular to elucidate the effect of particle shape in more detail, and to be able to decouple it from other parameters such as size, loading, support effects, etc. Further stability studies addressing the points raised in the previous paragraph would also be of value to the community.

6.1.4 Effect of Support and Catalyst-Ionomer Interaction

For any nanoparticle-based catalyst, a suitable support material is vital to ensure good dispersion and mechanical stability of the catalyst material. In addition, the interaction between support and nanoparticles can induce changes in the electronic structure of the catalyst and/or add interfacial sites, altering the performance of the catalyst. The support effect is utilized heavily in several industrial catalytic reactions, such as methanol synthesis on Cu/ZnO/Al₂O₃.³¹¹ However, only a limited number of studies investigating support effects in CO₂R have been reported to date. Song *et al.* showed that Cu nanoparticles supported on needle-shaped nitrogen doped carbon exhibit high selectivity towards ethanol production at high overpotentials, with a maximum Faradaic efficiency of 63% at -1.2 V vs. RHE.³¹² They attributed the high selectivity to the interaction between the nanoparticles and the highly textured support material. Subsequently, a number of further studies on Cu nanoparticles on various carbon supports reported significant selectivity towards ethanol³¹³ or ethylene.^{314,315}

Feng *et al.* synthesized Cu nanoparticles on graphene by physical vapor deposition, and observed a large number of grain boundaries.³¹⁶ From these non-equilibrium structures, they observe high selectivity towards ethanol and acetate from COR. Some works also report catalytic enhancement from metal-support interactions for CO₂R on Au and Ag.^{317,318} TEM images illustrating the geometry of these two studies are shown in **Figures 22a** and **22b**, respectively.

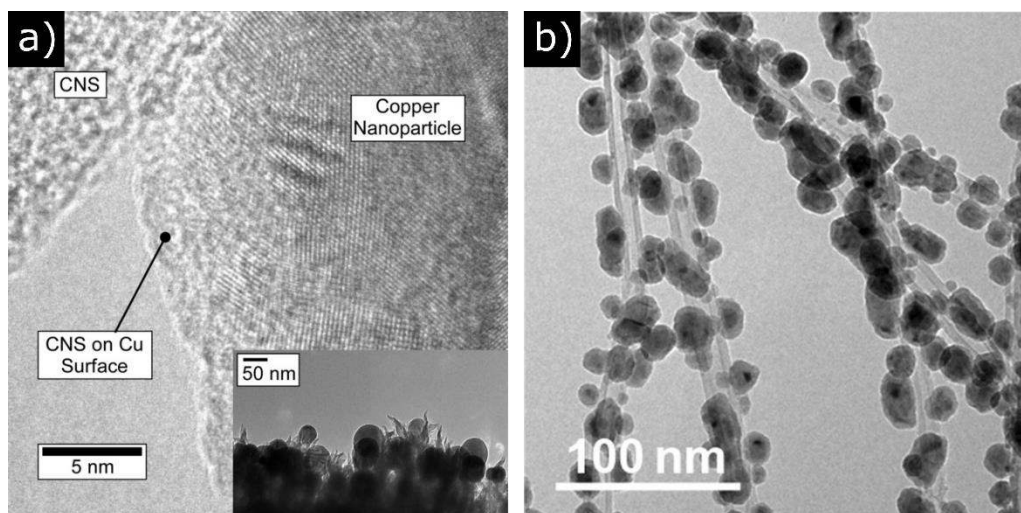


Figure 22: Transmission electron microscopy images of Cu nanoparticles on two different supports. **a)** Carbon nanospikes. Reprinted with permission from Song *et al.*³¹² Copyright © 2016, John Wiley and Sons. **b)** Carbon nanotubes. Reprinted with permission from Feng *et al.*³¹⁶ Further permissions related to this material should be directed to the American Chemical Society.

In moving towards more practical device designs, such as vapor-fed systems (Section 6.3), understanding how the other components including the support and ionomer materials impact CO₂R on Cu will become increasingly important. For example, it has previously been shown that an optimal ionomer loading exists for hydrogen oxidation electrocatalysts.³¹⁹ Gupta *et al.* tried to determine a similar ideal ionomer content for Cu nanoparticles, and found that optimal formate production occurs using 25% Nafion content in the catalyst ink.³⁰⁷ We would like to highlight the need for more fundamental studies in these areas in order to help translate aqueous-phase CO₂R catalysis to highly complex vapor-fed designs.

6.2 Three-Dimensionally Interconnected Catalyst Materials

Another approach to nanostructuring is the preparation of three-dimensionally interconnected (3-D) electrodes. In the following, we separate the discussion between oxide-derived and non-oxide-derived electrodes and consider how the different pretreatments influence CO₂R activity.

6.2.1 Oxide-Derived Copper

Rapid removal of oxygen during reduction of oxidized Cu is a straightforward means to achieve porous, inhomogeneous surfaces that exhibit altered CO₂R performance. Hori *et al.* were the first, to the best of our knowledge, to report CO₂R on this type of Cu electrode, which had significantly higher ECSA, as measured by the double-layer charging current.¹⁶⁰ Other early work by Karl W. Frese Jr. reported significant methanol production from CO₂R on intentionally oxidized copper electrodes.³²⁰ A large number of later works on similar catalysts have not reported methanol production; thus, it is still not clear how, if at all, methanol can be produced with significant selectivity from Cu electrodes. However, the preparation of nanostructured surfaces from oxidized precursors has still led to a number of interesting findings, which will be discussed subsequently. For ease of navigating the wide variety of materials that have been studied, we organize this subsection by the choice of synthesis method: thermal oxidation, anodic treatment, and other Cu₂O film-derived electrodes.

Thermal oxidation

Kanan and coworkers showed that calcination of planar Cu foils in air and subsequent electrochemical reduction resulted in high surface area 3-D electrodes.⁹⁰ An SEM image that illustrates the resulting surface structure can be seen in **Figure 23a**. When carrying out CO₂R on these electrodes, the selectivity towards CO and formate was improved between -0.2 and -0.7 V *vs.* RHE, compared to polycrystalline Cu foil. Similar studies have since been carried out using this thermal oxidation and electrochemical reduction method to alter the CO₂R activity of Cu electrodes, but a common approach has been to use a copper precursor material with a higher surface area than planar foils, such as Cu mesh, foam, and nanowire structures.^{92–94,321,322} Some of these studies report enhanced production of CO and formate, and little to no formation of >2e⁻ products.^{92–94} This corresponds well to the results by Kanan and coworkers.⁹⁰ On the other hand, two studies also showed enhanced selectivity for >2e⁻ products, such as hydrocarbons and alcohols, compared to polycrystalline Cu, which was not reported previously.^{321,322} Notably, CH₄ production was suppressed in favor of C-C coupled products. Possible causes for the discrepancy between these studies on calcined oxide-derived Cu electrodes could be

inadequate product analysis in some of the studies and varying mass transport conditions within the different catalyst morphologies and electrochemical cells used by the different research groups.

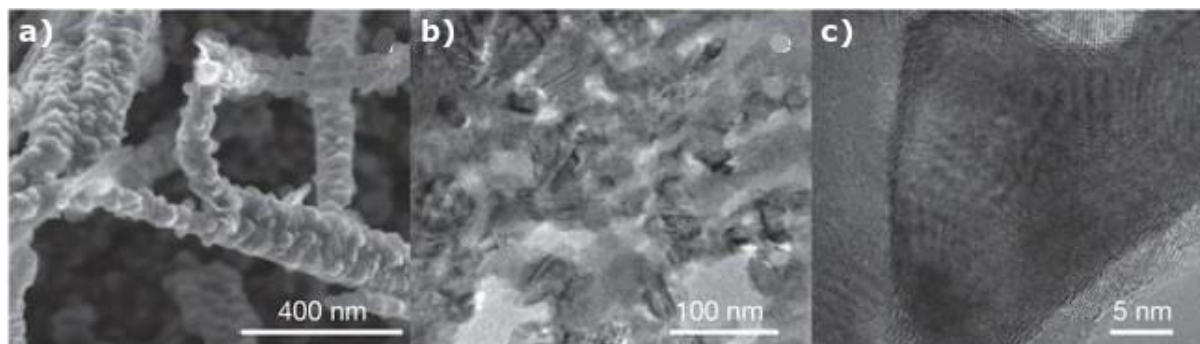


Figure 23: Electron microscopy images of calcined oxide-derived Cu electrodes. **a)** and **b)** SEM images. **c)** TEM image. Reprinted with permission from Li *et al.*⁷¹ Copyright © 2014, Springer Nature.

Kanan and coworkers also conducted CO reduction (COR) studies on their oxide-derived Cu foils.⁷¹ High COR selectivity was observed between -0.25 and -0.40 V vs. RHE, mostly towards the C₂ compounds ethanol and acetate. At -0.3 V vs. RHE, CO was reduced at a Faradaic efficiency of 57%, with an impressive 43% to ethanol production. Similarly high activity and selectivity towards COR was reported by Raciti *et al.* on Cu nanowires.³²³ However, due to the poor solubility of carbon monoxide in aqueous solutions,³²⁴ low maximum COR current densities were obtained in both of these studies. Nevertheless, such a high selectivity towards liquid products spurred much interest in this class of materials.^{91,316,325,326}

In the aforementioned COR study by Kanan and coworkers, a large number of grain boundaries in the calcined oxide-derived Cu electrodes were found using transmission electron microscopy (TEM), as illustrated in **Figures 23b** and **23c**.⁷¹ They hypothesized that the high selectivity could be caused by undercoordinated sites with special geometries that were stabilized by grain boundary surface terminations. By later studying nanoparticles with varying grain boundary density, they were able to correlate the COR performance to a high occurrence of grain boundaries.³¹⁶ Verdaguer-Casadevall *et al.* used CO temperature programmed desorption (TPD) to probe the binding strength of CO on oxide-derived Cu foils.³²⁵ A high temperature feature that was not present for planar polycrystalline Cu could be identified, suggesting the presence of strong-binding sites on the oxide-derived surface. The

occurrence of these sites could be correlated with COR activity, supporting the notion that certain sites present on oxide-derived Cu are responsible for its excellent performance. However, the TPD in this study was complicated by gas-phase mass transport and CO re-adsorption in the pores of the oxide-derived copper, and modeling was required to decouple this effect from the binding strength of particular sites. The modeling suggested that the high temperature feature was entirely due to strong binding of CO, rather than mass transport, but there is still some uncertainty to this result due to the inhomogeneity of the material.

Rather than specific morphological features being responsible for the high COR activity and selectivity to oxygenated products, other studies have suggested that this has more to do with the increased surface area of these materials.^{115,201} As shown in **Figure 24**, the production of both oxygenated and C–C coupled products are favored at lower overpotentials.²⁰¹ Thus, the performance of these very rough morphologies can be explained by their greater number of surface sites, which allow these electrodes to reach high geometric COR rates at more positive potentials where the production of C₂₊ oxygenates is favored. Importantly, when normalized by the ECSA, planar Cu²⁰¹ and these state of the art Cu materials^{71,323} exhibit very similar COR rates when compared at potentials that are free of diffusion limitations, suggesting that these potential-dependent selectivity trends are the key reason for the differing performance of these materials.

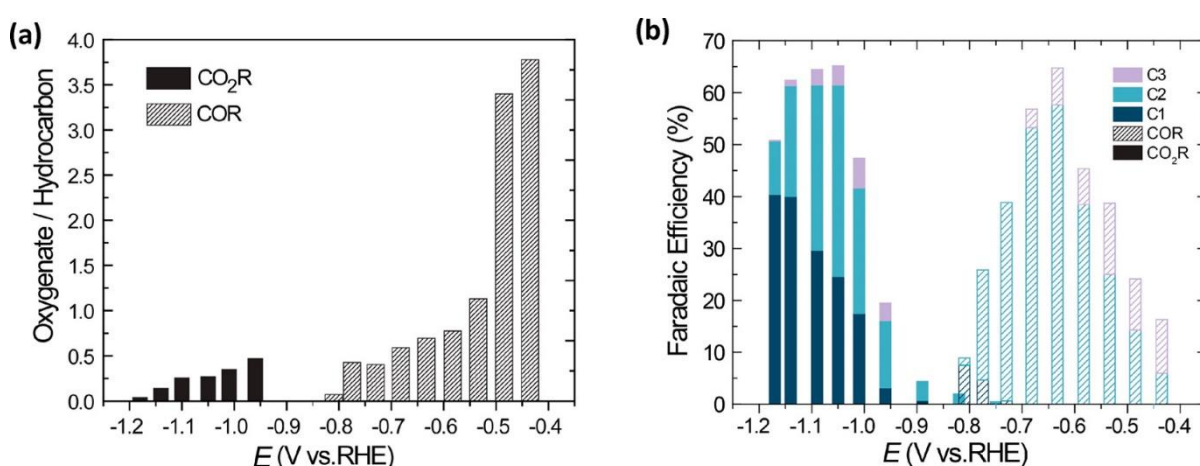


Figure 24: Potential-dependent selectivity of Cu toward CO₂R and COR. (a) oxygenate/hydrocarbon ratios of the reduction products as a function of potential, and (b) Faradaic efficiencies for C₁, C₂, and C₃ products, each as a function of potential. These potential-dependent selectivity trends reveal that the production of C₂₊ oxygenates is increasingly favored over hydrocarbons at Reprinted from Wang *et al.*²⁰¹ Copyright © 2018, American Chemical Society.

Anodic treatment

Another approach to prepare oxide-derived nanostructured electrocatalysts is *in-situ* anodic treatments. Oxidation-reduction cycles result in the formation of nanostructures on the surface of polycrystalline Cu.^{95,96,117,327} Similar to some studies on calcined oxide-derived Cu, the *in-situ* electrochemical oxidation-reduction treatment resulted in suppressed CH₄ evolution and enhanced production of C₂H₄ compared to planar Cu. C₂ and C₃ oxygenates were later identified as important liquid products from anodically treated Cu foils by performing rigorous product analysis.^{96,328} Roberts *et al.* followed up their CO₂R work on copper nanocubes synthesized by potential cycling in the presence of Cl⁻⁹⁵ by also testing these anodically nanostructured catalyst for COR.²⁸⁶ Ethylene formation was favored over methane on copper nanocubes compared to polycrystalline foils, confirming the trends they observed previously for CO₂R. In general, it seems that anodic nanostructuring of Cu surfaces favors production of C₂₊ over C₁ compounds. Using a different approach, Roldan Cuenya and coworkers created a thick, amorphous oxide film on the surface of Cu foils by oxygen plasma treatment.^{126,249,329} Depending on the exact pre-treatment conditions, this material exhibited high selectivity towards ethylene formation. A maximum Faradaic efficiency of 62% was observed at around -0.9 V *vs.* RHE.¹²⁶

Different reasons for the high ethylene selectivity of these materials have been suggested. Kwon *et al.*⁹⁶ reiterated the explanation given by Kanan and coworkers for calcined oxide-derived copper, attributing it to the high occurrence of grain boundaries and/or other defects on the surface.³¹⁶ In the case of the copper nanocubes, it has been speculated that the high degree of (100) surface orientation of the electrodes could play a role, due to the cubic geometry of the surface crystallites and the large number of undercoordinated sites present.⁹⁵ Eilert *et al.* used X-ray absorption spectroscopy to study the properties of the Cu electrodes as they were undergoing redox cycling to produce the cube-shaped surfaces, showing that these nanostructures are derived from Cu₂O.¹²⁵ They also prepared a catalyst derived from a CuO precursor, exhibiting very similar CO₂R performance. Interestingly, these electrodes showed a disordered surface morphology without cubic geometries. This points towards other causes for the high C₂H₄/CH₄ ratio than the occurrence of cubic facets with preferential (100) orientation. The higher roughness factors (ECSA/geometric electrode area) of these nanostructured

electrodes would lead to an elevated local pH close to the electrode surface, which has been shown to favor C_2H_4 over CH_4 , so this is another likely reason for the altered product distribution compared to more planar electrodes.

Other Cu_2O film-derived electrodes

A third class of oxide-derived materials are electrodes derived from copper(I)oxide films, prepared by electrodeposition or hydrothermal synthesis onto a substrate.^{116,129,216,330} A rough surface is again created after reduction of the oxide layer, although typically less rough than the calcined electrodes described above. Examples of such films of different thicknesses as-deposited and after reduction are shown in **Figure 25**, illustrating the change in morphology induced by removal of lattice oxygen. CO_2R measurements on this class of materials resulted in suppression of methane and enhanced C_2 product formation, with ethylene, ethane and ethanol being the main products. In the different studies, the effects of bulk crystal structure, film thickness and crystallite size were discussed, giving minor variations in product distribution. Interestingly, these methods for preparing oxide-derived, nanostructured electrodes overall yield similar results to the anodic treatments discussed above with regards to methane suppression and higher selectivity to C_{2+} products. On the other hand, some of the calcined oxide-derived copper electrodes were highly selective towards CO and $HCOO^-$ at low overpotential, but exhibited modest hydrocarbon productions. A possible reason for this discrepancy could be the significantly higher roughness factors resulting from the thermally oxidized precursors as compared to the other methods of obtaining oxide-derived electrodes. A very high roughness factor leads to higher activities at lower overpotentials, where the $2e^-$ products from CO_2R , CO and $HCOO^-$, are preferred. This could also lead to these catalysts being mass-transport limited in a region where they would otherwise produce significant amounts of $>2e^-$ hydrocarbon and/or oxygenates.

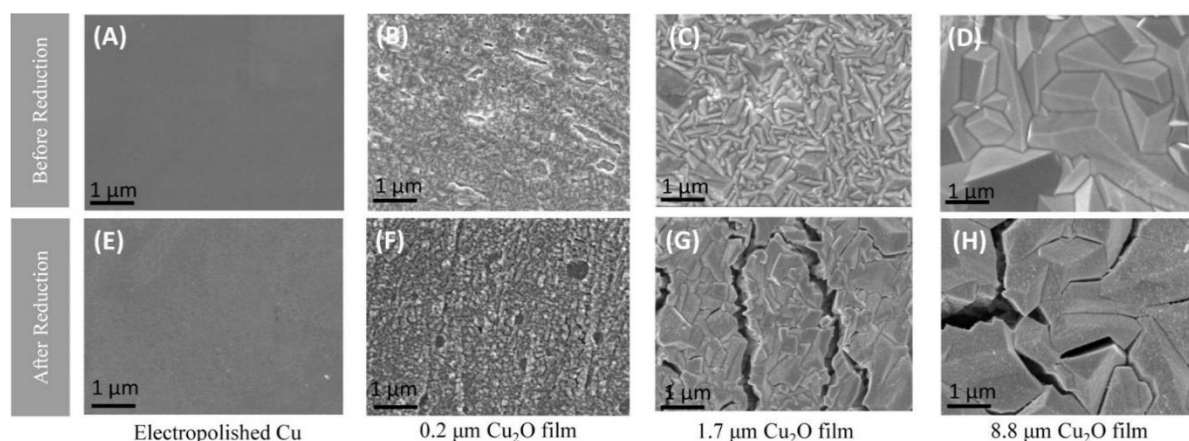


Figure 25: SEM micrographs of various Cu_2O films prepared by electrodeposition. (a)-(d) As-deposited and (e)-(h) after CO_2R at -0.99 V vs. RHE . Reprinted from Ren *et al.*¹²⁹ Copyright © 2015, American Chemical Society.

6.2.2 Non-Oxide-Derived Copper

While it is important to note that a thin native oxide surface layer is formed on Cu whenever exposed to ambient air, here we would like to briefly discuss ‘non-oxide-derived’ copper catalysts. By this we mean to highlight several approaches other than those based on the intentional formation and reduction of a thick copper oxide layer on the surface that have been utilized for preparing 3-D copper electrodes, such as sputter deposition, electrodeposition, and dealloying.^{131,331–336} Interestingly, similar trends as for the anodically treated and other Cu_2O -derived catalysts discussed previously were observed in all of these studies. Increased C_{2+} and lower C_1 product selectivity was reported compared to polycrystalline Cu, and specifically, ethylene and sometimes ethanol formation reached significant selectivity at lower overpotentials. It seems that many approaches can lead to significantly increased C_{2+} over C_1 product selectivity from CO_2R compared to polycrystalline Cu. The independence of the resulting product distribution on the preparation method suggests that the reason for the improved selectivity is related to the broader impacts of nanostructuring (such as increased surface area), and not necessarily an oxide precursor.

This hypothesis was supported by two recent works where multiple different nanostructured Cu electrodes were prepared and tested for CO_2R . Lum *et al.* synthesized four different types of oxide-derived Cu electrodes, spanning the three different groups discussed above, and studied their C_{2+} product selectivity from CO_2R between -0.7 and -1.0 V vs. RHE .⁹⁸ The varying ECSA of the different

catalysts enabled determination of an ideal roughness to optimize C_{2+} product selectivity at the two extreme potentials, as shown in **Figure 26**. The authors attributed this optimum to a compromise between elevated local pH, which has been shown to enhance C_{2+} product formation, and sufficient transport of CO_2 to the active sites. This hypothesis was corroborated by mass transport modeling.^{98,99} Ren *et al.* utilized a similar approach, where they prepared four different types nanostructured electrodes by electrodeposition; three were oxide-derived and one was not.²⁹⁰ The trends that they observed could all be related to the surface area of the electrode, regardless of whether the material was derived from an oxidized precursor or not. The authors concluded that in order to obtain selectivity towards certain products, the material should be designed to have a limiting current density in a potential region where Cu is selective for a certain product.²⁹⁰ If, for instance, $2e^-$ products are desired, the electrodes should exhibit very high roughness so that significant current can be achieved at low overpotential. As discussed previously, such electrodes reach mass transport limitations early, and therefore produce small amounts of $>2e^-$ products. Thus, if the aim is to produce oxygenates and/or hydrocarbons, intermediate to low roughness is desirable, as was also illustrated by Lum *et al.* in **Figure 26**.⁹⁸

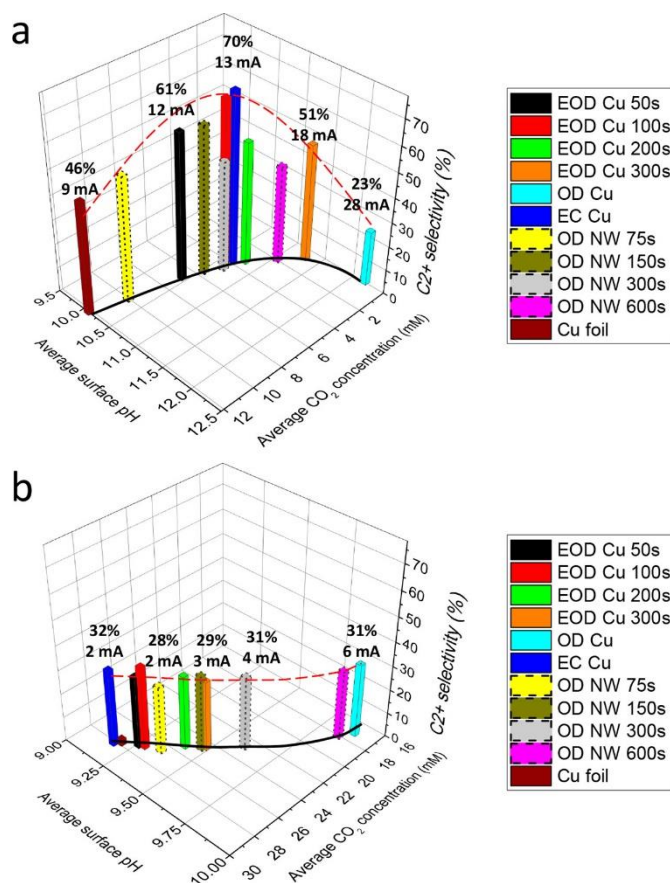


Figure 26: C₂⁺ product selectivity from CO₂ reduction on various oxide-derived Cu electrodes in 0.1 M KOH at a) -1.0 V and b) -0.7 V. Reprinted from Lum *et al.*⁹⁸ Copyright © 2017, American Chemical Society.

As previously mentioned, many nanostructured electrodes are ill-defined, making it difficult to deconvolute the influence of different possible reasons for changes in behavior. Effects that can play a role include changes in mass transport and increase in local pH, re-adsorption and further reduction of products, and higher occurrence of undercoordinated sites. One approach to try to deconvolute surface area effects from other effects is to prepare electrodes with ordered pore structure. Yang *et al.* prepared electrodes of more well-defined porosity by sputtering Cu onto a structured template.³³² This resulted in a Cu film with cylindrical pores of varying width and depth, as displayed in **Figure 27**. They found that pores of 30 nm diameter and 40 nm (**Figure 27a**) depth yield mainly C₂H₄ at -1.3 V vs. RHE, while CH₄ is the main CO₂R product on polycrystalline electrodes. Deeper pores (**Figure 27b**) led to enhanced C₂H₆ selectivity, while wider pores (**Figure 27c**) gave product distributions more similar to polycrystalline Cu. The authors attributed the increase in C₂ production for the electrodes with narrow

pores to an increased local pH. The change from ethylene to ethane with deeper pores could be caused by re-adsorption and further reduction of the products due to the longer retention time in the catalyst layer. Another similar study was performed by Song *et al.* on ordered, mesostructured Cu inverse-opal electrodes.³³⁷ As expected from the above arguments, they observed improved C₂₊ selectivity with increasing thickness of the porous Cu layer. This type of systematic studies is important in order to help identify of the factors that lead to improved performance of 3-D electrodes. We therefore suggest this as an area of increased attention in the future.

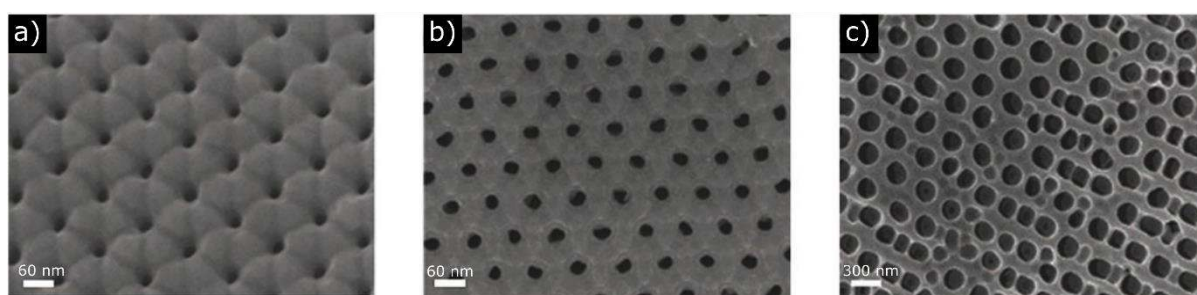


Figure 27: SEM images of mesoporous Cu films with holes of different dimensions. **a)** 30 nm width and 40 nm depth, **b)** 30 nm width and 70 nm depth and **c)** 300 nm width and 40 nm depth. Reprinted with permission from Yang *et al.*³³² Copyright © 2016, John Wiley and Sons.

6.2.3 The Role of Oxygen in CO₂R Electrocatalysis

The role of oxygen in CO₂ electroreduction has emerged as a topic of acute discussion within the field in the last few years. The topic has, however, been debated for decades already, starting with the previously mentioned report by Frese in the early 1990's.³²⁰ As described earlier, oxide-derived nanostructured materials have been shown to yield interesting selectivity effects for CO₂R and COR. An important question is whether this is a result of the nanostructure, or oxygen from the oxidized precursor remaining close to the surface under reaction conditions. Intuitively, one would expect any oxides to be reduced under the CO₂R conditions, due to the strong thermodynamic driving force from the negative potentials applied (see **Table 5**). Recent DFT calculations indeed suggested that reduction of Cu oxides is more favorable than CO₂R at the relevant potentials.¹³⁶ However, a number of reports

explain that some amount of the initial oxide can be stabilized and affects catalysis. In the following, we will discuss the relevant studies that argue the two points of view.

Table 5: Equilibrium potentials for the reduction various copper oxide species. Calculated with Thermochemistry data from NIST as described in Section 1 of the SI.

Reaction	$E^0 / \text{V vs. RHE}$
$\text{CuO} + 2 (\text{H}^+ + \text{e}^-) \leftrightarrow \text{Cu} + \text{H}_2\text{O}$	0.56
$2 \text{CuO} + 2 (\text{H}^+ + \text{e}^-) \leftrightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}$	0.66
$\text{Cu}_2\text{O} + 2 (\text{H}^+ + \text{e}^-) \leftrightarrow 2 \text{Cu} + \text{H}_2\text{O}$	0.46
$\text{Cu}(\text{OH})_2 + 2 (\text{H}^+ + \text{e}^-) \leftrightarrow \text{Cu} + 2 \text{H}_2\text{O}$	0.53
$\text{Cu}_2\text{CO}_3(\text{OH})_2 + 4 (\text{H}^+ + \text{e}^-) \leftrightarrow 2 \text{Cu} + 3 \text{H}_2\text{O} + \text{CO}_2$	0.55

DFT calculations have been applied both to study whether or not oxygen can be stable under reaction conditions and how it could potentially affect catalysis. Favaro *et al.* studied the effect of subsurface oxygen on the physisorption of CO_2 onto a Cu surface in a gaseous environment. Using DFT and ambient pressure X-ray photoelectron spectroscopy (APXPS), they showed that subsurface oxygen was critical to achieve stable adsorption of CO_2 onto the surface.³³⁸ Similarly, Kim *et al.* used XPS depth profiling before and after CO_2R as evidence that a copper oxide phase catalyzes the CO_2R .³³⁰ There remains a gap to be addressed, however, between these *ex-situ* results and true CO_2R conditions, since adding electrolyte to the system and applying negative polarization of the cathode are likely to have a significant influence. Liu *et al.* suggested that subsurface oxygen close to the surface can actually be stabilized by the disordered near-surface structure and roughness of oxide-derived copper.³³⁹ Furthermore, they argued that near-surface oxygen can enhance the CO binding strength by withdrawing electron density from surface atoms and reduce the σ repulsion between CO and surface Cu atoms. Other calculations showed that only oxygen in the topmost two subsurface layers can have a non-negligible influence on the reactivity of surface atoms, but that the barrier for diffusion of these oxygen atoms are too low for them to be stable under reaction conditions.^{340,341}

A number of further *ex-situ* studies have been carried out showing that oxygen is present after CO_2R .^{320,330,342–345} These groups applied techniques such as X-ray photoelectron spectroscopy, Auger

electron spectroscopy and TEM, showing copper oxides present throughout the catalyst. However, *ex-situ* studies after transfer through air are problematic when studying copper, because of the rapid re-oxidation upon exposure to O₂.^{346,347} As discussed previously, reduction of Cu oxide films before or during CO₂R leads to formation of nanostructured surfaces. The high abundance of defects on such surfaces ensures even faster oxidation in ambient air after CO₂R,³⁴⁷ making it even harder to draw conclusions about their oxidation state under reaction conditions. Recently, Cavalco *et al.* kept their electrodes under an inert gas atmosphere when transferring them to characterization by TEM, and still saw significant amounts of oxygen.³⁴⁴ It is, however, difficult to ensure that absolutely no oxygen reaches the sample at any point in the process. One way to get around oxygen contamination when applying *ex-situ* techniques is using isotopically labelled oxygen. Lum *et al.* carried out depth profiling of oxide-derived Cu that had been oxidized anodically in H₂¹⁸O.³⁴⁷ They saw that after only 10 minutes, less than 1% of the original content of ¹⁸O was remaining, similarly to ¹⁶O control samples, as shown in **Figure 28**. This suggests that at least a large fraction of the initial oxide is reduced under reaction conditions. Some recent studies have prepared Cu materials with other dopants than oxygen, such as sulfur^{144,348} and boron.³⁴⁹ This way materials can be prepared that are more resistant against reduction than those prepared with oxygen, while still retaining some of the effects that are thought to occur when O is present close to the surface. However, more work is needed to evaluate if this is actually a viable approach for future materials design.

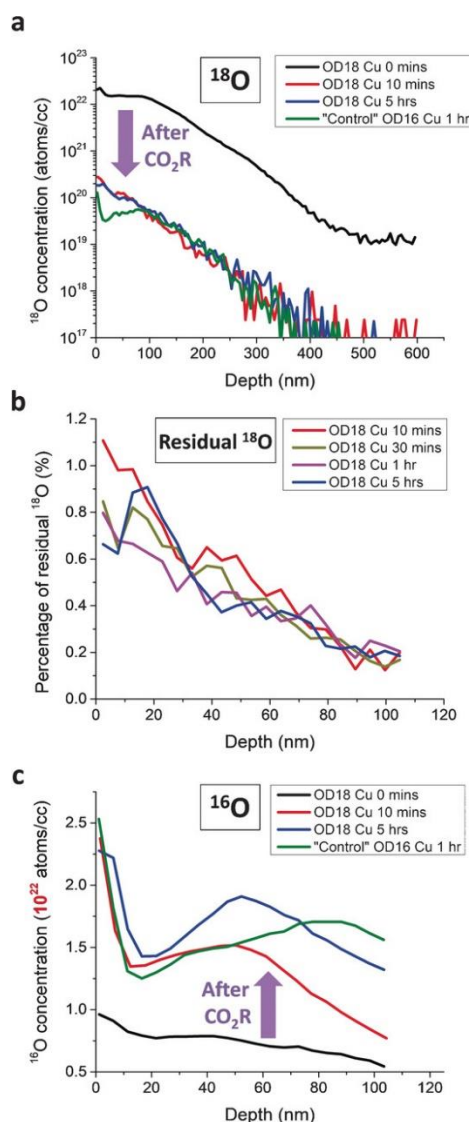


Figure 28: a) ^{18}O and c) ^{16}O content of OD Cu catalysts with different CO_2R durations measured by SIMS. b) The percentage of ^{18}O that remains in OD18 Cu after CO_2R . Reprinted with permission from Lum and Ager.³⁴⁷ Copyright © 2018, John Wiley and Sons.

Because of the rapid re-oxidation of Cu in air, *operando* techniques are useful to study the oxidation state of these electrodes during CO_2R . A number of studies showed reduction of the oxidized precursor under reaction conditions using *operando* measurements such as X-ray absorption spectroscopy (XAS),¹²⁵ Raman spectroscopy,^{96,129,130,136} and grazing incidence X-ray diffraction (GIXRD).¹⁷⁷ Other *operando* studies suggest that oxygen is present under reaction conditions.^{126,250,350} However, there is uncertainty regarding these techniques as well. Catalysis happens at the surface, and only the reactivity of the topmost layers of atoms matter. As discussed above, the presence of different species, such as oxygen, close to the surface can alter this reactivity and affect catalysis, but they need

to be within a few atomic layers underneath the surface.^{339,341} Most of the operando techniques employed thus far cannot clearly distinguish whether the oxygen is at or close to the surface, or deeper in the bulk where it will not affect catalysis. On the other hand, even small amounts of oxygen present at or close to the surface might affect reactivity, and most of the techniques would not be able to resolve such minute amounts of oxygen present at the surface.

As a general note, it is very challenging to design an experiment that conclusively determines the active site of a catalyst under reaction conditions. However, until evidence that oxygen species are stable close to the surface where they can influence catalysis is presented, it is the opinion of the authors that this is unlikely given the strong thermodynamic driving force for reduction. As discussed above, the fact that CO₂R on oxide-derived Cu materials lead to a similar product distribution as non-oxide-derived Cu further indicates that it is the nanostructure, and not the oxidation state of the precursor material, that gives the altered CO₂R performance.

6.2.4 Activity Comparisons

Throughout Section 6.2, we have grouped the different 3-D materials into two main categories; oxide-derived and non-oxide-derived catalysts. Although a number of different approaches to nanostructuring have been applied in the literature, which have yielded electrodes with highly diverse structures, there are many similarities in their performance for CO₂R. Importantly, studies on 3-D electrodes carried out at low overpotentials report improved selectivity towards carbon monoxide and/or formate compared to planar copper foils. At more negative potentials, some or full suppression of methane formation and enhanced selectivity towards ethylene and other C₂₊ products has been reported.

Nanostructuring gives electrodes with increased roughness factors, varying from 2 to 850 in the studies discussed herein. This results in increased current density when normalized by geometric surface area. In **Figure 29a**, geometric CO₂R current densities for many of the studies discussed throughout this section are shown, compared to data obtained on planar, polycrystalline Cu by Kuhl *et al.*⁶⁶ and Hori *et al.*⁸⁵ In this plot, all the nanostructured materials exhibit higher geometric activity at a given potential than polycrystalline copper, when not under mass transport limited conditions.

This does not, however, reflect the intrinsic activity of the material, as discussed in Section 2.1. Therefore, it is instructive to also compare the specific activity of the electrode, as shown in **Figure 29b**, where the activities are normalized to ECSA. Here we see that there is little or no difference in the total intrinsic CO₂R activity among the different types of nanostructured electrodes. Furthermore, the intrinsic activity of these various Cu nanostructures is similar to that of planar, polycrystalline Cu. The similar intrinsic activity of all Cu electrodes is underlined by the Tafel-like behavior observed in **Figure 29b**, prior to diffusion limited conditions. This explains why high roughness factor materials tend to exhibit earlier onset; higher roughness electrodes yield higher overall current densities, which allows for the detection of products at lower overpotential, even at low turnover frequencies per surface site. The magnitude of the diffusion limited current density also scales with surface roughness, with high surface area materials reaching mass transport limitation at lower overpotential. These findings strongly suggest that nanostructuring does not alter the intrinsic activity of copper in any significant manner, perhaps within a factor of 2-4, for any synthesis method used. Furthermore, it does not seem that intrinsic CO₂R activity is higher for oxide-derived materials (studies [C-J] in **Figure 29**), as compared to non-oxide-derived electrodes such as polycrystalline Cu (studies [A, B]) and mesostructured Cu (study [K]). This further corroborates the notion that the precursor material oxidation state is not a crucial factor for CO₂R performance,^{98,290} and that any subsurface oxygen that may or may not be present based on different preparations of Cu has little or no influence on intrinsic CO₂R activity.

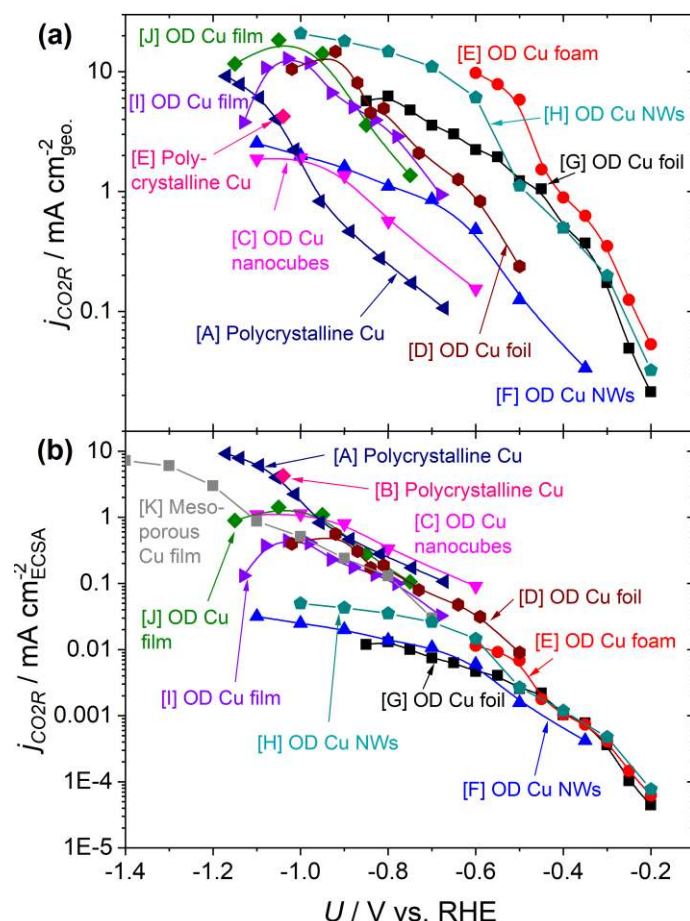


Figure 29: Comparison of CO₂R activity for various nanostructured Cu electrocatalysts with polycrystalline Cu. **(a)** CO₂R partial current density normalized to geometric surface area. **(b)** CO₂R partial current density normalized to electrochemical surface area (ECSA). The data were obtained from the following studies: [A] Kuhl *et al.*⁶⁶; [B] Hori *et al.*⁸⁵; [C] Kwon *et al.*⁹⁶; [D] Mistry *et al.*¹²⁶; [E] Min *et al.*⁹⁴; [F] Ma *et al.*^{93,321}; [G] Li *et al.*⁹⁰; [H] Raciti *et al.*⁹²; [I] Handoko *et al.*²¹⁶; [J] Ren *et al.*³²⁸; [K] Yang *et al.*³³². Studies [A,B] are polycrystalline Cu, [C-J] are oxide-derived, nanostructured Cu and [K] is non-oxide-derived nanostructured Cu.

Although the ECSA-normalized activity is similar for the various types of nanostructured electrodes, there are differences in the product distribution. First, as mentioned previously, mass transport conditions generally have a large influence on the product distribution obtained from a catalyst material. When approaching mass transport limited conditions, the local pH close to the electrode surface increases. Since electrodes with high surface area reach mass transport limitation at relatively low overpotentials, improved C₂₊ product selectivity can be observed under these conditions. However, as significant mass transport limitations are reached, too little CO₂ reaches the electrode surface, and H₂ evolution takes over. This is a likely reason for calcined oxide-derived Cu foils exhibiting a significant drop in CO₂R selectivity at potentials more negative than -0.6 V vs. RHE, and low

hydrocarbon formation in general. The very high roughness factors cause the bulk of the non-mass-transport-limited activity to be in a low overpotential region where CO_2R to CO and HCOO^- is favored; meanwhile, these systems favored C_{2+} oxygenates at low overpotentials when doing COR (since the overpotential to reduce CO_2 to CO is not a limiting factor), which can be understood by the potential-dependent selectivity trends shown in **Figure 24**. Thus, a key finding here is that the roughness factor of the electrode in effect shifts the potential window where kinetically-limited CO_2R can take place, which has a very large impact on the product selectivity.

Electrode roughness is not the only important parameter though; morphological features such as pore size and shape can also strongly influence product distribution, as well as the retention time of products and intermediates in the catalyst structure. A good illustration of this is that studies investigating catalyst layer thickness or pore depth generally find that thicker nanostructures lead to more ethane on behalf of ethylene. Ethane is generally not observed on planar electrodes, and can likely be attributed to re-adsorption and further reduction of ethylene. Although clear trends are outlined above, more work is still needed to improve our understanding of which effects drive selectivity to different products, and eventually give us the possibility to steer CO_2R towards desirable chemicals. Furthermore, since current densities of 100 mA cm^{-2} or higher seems to be a minimum for commercialization to be realistic,⁶⁰ more work needs to be done to enhance mass transport of CO_2 to achieve higher reaction rates. A key strategy towards that end will be discussed subsequently.

6.3 Vapor-Fed Systems

All of the catalysts described thus far have been tested using conventional aqueous-phase CO_2R reactors. While these have clearly been useful for gaining fundamental insights, the poor solubility of CO_2 in aqueous electrolytes ($\sim 34 \text{ mM}$), along with the acid/base buffer equilibria ($\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$) described earlier lead to significant challenges in achieving high CO_2R reaction rates. Vapor-fed systems can overcome these practical limitations by delivering gas phase CO_2 directly to the catalyst surface. Indeed, some of the best performing Cu catalyst systems reported today in terms of Faradaic efficiency, energy conversion efficiency, and stability use vapor-fed reactors.^{127,132,293,331,348,351–354} We

therefore wanted to take this opportunity to briefly discuss these reactor configurations and highlight promising developments in this area. For more information, we direct the readers to a recent perspective article that details the progress, challenges, and opportunities towards the development of practical CO₂ electrolyzers,³⁵⁵ as well as a recent review on the same topic.³⁵⁶

In commercial electrocatalytic systems, such as fuel cells and water electrolyzers, a gas diffusion layer is typically employed as a support material in order to maximize transport of reactants to the catalyst surface. These layers are comprised of open, three-dimensional structures of relatively inert materials, such as carbon. Together with the porous catalyst, this forms what is known as a gas diffusion electrode (GDE). A GDE can be used with either a liquid electrolyte or a solid-state polymer electrolyte membrane. A membrane electrode assembly (MEA) refers to the latter case, whereby an assembled stack is composed of a polymer electrolyte membrane sandwiched between two GDEs. Here, ionomers are used to extend the electrolyte membrane material into the GDEs to provide intimate contact with the catalyst and ensure efficient transport of ions to/from the surface. This is important because the relevant reactions can only take place at triple-phase boundaries, which are points where the gaseous reactant, electron-conduction catalyst, and ion-conducting polymer or liquid electrolyte meet. Vapor-fed systems are thus inherently more complex than aqueous-phase systems due to the multitude of heterogeneous interfaces across a range of length scales (**Figure 30**) and will present many challenges in optimizing CO₂R activity and selectivity.

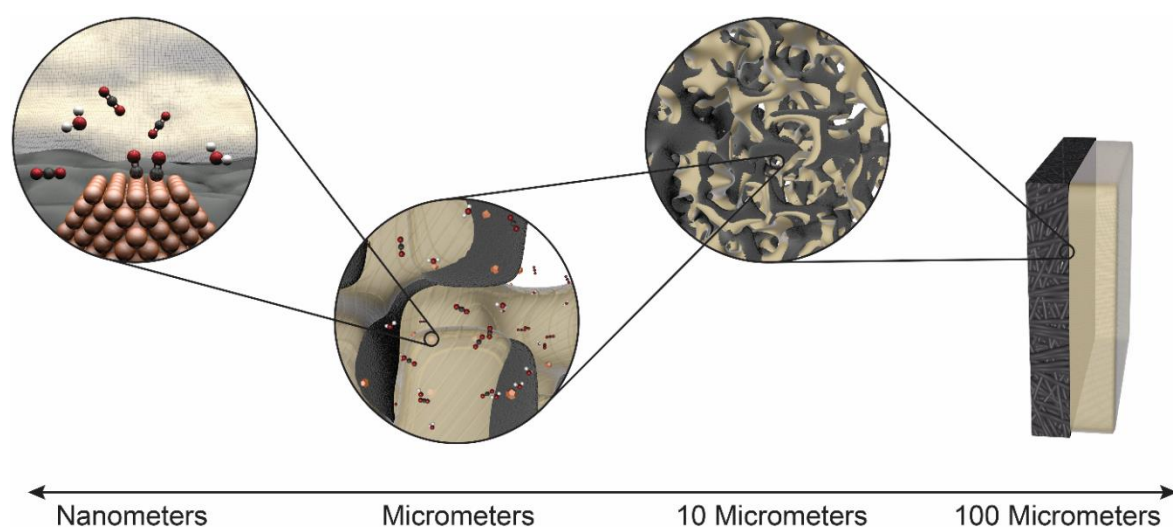


Figure 30: Schematic of a 3-dimensional GDE depicting the multiple length scales where phenomena are occurring during electrochemical CO₂R. Reprinted from Higgins *et al.*³⁵⁵ Copyright © 2018, American Chemical Society,

While still in its infancy, research in these areas have already demonstrated promising activity and selectivity improvements compared to conventional aqueous-phase reactors.^{127,132,293,331,348,351–353} For example, various vapor-fed reactors using Cu-based GDEs have achieved high CO₂R geometric partial current densities to ethylene of around 150 – 473 mA/cm²,^{127,132,293,331,352,353} and to ethanol of around 40 – 108 mA/cm².^{132,293,348,352,353} As discussed in Subsection 3.3.1, alkaline electrolytes can improve selectivities and energy efficiencies to C₂₊ products. This was illustrated in a recent report where researchers tested various electrolytes including KOH, KHCO₃, KCl, and K₂SO₄ in their microfluidic CO₂ flow cell electrolyzer and found that an optimal production of C₂₊ products (411 mA/cm² at -0.67 V vs. RHE, corresponding to 62% Faradaic efficiency) could be achieved in KOH.³⁵³ Another study employed a range of strongly basic conditions (1-10 M KOH) and could achieve a partial current density for C₂₊ products as high as 608 mA/cm² at -0.67 V vs. RHE (corresponding to 81% Faradaic efficiency).³⁵² These carbon-based GDEs were unfortunately found to degrade at such high reaction rates, but the stability was improved by incorporating a polymer layer to help prevent flooding. In this way, Sargent and coworkers were able to achieve ~70% Faradaic efficiency for CO₂R to C₂H₄ at -0.55 V vs. RHE for 150 hours in 7 M KOH (although the current slowly declined from 100 to 75 mA/cm²).³⁵² It is worth noting that for sustained CO₂R under alkaline conditions, reactor systems will have to be carefully engineered to avoid neutralization of the electrolyte via CO₂ conversion to bicarbonate; otherwise, regeneration of the KOH will add to the costs and detract from the overall energy balance of the system. This could also be one advantage of performing COR instead of CO₂R in such a device.

The studies discussed above demonstrate the promise of using vapor-phase CO₂ reactants in overcoming intrinsic limitations of aqueous-based systems, but there is still much work ahead in further developing and optimizing these practical device architectures for commercial application. The choice of electrolyte, catalyst, and GDE fabrication process will all have a significant impact on device performance and must ideally be designed to optimize transport of CO₂, products, electrons, and ions simultaneously. There is thus a large phase space to explore in tuning relevant properties of the gas diffusion layer(s), such as porosity, hydrophobicity, and thickness. Well-controlled studies that aim to

understand the effects of nanoparticle size, shape, and loading, as well as catalyst-support and catalyst-ionomer interactions will also be essential. Translating this and other fundamental knowledge gained from probing catalyst morphology and electrolyte effects in aqueous-phase reactors to these complex vapor-fed systems will aid in their advancement. Furthermore, since CO₂R in these 3-D architectures involves many processes over a range of length and time scales, it will become increasingly important to couple experimental and theoretical investigations. Continued development of microkinetic and 3-D transport modeling methods are promising candidates in that regard.

6.4 Summary

Nanostructuring gives electrodes with increased roughness factors, varying from 2 to 850 in the studies discussed in this chapter, which results in increased current density when normalized by geometric area of the electrode. However, when normalized by the ECSA of the electrode, it is found that the *intrinsic* activity of Cu catalysts is similar among all the different forms of electrodes reported to date, whether nanostructured or planar, and irrespective of the particular nanostructure or synthesis route. This highlights the importance of data normalization for determining whether higher catalytic activity results from a higher average turnover frequency or simply from an increased number of active sites.

While nanostructuring does not appear to change the intrinsic activity of Cu, interesting changes in product distribution have been observed. For example, many 3-D catalyst materials exhibit some or full CH₄ suppression and increased C₂₊ product selectivity. This has largely been explained by mass transport modeling studies, which have shown that an ideal compromise between pH increase and CO₂ supply at the electrode surface gives an optimal C₂₊ selectivity on rough electrodes.⁹⁸⁹⁹ More generally, since the number of active sites impacts the potential window where high reaction rates are achieved, the catalyst surface area has emerged as a key determinant of product selectivity. Other morphological factors such as preferential faceting, grain boundaries, and pore shape and size may also lead to changes in CO₂R selectivity due to surface structure effects and/or re-adsorption and further reduction of products.

Nanostructured electrodes are particularly relevant because of their potential compatibility with vapor-fed reactors, a promising technology platform capable of achieving industrially relevant current densities. However, substantial efforts will be needed in order to understand how CO₂R catalysts behave in such a different environment than the conventional aqueous-phase, lab-scale reactors that are typically employed today. We feel that research in these directions should be prioritized in order to begin accelerating the development of practical devices that convert CO₂ to high value fuels and chemicals.

7. Copper Bimetallics

Changing structural properties of the catalyst material (*e.g.*, via hierarchical nanostructuring, particle size/support effects, etc.) is one key tactic to alter the catalytic performance, as discussed in the previous chapter. Another approach being employed to improve the activity, selectivity, and stability of Cu for CO₂R is the preparation of bimetallic systems. Bimetallics can enhance performance compared to monometallic catalysts by a variety of mechanisms including electronic ligand and strain effects^{357–362} and geometric ensemble effects.^{357–359,363,364} The electronic effects refer to a change in the electronic structure of the host material after addition of another element, which alters the binding strength of intermediate adsorbates on the surface according to the *d*-band model.^{360,365} Geometric ensemble effects refer to a change in the atomic arrangement of active sites, which alters the way adsorbates interact with the surface and each other. In addition to simply changing the number or configuration of particular atoms in an ensemble, bifunctional active sites can also be created, where neighboring metals serve different catalytic roles. For example, it has been thought that bifunctional active sites for CO₂R could be created using a metal with higher oxygen affinity, allowing COOH* or CHO* to be stabilized by interacting with the surface through both the carbon and oxygen atoms compared to CO*, which tends to bind surfaces through the carbon atom in an upright geometry.^{203, 366} Additionally, isolated active sites can be formed that change the proximity of other adsorbates, which can impact the selectivity.³⁶⁷

There are a multitude of bulk systems that can be formed when two elements are mixed, including solid solutions, intermetallic compounds, and phase-separated systems. Details governing the formation of these bimetallics and their different properties are outside the scope of this review. Instead, we will focus on the resulting model systems that allow for the study of the aforementioned electronic and geometric effects. These include bulk alloys, surface alloys (alloy layer supported on a monometallic core), near surface alloys (alloy beneath one or a few monometallic layers), or guest metal modified surfaces (*e.g.*, islands or particles on a monometallic host). In addition, there are bimetallic overlayers, either planar or nanoparticulate (core-shell) structures, which refer to a monometallic surface supported on either a different metal, a bulk alloy, or a (near) surface alloy. Due to the large number of possible bimetallic combinations, with regard to both the composition and structural arrangements, computational screening approaches have been used to aid in the search for improved CO₂R catalysts.^{203,366–371} There have been a number of non-Cu-based bimetallics that have demonstrated synergistic activity or selectivity, primarily to 2e⁻ products.^{372–377} This chapter will only focus on the experimental results obtained for Cu-based bimetallic systems in aqueous solutions under ambient conditions.

As described in Subsection 1.2.2, early experimental work led by Hori and coworkers showed that on Fe, Ni, Pt, and Pd, the competing HER is primarily observed, on Ag, Au, and Zn the major product is CO, and on Cd, Pb, Hg, Tl, Sn, and In the major product is HCOO⁻.^{1,85} The Cu-based bimetallic combinations discussed in the following sections are thus organized according to these groupings by the dominant CO₂R selectivity of the guest metals. First, we will describe the structural properties of the studied model catalysts and summarize the main experimental findings with respect to their catalytic activity and selectivity for CO₂R compared to pure Cu. Then, we will provide some overall perspectives on the benefits of using bimetallics, pitfalls to avoid when investigating these systems, and suggestions for future studies.

7.1 Copper and H₂ Producing Guest Metals (Fe, Ni, Pt, Pd)

Mainly H₂ is formed during CO₂R on monometallic electrodes of group 8–10 transition metals.^{1,85} Thus, Cu-M bimetallic electrodes (where M = Fe, Ni, Pt) typically result in increased HER activity and selectivity compared to pure Cu. This has been shown for a variety of model systems: Cu electrodes modified with Fe, Ni, or Pt deposits,^{378,379} CuPt alloy nanocubes and nanocrystals,^{380,381} and Cu overlayers on Pt electrodes.^{382,383} Further, trends have been observed whereby increased guest metal coverage on Cu, increased Pt content in the nanoalloys, and decreased Cu overlayer thickness led to increased H₂ activity and/or selectivity. In the case of the Cu overlayers, only after the Cu layer was sufficiently thick (>5 nm) did the H₂ formation return to bulk Cu-like values.³⁸³ In a separate study, it was demonstrated using electrochemical scanning tunneling microscopy (ECSTM) that the presence of CO formed during CO₂R destabilizes thinner Cu overlayers due to the very high binding affinity of CO on Pt.³⁸² This causes restructuring from a flat morphology into more complex three dimensional particles, while simultaneously exposing the underlying Pt substrate, as shown in **Figure 31**.³⁸² Thus, the increased affinity for HER in the bimetallic systems likely results from increased exposure of these guest metals on the catalyst surface.

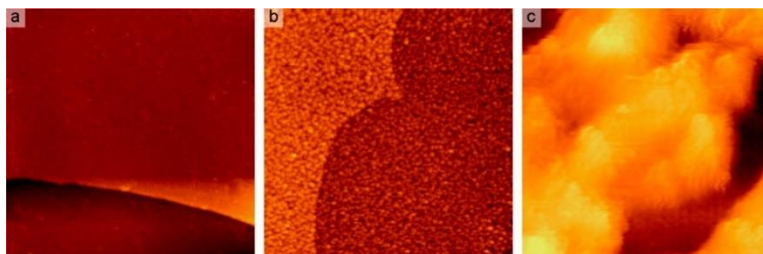


Figure 31: **a)** Atomically flat morphology of the Cu overlayer in a CO- free electrolyte (499 nm)², U = 0.02 V, U_B = 292 mV, I_T = 1 nA. **b)** Granular morphology of the Cu overlayer after exposure to a CO-saturated electrolyte (499 nm)², U = 0.01 V, U_B = 356 mV, I_T = 10 nA. **c)** Disordered Cu overlayer with (2 × 2)-CO structure inside the vacancies (13.6 nm)², U = 0.01 V, U_B = 356 mV, I_T = 10 nA. Reprinted from Varela *et al.*³⁸² Copyright © 2013, American Chemical Society.

As one might expect, these systems also exhibit a concurrent decrease in overall CO₂R activity and selectivity, and in general only mixtures of H₂, CO, CH₄, and C₂H₄ were detected. Interestingly, with increasing Ni or Fe coverage on Cu, Hori found a linear correlation between the HER selectivity and CH₄/C₂H₄ (C₁/C₂) selectivity ratio.³⁷⁸ It is worth noting, however, that the increase in C₁/C₂ ratio

was due to significant C₂H₄ inhibition rather than a boost in CH₄ production. This trend extends across many of these other systems, where C₂H₄ was only detected in trace quantities^{379,382} or not at all.^{380,381} Based on the mechanistic studies discussed earlier, this decreased C₂H₄ production may be attributed to increased H coverage on the surface, which can hinder C-C coupling. In the nanoalloys and guest metal modified Cu systems, this can also be due to a lack of adjacent Cu surface sites required for CO dimerization. However, for the thin Cu overlayer system, it was determined via ECSTM that even after sintering, the Cu ensembles would still be large enough to allow for C-C bond formation, but the C₂H₄ Faradaic efficiency did not exceed 0.6%.³⁸² Meanwhile, for thicker Cu overlayers (>5 nm), it was found that the ratio between CH₄ and C₂H₄ could be tuned as a function of overlayer thickness and potential.³⁸³ Both of these studies point to tensile strain on Cu from lattice mismatch with the Pt substrate playing a role in the CO₂R selectivity by altering the adsorption energy of reactive intermediates, as previously discussed. While these C₁/C₂ selectivity trends are interesting and merit further study to better understand, unfortunately it is clear that none of these bimetallics with highly HER active metals resulted in a more active CO₂R catalyst for >2e⁻ products (**Figure 36** in Section 7.4).

Interestingly, earlier reports from Watanabe *et al.*^{384,385} indicated that Cu-Ni alloys could have synergistic methanol production because they found that neither of the pure metals produced methanol, but their Cu-Ni alloys were shown to produce around 5-10% Faradaic efficiency. The different structural properties of the bimetallic electrodes (incorporating Ni as an overlayer/surface additive vs. mixing as an alloy) might be the cause for the different products observed between this and the other reports discussed above. With improved product detection, however, methanol production has since been confirmed for both monometallic Cu and Ni electrodes by Kuhl *et al.*²⁰⁴ Thus, it is unclear what, if any, synergistic effects were at play, and more thorough investigations are needed.

Palladium is somewhat unique in this grouping in that, according to Hori's data, Pd has very similar H₂ and CO Faradaic efficiencies (~27%), although there is ~40% of the current unaccounted for, which is likely from hydrogen absorption.¹ The ease with which hydrogen can be absorbed into Pd metal has attracted interest in this material for CO₂R, and early studies showed that Pd selectivity was heavily dependent on whether it was employed as a hydrogen-depleted or hydrogen-enriched surface,

with the latter leading to greatly enhanced formate production.³⁸⁶ Similarly, it was found that Cu-modified Pd and electrolytically charged Pd+H electrodes displayed different selectivities, where Cu/Pd+H electrodes led to higher Faradaic efficiencies for the production of methane and particularly for formate compared to Cu/Pd electrodes.^{387, 388} This effect was enhanced when the amount of absorbed hydrogen in the Pd electrodes was larger (Cu/Pd+H charged to 20 °C vs. 100 °C), and when the coverage of Cu was lower, likely because higher Cu coverages prevented hydrogen from discharging through the cracks in the Cu film.^{387, 388} Production of CO and C₂₊ products were not enhanced by the absorption of hydrogen.³⁸⁸ Another study found a complete shift in selectivity from C₂H₄ (32.1% → 3.4%) to C₂H₆ (<1% → 30.1%) at -1.0 V vs. RHE on a Cu₂O-derived catalyst after Pd(II)-chloride was added to the electrolyte, while the production of other carbonaceous species remained almost unchanged.³⁸⁹ Mechanistic studies on this system lead the authors to suggest that CO₂R on the Cu sites first produces C₂H₄, which is then hydrogenated to C₂H₆ with the assistance of adsorbed PdCl_x. Ultimately the practicality of this system may be limited since PdCl₂ served as a sacrificial dopant, resulting in less than 100% total Faradaic efficiency due to reduction of the PdCl₂ and decreasing C₂H₆ selectivity over time as this species was depleted. Regardless, both of these studies point to Pd serving as an active hydrogen source, shifting CO₂R selectivity towards hydrogenated products.

While these bimetallics utilized Pd or Cu as substrates for deposition of the other component, Cu-Pd alloys have also been reported and displayed a very different trend. Composition-dependent studies of Cu-Pd alloy nanoparticles³⁹⁰ and electrodeposited mesoporous films³⁹¹ resulted in enhanced activity and selectivity to CO, with optimum ratios of Cu:Pd producing around 80% CO at -0.8 V vs. RHE. Both studies attribute the enhanced CO production to a ligand effect, where Cu weakens the CO adsorption energy on adjacent Pd sites. Another reason for CO being the dominant CO₂R product reported in these studies could be due to a lower H* coverage resulting from Pd-H bond weakening in Cu-Pd alloys, preventing CO hydrogenation.^{391, 392} While electronic effects may certainly have an impact, other studies suggest that geometric effects play the primary role in governing selectivity of Cu-Pd bimetallics. A 1:1 ratio of CuPd gas diffusion electrodes was systematically studied in ordered, disordered, and phase separated atomic arrangements (**Figure 32**).³⁹³ Both intermetallic mixing patterns

primarily made CO over a range of potentials, similar to the other two Cu-Pd alloy systems reported, while the phase separated CuPd system showed a very clear difference in selectivity and made >60% C₂₊ products. Furthermore, a compositional study of disordered Cu-Pd electrodes also resulted in higher selectivity for C₂₊ products as the concentration of Cu increased from Pd<CuPd₃<CuPd<Cu₃Pd<Cu.³⁹³ Likely, the hydrogen absorption ability of Pd and the C-C coupling ability of Cu are both diminished upon increased mixing. Thus, bimetallic systems where Cu and Pd are sufficiently separated likely leads to more hydrogenated and/or C₂₊ products, whereas bimetallic systems with increased mixing between these two elements may lead to more CO. While this provides compelling evidence for geometric effects driving the selectivity, increasing the degree of mixing should enhance any ligand effects as well. This is why, in general, it is extremely challenging to deconvolute ligand/strain effects from geometric effects.

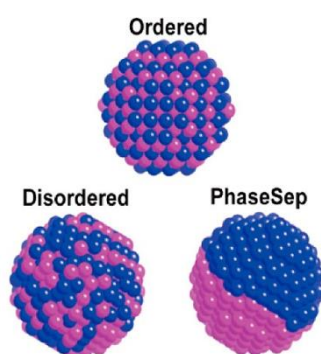


Figure 32: Schematics of ordered, disordered, and phase separated particles with 1:1 composition of CuPd. Reprinted from Ma *et al.*³⁹³ Copyright © 2017, American Chemical Society.

7.2 Copper and CO Producing Guest Metals (Ag, Au, Zn)

Silver, gold, and zinc are all highly selective for CO production from CO₂R in aqueous solutions under ambient conditions.^{1,85} As a result, many Cu-M bimetallic electrodes (where M = Ag, Au, Zn) have shown increased selectivity, and in some cases higher intrinsic activity, for making CO.^{155,394–398} Alternatively, some Cu-M bimetallic electrodes (where M = Ag, Au, Zn) have demonstrated synergistic effects leading to improved activity or selectivity for C-C coupled oxygenated products.^{73,123,128,130,132,399–403} The different factors leading to these two broader outcomes will be discussed subsequently.

7.2.1 Synergistic Effects for CO Production

Several composition-dependent studies have shown increasing CO selectivity with increasing guest metal content, and this was demonstrated for a variety of bimetallic structures including: Cu-Ag dendritic electrodeposits,³⁹⁴ small coverages of Au on Cu,³⁹⁵ $\text{Au}_x\text{Cu}_{1-x}$ pulsed laser deposition alloys with and without O_2 present,³⁹⁶ $\text{Au}_x\text{Cu}_{100-x}$ bulk alloys,¹⁵⁵ and ~10-11 nm Cu-Au alloy nanoparticles.³⁹⁷ This can be expected due to the weaker binding of CO on Ag and Au, favoring CO desorption in these systems.²⁷⁷ There does exist some synergistic effect though, since several Cu-Au bimetallics showed higher activities for CO production compared to pure Au electrodes tested in each study.^{155,397,398} Several explanations for this include: CO adsorbed on Cu sites can further promote CO desorption on Au sites due to dipole repulsion,¹⁵⁵ or that neighboring Cu atoms can instead form a bond with the oxygen end of COOH *via* a bifunctional mechanism, stabilizing this intermediate for CO production on Au sites.³⁹⁷ It is unclear to what extent these may be true, but both suggest that an optimal surface Cu:Au composition is required for enhanced CO activity in these alloys. It is worth noting that the optimal bulk composition was different in these two studies, but this could be due to a morphology effect for the planar *vs.* nanoparticle alloy configurations and/or the true surface compositions differed from the bulk.

Alternatively, a third study on CuAu (1:1) alloy nanoparticles actually ascribed their enhanced CO activity to a compressively strained Au surface layer that formed as a result of a disorder-to-order transformation.³⁹⁸ The disordered CuAu nanoparticles were largely selective for H_2 , in agreement with the group's previous composition-dependent study,³⁹⁷ but the ordered CuAu nanoparticles were found to have higher specific and mass activities for CO production compared to pure Au nanoparticles. Since surface characterization revealed that a three-atoms-thick Au shell formed on top of the ordered CuAu alloy core, bifunctional effects were ruled out in this specific system; instead, it was suggested on the basis of a complementary DFT study that 6% compressive strain and vertical ligand effects contributed to the catalytic activity.³⁹⁸ While enhanced CO activity has been demonstrated in these Cu-Au alloy and core-shell systems, it is worth noting that none have shown a higher average turnover frequency than the state-of-the-art Au catalysts (**Figure 37** in Section 7.4). Cu-Au bimetallics may offer an interesting

opportunity to rationally design electrocatalysts yielding optimal and tunable syngas (H_2 and CO) compositions, as demonstrated in a systematic study of Cu monolayer coverage on Au nanoneedles.¹³³

Another report sought to take advantage of strain and vertical ligand effects by synthesizing Au core Cu shell nanoparticles (Au@Cu) with different Cu shell thicknesses (7-10, 14-18, 30-40 layers).⁴⁰⁴ The cubic Au nanoparticle core resulted in epitaxial growth of Cu(100) for low and intermediate quantities of Cu layers, but this broke down for the largest number of Cu layers, which looked to be more (111) in character. Therefore, this system has several competing effects including strain, surface structure, roughness, and particle size differences that make it tough to ascribe the activity and selectivity to any one of these in particular. In addition, all three samples showed time-dependent selectivity over the course of an hour.⁴⁰⁴ While they do not confirm with structural characterization after electrochemistry, this could be due, at least in part, to Cu overlayer instability. Previous work investigating Cu overlayers on Au(100)⁴⁰⁵ and Au(111)^{405,406} observed alloy formation for Cu monolayers^{405,406} and multilayers⁴⁰⁶ under strongly cathodic potentials, while submonolayers⁴⁰⁵ relieved the interface tension by structural collapse. Thus, the significant (12.5%) tensile strain between Cu and Au may simply be too unstable to yield a certain benefit, especially given the already high mobility of Au and Cu at room temperature. The Au overlayer on intermetallic CuAu nanoparticles generated by the disorder-to-order transformation resulted in an intermediate compressive strain (6%) for Au.³⁹⁸ The reduced interfacial tension, plus the fact that the Au shell is already supported on an alloy phase, may decrease the driving force for overlayer instability. While extended tests over 12 hours do show some loss of activity (15%) and gold content,³⁹⁸ near surface alloys could still be a promising paradigm to investigate moving forward for achieving stable strain effects.

7.2.2 Synergistic Effects for $>2\text{e}^-$ Products

There are two key effects in some Cu-M bimetallic electrodes (where $\text{M} = \text{Ag}, \text{Au}, \text{Zn}$) that have led to improved activity or selectivity for C-C coupled and oxygenated products: CO spillover and electronic effects. In the first case, by co-locating domains of Cu with those of a CO-generating metal, such as Ag, Au, and Zn, additional CO can be supplied to Cu via eased surface diffusion over short

length scales and/or by simply increasing the local CO concentration within the diffusion boundary layer, which in turn can lead to a higher coverage of $^*\text{CO}$. One potential demonstration of this concept was shown in a study on Cu-Ag bimetallic electrodes using a pulsed CO_2 electroreduction technique, which yielded higher Faradaic efficiencies for the production of C_{2+} compounds such as CH_3CHO , $\text{C}_2\text{H}_5\text{OH}$, and C_2H_4 compared to pure Cu and Ag metal electrodes.¹²³ By alternating cathodic and anodic biases, it was expected that desorption of CO occurred on Ag but not from Cu, allowing for facile C-C coupling on Cu due to a higher partial pressure of CO near the surface of the electrode. Another group electrodeposited Cu-Au alloys onto a nanoporous Cu film (NCF) and found these led to higher alcohol selectivities compared to the NCF alone.³⁹⁹ They also compared the best Cu-Au alloy composition electrodeposited on the NCF to that deposited on a flat copper plate and found that the alcohol selectivity was much lower using the copper plate substrate, suggesting that the nanostructured morphology and/or surface area has a strong impact on this effect. Linear sweep voltammetry in CO yielded a higher current than in Ar, so while CO spillover is not mentioned explicitly, the authors use this result to suggest that catalyzing conversion of intermediary CO could be the cause for the improved alcohol selectivity.³⁹⁹ Unfortunately, the results are only presented in terms of selectivity (Faradaic efficiency), no current density information for the bulk electrolysis was provided, so we were unable to determine if the intrinsic activity towards alcohols was improved.

There have been a few recent reports that have more directly linked observed improvements in C_{2+} activity and/or selectivity to a CO spillover effect.^{128,130,132,400,401} One system that clearly exhibited synergistic activity and selectivity for C_{2+} alcohols superior to that of Cu, Au, or CuAu alloys was a polycrystalline Cu foil decorated with Au nanoparticles (Au/Cu).⁴⁰⁰ In fact, the Au/Cu catalyst reduced the overpotential by >260 mV for the production of alcohols and had a >100x higher rate of CO_2 reduction to $>2e^-$ products in this low overpotential region, as shown in **Figure 33**. These improvements are attributed to a tandem catalysis mechanism, where these two separate metals operate in close proximity with complementary surface chemistry. This hypothesis was supported by a control experiment performed on a surface alloy ($\text{Au}_{0.01}\text{Cu}_{0.99}$), which did not reproduce the trend of enhanced alcohol production at low overpotentials. The CO spillover effect was further corroborated by transport modeling, which indicated that the Au nanoparticles provide a higher concentration of CO near the

Au/Cu surface than what Cu could produce alone or than what could be sustained through transport of CO from the bulk.⁴⁰⁰ Having this local CO source within the electrode double layer sidesteps the issue of low CO solubility in aqueous electrolytes, leading to the increased activity for C_{2+} products at low overpotentials. A similar Au on Cu system mentioned earlier³⁹⁵ only reported on electrolysis data at -1.85 V vs. SCE, in the high overpotential region where this enhancement is minimized. In addition, Morales-Guio *et al.* found that there was an optimal range for Au nanoparticle loading required to observe the synergistic effect to $>2e^-$ products.⁴⁰⁰ These reasons, as well as differences in product detection capabilities, could possibly explain why this effect was not observed previously.

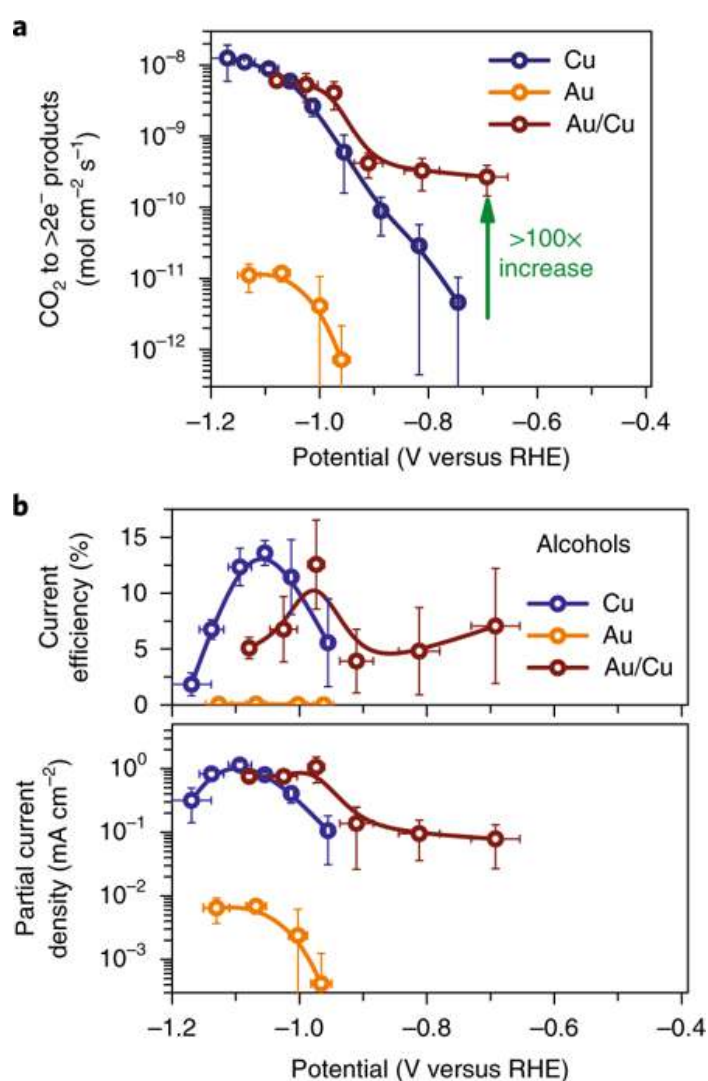


Figure 33: a) CO₂R rate to $>2e^-$ products; b) Current efficiencies and partial current densities to alcohols. Reprinted with permission from Morales-Guio *et al.*⁴⁰⁰ Copyright © 2018, Springer Nature.

Investigations of oxide-derived Cu_xZn phase separated electrodes¹³⁰ and Ag- Cu_2O phase blended and phase separated electrodes¹²⁸ showed enhancements in C_{2+} selectivity, particularly for ethanol, and a CO spillover mechanism was again proposed. These bimetallic electrodes achieve some of the highest ethanol Faradaic efficiencies reported (Ag- Cu_2O phase blended: 34% at -1.2 V vs. RHE¹²⁸; Cu_4Zn : 29% at -1.05 V vs. RHE¹³⁰). It is noteworthy, however, that the enhancements in ethanol selectivity compared to their monometallic Cu control samples only occur at high overpotentials ($E \leq -0.9$ V vs RHE). This is in stark contrast to the Au/Cu system, which achieves higher selectivities at lower overpotentials (-1.0 V vs. RHE $\leq E \leq -0.7$ V vs. RHE) and reaches a maximum in alcohol partial current density 90 mV earlier than on Cu.⁴⁰⁰ This can likely be rationalized by the higher overpotentials required for CO production on Ag and Zn compared to Au (see **Table 3**),¹ which may shift the potential region where CO spillover can be a benefit. As for why ethanol is preferred over ethylene in these systems, it is likely that the lower rates of hydrogen production on the Cu_xZn and Ag- Cu_2O electrodes and operation in the low overpotential region on Au/Cu could shift the selectivity towards oxygenated C-C coupled products (*i.e.* ethanol) rather than hydrogenated C-C coupled products (*i.e.* ethylene). As discussed previously, while the selectivity is an important metric to consider, this alone does not tell you about the activity of the catalyst for CO_2 reduction; for this, we must examine the (partial) current densities. Since the authors primarily discuss activity based on the geometric current density despite the different roughness factors (RF) of these catalysts¹³⁰ or do not report the catalysts' RF,¹²⁸ we will address their activity in Section 7.4.

Finally, it is worth discussing another report that has studied this tandem/sequential catalysis mechanism in detail using a series of microfabricated electrodes (**Figure 34**).⁴⁰¹ In the first design, separate, interdigitated Au and Cu electrodes on an insulating SiO_2 substrate allow for each electrode to be actuated individually or simultaneously. When the electrodes were actuated simultaneously, there was a significant drop in the CO partial current density compared to when only Au was actuated, which suggests that the CO formed on Au lines is consumed by the Cu lines, validating the sequential catalysis concept.⁴⁰¹ Interestingly, there was also a subtle shift in C_{2+} product distribution to favor oxygenates

over ethylene production with decreasing Cu coverage, while all variations of the device maintained a lower oxygenates to ethylene ratio when only Cu was actuated.

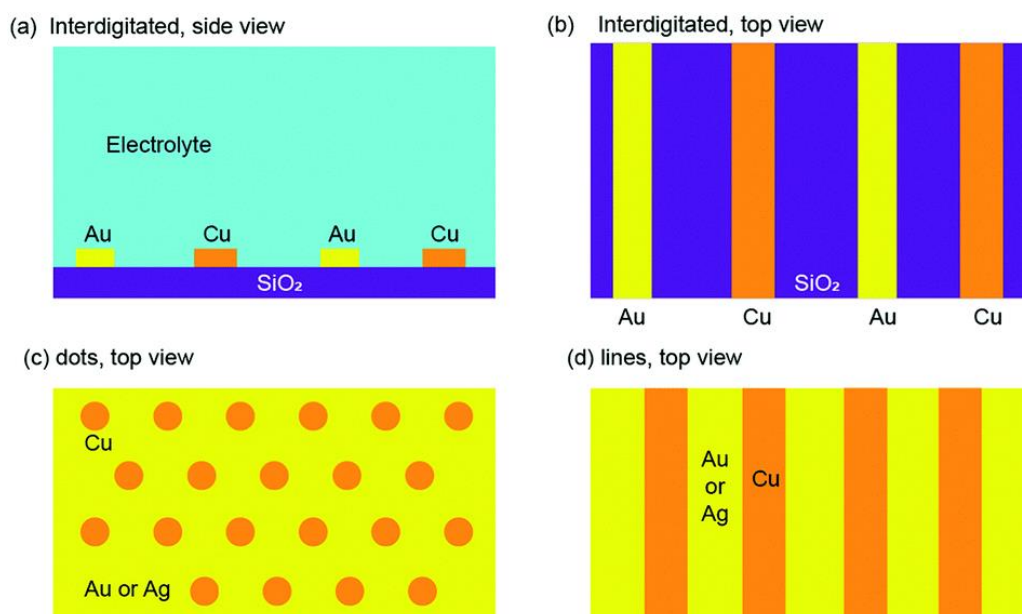


Figure 34: Schematics of interdigitated bimetallic electrodes, **a)** and **b)**, and micropatterned electrodes, **c)** and **d)**. Separation of the two metals in the interdigitated design allow for their independent operation. In all three designs, the areal ratio of the CO-producing metal, Au or Ag, to Cu can be varied. Reproduced from Lum *et al.*⁴⁰¹ with permission from the Royal Society of Chemistry.

The researches then probed this effect further by systematically fabricating a series of electrodes where Cu was patterned directly onto Au or Ag substrates, which allowed for fine control over the spacing and coverage of Cu. As the coverage of Cu was decreased from 77.2% to 2.4%, the ratio of oxygenates to ethylene Faradaic efficiency increased from 0.72 to 2.39, which mainly resulted from a decrease in ethylene and increases in acetaldehyde, acetate, and propionaldehyde selectivities.⁴⁰¹ Meanwhile, the total C₂₊ Faradaic efficiency was maintained in the 50-65% range regardless of Cu coverage in these tandem/sequential catalyst devices; although, as one may expect, the partial current densities dropped with decreasing Cu coverage. Through a combination of control experiments and modeling, the reason behind the improved selectivity towards oxygenates in these devices was proposed to be due to CO transfer from the Au or Ag substrate inducing a higher coverage of *CO on the Cu surface.⁴⁰¹ This increased *CO would likely come at the expense of *H coverage, which could result in slower surface hydrogenation rates and, in turn, favor the formation of oxygenates instead. All in all, the studies discussed thus far in this subsection showcase a new design principle for tandem or

sequential catalysis; by employing a co-catalyst that generates an *in-situ* source of mobile CO, CO₂R to >2e⁻ products, particularly C₂₊ oxygenates, can be enhanced. Future work can advance tandem catalysis system designs by tuning the materials' surface structures, morphologies, and compositions.

Bimetallic Cu-Ag thin films have also been reported to exhibit HER suppression and higher selectivity for C₂₊ oxygenates through other means.^{73,402} While CO spillover could still be a contributor in these systems, the dominant cause thought to be leading to these selectivity enhancements was tuning of adsorbate and reaction intermediate binding energies by incorporation of Ag into Cu. In the first case, CuAg metal foils consisting of segregated Cu and Ag phases were prepared by arc melting, quenching, and cold rolling, and it was suggested that formation of CuAg surface alloys under electrochemical reaction conditions leads to compressive strain on Cu surface atoms.⁷³ This compressive strain, as evidenced by an observable shift of the valence band structure of Cu to deeper levels, weakens the adsorption energy of H*, resulting in a 60–75% reduction in the HER activity. Interestingly, this was also correlated to a 10–15% increase in the total selectivity for C₂₊ products and a product distribution shift from hydrocarbons to oxygenates. Moreover, acetate and acetaldehyde accounted for a substantial portion of the C₂₊ oxygenate selectivity, reaching up to a combined 15% Faradaic efficiency, which is noteworthy given that these are typically minor (<1%) products on pure Cu. This selectivity modification is attributed to reduced rates of C–O bond scission resulting from the HER suppression and the reduced oxophilicity of the compressively strained Cu, which presumably inhibits the ability of Cu to reduce these carbonyl-containing products further.⁷³ It is worth noting though that this did not impact the ability of Cu to make products derived from CO (*i.e.* the activity to >2e⁻ products remained unchanged when normalized to the nominal Cu composition).⁷³

In the second case, CuAg thin films across a range of nominal CuAg compositions were formed via physical vapor deposition, and many of the same trends were observed including HER suppression, decreased hydrocarbon selectivity, and increased oxygenate selectivity, particularly for the carbonyl products.⁴⁰² In this case, however, the overall intrinsic CO₂R activity toward further reduced products was decreased for CuAg versus Cu. This is attributed to the significant nonequilibrium bulk-phase miscibility between Ag and Cu achieved in these films,⁴⁰² compared to the previous work which had

minimal miscibility of Ag in Cu (< 3 at.%).⁷³ This significant Ag miscibility in Cu is also thought to be responsible for the observed selectivity enhancements by tuning the electronic structure of Cu, decreasing the binding energy of H* and oxygenated reaction intermediates. Further trends in product distribution were also discussed, including the significant suppression of CH₄ leading to an overall higher selectivity for C-C coupled products in these CuAg films compared to pure Cu.⁴⁰² With careful catalyst characterization, these studies demonstrate how formation of alloys using two metals that are thermodynamically immiscible under ambient conditions can be an effective strategy to alter CO₂R activity (reduced HER) and selectivity (increased C₂₊ oxygenates) in bimetallic systems.

Another Cu-Ag system has also demonstrated a higher selectivity for acetate formation (~21% at -1.33 V vs. RHE at 0 °C).⁴⁰³ In this case, however, they were separate ~6 nm Cu and Ag nanoparticles immobilized on a polymer/glassy carbon electrode, and acetate was only observed over the bimetallic when benzotriazole (BTA) was in the electrolyte (over the Cu control sample it was observed in minor quantities, <1% Faradaic efficiency, both with and without BTA). While the selectivity changed with the ratio of Ag present, indicating the Ag clusters may play an important role through the CO spillover mechanism discussed earlier, clearly the electrolyte additive has a dominant impact on the product formation since without BTA, the main CO₂R product over the bimetallic electrode was CO.⁴⁰³

7.3 Copper and HCOO⁻ Producing Guest Metals (In, Sn)

The *p*-block metals are generally characterized by their high selectivity for formate production at high overpotentials.^{1,85} They also require a relatively high overpotential for the HER, which has drawn significant interest in employing them in bimetallic Cu systems as a strategy to reduce the selectivity for this competing side reaction. In addition, In and Sn electrodes have previously been demonstrated to exhibit a kinetically meta-stable oxide at the electrode/electrolyte interface at potentials where CO₂R is observed, which can strongly influence the electrocatalytic properties of these systems.^{142,407} This also widens the range of surface chemistries that can be created by these bimetallic systems, so careful characterization of the electrode surface is crucial. Unfortunately, *ex-situ* characterization methods are

often complicated by the oxophilicity of these elements and are particularly difficult given the nanostructured nature of the bimetallic catalysts in this section. Thus, comparisons and conclusions based on composition and/or oxidation state need to be taken with caution. In addition, it is impossible to identify which catalysts have a higher average turnover frequency because almost all of these studies reported current densities using the geometric electrode area. Thus, we will focus much of the remaining discussion of these Cu-M bimetallics (where M = In, Sn) on selectivity trends.

The key trends observed in Cu-M (where M = In, Sn) systems include synergistic CO production, HER suppression, and suppression of further reduced ($>2e^-$) products.^{408–419} In addition, several bimetallics maintained a higher selectivity to HCOO^- .^{408,409,420,421} In two of these cases, thick Sn deposits were employed on top of Cu substrates and resulted in overall Sn-like behavior with high selectivity ($>80\text{--}90\%$) to HCOO^- formation.^{420,421} Thus, the Cu here mainly seems to serve as a support to provide a route for making high surface area Sn electrodes to increase the yield of HCOO^- , rather than engendering any bimetallic effects. On the other hand, Cu core SnO_2 shell nanoparticles (Cu@SnO_2) were investigated for CO_2R , and while the thicker (1.8 nm) Sn shell was again more selective for HCOO^- ($<1\%$ CO), the thinner shell (0.8 nm) instead resulted in very high selectivity for CO ($>90\%$ from -0.6 to -0.9 V *vs.* RHE).⁴⁰⁸ DFT calculations suggested that the combination of compression ($\sim 10\%$) due to the lattice mismatch between the core and shell and self-doping of Cu atoms diffusing out from the core resulted in the selectivity towards CO over HCOO^- on SnO_2 . An analogous study on Cu core In_2O_3 shell nanoparticles reported similar results and reasoning; lattice compression and Cu doping of the In_2O_3 shell led to enhanced CO generation, particularly for the thinnest shell (68% at -0.7 V *vs.* RHE), while the thickest shell had a higher selectivity for HCOO^- .⁴¹⁸ These core-shell catalysts both show that the existence of Cu at the surface is an important factor governing the CO selectivity; there is further support for this design criteria in the studies discussed subsequently.

Two studies of Sn deposited on Cu oxide nanowires⁴¹² and oxide derived Cu substrates⁴¹³ both demonstrated very high CO selectivity for optimized samples (90% CO at -0.8 V *vs.* RHE⁴¹²; $>90\%$ CO between -0.5 to -0.8 V *vs.* RHE⁴¹³), which drastically falls after there is enough Sn on the surface to surpass a full monolayer of coverage on Cu. Similarly, a Cu foam sparsely decorated with Sn (2–3 at.%) was found to achieve $>90\%$ CO selectivity from -0.6 to -1.0 V *vs.* RHE.⁴¹⁹ Two studies of Cu-In

alloys synthesized from reduction of an oxide-derived Cu substrate in In solution⁴¹⁴ and reduction of CuInO₂⁴¹⁵ also demonstrated high CO selectivity (>75% CO between -0.4 to -0.7 V vs. RHE⁴¹⁴; 70% at -0.8 V vs. RHE⁴¹⁵). While the resulting bimetallic structures range from no evidence of alloy formation,^{412,419} to near surface alloy formation,^{413,414} to bulk alloy formation,⁴¹⁵ similar reasoning for the enhanced CO selectivity is proposed; namely, it is thought that incorporation of In/Sn disrupts favorable multi-Cu binding sites for protons while leaving CO binding sites unaffected, leading to HER suppression and enhanced CO selectivity at moderate overpotentials.^{412–415,419} This is supported by complementary DFT studies by the Takanabe group.^{413–415}

Alternatively, it has also been proposed that a meta-stable In(OH)₃ phase generated *in-situ* is responsible for enhanced CO selectivity in oxide-derived Cu-In bimetallics.⁴¹⁶ In this report, several CuIn catalysts were synthesized from different starting oxide materials, and while they initially showed different performance & morphologies, these catalysts evolved over repeated catalytic cycles to achieve similar CO selectivity (~50%) in parallel with appearance of an In(OH)₃ shell. Furthermore, when In(OH)₃ was etched off, the CO selectivity decreased until the hydroxide reappeared.⁴¹⁶ Thus, it was hypothesized that the synergistic effect observed in these systems was due to the existence of bifunctional active sites at metal-oxide interfaces. Therefore, following this study, the same researchers conducted systematic experiments on a series of microfabricated electrodes seeking to establish a relationship between the CO activity and the length of these metal-oxide interfaces.⁴¹⁰ By varying the amount of In/In₂O₃ dots patterned onto Cu/Cu₂O substrates, the interfacial density (ρ_{int}) could be varied across 2 orders of magnitude; meanwhile, the total geometric surface area of each single-phase component was kept constant so as to avoid contributions from differences in coverage. In this way, the researchers did observe a positive correlation between the CO activity and ρ_{int} for 2/3 of the variations studied (In₂O₃/Cu₂O and In/Cu₂O, not In₂O₃/Cu), but not for the reason they initially expected.

Ultimately, it was found that oxidic indium was not important, but the presence of Cu₂O, which was reduced to metallic Cu under reaction conditions, was necessary for this synergistic effect to occur. By contrast, all electrodes using a Cu substrate showed similar activity for CO regardless of ρ_{int} (**Figure 35a**).⁴¹⁰ As shown in **Figure 35b**, only the two electrode versions using Cu₂O substrates displayed significant diffusion of In from the dots into the surroundings. Taken together, these results indicate

that these In-modified Cu “halos” around the dots were responsible for the high activity for CO evolution rather than metal-oxide interfaces (both Cu and In were found to be metallic under reaction conditions anyway).⁴¹⁰ Thus, with regards to their previous work, it is now suggested that the succession of reduction/oxidation cycles would aid in the formation of highly active, indium-poor metallic Cu compositions similar to those found in this study by accumulating In into an $\text{In}(\text{OH})_3$ sink; although the possibility of active sites existing at metal-oxide interfaces cannot be completely ruled out at this time.⁴¹⁰

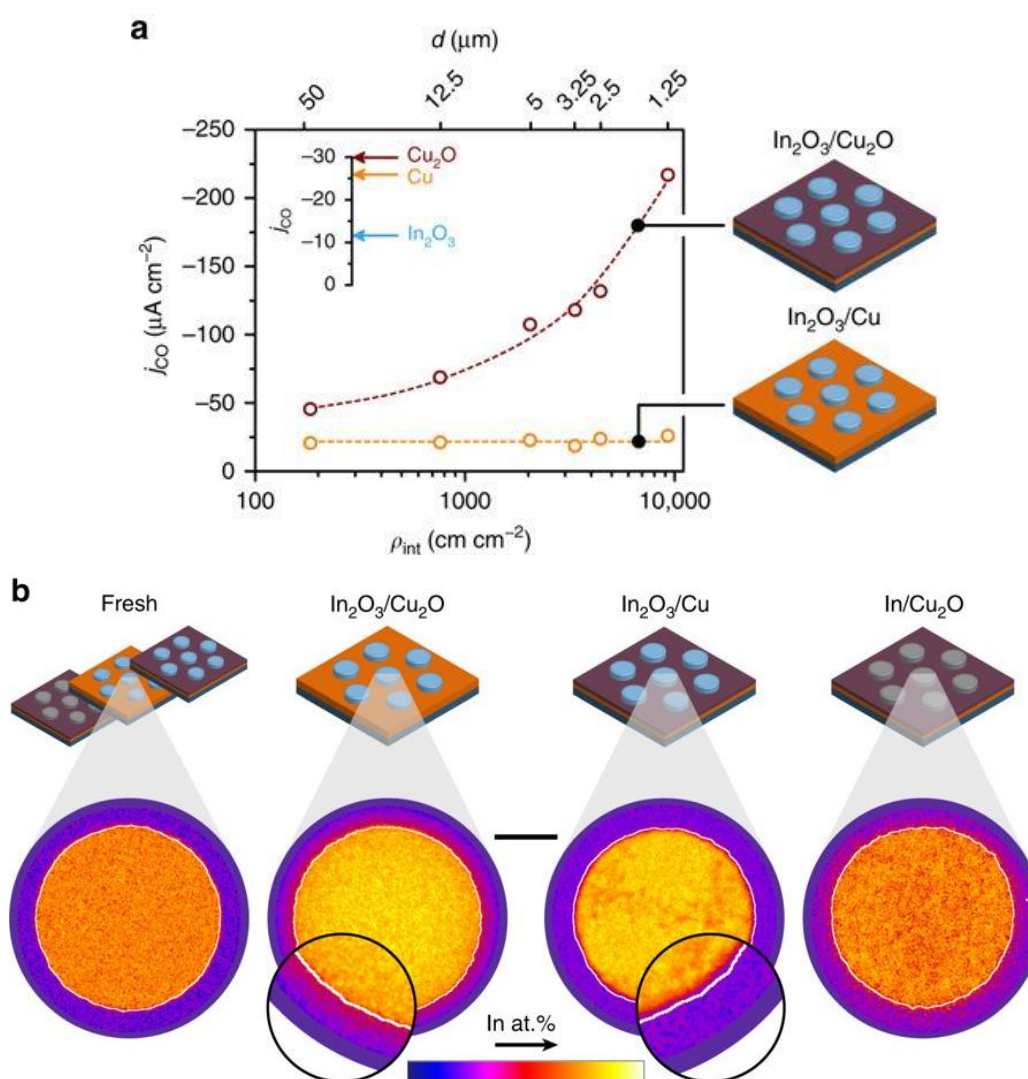


Figure 35: a) Partial current density for CO evolution (j_{CO}) over microfabricated $\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$ and $\text{In}_2\text{O}_3/\text{Cu}$ electrodes as a function of the interfacial density (ρ_{int}) at -0.6 V vs. RHE. Note: the corresponding island diameter (d) is indicated on the top x-axis, the trendlines were added as a visual aid, and the inset shows the corresponding partial current densities measured over the single-phase control samples. **b)** Elemental distribution of indium over individual islands for the 3 electrode variations ($\text{In}_2\text{O}_3/\text{Cu}_2\text{O}$, $\text{In}_2\text{O}_3/\text{Cu}$, $\text{In}/\text{Cu}_2\text{O}$), with a representative island prior to the reaction shown as reference (Fresh). Note: the white contours indicating the border of the corresponding fresh islands were added as a visual aid, and the scale bar is 5 μm . Reprinted from Larrazábal *et al.*⁴¹⁰ This work is licensed

In light of this follow-up study by Larrazábal *et al.*, it is clear that the interfaces between In/Sn and Cu on the surface is emerging as a key factor governing the high CO selectivity observed in these bimetallic electrodes. This is further supported by a combined theory-experiment study on In-modified (Cu(OH)₂-derived) Cu nanowires.⁴¹¹ The composition where the highest number of Cu-In interfacial sites were formed was found to be the optimal sample, achieving ~93% Faradaic efficiency for CO at -0.6 to -0.8 V *vs.* RHE. DFT calculations also confirmed the crucial role of metallic Cu-In interfaces in tuning the stability of key reaction intermediates; these interfacial sites were found to significantly decrease the barrier for *COOH formation while still allowing for facile release of *CO, and weakly adsorbed *H and strongly adsorbed *OCHO on these sites could be the cause for suppression of H₂ and >2e⁻ products.⁴¹¹

Finally, it is worth briefly revisiting the role of the oxide(s) in these bimetallic electrodes. Many of these studies suggested that the structure of the oxide precursor(s) governs the alloy formation and resulting CO activity several reasons including compositional⁴¹⁷ and morphological effects.^{409,414,415} Interestingly, in the work by Larrazábal *et al.*, a control experiment where indium was deposited on an already oxide-derived Cu substrate did not exhibit the same synergistic effect, which indicates that the *in-situ* reduction of the Cu₂O-based electrodes is required for diffusion of In to create the CO-selective, In-modified Cu “halos”.⁴¹⁰ This could perhaps explain the formation of highly active Cu-In and Cu-Sn surfaces that started with an oxide precursor mentioned earlier in this section. Although the oxidation state of Cu, In, and Sn during CO₂R is still an open area of debate, at least partial (if not full) reduction of these oxide species under reaction conditions seems beneficial to encourage diffusion of these components to create optimal interfacial sites. Unfortunately, untangling the complex tradeoff between the various possible effects in these nanostructured, bimetallic catalysts is incredibly difficult, so again, caution must be taken when trying to draw comparisons between systems or identify concrete structure-activity relationships. While there is clearly more work that needs to be done to better understand the factors governing the activity and selectivity of Cu-In and Cu-Sn, these high surface area Cu bimetallics

with p-block metals have certainly shown promising CO selectivities and geometric activities (**Figure 37** in Section 7.4).

7.4 Activity Comparisons

In this chapter, we presented the main findings for different classes of Cu-based bimetallic systems. Before reiterating the key selectivity trends and presenting activity comparisons, we wish to start by providing some overall perspectives on the challenges faced in studying and comparing the activity of bimetallic catalysts. First, as discussed in Section 2.4, benchmarking and reporting how the pure metal components perform in a given experimental setup is highly recommended to help validate trends observed for a given bimetallic catalyst. Second, identifying active sites on the surface of bimetallics under *operando* conditions can represent a major challenge. In particular, the composition at the surface of a bimetallic can be very different than in the bulk due to segregation of one component. This can be induced by fundamental differences in the materials' properties (oxophilicity, CO binding strength, miscibility, etc.) upon exposure to different environments (air *ex-situ*, electrolyte and/or applied potentials *in-situ*), as well as result from different catalyst synthesis methods and pretreatment procedures. Indeed, many studies discussed herein observed surface enrichment of one component either as a result of the synthesis method^{133,390,391,394,398,418} and/or electrochemical testing.^{73,382,391,396,405,406,414,416} Unfortunately, this makes comparisons between bimetallic catalysts more difficult; for example, two different bulk compositions may ultimately have similar surface compositions during electrolysis, and *vice versa*. This, in turn, can limit the scope of theoretical predictions and/or hinder our ability to match them with experimental results.

Third, while nanostructured bimetallics are interesting to explore in their own right, one must be careful when trying to draw structure-composition-activity relationships from these systems. Some reports on high surface area bimetallic electrodes noted different morphological features as a function of composition, which increases the difficulty of making systematic assessments.^{130,391,394,404,409} In addition, some studies tried testing a flat bimetallic catalyst to serve as a standard for comparison to their nanostructured catalyst,^{413,414} but this still has its pitfalls because the same surface ratio and

dispersion of individual metal components may not be readily replicated between low and high surface area catalysts. In general, trying to decouple the impacts resulting from nanostructuring (increased surface area, faceting, grain boundaries, nanoparticle size and support effects, mass transport limitations) and those resulting from the bimetallic ensemble (composition/phase, atomic arrangement of each component, strain) is extremely difficult. Thus, when trying to draw conclusions about the intrinsic activity or selectivity of bimetallics, planar catalysts that minimize the effects of nanostructuring are ideal.

Finally, it is crucial to measure the ECSA of tested electrodes in order to determine whether a higher surface area catalyst truly has a greater average turnover frequency rather than greater activity simply resulting from an increased number of active sites. In light of the challenges in comparing bimetallic electrodes that were just discussed, getting an accurate measure of the ECSA of bimetallics can be especially difficult. As mentioned previously in Section 2.1, there exists a variety of methods for determining the ECSA, and researchers should keep in mind the limitations of each in order to choose the technique most suitable for the materials being studied. The most common method for estimating the ECSA of CO₂R electrocatalysts has been to use double-layer capacitance (C_{dl}) measurements. Ideally, a rough Cu-M catalyst would be compared to a planar Cu-M catalyst of the same surface composition; although as discussed earlier, this can be difficult to replicate and validate since changes in surface composition and morphology may also occur under reaction conditions. These discrepancies in composition may only have a small impact if the capacitance of the two materials are similar, but this introduces more uncertainty when the capacitance of the two materials are quite different. In the case of Cu-M materials, since other M do not convert CO₂ to >2e⁻ products to any appreciable degree, ECSA estimates for Cu-M catalysts can compare the C_{dl} of Cu-M to the C_{dl} of planar Cu when looking to see if the intrinsic activity has been improved beyond that of pure Cu. In any case, it should be noted that the ECSA of bimetallic systems as determined by C_{dl} ratios is typically a conservative estimate for the total number of active sites, since it is unlikely that the entire surface will be active in a bimetallic electrode. Still, any promotion in activity observed using this conservative estimate indicates that at least part of the enhancement is due to improved intrinsic reaction rates and not purely resulting from

an increased number of active sites. Therefore, despite the difficulties and limitations, we urge researchers to make their best attempts to measure and report the ECSA of tested electrodes.

Unfortunately, only a limited number of Cu-M bimetallics have been reported with the requisite information to compare catalytic activity on an average turnover frequency basis. **Figures 36** and **37** provide the total CO₂R current density to >2e⁻ products and CO, respectively, normalized by both the exposed geometric area and ECSA when available for catalysts tested in aqueous-phase reactors. The few bimetallic CO₂R catalysts that have been tested in vapor-fed reactors were not included for this direct comparison due to the vastly different reactant mass transport conditions. Also, in cases where multiple variations of Cu-M bimetallics were studied, only the optimal material was generally included for clarity, in addition to the monometallic control sample if tested.

In **Figure 36**, both planar⁶⁶ and high surface area⁹⁰ Cu control samples are included for reference. While a number of studies have reported bimetallics with increased selectivity to >2e⁻ products, **Figure 36a** shows that this improvement is generally accompanied by a similar or lower geometric activity as compared to the corresponding Cu standard. It is worth noting that despite the decreased partial current densities, in some cases the CO₂R energy efficiencies may be higher on the bimetallics compared to the Cu control samples. This was demonstrated by Lum *et al.*; the 4.3% Cu dots on Ag sample shown in **Figure 36a** had the highest energy efficiency (21.4%) for generation of C₂₊ products, while the 2.3% Cu dots sample had the highest total CO₂R energy efficiency (32.8%).⁴⁰¹

Looking at **Figure 36b**, it quickly becomes clear that the only aqueous-phase bimetallic catalyst system with a higher activity than pure Cu is the Au nanoparticles on Cu foil catalyst.⁴⁰⁰ The OD-Cu₄Zn catalyst¹³⁰ has a larger RF than the OD-Cu standard, so while it achieves an equivalent CO₂R rate to >2e⁻ products when normalized by the geometric electrode area, this results in a lower average turnover frequency when normalized by the ECSA. Another bimetallic catalyst system that demonstrated higher activity than pure Cu was the CuAg wire reported by Hoang *et al.*¹³² While the Cu wire catalyst initially shows higher current densities to C₂₊ products at lower overpotentials then levels off (likely due to the lack of *CO resulting from the high turnover rate in this region), the C₂₊ activity of the CuAg wire catalyst continues to increase and surpasses that of the Cu wire at -0.7 V vs. RHE. These results were not included in **Figure 36** since they were obtained in a vapor-fed device, but it is worth noting the

impressive C_{2+} activity and selectivity metrics achieved by the CuAg wire catalyst at this potential: 60% C_2H_4 and 25% C_2H_5OH at a total current density of $\sim -300 \text{ mA/cm}^2$.¹³² This cannot be explained by surface area differences alone because the bimetallic has a 10% higher ECSA but 60% higher current density than the Cu wire at this potential. Experiments where CO is mixed into the vapor feed during CO_2R show that the C_{2+} saturation region displayed by the Cu wire catalyst disappears, and instead the current continues to increase like that of the CuAg wire.¹³² Therefore, CO spillover from Ag is likely a key mechanism by which the bimetallic wire achieves the improved performance at higher overpotentials. This once again highlights the potential of tandem catalyst systems that can effectively decouple multiple CO_2R steps, bypassing design limitations intrinsic to monometallic electrodes.

In **Figure 37**, both planar^{66,422} and high surface area^{90,423} Cu and Au control samples are included for reference. In **Figure 37a** we can see that many rough Cu-based bimetallics have had activity comparable to pure Au on a geometric area-normalized basis. While this is encouraging for increasing cost-effectiveness for CO_2R to CO catalysis by reducing noble metal usage, we can see in **Figure 37b** that pure Au is still orders of magnitude more active on an average turnover frequency basis. Also, it is interesting to note that the ECSA-normalized CO partial current densities for Cu-M bimetallics with In or Sn essentially fall in between the planar and high surface area Cu standards; only those with Au have activity higher than Cu, closer to that of Au. Thus, while many of these high surface area Cu-M catalysts with p-block metals have demonstrated impressive CO selectivity (>90%), the *intrinsic* activity for CO_2R to CO on copper does not seem to have been enhanced in these systems. Again, the sample pool is very limited here though due to a lack of reporting the ECSA of these materials. Future studies on Cu-M bimetallics should strive to include the roughness factors of these materials so that the intrinsic activity can be more readily compared.

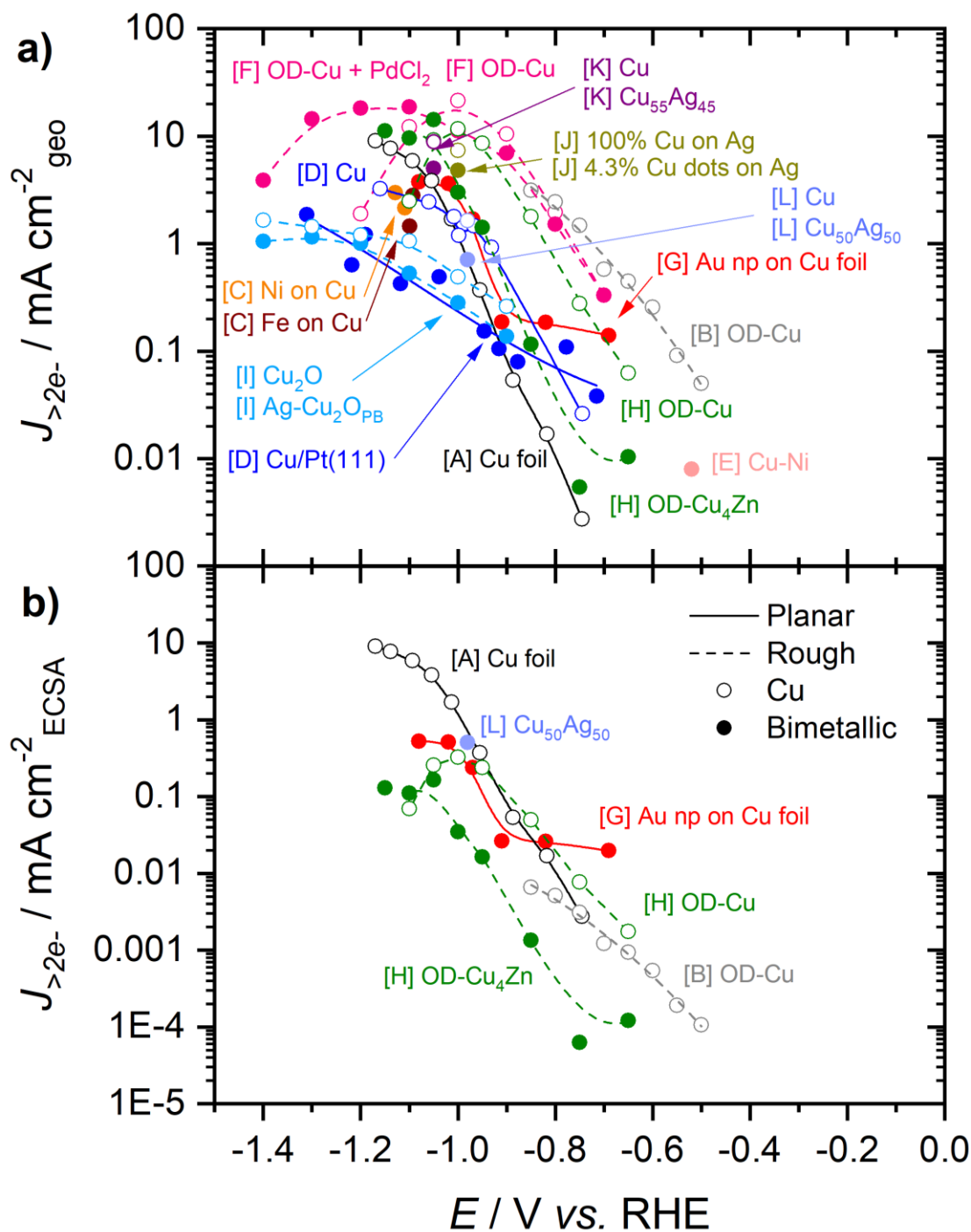


Figure 36: Cu-based bimetallic catalysts' total current density to further reduced ($>2e^-$) products normalized by **a)** the geometric area and **b)** the ECSA. The data were obtained from the following studies: [A] Cu foil by Kuhl *et al.*⁶⁶; [B] OD-Cu by Li *et al.*⁹⁰; [C] Ni and Fe deposits on Cu (two points shown for the beginning and end compositions formed by the *in-situ* electrodeposition) by Hori *et al.*³⁷⁸; [D] Cu overlayer on Pt(111) and Cu control sample by Varela *et al.*³⁸²; [E] Cu_{90.5}Ni_{9.5} alloy by Watanabe *et al.*³⁸⁵; [F] OD-Cu with PdCl₂ in the electrolyte forming deposits on the surface, as well as an OD-Cu control sample, by Chen *et al.*³⁸⁹; [G] Au nanoparticles on Cu foil by Morales-Guio *et al.*⁴⁰⁰; [H] OD-Cu₄Zn and OC-Cu control sample by Ren *et al.*¹³⁰; [I] Ag-Cu₂O_{PB} (PB = phase blended) and Cu₂O standard both deposited on Toray paper by Lee *et al.*¹²⁸; [J] 4.3% Cu dots patterned on an Ag substrate and a 100% Cu (fully coated on Ag substrate) control sample by Lum *et al.*⁴⁰¹; [K] Cu₅₅Ag₄₅ bimetallic

foil and Cu foil standard by Clark *et al.*⁷³; [L] Cu₅₀Ag₅₀ thin film bimetallic and Cu control sample by Higgins *et al.*⁴⁰²

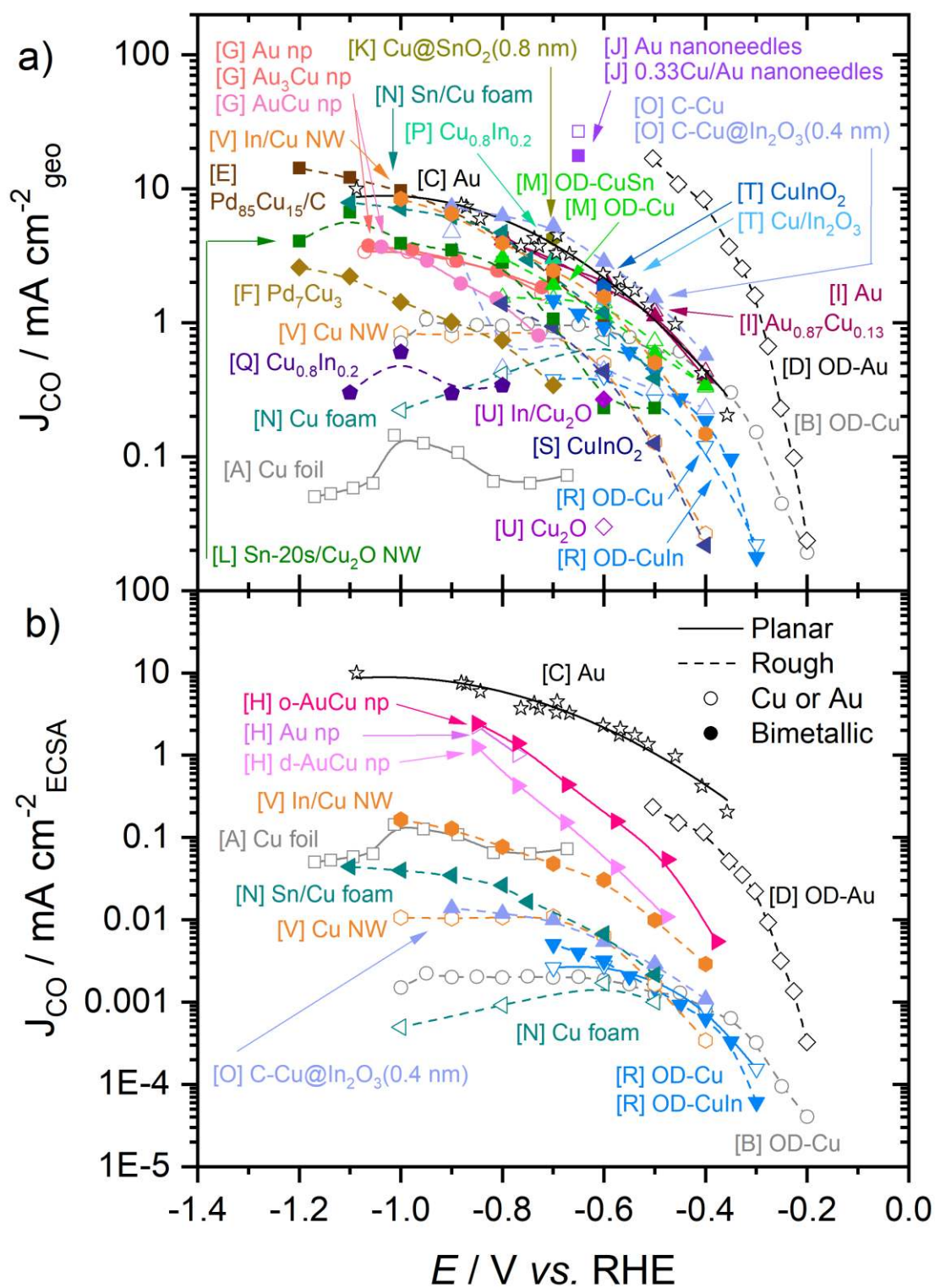


Figure 37: Cu-based bimetallic catalysts' total current density to CO production normalized by **a)** the geometric area and **b)** the ECSA. The data were obtained from the following studies: [A] Cu foil by Kuhl *et al.*⁶⁶; [B] OD-Cu by Li *et al.*⁹⁰; [C] Au by Hori *et al.*⁴²²; [D] OD-Au by Chen *et al.*⁴²³; [E] Pd₈₅Cu₁₅/C alloy nanoparticles supported on carbon black by Yin *et al.*³⁹⁰; [F] Pd₇Cu₃ electrodeposited mesoporous films by Li *et al.*³⁹¹; [G] AuCu, Au₃Cu, and Au nanoparticles by Kim *et al.*³⁹⁷; [H] ordered (o-) and disordered (d-) AuCu nanoparticles and Au nanoparticle control sample by Kim *et al.*³⁹⁸; [I] Au and Au_{0.87}Cu_{0.13} prepared by pulsed laser deposition in 220 mtorr O₂ by Roy *et al.*³⁹⁶; [J] 33% Cu coverage on Au nanoneedles and Au nanoneedles by Ross *et al.*¹³³; [K] Cu@SnO₂(0.8 nm) core-shell nanoparticles by Li *et al.*⁴⁰⁸; [L] Sn deposited for 20 sec on Cu₂O nanowires by Zhao *et al.*⁴¹²; [M] OD-CuSn and OD-Cu control sample by Sarfraz *et al.*⁴¹³; [N] 2-3 at.% Sn on Cu10 foam (Sn/Cu foam) and Cu10 foam standard (Cu10 = 10 min electrodeposition) by Zeng *et al.*⁴¹⁹; [O] Carbon-supported Cu@In₂O₃(0.4 nm) core-shell nanoparticles and carbon-supported Cu nanoparticle control sample by Xie *et al.*⁴¹⁸; [P] Cu_{0.8}In_{0.2} by He *et al.*⁴¹⁷; [Q] Cu_{0.8}In_{0.2} by Hoffman *et al.*⁴⁰⁹; [R] OD-CuIn and OD-Cu control sample by Rasul *et al.*⁴¹⁴; [S] CuInO₂-derived by Jedidi *et al.*⁴¹⁵; [T] Cu/In₂O₃-derived and CuInO₂-derived by Larrazábal *et al.*⁴¹⁶; [U] In dots microfabricated on Cu₂O substrate (In/Cu₂O) and Cu₂O control sample by Larrazábal *et al.*⁴¹⁰; [V] In deposited on Cu nanowires (Cu(OH)₂ derived) using 20 mM InCl₃ solution and Cu nanowire control sample by Luo *et al.*⁴¹¹

7.5 Summary

Here we examined Cu-M bimetallic combinations across three groups, where the guest metal M is either highly selective to H₂, CO, or HCOO⁻. In all cases, the synergistic effects are generally diminished when the surface is dominated by the guest metal, causing the activity and selectivity to mimic that of the pure M component. For H₂-selective metals, increased HER activity and decreased CO₂R activity have typically been observed. Interestingly, the C₂₊ pathway(s) in particular get disrupted, as the main further reduced product formed in these systems was CH₄, with C₂H₄ formation significantly suppressed. For CO-selective metals, high activity and selectivity for CO has been noted, as well as some synergistic activity and selectivity to C₂₊ products (especially oxygenates) resulting from CO spillover and electronic effects, respectively. Finally, for HCOO⁻-selective metals, HER suppression and high selectivity for CO, along with inhibition of all further reduced products, have typically been observed.

At this time, it appears that the intrinsic activity of Cu (for >2e⁻ products) and Au (for CO) have not been outmatched by bimetallic systems, except in the two demonstrations of tandem catalysis via CO spillover from Au nanoparticles on Cu foil⁴⁰⁰ and from Ag in a CuAg wire gas diffusion electrode.¹³² In these cases, the two monometallic catalysts operate in synergy whereby Au/Ag provides a higher concentration of CO near the electrode surface than what Cu could produce alone or than what could

be sustained through transport of CO from the bulk electrolyte, allowing for increased rates of C₂₊ product formation compared to pure Cu. While there have been notable electronic and geometric effects demonstrated in Cu bimetallic systems, it appears that these have predominantly contributed to product distribution trends such as HER suppression, >2e⁻ products suppression, increased CO selectivity, and/or increased selectivity to C₂₊ oxygenates including ethanol or the carbonyl products. In these cases, weakening or disrupting sites for *H binding seems to be a key factor leading to enhanced CO₂R selectivities. It is possible that poisoning of oxophilic sites by formate may prevent the predicted ability of bifunctional active sites to break scaling relations for CO₂R to >2e⁻ products.^{203,366} Therefore, electrochemical CO reduction (COR) on Cu-based bimetallics may be of interest for future work, since starting from CO as the reactant both eliminates the HCOO⁻ pathway and allows for a broader range of pH conditions to be tested. Characterization and stability of these bimetallic system has also presented major challenges, as segregation and/or oxidation state changes of the individual metals can occur under reaction conditions and/or upon exposure to air for *ex-situ* characterization. Therefore, another area for future work includes further development of *operando* spectroscopic techniques to help elucidate the true chemical state and structure of active sites in Cu bimetallics during electrochemical CO₂R.

8. Conclusions and Future Outlook

Coupling electrochemical CO₂ reduction (CO₂R) with a renewable energy source to create high value fuels and chemicals is a promising strategy to help achieve a sustainable global energy economy. Not only could this serve as a renewable source of traditionally fossil-derived resources, but it could also enable storage of energy from intrinsically variable electricity generators such as wind and solar. In this review, we took a detailed look at the state of electrochemical CO₂ reduction on Cu and the key levers that have been used to tune its activity & selectivity, including surface faceting, electrolyte effects & electrochemical conditions, nanostructuring, and preparation of bimetallics. First, we would like to emphasize the following key points:

- 1) **Nanostructuring does not alter the *intrinsic activity* of copper in any significant manner, independent of the method used.** While other morphological features may also play a role,

we believe that increased surface area is the key factor altering the product selectivity of nanostructured materials, since this impacts the potential window where CO₂R/COR current densities are optimized.

- 2) **a) Significant methods to increase the intrinsic activity of copper through bimetallic electronic or geometric effects have not yet been found.** Notably, a tandem/sequential catalysis scheme has emerged as a promising paradigm for achieving higher activity and selectivity to C₂₊ products, particularly oxygenates. By co-locating domains of Cu with those of a CO-generating metal (*e.g.* Ag, Au, and Zn), additional CO can be supplied to the Cu surface.
b) Bimetallic electronic and geometric effects have, however, resulted in product distribution changes such as HER suppression, >2e⁻ products suppression, and/or increased CO selectivity compared to pure Cu. It is also worth noting that higher selectivities to oxygenates such as acetate and acetaldehyde have been achieved in several Cu-Ag systems.
- 3) **It is important to consider the chemical potential of the reactants and electrolytes since this could easily change the catalyst surface structure and composition.** The inherent mobility of copper and the ease with which it is oxidized present challenges in maintaining stable surfaces. This can explain the large observed dependency on the catalyst preparation and testing methods.
- 4) **Theoretical studies have indicated that step sites may very well dominate CO₂R activity, although experimental validation of this remains a challenge.** Copper surfaces have been shown to reconstruct under reaction conditions. Thus, the formation of undercoordinated defects or step sites during preparation or testing of single crystal electrodes could explain why they have demonstrated similar overall activity.
- 5) **It is crucial to report the electrochemically active surface area (ECSA) of tested electrodes whenever possible in order to determine if greater catalytic activity can be attributed to improved intrinsic activity (higher average turnover frequency) rather than an increased number of active sites (larger surface area).** It is also important to keep in mind the ambiguities of measuring ECSA and choose the method most appropriate for the system at hand.

- 6) Catalysts with different roughness factors and/or catalysts tested under different electrolyte and electrochemical conditions will reach mass transport limitations at different rates.** Thus, it is not always straightforward to compare electrodes tested at the same applied potential, since these different conditions may lead to different kinetic overpotentials. When investigating the *intrinsic* behavior of novel electrocatalyst materials, we underline the importance of comparing data in potential windows governed by the intrinsic reaction kinetics, so as not to convolute the impacts of catalyst properties and mass transport effects.

Electrochemical CO₂ reduction on copper catalysts holds significant promise, but there is still much work to be done before low-cost, scalable deployment of CO₂R technologies can be realized. Towards this end, we not only need greater fundamental understanding of CO₂R mechanisms, but increased practical performance metrics as well. We will briefly discuss our outlook on key areas for future studies in these spaces.

To date, most of the catalyst characterization techniques have been conducted *ex-situ* before and/or after CO₂R due to the complexity of the electrified electrode/electrolyte interface. There has been an increasing trend, however, in the development and implementation of *in-situ/operando* characterization techniques, with recent studies providing new insights highlighted in each section of this review. We urge the further advancement of these techniques, as they can provide crucial insights regarding the catalyst surface structure, composition, oxidation state, and adsorbed intermediates under reaction conditions. These will be invaluable tools for providing better understanding of active sites, elucidation of reaction mechanisms, and validation of predictions from theoretical studies. For more details on the state of surface characterization techniques for CO₂R and the progress in this area of research, we direct the reader to a reference module by Soriaga *et al.*⁴²⁴ in addition to a recent review article by Handoko *et al.*¹⁰

The developments in theoretical modeling of the electrochemical interface have yielded significant progress in identifying key active site motifs, reaction intermediates and descriptors, solvation and ion promotion effects, and CO₂R pathways. While much of the previous focus has been

on analyzing the reaction energetics and thermodynamics, further developments in kinetic modeling will be required to better understand the interplay between coverage, potential dependence of activation energies, adsorbate-adsorbate interactions, and pH effects. The development of machine-learning algorithms also presents an opportunity to develop predictive capabilities and screening methods, which can aid materials discovery efforts and promote the rational design of CO₂R catalysts.^{425–427} Challenges remain in the reconciliation of conclusions between existing theoretical approaches, the advancement of functionals for describing charge at the electrochemical interface, and the evaluation of kinetics and reaction barriers of elementary steps under reaction conditions. Multi-scale modeling of transport effects will also be critical for better understanding of interfacial processes, especially for more practical high surface area catalysts and vapor-fed reactors. These developments will lead to increased and improved coupling between experimental and theoretical CO₂R studies.

Next, we feel that the field must begin developing the necessary catalysts and reactor systems to enable scalable (low cost), selective and energy efficient conversion of CO₂ to useful fuels and chemicals. It is often cited how Cu typically requires ~ 1 V overpotential to form valuable hydrocarbons and alcohols,¹ but this mainly applies to planar systems. Nanostructuring, along with the use of alkaline electrolytes and larger-sized alkali cations, has provided a route to decreasing the required overpotential and altering the selectivity to certain products. Most notably, immense progress has been made in recent years in development of gas diffusion electrode (GDE) and continuous flow devices.^{13,127,132,293,331,348,351–355,428} For example, a recent report achieved a very high C₂H₄ selectivity of ~70% over 150 hours of operation between 75 and 100 mA/cm², and a full-cell energy efficiency for CO₂ conversion to C₂H₄ of 34%.³⁵² While this value is lower than the 60 – 80% energy efficiency typically achieved for water splitting, this is quite reasonable based on the relative maturity of that field, as well as the significant difference in potential product values. Thus, while there is always a need for fundamental research, the field is at a stage where we can start accelerating the development of practical devices. This includes optimization of device components (catalysts, supports, membrane, electrolyte) and conditions (flow rate, temperature, pressure, etc.), as well as testing the tolerance to more realistic conditions. For example, many potential CO₂ sources for initial commercial applications (such as industrial plant flue

gas, biogas, etc.) will have diluted CO₂ streams with different potential contaminants.⁴²⁹ Renewably-powered CO₂R may also have interrupted/variable power input depending on the source (such as intermittent wind & solar), so tolerance to factors like these must be taken into account for large scale deployment of CO₂R technology. In addition, complicated product separations may result in significant additional energy requirements, which should ideally be minimized.⁴²⁹

Lastly, we will briefly discuss three other focus areas for improving CO₂R activity & selectivity. The competing HER remains a significant issue for CO₂R in aqueous systems. While progress has been made in improving CO₂R selectivity by employing basic electrolytes, we additionally suggest the investigation of CO₂R in nonaqueous and solid polymer electrolytes. While this review focused on Cu catalysts, there are also several emerging classes of catalysts that hold the potential to break scaling relations between reaction intermediates, including stable alloys, single atom catalysts, (doped) carbon materials, metal organic frameworks (MOFs) and covalent organic frameworks (COFs), materials with 3 dimensional active sites that can induce confinement effects, and functionalized surfaces (tethering promoters/ligands to the electrode surface).^{58,203,374,430} Materials discovery efforts should continue in these directions to identify novel catalyst materials with enhanced properties. Finally, CO reduction has been increasingly studied in recent years, both as a proxy to better understand CO₂ reduction mechanisms, as well as for fundamental understanding of this important reaction in its own right. If viable COR catalysts are developed, this could enable tandem or cascaded reaction systems in which CO₂R is split into two separate steps: 1) CO₂ reduction to CO, then 2) CO reduction to the desired product(s). Unique synergies could also be achieved by coupling CO₂ electroreduction with alternate types of catalytic processes (biological, thermal, etc.).

In summary, while many challenges and opportunities remain in developing catalysts and reactor systems with high activity, selectivity, stability, and scalability, much progress has also been attained in recent years, priming this technology for commercial application. With continued research & development, electrochemical CO₂ reduction could have a substantial impact on the sustainability of our global energy economy.

Acknowledgements

The material from Stanford/SLAC researchers is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award No. DE-SC0004993.

The work by researchers at the Technical University of Denmark was supported by a research grant (9455) from VILLUM FONDEN.

B.S. also acknowledges a grant from Innovation Fund Denmark (8057-00018B ECOethylene).

Supporting Information

1. Thermochemistry: Raw Data and Calculations. Includes Table S1: Thermochemistry data for carbon products and copper phases, calculation of equilibrium potentials, energy content of carbon products calculations, and discussion/calculations of pH dependence on the RHE and SHE scales.
2. Economics: Raw Data and Calculations. Includes descriptions of global non-energy carbon in industry, economics of CO₂ reduction products
3. Computational Studies: Energetics and Kinetics of Elementary Steps. Includes Table S2: Calculated barriers for CO₂R to CO via various methods, Table S3: Calculated barriers for CO reduction to C₁ products via various methods, Table S4: Calculated barriers for C-C coupling via various methods.

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Biographies

Stephanie A. Nitopi was in the Schreyer Honors College at The Pennsylvania State University where she received her B.S. in Chemical Engineering in 2014. She is now a Ph.D. candidate in the Chemical Engineering department at Stanford University, and a member of Professor Tom Jaramillo's group and the SUNCAT Center for Interface Science and Catalysis. She was a recipient of a Stanford Graduate Fellowship in Science & Engineering, and her current research is focused on the electrochemical conversion of carbon dioxide to fuels and chemicals on copper catalysts.

Erlend Bertheussen received his Bachelor's degree in Nanotechnology from the University of Bergen in 2012. He then moved to Denmark to do a Master's in Physics and Nanotechnology at the Technical University of Denmark (DTU), where his interest for electrochemical energy conversion started. He subsequently started a PhD degree in Physics at DTU, where he performed work within the field of CO reduction on copper electrodes. After graduating in the spring of 2018, he took a position as an R&D Engineer in the start-up company RenCat ApS.

Soren B. Scott received a Bachelor's in Chemistry from the University of Copenhagen in 2013 before being introduced to the idea of CO₂ electroreduction while working as a research assistant at the Joint Center for Artificial Photosynthesis at Lawrence Berkeley National Lab. He returned to Denmark for a Master's in Chemical Engineering at the Technical University of Denmark (DTU, 2016) and has since then been a Ph.D. student at DTU's Department of Physics. In 2018, Soren was awarded an EliteForsk travel grant from the Danish Ministry of Higher Education and Science. His current research uses in-situ mass spectrometry to probe electrocatalytic interfaces.

Xinyan Liu received her B.S. in chemical engineering from Tsinghua University (Beijing, China) in 2013. She then obtained her Ph.D. in chemical engineering from Stanford University in 2018 under the supervision of Prof. Jens K. Nørskov, during which she has worked on density functional theory based microkinetic modeling of Fischer–Tropsch synthesis, electrochemical hydrogen evolution reaction, and

electrochemical carbon monoxide/dioxide reduction reactions. Her expertise is in microkinetic modeling and data mining.

Albert K. Engstfeld (1983, Germany) graduated from the Ulm University in 2009 in chemistry with specialization in physical chemistry and surface science. He received his Ph.D. in 2015 from Ulm University on “Design and electrochemical / –catalytic properties of well defined bimetallic model catalyst electrodes,” research conducted under the supervision of Prof. R.J. Behm. After a Post Doc position at the Institute for Surface Physics & Catalysis (Technical University of Denmark), he returned in 2017 to Ulm University. He is currently working as a group leader (Nano-structured metal surfaces) at the Institute of Surface Chemistry and Catalysis. Combining an ultrahigh vacuum system with electrochemical methods he focusses on a fundamental understanding of restructuring/corrosion processes and electrocatalytic properties of nanostructured (bi)metallic single crystal model electrodes on an atomic scale level.

Sebastian Horch received his Ph.D. degree in Physics (1994) from Bonn University, Germany. He was Feodor Lynen Research Fellow at Arizona State University in 1995. Until 1999, he was Assistant Research Professor in the Center for Atomic-scale Materials Physics (CAMP) at Aarhus University, Denmark. Since 1999, he is Associate Professor at the Department of Physics, Denmarks Technical University (DTU). His main area of research is Surface Science using high resolution scanning probe microscopy.

Brian Seger completed his PhD in chemical engineering from Notre Dame under Prof. Prashant Kamat in 2009. After completing postdocs at the University of Queensland under Lian Zhou Wang and at DTU under Prof. Ib Chorkendorff, he became an assistant professor in the Surface Science and Catalysis section of DTU Physics in 2014 and then promoted to associated professor in 2017. He has published 45 peer reviewed papers that have been cited over 5,000 times. His research focuses on electrochemical CO₂ reduction, photoelectrochemistry, semiconductor-electrolyte interfaces, and electro-synthesis reactions.

Ifan E.L. Stephens was appointed as Senior Lecturer at the Department of Materials at Imperial College London in July 2017. Prior to Imperial, he was at the Department of Physics at the Technical University of Denmark (DTU); he was first employed as a postdoctoral researcher, then as assistant professor and finally as associate professor and leader of the Electrocatalysis Group there. In 2015, the Department of Mechanical Engineering at Massachusetts Institute of Technology (MIT) awarded Ifan the Peabody Visiting Associate Professorship. His team conducts model electrocatalysis experiments to enable the large-scale conversion of renewable energy to fuels and valuable chemicals and vice versa.

Karen Chan is an Associate Professor at the Department of Physics, Technical University of Denmark. Prior to this she was Associate Staff Scientist at SLAC National Accelerator Laboratory as part of the Joint Center for Artificial Photosynthesis. Her expertise is in the atomistic and continuum level modeling of electrochemical interfaces with applications in sustainable energy conversion. She obtained her PhD in 2013, advised by Michael Eikerling and held a postdoc fellowship from 2013-2016 at Stanford University, advised by Jens K. Nørskov.

Christopher Hahn completed his doctorate at the University of California Berkeley in 2012, where he studied bandgap engineering of 1-dimensional nitride and oxynitride materials for solar water splitting. After receiving his Ph.D., he conducted his postdoctoral research on catalyst discovery for electrochemical CO₂ reduction at Stanford University within the SUNCAT Center for Interface Science and Catalysis. He began his current position at SLAC National Accelerator Laboratory in 2015, where he is conducting research with the Joint Center for Artificial Photosynthesis on catalyst discovery and understanding reaction mechanisms for electrochemical CO₂ reduction.

Jens K. Nørskov is the Villum Kann Rasumussen professor at the Technical University of Denmark. His research aims at developing theoretical methods and concepts to understand and predict properties of materials. He is particularly interested in surface chemical properties, heterogeneous catalysis, electro-catalysis, and applications in energy conversion.

Thomas Francisco Jaramillo is an Associate Professor of Chemical Engineering at Stanford University and of Photon Sciences at SLAC National Accelerator Laboratory, where he is the Director of the SUNCAT Center for Interface Science and Catalysis. A native of Puerto Rico, Prof. Jaramillo earned his B.S. in Chemical Engineering at Stanford University, followed by M.S. and Ph.D. in Chemical Engineering at the University of California at Santa Barbara (UCSB). Prof. Jaramillo conducted post-doctoral research in the Department of Physics at the Technical University of Denmark (DTU) as a Hans Christian Ørsted Post-doctoral Fellow. Prof. Jaramillo's research efforts are aimed at developing catalysts and processes that can accelerate important chemical transformations related to energy conversion with improved sustainability, efficiency, and durability. Prof. Jaramillo has earned a number of honors and awards for his efforts, including the Resonate Award from the Resnick Institute (2014), the Presidential Early Career Award for Scientists & Engineers (PECASE, 2011), the U.S. Dept. of Energy Hydrogen and Fuel Cell Program Research & Development Award (2011), the National Science Foundation (NSF) CAREER Award (2011), and the Mohr-Davidow Ventures (MDV) Innovator Award (2009).

Ib Chorkendorff is Professor in Heterogeneous Catalysis at DTU Physics. He earned his PhD in 1985 at Odense University Denmark, and after a post-doc at University of Pittsburgh, USA, he was employed in 1987 at DTU as Associate Professor for starting up the field of experimental surface science and catalysis. From 2005-2016 he was director of the Danish National Research Foundation Center for Individual Nanoparticle Functionality (CINF) and from 2016 he has been director of The Villum Center for the Science of Sustainable Fuels and Chemicals (V-SUSTAIN). Ib Chorkendorff's research activities focus on finding new catalysts for improving energy production/conversion and for environmental protection. He has author or coauthored more than 330 scientific papers, 18 patents and one textbook "Concepts of Modern Catalysis and Kinetics". He is co-founder of three start-up companies RENCAT APS, HPNOW APS and Spectroinlets APS. Ib Chorkendorff has received numerous prizes and honors among others the Ulrik and Marie Brinch award and the Ingeborg and Leo

Dannin's Prize for Natural Science Research. He is elected Fellow of The Academy for Technical Sciences (ATV) and Elected member of the Royal Danish Academy of Sciences and Letters.

TOC Figure

