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## 2022 roadmap on low temperature electrochemical CO<sub>2</sub> reduction

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## ROADMAP

2022 roadmap on low temperature electrochemical CO<sub>2</sub> reduction

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**Keywords:** electrocatalysis, CO<sub>2</sub> reduction, electrochemistry, solar fuels

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**Abstract**

Electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>R) is an attractive option for storing renewable electricity and for the sustainable production of valuable chemicals and fuels. In this roadmap, we review recent progress in fundamental understanding, catalyst development, and in engineering and scale-up. We discuss the outstanding challenges towards commercialization of electrochemical CO<sub>2</sub>R technology: energy efficiencies, selectivities, low current densities, and stability. We highlight the opportunities in establishing rigorous standards for benchmarking performance, advances in *in operando* characterization, the discovery of new materials towards high value products, the investigation of phenomena across multiple-length scales and the application of data science towards doing so. We hope that this collective perspective sparks new research activities that ultimately bring us a step closer towards establishing a low- or zero-emission carbon cycle.

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## Introduction

Ifan E L Stephens and Karen Chan

The electrochemical reduction of CO<sub>2</sub> offers enormous potential as a carbon neutral or carbon negative route to the production of platform chemicals and fuels. Since the seminal works by Horii in the 1980s through to the early 2000s [1, 2], the field had remained relatively static until 2010, when Peterson *et al* [3], Schouten *et al* [4], and their respective co-workers reignited interest. Since then, enormous progress has been made in reactor design and in tailoring materials. Even so, we still face numerous challenges on the road to large scale industrialization. In this roadmap, leading international researchers in the field provide a comprehensive overview of the state-of-the-art and also identify avenues for future progress.

We have focussed specifically on low temperature electrochemical CO<sub>2</sub> reduction, i.e. occurring below 100 °C. Nonetheless, as we acknowledge at several points in the manuscript, high temperature CO<sub>2</sub> reduction can sometimes offer advantages over the low temperature counterpart and may even complement it (e.g. chapters 19 and 21). However, low temperature routes are at a more early stage in their technological development. Within this roadmap, for the purpose of brevity, and to maximise the scientific common ground, we have chosen not to include high temperature CO<sub>2</sub> electrolysis and to focus on the more nascent, low temperature routes towards CO<sub>2</sub> electro-valorisation.

Kuhl *et al*, from the start-up, Twelve, commence the roadmap by establishing the industrial priorities for CO<sub>2</sub> reduction (CO<sub>2</sub>R), emphasizing the technological and commercial challenges and opportunities ahead. Yadegari, Zhong and Ryan discuss the upstream challenges associated with capturing CO<sub>2</sub>; progress in this area will be essential if CO<sub>2</sub>R is to transition from a carbon *neutral* technology—contingent on waste CO<sub>2</sub>—to a carbon *negative* technology. Roy, Karimi and de Luna identify CO and ethanol as the most promising products for closing the carbon cycle.

There are several challenges for experimentalists in evaluating the performance of CO<sub>2</sub>R. In particular, measuring the myriad products in a rigorous, transparent and meaningful manner is an untrivial task: Jayatilake and Hahn summarize best practices and also outline how they see testing progressing in the future. Jovanov, Ferreira de Araujo and Strasser explain the possibilities afforded by electrochemical mass spectrometry (EMS), both for quantifying performance in real time and also to elucidate reaction pathways.

Benchmarking the performance is particularly challenging under conditions that resemble those in industrial devices; to that end, Hansen and Jiao outline the most important aspects to the employment of gas diffusion electrodes (GDEs). Within GDEs, there is a complex interplay between transport phenomena, solution phase reactions and charge transfer kinetics. Boutin and Haussener explain the challenges and opportunities in multi-scale modeling to rationalize these phenomena. Ma and Seger address a particularly important, but sometimes overlooked, challenge: how to maximize CO<sub>2</sub> utilization. One means to do so is to employ bipolar membranes (BPMs), which Boettcher reviews in detail.

Da Silva, Vos, Liang, Liu and Koper have identified some of the key open questions in the mechanistic understanding of CO<sub>2</sub>R; they suggest that exploring CO<sub>2</sub>R outside 'normal' conditions, such as in non-aqueous solvents or at high pressures, may yield new insights and open up new reaction pathways and products.

Several contributions call for an increasing role for data science to understand CO<sub>2</sub>R, from the stack level, as described by Janaky and Endrődi, to the atomistic scale, as described by Bagger and Rossmeisl. Wang and Sargent advocate for machine learning techniques to accelerate the discovery of new materials. On a similar note, Chee, Roldan Cuenya, Xu, Chang, Lee, Oh and Hwang in their separate contributions all advocate for greater integration of multiple *operando* characterization techniques with catalytic testing to map out structure-property relationships in CO<sub>2</sub>R; they suggest that much complementarity is to be gained by comparing multiple techniques in a coherent and integrated manner.

Sebastian Pascual and Escudero-Escribano describe the unique opportunities afforded by single crystals of copper in providing insight into CO<sub>2</sub>R; they envision how single crystal studies could be integrated with other spectroscopic techniques. Buonsanti discusses how findings on single crystals can be translated to more technologically relevant conditions by using well-defined nanoparticles.

While copper is the most studied material for CO<sub>2</sub>R and is the only synthetic material to produce C<sub>2+</sub> products at significant rates, several of our contributors, including Steier and Varela, have advocated the study of alternative materials. Einsle explains the key features that enable the nitrogenase enzyme to produce C<sub>2+</sub> products. Boutin, Bonin and Robert discuss how well-defined molecular catalysts can reduce CO<sub>2</sub> and CO. The solid state analogues to homogenous catalysts are single metal site doped carbon, which Varela has reviewed; while such catalysts can produce CO efficiently, she proposes that dual site catalysts—emulating

nitrogenase—may be able to yield more reduced energy rich products than CO. Finally, going beyond merely reducing CO<sub>2</sub>, Figueiredo discusses the possibilities afforded by electrochemistry in the formation of C–N bonds.

Despite the open fundamental and technological challenges that remain, significant fundamental and technological developments have been made over the past decade. We envision that continued and coordinated research efforts will pave the way towards the commercialization of CO<sub>2</sub> electrolyzer technology, enabling the sustainable and scaleable production of some of our most important fuels and chemicals.

### **Acknowledgments**

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## 1. What are the industrial priorities in the commercialization of CO<sub>2</sub> electrolyzers?

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### Status

The development of CO<sub>2</sub> electrolysis has gained momentum within the past 10 years. Recent efforts have shifted toward understanding how the design of the electrolyzer itself affects the speed and efficiency of the reaction. Factors such as CO<sub>2</sub> availability, pH, temperature, and electrolyte composition can greatly affect performance. CO<sub>2</sub> as a feedstock can be particularly challenging due to the formation of bicarbonate and carbonate in aqueous solutions, this complicates the reactor design and reaction conditions. To achieve high current density (CD) and selectivity for CO<sub>2</sub> electrolysis products, electrolyzers must be designed to deliver the requisite amount of CO<sub>2</sub> to the cathode catalyst, which is challenging in the traditional purely aqueous systems due to the low solubility of CO<sub>2</sub> in water.

At this time, electrolyzer/catalyst combinations that reduce CO<sub>2</sub> by 2e<sup>-</sup>'s, to make CO or formate/formic acid, are the most developed at the lab scale. Performance metrics for these systems—including CD, current efficiency, cell voltage, product output concentration, and lifetime—have achieved market entry-level and are ready to scale to the MW-level for industrial applications. Efforts are underway to push this further, with the goal to achieve the industrial tons per day scale utilizing a similar electrolyzer design.

Continued electrolyzer/catalyst development for CO<sub>2</sub> electrolysis, to further reduced products such as hydrocarbons and alcohols, is still necessary to make these processes commercially viable at scale. Unfortunately, few reports of electrolyzers with high selectivity to the desired product and high CD (e.g. greater than 200 mA cm<sup>-2</sup>) have been reported (see table 1). A better understanding of the reaction mechanism, impact of catalyst environment on performance, and how the environment can be controlled by electrolyzer design would accelerate commercial application. Those are the top industrial priorities for mass commercialization of CO<sub>2</sub> electrolysis at this time.

### Current and future challenges

Larger-scale commercialization of CO<sub>2</sub> electrolysis faces performance challenges in the following areas: faradaic efficiency (FE), energy efficiency (EE), and CDs. Energy consumption (EC) per unit mass of the product is also used in industry to evaluate energy input for different chemical production processes. To make CO<sub>2</sub> electrolysis competitive with conventional chemical production at large scales, EC needs to be further decreased, requiring a significant improvement in cell voltage and selectivity.

In addition to EC challenges, CO<sub>2</sub> utilization and lifetime are crucial factors that determine the success of commercializing the technology. These two important metrics were frequently ignored until recently. High CO<sub>2</sub> utilization decreases the reactant and downstream purification costs, while long lifetimes of the membrane electrode assembly (MEA) ensures low operating costs and effective utilization of capital costs. Both are fundamental for expanding the technology to a wider market. Lifetime is mainly governed by the key components of the electrodes (or MEAs)—including electrocatalysts, polymer membranes and/or polymer binders, and gas diffusion layers (GDLs)—as well as the way they integrate together. GDL properties, which are relevant to CO<sub>2</sub> utilization and lifetime, could also change during operation. For example, the wettability tends to increase under potential over time, which could cause the pores of GDLs to fill with water, thus blocking the pores for mass transfer of gaseous reactant into and product out of the active sites. Operating for more than 50 000 h is the current lifetime of commercial proton exchange membranes (PEMs) water electrolyzers; this is also the target of Twelve's PEM CO<sub>2</sub> electrolyzers (see figure 1), which utilize the same reactor design. To reach this lifetime goal, it is necessary to demonstrate and understand the root causes of degradation and use this to guide improved materials development.

### Scaleup

Another challenge the industry faces to commercialize this technology is adapting the system for larger applications. The controlling units, electrolyzers, as well as everything within the electrolyzer (such as catalyst amount, flow fields, and bipolar plates) all need to be scaled up. As reactor size increases, the heat distribution and transfer within the electrolyzer will change, requiring a well-designed temperature control system to manage the actual operating temperature of the entire process. Water removal is critical to ensure efficient mass transport within the CO<sub>2</sub> electrolyzers. As the system size increases, water removal from each cell within the stack and uniform distribution of gas to each cell must be regulated. CO<sub>2</sub> electrolysis uses new electrocatalysts that are not off-the-shelf, thus scaling the manufacturing of these new active catalysts to support the requirements of larger units is necessary. Identifying proper materials and sourcing the right



**Table 1.** Key performance metrics for industrially-relevant CO<sub>2</sub> electrolysis.

Key performance metric	Desired range
Current density (CD)	>200 mA cm <sup>-2</sup>
Stack energy efficiency (EE)	Up to 75%
Lifetime	Up to 50 000 h

**Figure 1.** Shows twelve's proton exchange membrane (PEM) CO<sub>2</sub> electrolyzer for CO production. This system has reached the kg per day scale.

manufacturers for large-scale electrolyzer development is essential in building the hardware and expanding CO<sub>2</sub> electrolysis to larger systems.

#### *Commercialization*

Beyond the technical priorities, there are commercial headwinds that emerging technologies must surmount. Often potential customers have CO<sub>2</sub> emissions they want to eliminate but they lack the technology and knowledge to do so. Early conversations begin with a discussion on access to low-cost, carbon-free electricity, which is often the highest cost input for CO<sub>2</sub> electrolysis. Subsequent conversations usually focus on the end product of the CO<sub>2</sub> electrolysis, i.e. methanol, ethanol, polymers, liquid fuels. Typically sites do not have the demand for the end product, thus an off-taker needs to be identified and new value chains must be formed that introduce the CO<sub>2</sub>-based product into an pre-existing, petroleum-based market. This involves conversations among all parties regarding costing, supply, and other incentives for adopting low carbon fuels or products. This type of project development is often outside of the CO<sub>2</sub> emitter's core business operations.

The cost of capital for a first-of-a-kind system can make the project unpalatable to a risk-averse company seeking to reduce its CO<sub>2</sub> emissions. Often the available commercial loans for emerging technologies have above-market interest rates, which can challenge the economic value of the overall project.

Early technology developers must also be project developers, bringing the entire CO<sub>2</sub> ecosystem to a site to ensure sufficient upstream (CO<sub>2</sub> capture) and downstream components (thermochemical and biochemical upgrading) are integrated into one plant. This introduces the added challenge of providing internal project management, contract, and contingency expertise on the developer's side to support large-scale commercialization. Siting is another logistical challenge. Ideally CO<sub>2</sub> electrolyzers would be located near areas with large amounts of cheap renewable electricity, and also adjacent to customer premises for direct integration into downstream process and to minimize the need for constructing new infrastructure. In some cases, where customer sites are not located in optimal cost conditions for electrolysis, the use of existing pipeline infrastructure could provide an economical method for transporting CO<sub>2</sub> or downstream liquid fuels to customers.

Despite these challenges, the industry is primed to expand CO<sub>2</sub> electrolysis to larger commercial applications. With stricter regulations on the horizon and the impacts of climate change becoming more apparent, this technology is a necessary means to integrate industrial production into the future.

## Advances in science and technology to meet challenges

### *Performance*

While there are many challenges to the commercialization of CO<sub>2</sub> electrolyzers, the industry is effectively prioritizing research and development to overcome these challenges. A variety of recent works in the areas of membrane and catalyst development, device design, and device operation have targeted improving CO<sub>2</sub> utilization and lifetime, decreasing EC, and scaling up reactor sizes. Recent studies characterizing how CO<sub>2</sub>R catalysts change under operational conditions [5, 6] and over time [7] yield insights into the relationship between catalyst structure and performance, and how these catalysts might be further optimized for improved performance and lifetime. Membrane durability may also impact system lifetime; there are several known decomposition pathways that may alter the properties of the membrane over time [8]. Continued development of more durable and more conductive membranes, through such strategies as crosslinking and new structural motifs, are necessary for improving device lifetime and efficiency [9]. Tuning of the device design and operational parameters will also be necessary to target limitations on lifetime, including the management of water or salt buildup, maintenance of CO<sub>2</sub> mass transport, and sustained hydration of the membrane [10].

Improving the quality of MEAs with a scalable and economical pathway will substantially enhance the performance of the CO<sub>2</sub> conversion platform and make the electrolytic conversion more competitive in the market. Recent advances in MEA fabrication for CO<sub>2</sub> electrolysis could be classified into two groups based on the supporting substrate for the catalyst layer: GDE with deposition upon a GDL, and catalyst coated membrane (CCM) with the integration of the catalyst layer on the polymer membrane [11, 12]. Either would inherently involve the catalyst ink preparation and sequent integration (deposition) process. To obtain high-quality and consistent inks, the active ultrafine powder and ionomer need to be mixed homogeneously and dispersed into desirable solvents by ultrasonication. At commercial scale, large volume, high shear mixing devices are required for ink preparation and continuous flow cell systems must be optimized to prevent ink separation during longer term storage. Among the latest advanced fabrication technologies, the ultrasonic spray coating system exhibited numerous advantages through manipulation of flow rate, nozzle power, etc. This allows for a series of layered structures where thickness, porosity, and mass loading can all be controlled. Other methods physical and chemical coating techniques [13] have advanced such that they are also viable options for low-cost mass manufacturing of CCMs. An optimized ink associated with the appropriate fabrication method is essential for high-end MEA production, and as catalyst ink technology advances so can CO<sub>2</sub> electrolysis.

### *Commercialization*

Along with technological advances, there are several commercial and financial opportunities that will aid the deployment of CO<sub>2</sub> electrolysis. Manufacturing advances and cost reductions are progressing with the CO<sub>2</sub> electrolyzer itself. By using a standard module size, the CO<sub>2</sub> electrolysis industry can capture manufacturing cost reductions as seen in the photovoltaics and battery sectors.

Larger-scale CO<sub>2</sub> electrolysis is dependent on low-cost carbon-free electricity. Power purchase agreements provide remote access to wind, solar and geothermal electricity and are on a steady downward cost trajectory according to BloombergNEF. Performance guarantees are another risk mitigation tool that can make deploying early-stage technology more palatable. With these guarantees, an insurer will cover any losses to the off-taker, if the new technology does not produce the desired output.

Lastly, public-private partnerships where the federal and state governments co-invest alongside private investors will greatly increase the output of new technologies. The US Department of Energy, for example, has below-market-rate loans for clean energy that can reduce the cost to deploy a first-of-a-kind unit like a CO<sub>2</sub> electrolysis system.

These developments within the carbontech ecosystem are rendering CO<sub>2</sub> electrolysis more reliable and economical, and their advancement helps set priorities for the industry as it expands to bigger commercial markets.

### **Concluding remarks**

The CO<sub>2</sub> electrolysis market is accelerating by leveraging learning from related technologies (water electrolyzers, fuel cells, chlor alkali) and past research. Intensive interest in this technology, which began in academic labs, is now ready to scale to commercial industries. As CO<sub>2</sub> technology becomes mainstream, we see a world where more and more products are made from CO<sub>2</sub>, and no CO<sub>2</sub> is 'wasted' by being emitted to the atmosphere. CO<sub>2</sub> electrolysis at scale can be a piece of the puzzle that mitigates the effects of climate change and the industry will rise to this call.

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## 2. What is the future of CO<sub>2</sub> capture for CO<sub>2</sub> utilization?

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### Status

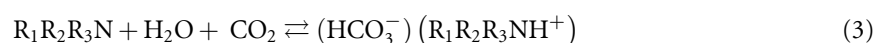
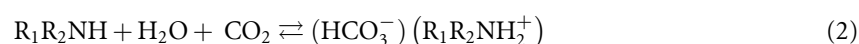
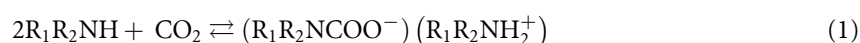
Carbon capture and storage (CCS) generally refers to technologies which selectively capture CO<sub>2</sub> from the atmosphere and durably store it in geological, terrestrial or ocean reservoirs for multiple hundreds or thousands of years. However, achieving a close carbon cycle requires efficient capture followed by CO<sub>2</sub> conversion to products or controlled release in a concentrated form for subsequent utilization. Anthropogenic activities have released a total of ~2400 GtCO<sub>2</sub> over the period 1850–2019, causing (to date) a 1.07 °C raise in global surface temperature [14]. The 2021 AR6 Climate Change report assessed a likely 0.45 °C raise in earth temperature with each 1000 GtCO<sub>2</sub> of cumulative CO<sub>2</sub> emission. Accordingly, remaining carbon budgets (starting from 2020) for limiting global warming to 1.5 °C, 1.7 °C, and 2.0 °C are estimated at 500, 850 and 1350 GtCO<sub>2</sub>, respectively, based on the 50th percentile of transient climate response to cumulative CO<sub>2</sub> emissions (figure 2(a)). Hence, stabilizing or reversing CO<sub>2</sub>-induced global surface-temperature increase requires achieving global net zero or negative CO<sub>2</sub> emissions. However, current commercial-scale CCS projects have a combined potential for capture and storage of only ca.100 million tons of CO<sub>2</sub> per year, accounting for just 0.3% of global annual CO<sub>2</sub> emissions [15, 16].

Electricity and heat generation produced 41% of global CO<sub>2</sub> emission in 2017 (figure 2(b)) [15]. Therefore, most of the CCS research is focused on high concentration point-sources (~4%–15% CO<sub>2</sub>) from fossil fuel power plants. Industrial processes such as cement manufacturing, iron and steel making and natural gas treatment which produced 24% of global CO<sub>2</sub> emission can also be targeted with CCS technologies [17]. Meanwhile, direct air capture (DAC) is also envisioned as a near-term strategy toward negative emissions. Economical and environmental considerations have narrowed down the commercially deployed CCS technologies to post-combustion CO<sub>2</sub> capture, i.e. chemical absorption, and solid looping technologies (figure 2(c)). Amine scrubbing and calcium looping are the two most commercially adopted technologies due to their efficient absorption reaction and compatibility with existing power stations [18]. However, the energy-intensive regeneration of diluted amine solvents and high-temperature thermal swing in calcium looping has motivated the search for more efficient CCS technologies using nanomaterials and electrochemistry [15, 19].

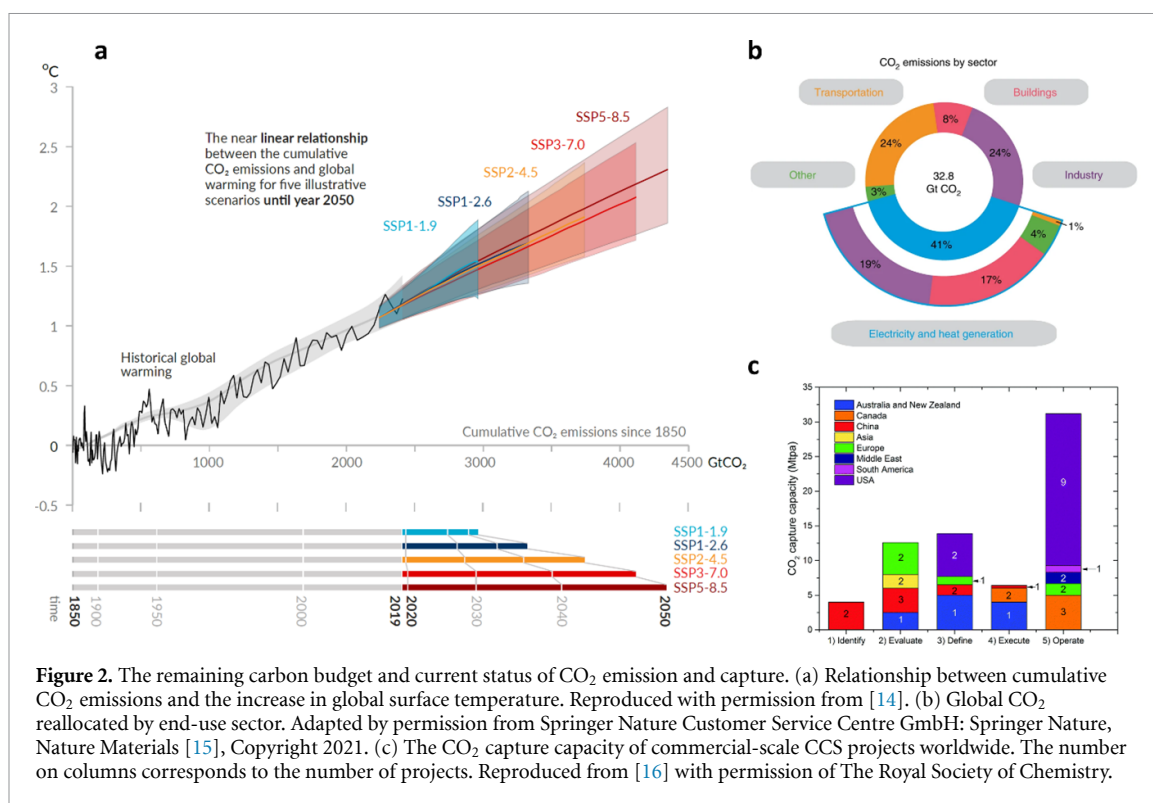
### Current and future challenges in carbon capture

Despite the industrial deployment of solid looping and amine scrubbing, significant challenges still remain in regard to total EE, capacity and lifetime of sorbents, and toxicity and environmental hazards of the employed materials. Solid looping method applies temperature and pressure swing adsorption under relatively high temperatures (usually larger than 300 °C) [20, 21]. Metal oxides, hydrotalcites, and zeolites are often used as solid sorbents. Among them, CaO is one of the most promising and well-studied CO<sub>2</sub> capture materials because of the wide distribution of limestone in nature. Taking calcium looping method as an example, the carbonation reaction of CaO occurs at around 600 °C, whilst the backwards endothermic CO<sub>2</sub> releasing (calcination) reaction proceeds at above 800 °C [18]. Thus, significant thermal energy is required during the absorption/desorption cycle. High temperature also causes additional materials challenges such as sintering and catalyst surface poisoning. It has been shown that the carbonation conversion of CaO significantly decreased from 70% on the first cycle to <10% after 30 cycles due to the formation of surface CaCO<sub>3</sub> blocking layer [18]. Therefore, the rate limiting step changes from surface carbonation reaction to CO<sub>2</sub> diffusion, dramatically decreasing the CO<sub>2</sub> capture capacity and catalyst lifetime.

Amine scrubbing is based on reversible absorption and desorption of CO<sub>2</sub> through formation of water-soluble salts in contact with aqueous amine solutions through following reversible reactions:



where CO<sub>2</sub> can be stored as carbamates via zwitterionic intermediates which will be subsequently be deprotonated and stabilized by base. For primary and secondary amines, both amines and water molecules can serve as the base for deprotonation as shown in reactions equations (1) and (2). However, only



**Figure 2.** The remaining carbon budget and current status of CO<sub>2</sub> emission and capture. (a) Relationship between cumulative CO<sub>2</sub> emissions and the increase in global surface temperature. Reproduced with permission from [14]. (b) Global CO<sub>2</sub> reallocated by end-use sector. Adapted by permission from Springer Nature Customer Service Centre GmbH; Springer Nature, Nature Materials [15], Copyright 2021. (c) The CO<sub>2</sub> capture capacity of commercial-scale CCS projects worldwide. The number on columns corresponds to the number of projects. Reproduced from [16] with permission of The Royal Society of Chemistry.

bicarbonates will be generated for tertiary amines. Since the amine solutions are thermally regenerated, amine scrubbing is also considered as a temperature swing method. Although much lower temperature is usually required compared with solid looping, the inevitable associated water evaporation decreases the EE. High temperature also results in amine loss due to the evaporation. Besides their corrosive and toxic nature, amines are also involved in parasitic reactions such as polymerization and oxidation to amides, ammonia, or nitrosamines under high temperatures, leading to poor capacity and short lifetime.

### Advances in science and technology to meet challenges

Nanoscience and electrochemistry in the past decades have been applied to address the low EE and poor capacity of carbon capture technologies. Surface modification [22], nanosizing of metal oxides via ball-milling and sol-gel [23], and introduction of inert metal oxides [24] or calcium metal oxides [23] to minimize the formation of surface blocking layer have been employed in solid looping technology. The uptake capacity of these calcium-based solid catalysts can reach as high as 0.64 g of CO<sub>2</sub> per gram of sorbent after around 20 cycles [23, 25]. However, application of high temperature is inevitable due to the intrinsic thermodynamics of carbonation reactions, so requires energy input and leads to low efficiency.

Elimination of the aqueous solvent through fixing amines onto solid substrates has been pursued to address the low EE in amine scrubbing technology. A variety of nano-structured amine-functionalized sorbents including high surface carbon-based materials, inorganic oxides, metal-organic frameworks (MOFs), porous polymeric materials, and zeolites have been reported. In an innovative design, Voskian and Hatton used a quinone polymerized into a solid, demonstrating an *electro-swing* CO<sub>2</sub> absorption with high FE and low EC (40–90 kJ mol<sup>-1</sup>) [26]. Meanwhile, porous materials have been widely considered as an emerging technology due to their high EE for CO<sub>2</sub> capture. The adsorptive mechanism in porous materials is projected to reduce the parasitic energy by 30%–40% compared to the absorption process in amine scrubbing and solid looping. In addition, solid-state adsorbents provide tunability of the capture process by altering the pore size and shape, while avoiding toxic and corrosive sorbents. Various organic and inorganic adsorbents including activated carbons, zeolites, amine-functionalized silicas, porous organic networks, and MOFs have been introduced to achieve high selectivity and capacity with low-energy regeneration kinetics [15]. Solid-state adsorptive approach promises higher EE, wider tunability, improved stability and environmental friendliness, but it requires higher capital cost compared to the industrially adopted technologies.

Electrochemical CO<sub>2</sub> capture (ECC) as another promising carbon capture technology uses electro-swing instead of pressure or temperature swing for capturing and releasing CO<sub>2</sub>. ECC methods are mainly appealing for their potential-dependent control of CO<sub>2</sub> absorption/desorption through altering the nucleophilicity of intermediate species under ambient conditions. In addition, ECC methods are compatible

with electrified industry, demonstrate higher flexibility to address decentralized emissions, and offer lower theoretical energy penalties of capture/release processes [19]. Direct ECC is based on altering the nucleophilicity of a redox-active sorbent, while indirect ECC employs a redox mediator which competes with the redox-inactive sorbent for CO<sub>2</sub> binding. Organic redox-active sorbents of quinones, bipyridines, and disulfides, as well as transition metal complexes with macrocyclic amino and pyridine ligands have been explored for direct ECC [27].

Indirect capture mediated with Cu<sup>2+</sup>/Cu<sup>0</sup> (competitor) for the electrochemical regeneration of amines is also investigated as an alternative to thermal generation [28]. Substituting the thermal regeneration with an electro-swing in an amine-based absorption capture could halve the EC of the desorption process [19]. Moreover, electrochemically mediated pH-swing through reversible switching from a basic pH capture to an acidic pH release over ca. 2–3 pH units in aqueous hydroxide or carbonate solutions is particularly attractive for application of inexpensive and environmentally benign mediators [19]. However, irreversible gas evolution during pH-swing decreases the EE. Other potential ECC technologies based on proton coupled electron transfer and membrane capacitive deionization exhibit higher energy efficiencies, but more research and development are required to decrease their capital and operational costs and increase the technology readiness level [19].

### Concluding remarks

CO<sub>2</sub> capture capacity as the basis for CO<sub>2</sub> usage is still under 1% of global emission and requires a significant increase to provide an effective source of CO<sub>2</sub> for scale up of utilization approaches toward zero or negative carbon emissions. The industrially adopted amine scrubbing and solid looping exhibit high EC, poor capacity, and short lifetime due to the intrinsic high temperature desorption cycle. The recent development in utilizing advanced nanomaterials and electro-swing offer potential energy-efficient solutions for the diverse emission sources. The dry adsorptive mechanism using porous sorbents provides a tuneable approach for various-sized plants with different gas mixtures. However, the large-scale synthesis, thermal decay mechanisms, disposal/recycling of the sorbents and its environmental impact should be rigorously analyzed. Electrochemically mediated CO<sub>2</sub> capture is another emerging technology, promising low theoretical energy penalties, ambient operation, use of less toxic materials, and high adaptability with electrified industries. However, further research is required to improve CO<sub>2</sub> absorption rate by enhancing electron and charge transfer kinetics. Moreover, operation under high CD and low-cost membranes should be attained before scaling up. Moreover, recent strategies in combining CO<sub>2</sub> capture with electrochemical conversion into chemicals and fuels [29] has a potential to eliminate expensive separation, storage, and transfer steps and increase the overall EE. Developing efficient technologies combining CO<sub>2</sub> capture with conversion/utilization methods is required for closing the carbon cycle and moving toward zero emission.

### Acknowledgment

H Y acknowledges Marie Skłodowska–Curie Fellowship H2020-MSCA-IF-2019 (897014).

### 3. What are the ideal CO<sub>2</sub> reduction (CO<sub>2</sub>R) products for closing the carbon cycle?

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#### Status

While electrochemical conversion of CO<sub>2</sub> to high-carbon products is favorable, it comes at a significant energy cost and with lower selectivity. As the number of proton-coupled electron transfers increase with higher-carbon molecules, the overall efficiency of energy transformation decreases [30]. Simply put, the larger you go, the more energy you need to get there, and the less efficient you become. Thus, the highest priority should be placed on simple, small building-block molecules that can then be up-converted to a variety of products.

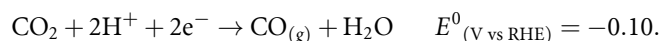
The ideal CO<sub>2</sub>R product is one that can be scaled, is cost competitive with fossil fuel incumbents, and has a sizeable market share such that emissions reductions would be significant when switching from petrochemical production to electrosynthesis. From an emissions reduction capability, renewable electrosynthesis of liquid fuels could comprise 10 700 megatons of CO<sub>2</sub> avoided by 2030 [31]. Carbon monoxide and ethanol represent two ideal CO<sub>2</sub>R products that can be either upgraded to fuel or used directly as a drop-in replacement. Ethylene is also considered a great CO<sub>2</sub>R product that could be used as a building block in chemical industry; however, electrochemically synthesized ethylene has a higher production cost compared to ethanol [30] and hence it is not included here.

Carbon monoxide, when mixed with hydrogen, forms syngas—a precursor of many transportation fuels such as jet fuel, diesel, and gasoline via Fischer–Tropsch upgrading. CO is the most industrially advanced CO<sub>2</sub>R product with companies developing CO<sub>2</sub> electrolyzers at industrially relevant CD<sub>s</sub> (300 mA cm<sup>-2</sup>) and >90% FE, and thousands of hours recorded [32]. CO can also be produced from carbonates directly from CO<sub>2</sub> capture solutions which simplifies process steps and reduces capex [33]. CO as a gaseous product is also easier to separate than products that are dissolved in electrolyte.

Ethanol is a liquid alcohol that can be directly used as a drop-in replacement fuel like ethanol biofuel produced from corn. To date, copper-based catalysts are the only metal type capable of C<sub>2+</sub> products. Ethanol electrosynthesis has been demonstrated at industrially relevant CD<sub>s</sub> in flow cell device, but its FE remains relatively low (50%) [34]. While there is much to be done to improve ethanol electrosynthesis in terms of efficiency, selectivity, and stability, doing so would allow direct conversion to a drop-in fuel and eliminate the need for Fischer–Tropsch.

#### Current and future challenges

Carbon monoxide and ethanol production at high efficiency and conversion rate relies on optimized catalyst design, reactor architecture and process conditions. Catalyst design is central to product selectivity as the binding energy between the surface of the catalyst and the reaction intermediates is a determining factor in product formation. The higher the number of proton–electron exchange, and steps, the more tedious the reaction. CO production is a simple two-electron transfer:

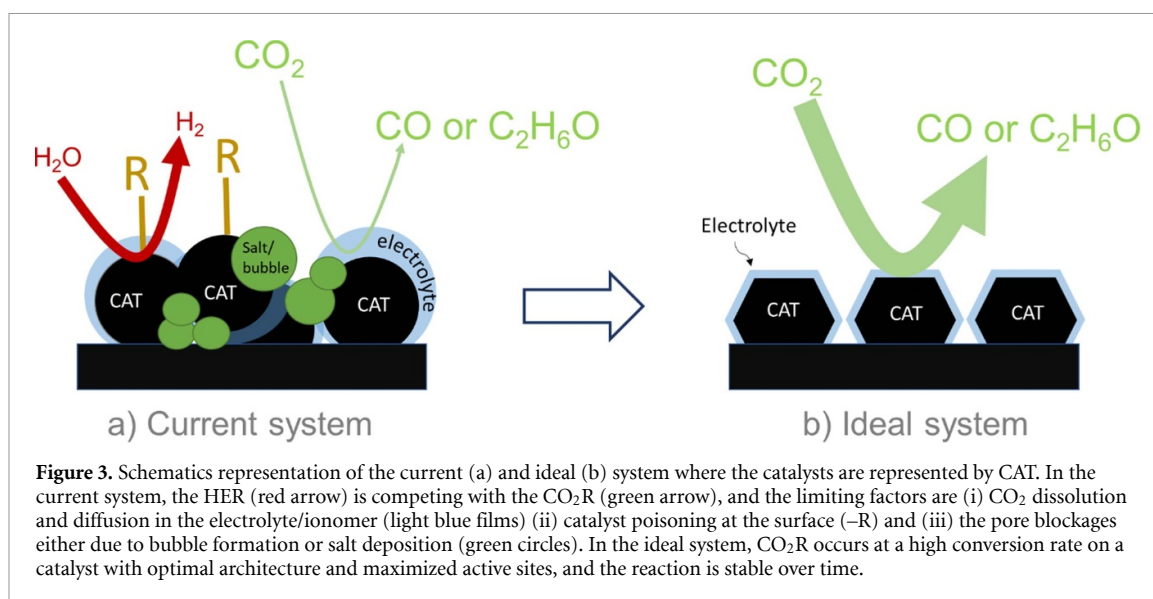


CO conversion is possible at high selectivity with gold, for which the smallest overpotential was reported but gold is a scarce and expensive noble metal. Silver is the most used for industrial applications due to its good catalytic activity, high abundance, and affordability. The challenges with CO production remain in further scaling-up the device, i.e. going from cm<sup>2</sup> cell size to the m<sup>2</sup>, loss of CO<sub>2</sub> in the electrolyte as carbonate, and increasing the CO concentration gas product which is currently reported to be limited to 30% [32]. Ethanol production is more complex and involves 12-electron transfer:



Also, the energy required on top of the thermodynamic potential to drive the reaction is substantial (around 1 V overpotential). The mechanistic understanding that enables C–C coupling beyond the self-coupling of CO to ethanol production is lacking [35], but it has been suggested that higher uncoordinated sites such as steps, edges, and kinks favor ethanol production over ethylene [36]. On top of the limited 50% FE reported, stability also needs to be addressed as the longest operation reported to date was in the hundreds of hours.

For both CO and ethanol production, mass transport limitation of CO<sub>2</sub> is a limiting factor in reaching higher FE. In addition to the limited CO<sub>2</sub> solubility in aqueous electrolyte, the competing hydrogen evolution reaction (HER) should be avoided. Stability is among the main challenges limiting the economic



viability of the technology in both cases. Loss in activity that affects product selectivity is common and can be caused by (a) surface poisoning from electrolytes impurities and/or reaction intermediates, (b) surface restructuring under operating conditions, and/or (c) pore blockage through bubble formation or salt deposition. Figure 3 depicts the current system with the above-mentioned challenges and compares it to the ideal system where only the CO<sub>2</sub>R reaction (CO<sub>2</sub>RR) would occur.

#### Advances in science and technology to meet challenges

For CO<sub>2</sub>-to-CO conversion, rapid improvement in device architecture is needed to tackle stability issues at larger scales, while for CO<sub>2</sub>-to-ethanol, further progress on catalyst development for higher activity, selectivity, and stability are still required.

The use of gas-fed devices for CO<sub>2</sub>RR reduces challenges related to mass-transport limitation of CO<sub>2</sub>, and hinder competing HER as the CO<sub>2</sub>-to-H<sub>2</sub>O ratio increases at the catalyst interface. While the use of GDL compared to H-cell setups, allows to reach much higher CDs, problems such as flooding, salt deposition or catalyst poisoning limit the long-term performance [37].

To avoid flooding issues, GDLs should be made of materials with stable hydrophobic properties to efficiently repel water, without sacrificing two other important GDL characteristics: electrical conductivity and porosity. Additionally, to avoid other challenges such as salt-deposition or catalyst deactivation (associated to liquid electrolytes), future research should also be dedicated to development of zero-gap devices, ideally with entirely solid-polymer-electrolytes. For this purpose, it is critical to develop anion-exchange-membranes (AEMs) with high chemical and mechanical stability, high ionic conductivity, that also reduce CO<sub>2</sub> crossover to the anode side [9].

CO<sub>2</sub>-to-ethanol reduction is a more complex reaction and main challenges rise from the lack of a reliable catalyst. Obtaining a better understanding of the surface composition/structure and gaining a deeper knowledge of the reaction mechanism and events occurring at the surface under real operating conditions are key to development of more reliable catalysts. For this purpose, *in-situ* spectroscopy/microscopy techniques such as infrared/Raman spectroscopy (to detect reaction intermediate/adsorbed species on the catalyst), and x-ray adsorption/photoelectron spectroscopy (to probe elemental composition, chemical/oxidation state, electronic structure, and coordination number, etc.) are promising techniques. Each of these techniques face very specific challenges [38], but the lack of appropriate cells that closely mimic the actual catalyst working condition and lack of reproducibility in the measurement, are common to both and should be addressed first. In complement, data collected during *in-situ* measurements should be combined with artificial intelligence/machine-learning models, to help with the design and development of new catalysts.

#### Concluding remarks

In conclusion, we have identified that CO and ethanol are the two most promising CO<sub>2</sub>R products because they are easily scalable, cost-competitive and have sizeable market shares. Electrochemical CO production is considered one of the most promising candidates because of its technologic and economic feasibility.



CO<sub>2</sub>-to-ethanol is considered one of the other most interesting strategies to convert CO<sub>2</sub>. Ethanol is a widely used chemical with a high-energy-density that is also commercially attractive. While the challenges related to the production of CO lie in the device architecture affecting long-term stability in larger scales, ethanol production is an early technology where catalyst activity, selectivity and stability are still limiting its development. CO<sub>2</sub> to ethanol conversion is particularly the process where the use of *in-situ* and *in-operando* techniques coupled with artificial intelligence and machine learning could greatly help to advance catalyst development.

### Acknowledgment

We acknowledged the support from the National Research Council of Canada's (NRC-CNRC) Materials for Clean Fuel (MCF) Challenge Program.

## 4. What guidelines must we have for product detection and benchmarking?

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### Status

Benchmarking provides an unbiased, reproducible, and meaningful performance assessment of novel catalysts in comparison to standards. Generally, there are two purposes to benchmarking catalysts for electrochemical CO<sub>2</sub>R. The first is to assess and compare intrinsic activity and selectivity, which signifies the true rate and selectivity at which the active sites turnover CO<sub>2</sub>. The second is to assess the geometric activity of an electrocatalyst integrated within a high surface area electrode that is designed to optimize overall performance. Both are important to technology development as the former quantifies the discovery of new catalysts, while the latter assesses the viability of these catalysts in real systems where the productivity scales with surface area.

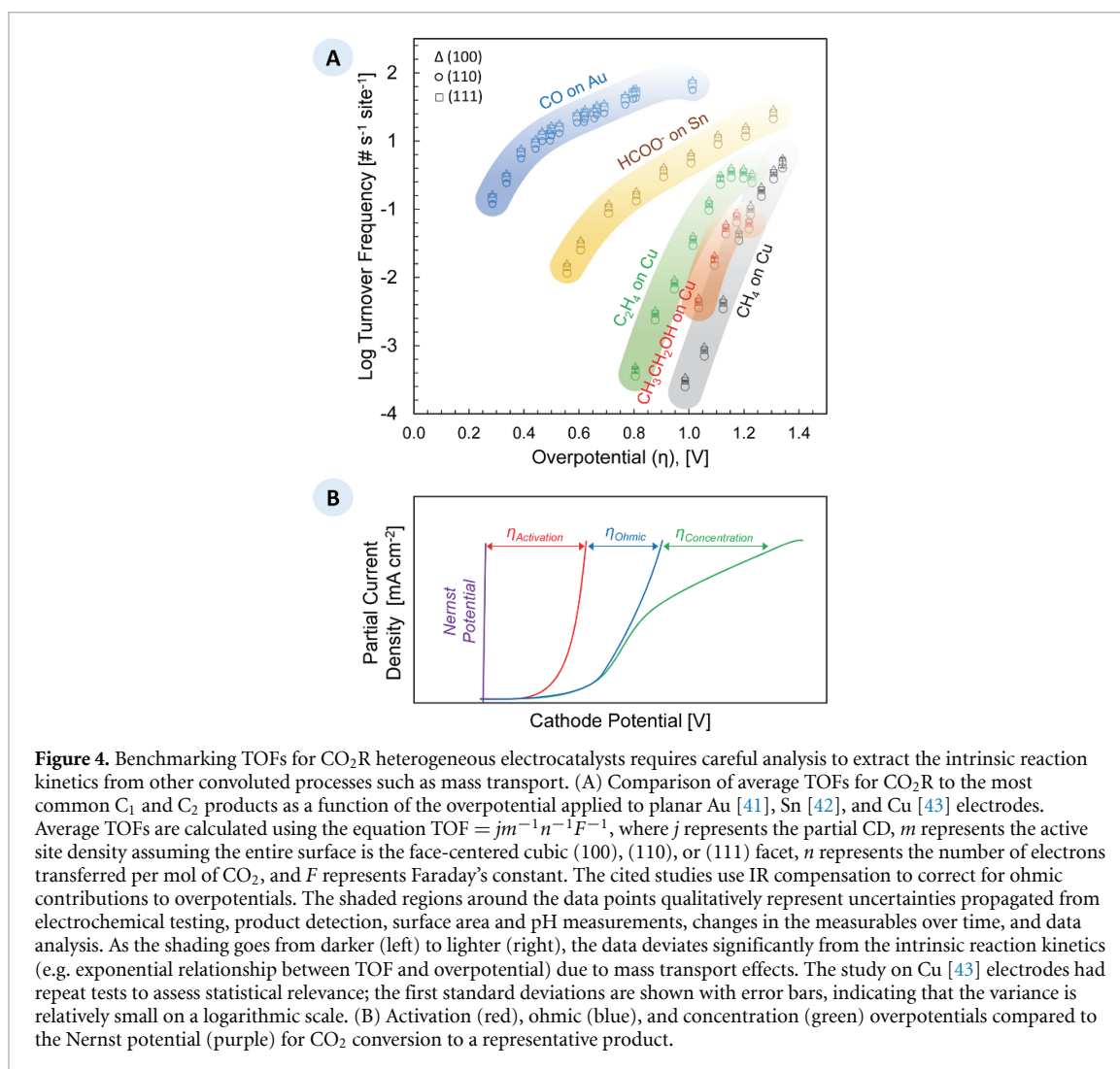
Benchmarking electrocatalysts for CO<sub>2</sub>R necessitates a multimodal characterization approach integrating electrochemistry analysis with product detection, as many different CO<sub>2</sub>R products can be formed, and the HER is a ubiquitous competing pathway (see section 15). Liquid and gas phase products are oftentimes simultaneously evolved, and the field has widely accepted the use of conventional analysis techniques such as gas and liquid chromatography (GC, LC) and nuclear magnetic resonance (NMR) spectroscopy to analyze selectivity. Mass spectrometry and Raman and infrared spectroscopy have been used as *in situ* tools to analyze real time electrocatalyst performance through higher frequency detection of products and intermediates (see sections 8–10) [39].

Extensive research using three electrode configurations within H-cells and their equivalents has identified heterogeneous catalysts that are selective and geometrically active for CO<sub>2</sub>R to CO, formate, and multi-carbon products in aqueous bicarbonate electrolytes. Measuring catalyst surface areas and active site distributions [40] to assess turnover frequencies (TOFs) has been far less abundant, although this is the most objective way in which intrinsic activity can be compared. Our analysis compares TOFs for the most common C<sub>1</sub> and C<sub>2</sub> products measured from planar Au [41], Sn [42], and Cu [43] electrodes (figure 4(A)). The selected data is not meant to represent the state-of-the-art, but rather to demonstrate how TOF analysis on detailed studies of catalysts can be used to quantitatively assess progress in catalyst development.

### Current and future challenges

The benchmarking uncertainties in figure 4(A) emphasize several research challenges for the CO<sub>2</sub>R field. Notably, even for these detailed studies there are few data points to assess and compare the intrinsic reaction kinetics, which presents issues for a complex multistep reaction such as CO<sub>2</sub>R as the rate-determining step may change as a function of the electrode potential. Conventional product detection methods such as GC, LC, and NMR have provided common frequencies of data acquisition in the timeframes of minutes and hours due to either limited detection sensitivity or inherent separation times required for product identification and quantification. This is significantly slower than the timescales of reactive events (figure 4(A)), providing limited feedback on transients in the CO<sub>2</sub>R kinetics. Uncertainties in product analysis are propagated, as these detection methods are coupled with steady state electrochemistry to assess partial activities. Taken together, these factors have led the CO<sub>2</sub>R field to have less data per report with more uncertainty than related cathode reactions such as hydrogen evolution and oxygen reduction. Analysis of TOFs for polycrystalline metals (figure 4(A)) illustrates how active site distributions lead to additional uncertainty. Characterizing the physicochemical properties and dynamics of active sites is a grand challenge in catalysis that is compounded for CO<sub>2</sub>R by the need for concomitant product analysis.

Another challenge is rationally extracting the intrinsic reaction kinetics from benchmarking, which is important to accurately compare data for catalysts measured in different electrochemical cells [44]. This requires measuring the electrokinetics under reaction conditions that are free of mass transport effects, and/or mathematically deconvoluting the activation overpotential from ohmic and concentration overpotentials (figure 4(B)). While ohmic overpotentials are typically compensated through IR correction, concentration overpotentials are germane to CO<sub>2</sub>R as CO<sub>2</sub> has relatively low solubility in aqueous electrolytes and measurements are typically conducted in neutral pH without strong buffering agents. Rotating disk electrode (RDE) measurements (figure 5(A)), that hydrodynamically control external diffusion within the boundary layer, are uncommon in CO<sub>2</sub>R as it is challenging to form a gas-tight seal for product analysis [45, 46]. Thus, conventional analytical methods to deconvolute mass transport effects, such as Koutecky–Levich analysis at various rotational rates ( $\omega$ ) (figure 5(B)), are typically not used for CO<sub>2</sub>R, and researchers are left with difficult decisions hypothesizing which data represents the intrinsic reaction kinetics.

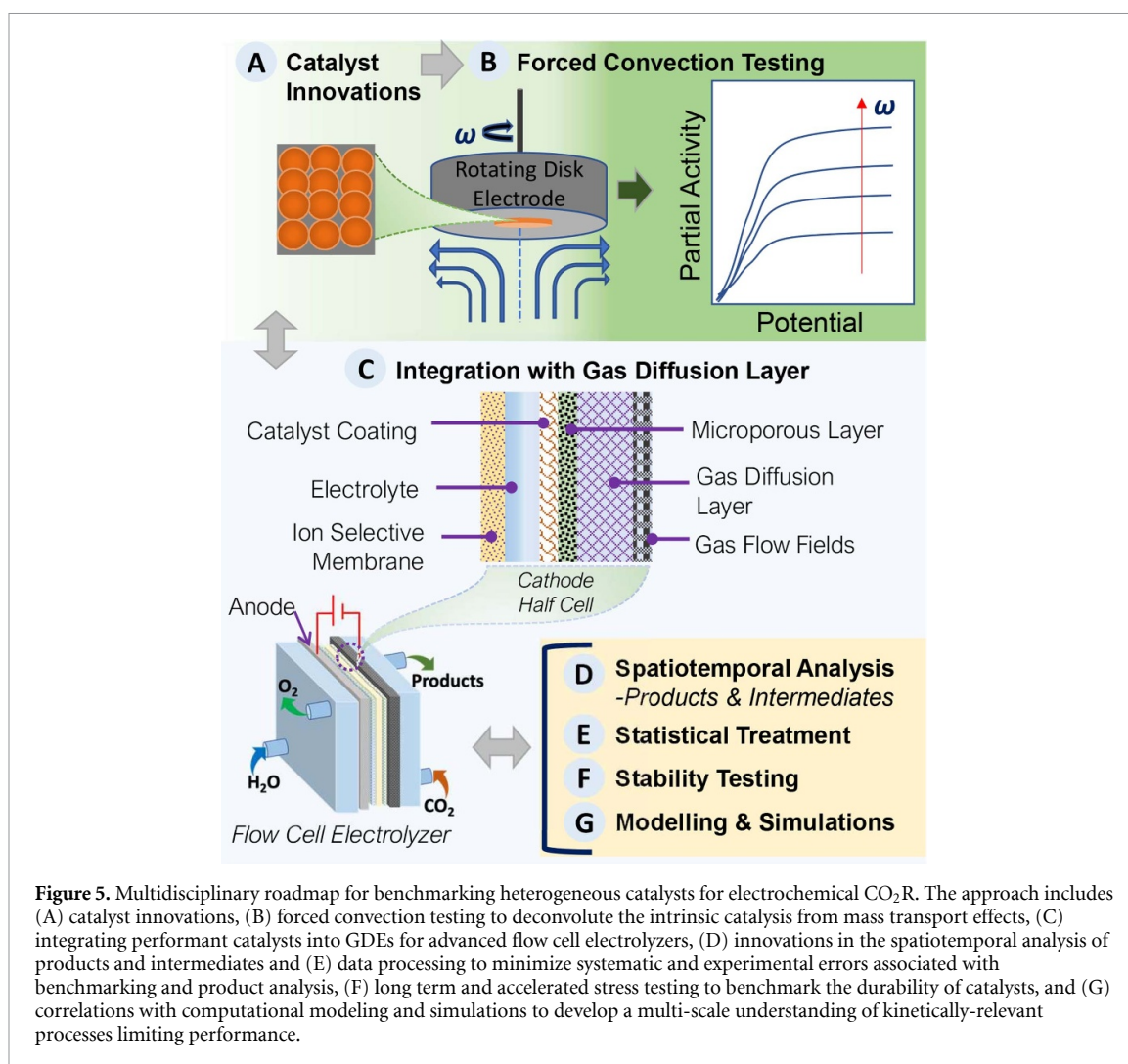


These challenges are compounded when benchmarking porous catalysts, as they can have different active site distributions for TOF analysis and form complex internal diffusion gradients during electrolysis that further obfuscate the intrinsic reaction kinetics (see section 6) [47].

### Advances in science and technology to meet challenges

Looking ahead, a concerted multidisciplinary approach is needed to provide breakthroughs in both the accuracy and speed of benchmarking (figure 5). Development and more widespread adoption of product analysis tools with improved detection sensitivity and temporal resolution provide a means to bridge the vast gap in timescales between conventional product measurements and reactive events (see section 10) [39]. Inspiration can be drawn from the development of TAP reactors for transient studies of thermal catalysis [48]. Benchmarking can be accelerated by coupling rapid product analysis with high-throughput electrochemical methods such as scanning droplet cells (SDCs). *In situ* characterization methods are needed to measure the specific types, quantities, and dynamics of catalyst active sites for analyzing TOFs and establishing accurate theories for CO<sub>2</sub>R (see sections 5 and 7).

Further development and more widespread adoption of gas-tight RDE and liquid flow cells for benchmarking will deconvolute intrinsic reaction rates from mass transport effects [45, 46]. Reporting uncertainties in data, and importantly, propagating the error through all analyses is strongly encouraged. A *t*-test can be used to determine confidence intervals that aid in establishing a statistically relevant conclusion. Data science tools such as Bayesian analysis can provide unbiased selections of data for extracting the intrinsic reaction kinetics [49]. Although benchmarking flat catalysts is recommended when assessing and comparing intrinsic activity, controllably tuning the catalyst mesostructure provides information about internal diffusion gradients and how the catalyst will perform in real systems [50]. These phenomena can be deterministically controlled by developing advanced manufacturing methods that can realize complex mesostructures predicted by modeling.



Recently, greater attention has been focused on catalyst integration into GDEs [51] for scale-up of CO<sub>2</sub> electrolyzers (see sections 6 and 18). Decades of research from the fuel cell community has shown that this is not a trivial step. More collaborations are encouraged between researchers that are focused on catalyst development and those on systems prototyping to benchmark catalysts under real operating conditions at earlier stages of research. A useful endeavor would be for the CO<sub>2</sub>R field to establish, disseminate, and widely adopt a few GDE platforms [52] for routine half-cell benchmarking of new cathode catalysts. As the field matures, more focus is needed on long-term testing and durability. Accelerated stress testing of related technologies, such as fuel cells and water electrolyzers, provides a knowledge base for the CO<sub>2</sub>R field to develop and adopt new protocols (see section 18) [53].

### Concluding remarks

Here, we discuss the current status and challenges for benchmarking heterogeneous CO<sub>2</sub>R electrocatalysts and characterizing products and other relevant reaction species. We provide an analysis of catalytic TOFs for different metals and reaction pathways that emphasizes the importance of benchmarking the intrinsic reaction kinetics to quantitatively assess and drive catalyst innovations. Mass transport effects and uncertainties propagated from electrochemistry experiments, product analysis, and surface area and active site characterization are key challenges for improving the accuracy and speed of benchmarking. We provide a multidisciplinary roadmap with some general guidelines to encourage accurate comparisons of catalytic performance and more collaborations, which will aid in focusing catalyst development on key research gaps.

### Acknowledgments

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## 5. What does DFT tell us about electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>R)?

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DFT and atomic modeling does not tell anything unless asked. It is like the ancient Greek oracles, you have to ask the questions specifically and you have to make a careful analysis of the answers to get useful insight.

For CO<sub>2</sub>R the question is what kind of questions we should ask and what kind of insight we can obtain. One of the main questions is how to discover better catalyst materials. A better catalyst is active (energy efficient) and selective (making the desired products). In reality, you want to find a catalyst that makes the most valuable product and optimize the activity for the product. For CO<sub>2</sub>R, this means that most studies are related to Cu, which has the most interesting product distributions.

For simple reactions (one reactant—one product) one can postulate a reaction mechanism from chemical intuition and analyze it deductively to predict trends in catalytic activity between different materials. For the postulated reaction it is possible to find descriptors, usually adsorption energies, which by the use of linear scaling and Brønsted–Evans–Polanyi relations are causally linked to the activity by Sabatier volcanos. The most active catalyst will be the one with an adsorption energy closest to the value corresponding to the top of the volcano. For electrochemistry this means the catalyst with the smallest overpotential.

The challenge is how to approach complicated reactions (multiple reactants—multiple products) where one can imagine many different reaction paths resulting in different products. For addressing selectivity, the relative activity of different reaction paths needs to be compared. There are several volcanoes; one for each possible reaction path. This makes the selectivity challenge more complicated than the activity and multi-dimensional. It is therefore challenging even to postulate all the different reaction mechanisms, neatly illustrated by Nitopy *et al* [54] for CO<sub>2</sub>R on Cu.

However, it is in some cases possible for gas phase catalysis e.g. selective dehydrogenation of light alkanes, to derive selectivity maps with a couple of important variables from extensive microkinetic models, binding energies and barriers [55]. Whereas the electrochemical catalytic reactions involving the electrolyte and potential challenge the deep detailed mechanistic description. In other words, the mechanistic conclusions for complicated electrochemical reaction are typically sensitive to choices of method and interface models [56]. Hence, the challenge is that it might be impossible to *a priori* postulate reaction paths and analyze the selectivity by deduction of the model.

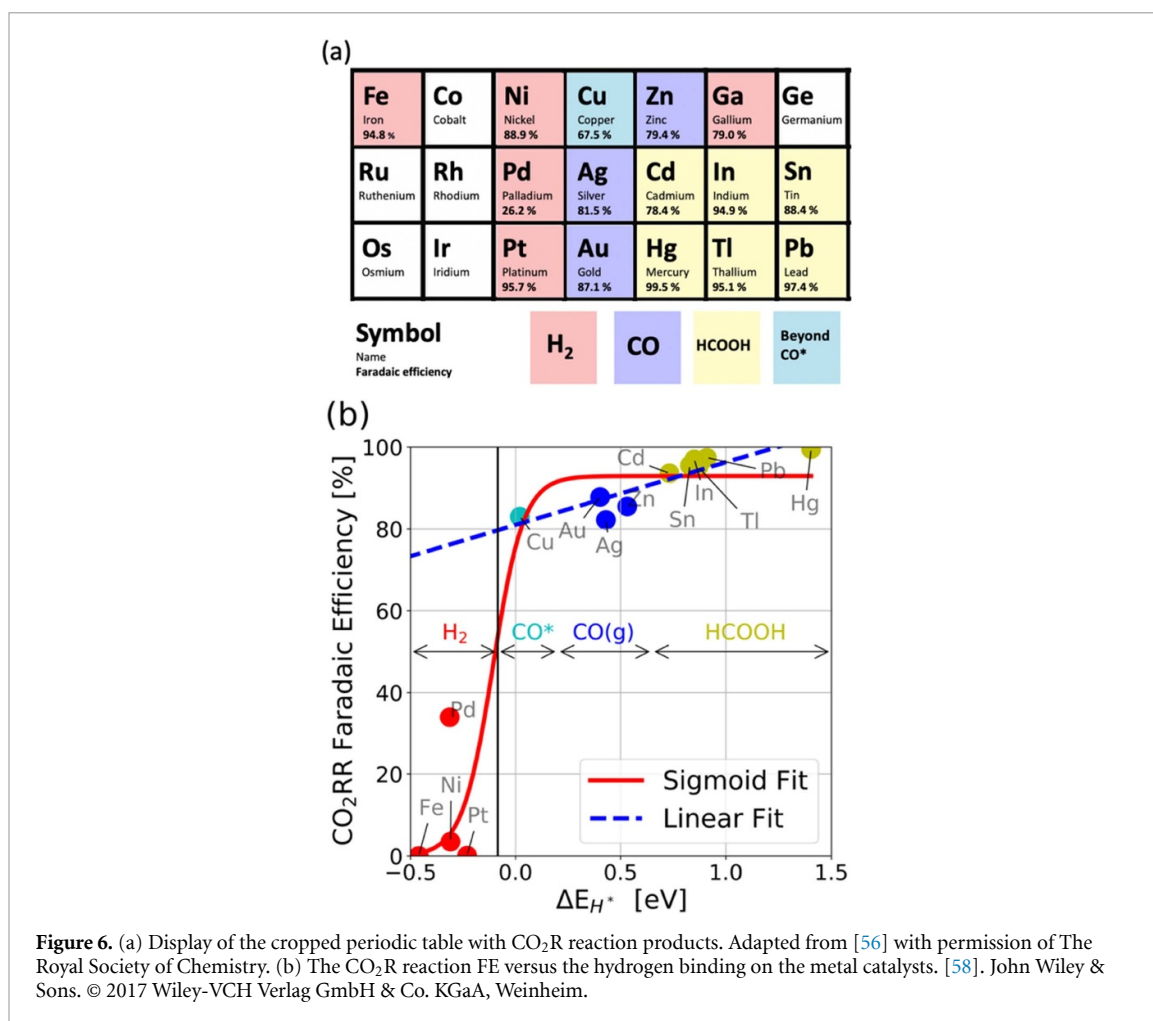
We will argue that we actually need a simpler approach to address complicated electrochemical reactions. The product distribution over metal catalysts from CO<sub>2</sub>R is depicted in the periodic table of figure 6(a), visualizing such a selectivity challenge [57, 58]. To get robust conclusions for the CO<sub>2</sub>RR, the analysis we carry out is at the level of *energy-selectivity* and *structure-selectivity correlations* rather than on the level of exact causal connections between descriptors and selectivity. So why is it better to look for correlations than causal connections?

Deriving a multi-dimensional model, looking only at the *correlations* is empirical and statistical—allowing the most dominant parameters to carry the weight of the model, without the need to be a reaction intermediate. In this sense, it may or may not allow us to speculate about the underlying reaction mechanism, but it will allow us to determine design principles for better catalysts.

Figure 6(b) show the CO<sub>2</sub>RR FE versus the hydrogen binding [56, 58]. A one-dimensional analysis with four groupings based on the primary product of the CO<sub>2</sub>R; H<sub>2</sub>, beyond CO\*, CO(g) and HCOOH. A sigmoid fit to the FE of the CO<sub>2</sub>R shows that hydrogen underpotential deposited (H<sub>UPD</sub>) is an ‘on’/‘off’ descriptor for CO<sub>2</sub>RR. If there is H<sub>UPD</sub> (‘off’ region) the material mostly catalyzes the parasitic hydrogen evolution and not CO<sub>2</sub>R. In the ‘on’ region a linear fit illustrate that the CO<sub>2</sub> conversion selectivity is correlated with the adsorption energy of hydrogen. This ‘most simple analysis’ shows that for the selectivity challenge of CO<sub>2</sub>, a one-dimensional analysis in the hydrogen binding shows that the selectivity descriptors does not need to be linear with the product distribution or overpotential. However, it does not allow us to distinguish the important Cu catalyst from the rest—and a multi-dimensional description is needed.

Figure 7 show how to carry out a statistical analysis to gain insights into the CO<sub>2</sub> reaction at a series of Cu facets [2, 59]. Figure (a) show a two-dimensional analysis with the CO versus the hydrogen binding energy and (b) is an enlargement of the dashed box, with the C<sub>2+</sub> FE given by the colorbar. The CO vs H binding show that Cu is special from the rest of the metals, due to its ability to bind CO while not having H<sub>UPD</sub> and the zoom of the data present how close energetically the different Cu facets are in terms of CO and hydrogen binding.

Focusing on the selectivity at the Cu catalyst; (c)–(e) depict principal component analysis of the products, coordination number and selected binding energies, respectively. Figure (c) shows that 78% of the variation in products can be explained by only two product variables, hinting a simple correlation model of



two parameters should be able to capture the majority of product variation. Elegantly, it allows the products to group by their original vectors, giving insights into which reaction paths could be similar. Figure (d) correlate how important the local structure is for the catalyzed product. Figure (e) express that simulating multiple binding energy descriptors, can be reduced to a two-dimensional analysis carrying 70% of the variation in binding energies.

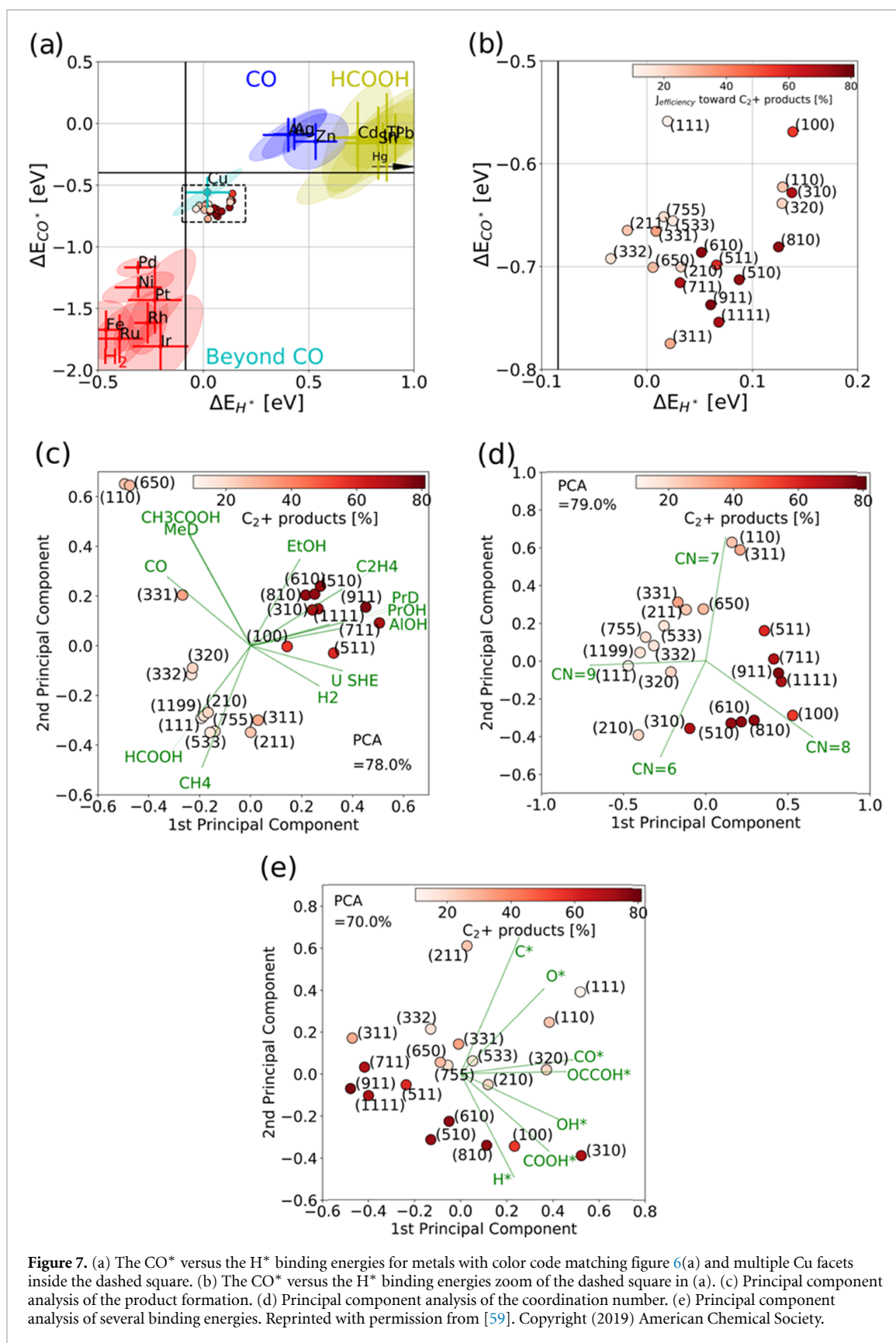
Given by the statistical *correlations*, there is no need for rigorous screening of different bindings or reaction paths at Cu facets to explain products, when two selected binding energies carry the difference. One example would be to choose the intuitively CO vs H binding energies, that are almost orthogonal in figure 7(e). The analysis does not give us the reaction path; however, it most importantly gives us design principles for better catalysts.

### Current and future challenges

The big research issue with the selectivity challenge of CO<sub>2</sub>R is to understand the reaction and building robust models based on *energy-selectivity* and *structure-selectivity correlations* as a framework. There is an urgent need for a whole series of well-defined experiments to allow statistical understanding of the reaction, such as a data-driven high-throughput experimentation approach combining with model frameworks. High-throughput experimentation can be achieved through e.g. combinatorial co-sputtering from multiple elemental targets in combination with SDC measurements [60].

### Concluding remarks

Activity and volcano constructions is highly challenging for complex reaction as CO<sub>2</sub>RR, and we suggest a different approach. For complex reactions, *energy-selectivity* and *structure-selectivity correlations* allow for robust analysis frameworks that can describe the selectivity challenge in a multidimensional space of descriptors/parameters. To improve the understanding, advanced models beyond correlation is needed. For this to succeed, there is an urgent need to improve the statistical experimentation, to allowing advanced models to describe the selectivity phenomenon of these reactions without discussing deterministic models.



**Figure 7.** (a) The CO\* versus the H\* binding energies for metals with color code matching figure 6(a) and multiple Cu facets inside the dashed square. (b) The CO\* versus the H\* binding energies zoom of the dashed square in (a). (c) Principal component analysis of the product formation. (d) Principal component analysis of the coordination number. (e) Principal component analysis of several binding energies. Reprinted with permission from [59]. Copyright (2019) American Chemical Society.

## Acknowledgments

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## 6. Modeling transport effects in CO<sub>2</sub> electrolysis

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### Status

Activity and selectivity of CO<sub>2</sub>R is sensitive to local conditions at the electrode/electrolyte interface (i.e. concentrations of reactant, product, electrolyte, and catalysts or local potential). Due to the necessary presence of protons to equilibrate most CO<sub>2</sub>RRs, the concomitant HER ( $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$ ) constitutes a permanent threat to selectivity. This effect is even more important for catalysts that are able to reduce CO<sub>2</sub> into various products (e.g. copper) as only one product is desired per process in order to reduce expenses in downstream separation. CD and selectivity, along with charge transport and fluid dynamics will determine these local conditions that often deviate from bulk concentration or potential measured at the current collectors. While experiments provide typically one applied potential and CD per product as a function of one bulk concentration of reactant and electrolyte, models can predict locally resolved values. Previous work has already investigated such relations, starting from ideal cases (flat electrode/electrolyte interface, constant diffusion layer thickness) [61, 62] or quasi-ideal cases (controlled electrode rugosity) [63, 64]. These studies have correlated high local pH with favoring C–C coupling on copper or suppressing HER on silver, but also with the suppression of CO<sub>2</sub>RR CD (as CO<sub>2</sub> interfacial concentration almost completely depleted via the homogeneous reaction with hydroxide anions,  $\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-$ ) [62].

Such detailed computational models allow to define guidelines for optimal pH conditions and electrode design (pore size, electrode thickness, etc). In these cases, CO<sub>2</sub> reacts as a dissolved species at an electrode/electrolyte interface. Because of the low solubility of CO<sub>2</sub> in water, the CO<sub>2</sub>RR CD is limited to tens of mA cm<sup>-2</sup>. As industrialization perspectives are starting to drive the activities, GDEs have been introduced to significantly increase the CDs. The generalization of this technology, along with the fact that gas bubbles are evolving even in the simplest designs, is requesting more complex and complete models. For example, the model need to be extended as mass transport at such CD is also impacted by the device geometry and the nature of the separator material. Modeling of such complex processes have only recently started [65]. At the other extremum of the scale, there is an emerging interest in understanding mass transport phenomenon of charged species due to migration in the nanometric vicinity of the electrode, where the electrical potential drops sharply due to double layer (DL) charging effect. On this narrow region, electrolyte cations accumulation have been shown to affects diffusion of species, while accumulation of hydronium cation is producing important pH deviation from the usual reaction-diffusion model [66, 67]. This interrelation of various mass transport modeling scales is depicted in figure 8.

### Current and future challenges

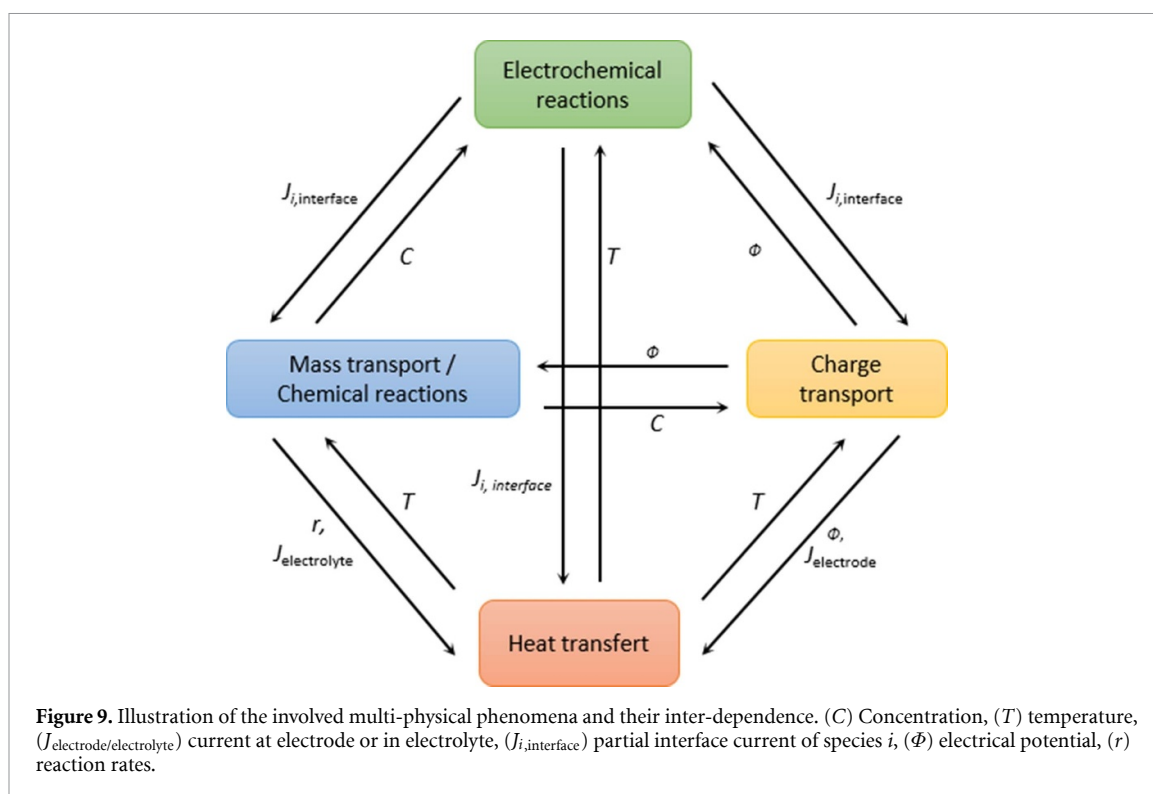
One challenge in multi-scale modeling is to accurately implement kinetics, mainly the intensity of the partial CDs as a function of potential, reactant and product concentration, electrolyte, etc. The experimental determination of such parameters requires full control over the local concentration of species, i.e. experimental conditions where the mass transport phenomena are understood. To deconvolute kinetic and mass transport effects, conditions of known fluid dynamics behavior at flat electrode surfaces are preferred. This is the case for flat rotating electrodes that, despite their simplicity, are still posing a challenge for CO<sub>2</sub>RR due to the evolution of gas bubbles [68, 69].

Modeling at the molecular scale such as by density functional theory (DFT) is expected to provide complementary information toward complete kinetics model. Although, the entanglement of mass transport phenomena at many different scales makes the definition of the relevant scale a pending question. DFT studies are usually made for a few molecules (Å scale). But migration induced accumulation of ions in the DL (nm scale) is impacting DFT results [70]. This migration, coupled with diffusion and steric interaction of charged species near the surface induce a deviation from usual diffusion layer models (~10–200 μm scale). But the intensity of this DL charging effect will be influenced by the mass transport of electrolyte ions in the electrode porous layer (μm scale) and by the size of the pore (as screening effects could happen for nanometric pores). Consequently, phenomena at specific scales cannot be independently modeled and it remains a significant challenge to establish a model that considers all scales simultaneously.

The modeling of the reaction is also complicated by the concomitant contribution of various interfacial configurations: while CO<sub>2</sub>R is mostly considered in a solvated environment at an electrode/electrolyte interface, improvements enabled by GDE technology are often explained by the development of a triple phase interface in which gaseous CO<sub>2</sub> is reduced at a gas/electrode/electrolyte interface. In reality, the







### Advances in science and technology to meet challenges

New parameters need to be implemented in a standardized CO<sub>2</sub> electrochemical model. These parameters include supersaturation and nucleation of bubbles; gas bubbles motion into porous GDE; deconvolution of triple phase, double phase, and double near triple phase interfaces contributions; concentrated species model for strong electrolyte; etc. New models also have to be developed for more specific application such as mass transport in solid electrolytes or BPMs (see section 20 from Boettcher). Due to the convolution of many parameters in the model, it is important to separately validate each assumption. Therefore, experiments conducted under controlled fluid dynamics conditions should be correlated with relevant models to connect local activity/selectivity to local parameters. For the case of bubble transport modeling validation inside the GDE, *operando* tomography could be used.

The complete integration of the various scales (figure 8) into a coupled multi-scale model will require the development of relevant interfaces between *ab-initio* DFT models, molecular dynamics models, meso-scale pore-level models, and continuum-scale device models. While this will cover the spatial variability, similar methods will be required for the temporal resolution that span from fs for fastest electron transfer and chemical steps, ms to s for the transport processes, and significantly longer timescales to capture degradation phenomena.

Other transport related physics will have to be implemented in the model, including electron transport in the conductive part of the device or heat transport (induced by ohmic phenomena or others). Extraction of effective ohmic resistance or heat conductivity of the porous media can be facilitated by the emergence of nano-tomography performed on such substrates [73]. Due to temperature gradient within the device, the determination of temperature dependence of all physics involved represent an important step to accomplish. Eventually the evolution of the steady-state regime over time has to be resolved, requiring the extraction of kinetics parameters relevant for deactivation processes from specially developed experiments. This transient modeling will shed light on the role of mass transport limitation in catalytic deactivation. Such effects are suggested by recent studies where the system lifetime was increased by pulsed potential electrochemistry, buffering mass transport limitation effects [74].

### Concluding remarks

Transport modeling of CO<sub>2</sub>R is a promising method that has the potential to rationalize the relationship between the various physics involved in an electrochemical device. Advanced multi-scale and multi-physics modeling is the only way to deconvolute their respective contributions in devices. This applies even more so for devices that are operated under more and more intense conditions. Once predictive models and digital

twins are established, screening of all parameters can be performed within time scale and costs unattainable by experiments. Consequently, transport modeling could ultimately guide researchers in the optimization of their device designs, and provide a way for full transport control in a CO<sub>2</sub>RR device. Furthermore, such models allow for a finer understanding of the interrelation between experimental conditions and performance, potentially allowing to revisit previous studies that were relating homogeneously distributed CD to bulk concentrations of species in the absence of accurate estimation of current partition and local concentrations.

### Acknowledgments

This material is based upon work performed with the financial support of a Starting Grant of the Swiss National Science Foundation, as part of the SCOUTS project (Grant #155876), the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 85144 (SELECT-CO<sub>2</sub>) and No. 862453 (FlowPhotoChem).

## 7. Mechanistic insight into the electrocatalytic reduction of CO<sub>2</sub> via *operando* spectroscopy and microscopy methods

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### Status

In this contribution, we will assess whether the electrocatalyst's morphology under reaction conditions is the same as in its pre-catalyst state, or if drastic structural and chemical changes are likely to occur. This aspect has been beautifully exemplified in the literature related to Cu materials, the premier catalyst for the electrochemical CO<sub>2</sub>R to C<sub>2+</sub> hydrocarbons and alcohols. In particular, the selectivity of Cu-based materials is known to be strongly affected by different environmental factors which determine the evolution of their surface structure and composition such as the electrolyte and the applied potential [7, 75]. Furthermore, these changes are expected to be more severe at the high CDs in industrial CO<sub>2</sub> flow electrolyzer applications [10]. To date, our fundamental understanding of a catalyst morphology is still largely rooted in descriptors derived from surface science thermal catalysis studies, with the operating temperatures influencing surface atomic diffusion and the most stable morphology. Such descriptions are unlikely to hold for electrocatalysts that operate in an electrolyte, under applied potential and mostly at ambient temperature, which can lead to thermodynamically unfavorable motifs. These dynamical motifs are, however, non-trivial to investigate because of the challenges associated with characterizing samples in a 'vacuum-incompatible' liquid environment. Moreover, the critical features can be lost once the catalysts are removed from the reaction conditions.

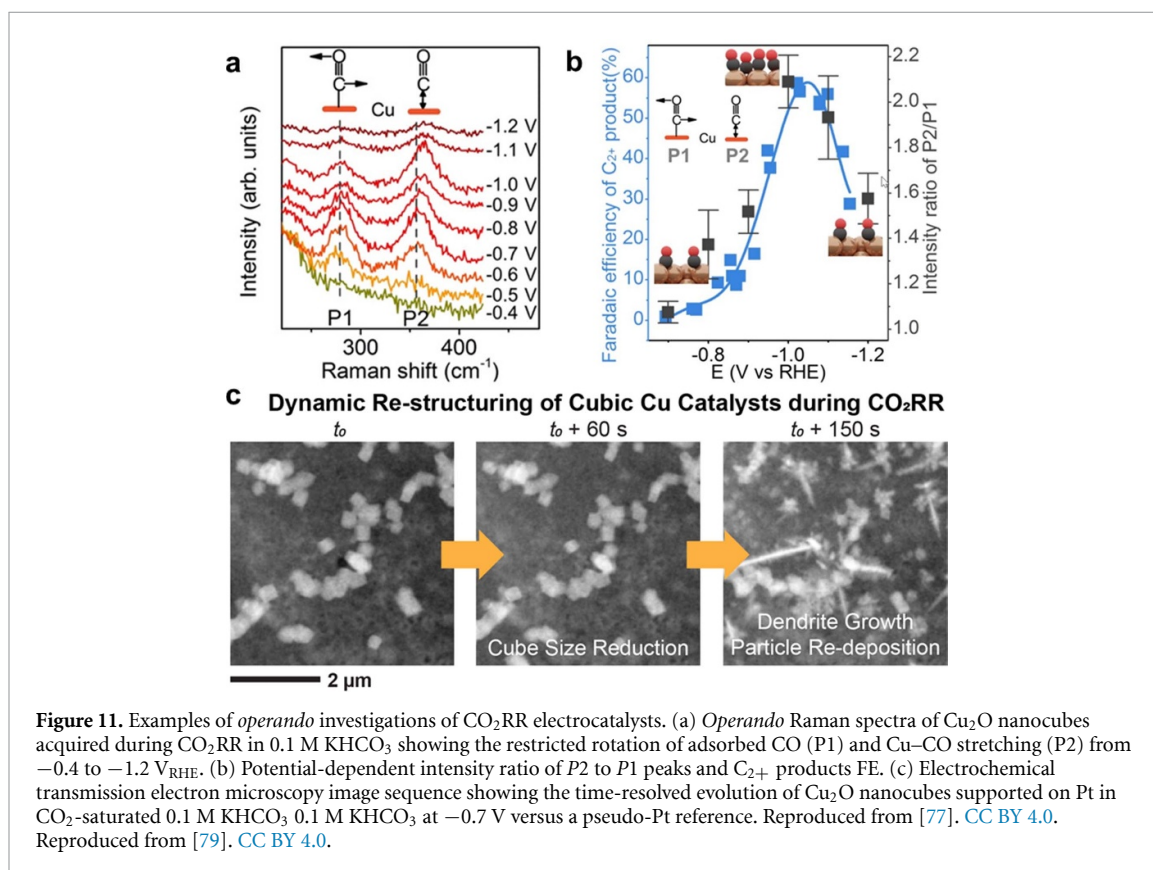
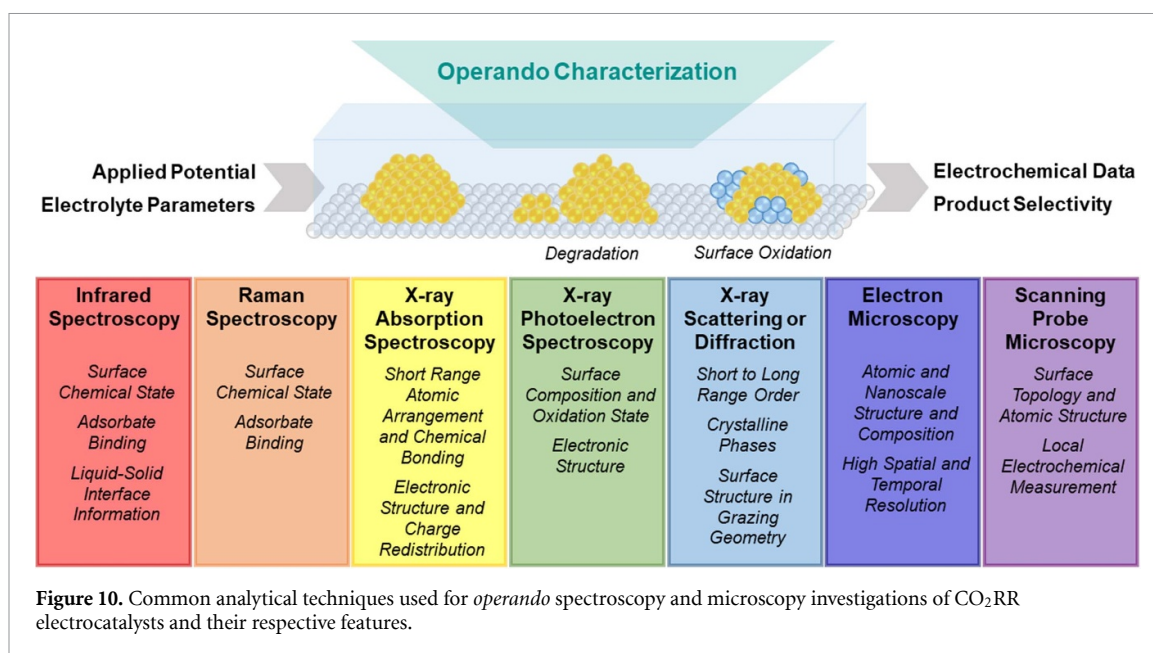
To enable direct studies during reaction, significant efforts have been invested in recent years to develop electrochemical cells that can circumvent the limitations of conventional surface science methods [76]. Some analytical techniques where such setups have been implemented for electrocatalysis studies are summarized in figure 10. *Operando* spectroscopy is the more established approach, where a broad probe beam is used to interrogate the samples and their averaged properties are measured. For example, Raman spectroscopy can track the surface binding of reaction intermediates during CO<sub>2</sub>RR [77], whereas x-ray absorption spectroscopy (XAS) allows us to probe the catalyst structure, composition and oxidation state [78]. The use of *operando* microscopy to track nanoscale structural [79] and surface [80] changes that occur under CO<sub>2</sub>RR reaction conditions using specialized electrochemical reaction cells is, comparatively, in its infancy. Examples of *operando* work describing the behavior of cubic Cu<sub>2</sub>O catalysts during CO<sub>2</sub>RR are provided in figure 11. Ideally, the experiments will also be coupled with online monitoring of the reaction products for structure-property correlation, although examples of such implementations are still very scarce.

For more details on the use of *in-situ* spectroscopy to probe the structure of the electrochemical DL, we refer readers to section 8; conversely, section 9 elaborates on the use of *in-situ* spectroscopy to probe adsorbed intermediates.

### Current and future challenges

There are several challenges associated with performing *operando* spectroscopy and microscopy studies to probe the dynamic behavior of electrocatalysts. First, high temporal resolution is needed in electrochemical CO<sub>2</sub>RR to resolve the rapid changes in morphology and oxidation state observed in Cu during fast or pulsed potential sweeps. Furthermore, in a system with significant gas evolution, the formation of bubbles on the working electrode can also lead to unstable local electrolyte conditions on the timescale of the measurements. Within the different techniques described in figure 10, there is already considerable spread in their temporal resolution, ranging from ms resolution in advanced quick x-ray absorption setups, subsecond resolution in surface-enhanced Raman spectroscopy and surface x-ray diffraction and a few seconds in electron microscopy. A number of scanning probe approaches [81] allow monitoring electrochemical reactions locally, but their temporal resolution is still insufficient to track fast intermediate reaction steps taking place during CO<sub>2</sub>RR. In many cases, the changes in the catalyst morphology are already probed at higher time resolution compared to the accumulation times (typically tens of minutes) required for the analysis of the reaction products from CO<sub>2</sub>RR using, for example, GC, making the impact of these changes on the catalyst functionality difficult to decouple. The generally slow response of the product measurements, especially for low yield products, is another significant bottleneck for advancing the mechanistic understanding that can be derived from *operando* studies of CO<sub>2</sub>RR electrocatalysts.

In addition, the cell geometry or materials need to be optimized for each technique and these compromises often mean that the experimental conditions applied in different experiments do not exactly match, making the generalization of the results sometimes complicated. Each technique also has its



limitations with most *operando* spectroscopy techniques being ensemble-averaging and, hence, only sensitive to the majority species in the sample. The role of minority and spectator species is difficult to decouple from such studies. *Operando* microscopy studies, on the other hand, suffer from limited statistics due to the narrow view associated with the high spatial resolution imaging. It should be also noted that most *operando* techniques employ energetic probes (high energy electrons, x-rays, lasers), which can alter the state of the catalysts being studied. Beam damage effects are especially critical in synchrotron-based spectroscopic/diffraction studies and high-resolution transmission electron microscopy where radiolysis can lead to the formation of reductive/oxidative species or alter the local pH of the sample environment. While such issues are generally mitigated with low radiation dose methods and comparative control experiments,

one cannot keep reducing the dose without running into signal-to-noise ratio issues or sacrificing temporal resolution with longer acquisitions.

As *operando* methods become more common and the instrumentation improves, data management becomes a looming problem. In this aspect, there are already emerging challenges in both the processing and interpretation of large *operando* datasets, and in the compilation of data streams from different instruments. In this respect, machine learning approaches would become increasingly important in the analysis and interpretation of *operando* microscopy and spectroscopy data [78].

### Advances in science and technology to meet challenges

We envision that future technical advances in *operando* characterization will mostly be associated with improving the spatial and temporal resolution of these methods, including enabling online product analysis of the electrolyte stream. The latter is essential to correlate the catalyst selectivity with its corresponding structure. There is also a considerable gap between the nanoscale morphological data that can be obtained from electron and scanning probe microscopy methods with the microscale probe sizes of the different *operando* spectroscopy techniques. Here, improving the spatial resolution of scanning methods such as scanning x-ray microscopy and confocal Raman spectroscopy will allow us to bridge the results obtained using different methods. Future developments in the *operando* characterization of electrocatalysts will also involve the use of multiple techniques simultaneously, or, when the requirements of the different methods do not allow it, to employ transferrable reactor cells that are compatible with the different experimental setups.

Tracking electrochemical transformations and detecting elusive transient species and reaction intermediates that might be intermittently present on the catalyst surface or in its vicinity will require improving the temporal resolution of the different techniques through more sensitive detectors. The improvement required in this case is not limited to the tracking of structural changes. Compositional maps obtained, for instance, using energy dispersive x-ray spectroscopy within an electron microscope can provide extremely valuable information about a catalyst's elements and their distribution. The time resolution of such investigations must be, however, drastically improved to follow the rapid transformations of electrocatalyst under potential control. Other improvements will involve incorporating more capabilities into the reactor cells, such as including local pH measurement close to the working electrode, where pH effects remain one of the more challenging issues to rationalize in CO<sub>2</sub>RR [54].

Lastly, the interpretation of *operando* spectroscopy data can be enhanced by better theoretical support, such as using calculations to understand the features in the Raman or infrared spectra and how they relate to different reaction intermediates and modeling of near-edge or extended x-ray absorption data [77]. Here, machine learning approaches are expected to significantly aid these efforts [82].

### Concluding remarks

We envision that the knowledge that will be extracted from *operando* spectroscopy and microscopy studies will aid the rational design of a new generation of active but even more importantly, highly selective and durable CO<sub>2</sub>RR catalysts. Clearly, it is not sufficient to only enable better data collection; the data must be processed and weaved together into a consistent picture. We expect future efforts to focus on combining multiple *operando* techniques to mitigate the weaknesses of a single method, i.e. where electron microscopy provides the morphological details needed for interpreting spectra from ensemble-averaging techniques such as Raman or x-ray absorption spectroscopy. How to merge such data meaningfully, especially for complex reactions like CO<sub>2</sub>RR, with multiple possible underlying processes or a multi-element material remains a largely unsolved problem, specially when each technique uses a different electrochemical cell configuration. This is especially critical if, for example, confinement and mass transport limitation effects in such cells lead to artifacts in the data and result in findings that are not representative of the processes in benchtop or industrial electrochemical experiments. Finally, we see significant promise in the use of data science, thanks to recent breakthroughs in machine learning methods, for providing an effective solution for analyzing and combining several complementary large *operando* spectroscopy/microscopy datasets.

### Acknowledgments

We appreciate funding by the European Research Council (ERC-725915, OPERANDOCAT) and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—Project No. 406944504—SPP 2080.

## 8. Understanding the interplay between electrolytes and electrode-mediated reactions via *in-situ* spectroscopies

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### Status

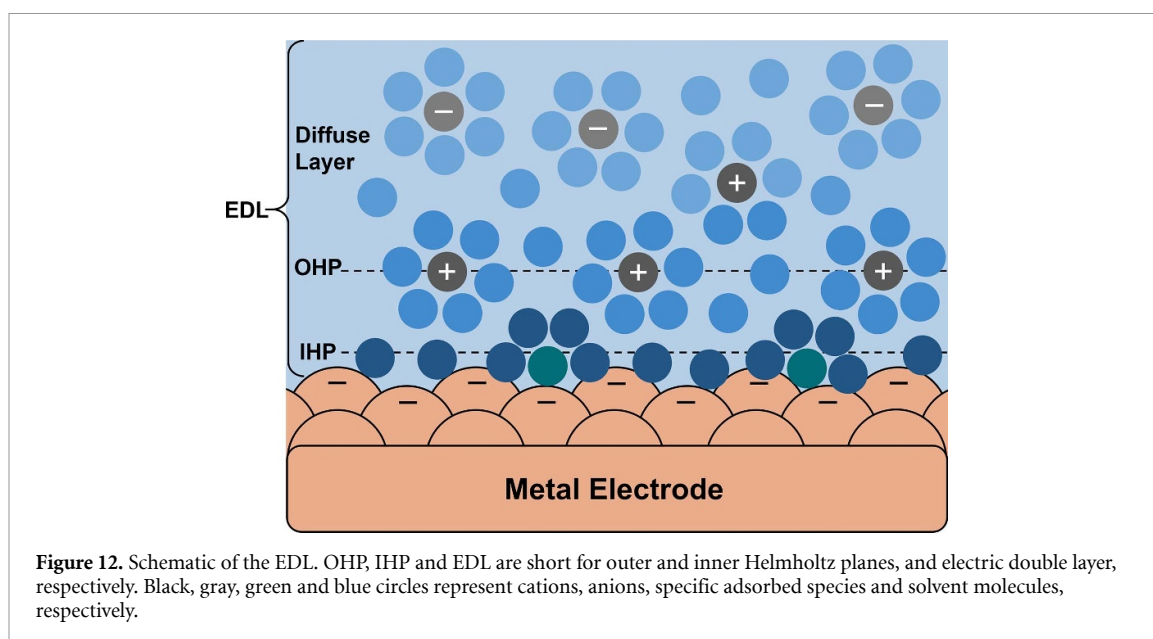
Electrode surface, ions in the electrolyte and solvent form the immediate environment (figure 12) in which electrocatalytic reactions occur, i.e. the electric DL (EDL). In this crowded interfacial space, there are intricate interplays among all species present through a multitude of modes of interactions, e.g. covalent, ionic and van de Waals [83]. Thus, any interfacial species has the potential to substantially alter the energetics and activation barriers of reactions taking place on the electrode surface [84]. Upon applying a potential, ions in the electrolyte of the opposite charge to the excess charges on the electrode are attracted to as close as the outer Helmholtz plane (OHP). With sufficient concentrations of the electrolyte, the majority of the potential change is only felt within the EDL, where an intense interfacial electric field ( $>10^8 \text{ V m}^{-1}$ ) is present [85]. This interfacial field is proposed to impact the stability of reactants and intermediates within the EDL to varying degrees depending on their molecular structures and adsorption configurations [86]. Since the OHP is defined as the closest plane non-specifically adsorbed ions can approach the electrode surface, the distance between the OHP and the electrode is sensitive to the structure and properties of the ions. In the absence of specific adsorption, the size of ions (together with their solvation layers) balancing the excess charges on the electrode determines the thickness of the EDL, and in turn the interfacial field strength at a given potential. This could be regarded as the electrostatic component of the electrolyte effect. Specific adsorption of ions, especially anions, could be considered as one type of (electro)chemical interaction between the electrolyte and the electrode, which could result in site blockage. Although effects of other chemical interactions on the reactivity have been reported [87], their nature and mechanism remain elusive.

### Current and future challenges

The key conceptual challenge to understand the impact of the electrolyte is the difficulty in isolating individual variables as species in the EDL interact with one another through several mechanisms, e.g. change in the size of alkali metal cations also affects their hydration shells [87]. Thus, understanding the electrolyte effect is like reverse-engineering a black box with complex circuitry using a number of inputs and outputs. In this crude analogy, the greater the number of inputs/outputs and the closer to the core circuitry, the easier the task becomes. Reactivities and kinetics constitute an important group of inputs and outputs, with many experimentally accessible variables such as concentrations (partial pressures), potential, rates and selectivities [88]. They form the boundary conditions to which any reverse-engineered black boxes should compile, however, they are several steps away from the reaction sites. *In-situ* characterizations, especially interfacial specific spectroscopies, provide more informative inputs/outputs. For example, x-ray absorption and Raman spectroscopies could probe the impact of the electrolyte on the oxidation state, composition and structure of the electrode. Electrochemical scanning tunneling and atomic force microscopies (STM and AFM) afford nanometer scale resolutions, which could provide direct evidence for specific adsorption of species from the electrolyte [89]. Importantly, vibrational spectroscopies are able to determine the interfacial field strength based on the vibrational Stark effect with a proper probe molecule such as CO [90]. Unfortunately, few works in the literature have taken full advantage of these techniques at our disposal to obtain complementary information on well-defined systems and construct frameworks of understanding regarding the electrolyte effect, for following reasons: (a) different sample requirements or preparation procedures make it hard to combine multiple techniques to investigate the same system, e.g. spatially resolved techniques such as STM and AFM require relatively flat surfaces while reactivity tests are more accurate on supported particulated catalysts. (b) Complementarity of different interfacial characterization techniques remains underexplored. It is well known that infrared and Raman spectroscopies provide complementary information as molecular spectroscopies, however, the complementarity of surface enhanced infrared and Raman techniques remains largely unknown, leading to uncertainty in combining these techniques [91]. (c) Over-reliance on simplistic computational models. While the accuracy of calculations has been continuously improved with computation power and method, computational results are as reliable as the model representing the physical system under study. The disconnect between idealized models typically employed in computations and the complexity in real electrochemical interfaces introduces uncertainties in the mechanistic interpretations.

### Advances in science and technology to meet challenges

Advances in the understanding of how species in the EDL impact electrocatalysis demand better correlations of variables intrinsic to the EDL with kinetic rates of catalytic materials. Kinetic rates, i.e. free of the mass



**Figure 12.** Schematic of the EDL. OHP, IHP and EDL are short for outer and inner Helmholtz planes, and electric double layer, respectively. Black, gray, green and blue circles represent cations, anions, specific adsorbed species and solvent molecules, respectively.

transport effect, are far less commonly reported in electrocatalytic literatures than in thermocatalysis [88]. This makes quantitative correlations between the EDL properties and catalytic performance untenable, though qualitative trends can still be identified. More rigorous rate measurements, as well as reactor and electrode designs that minimize mass transport limitation, are needed in electrocatalytic research. Surface enhanced vibrational spectroscopies are informative tools to investigate the EDL due to their interfacial specificity. However, the understanding of the selective enhancement of, as well as the effect of the interfacial environment on, vibrational modes with these spectroscopies remains incomplete, leading to ambiguous spectral interpretations. For example, few organic species involved in the electrocatalysis exhibit the vibrational Stark effect, which could be interpreted as either these species are not in the EDL or their vibrational modes are insensitive to the interfacial field strength [92]. These aspects need to be clarified to gain reliable knowledge of the composition and structure of the EDL. Beyond the level of individual techniques, the development of spectroscopic configurations and cells that enable simultaneous operation of multiple techniques is needed. This would not only offer a more complete picture of the EDL, but also help elucidate the complementarity of different techniques. Enhanced spatial and temporal resolutions of characterization tools would be a prerequisite in reaching molecular level understanding of the dynamic nature of the EDL during electrocatalysis. Further, the causal effect between the EDL structure and the catalytic performance can only be reached by close integration of experimental and computational investigations. This is because the multiple variables that are hopelessly intertwined in physical systems could be neatly deconvoluted in computational models and independently varied. The accuracy of the computational modeling is rested upon two factors, i.e. the quality of the computational method and the model employed. In this regard, qualitative and quantitative comparison between simulated and experimental spectroscopic results could serve as an accessible measure of the representativeness of the computational model, and in turn an effective approach to hone the reliability of combined experimental and computational research.

### Concluding remarks

The interplay between the electrolyte and surface-mediated electrochemical reactions takes place in the EDL, which is a crowded space with numerous interacting species. *In-situ* spectroscopic techniques play key roles in deconvoluting the impact of individual species or variables in the EDL on catalytic performance. Integrating multiple existing spectroscopies to allow for simultaneous operations and developing techniques with enhanced spatial/temporal resolution are expected to foster breakthroughs in fundamental understanding. In addition, spectroscopic results could also serve as the anchoring point enabling reliable interactive experimental and computational investigations.

### Acknowledgment

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## 9. What can *in situ* spectroscopy tell us about adsorbed intermediates?

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### Status

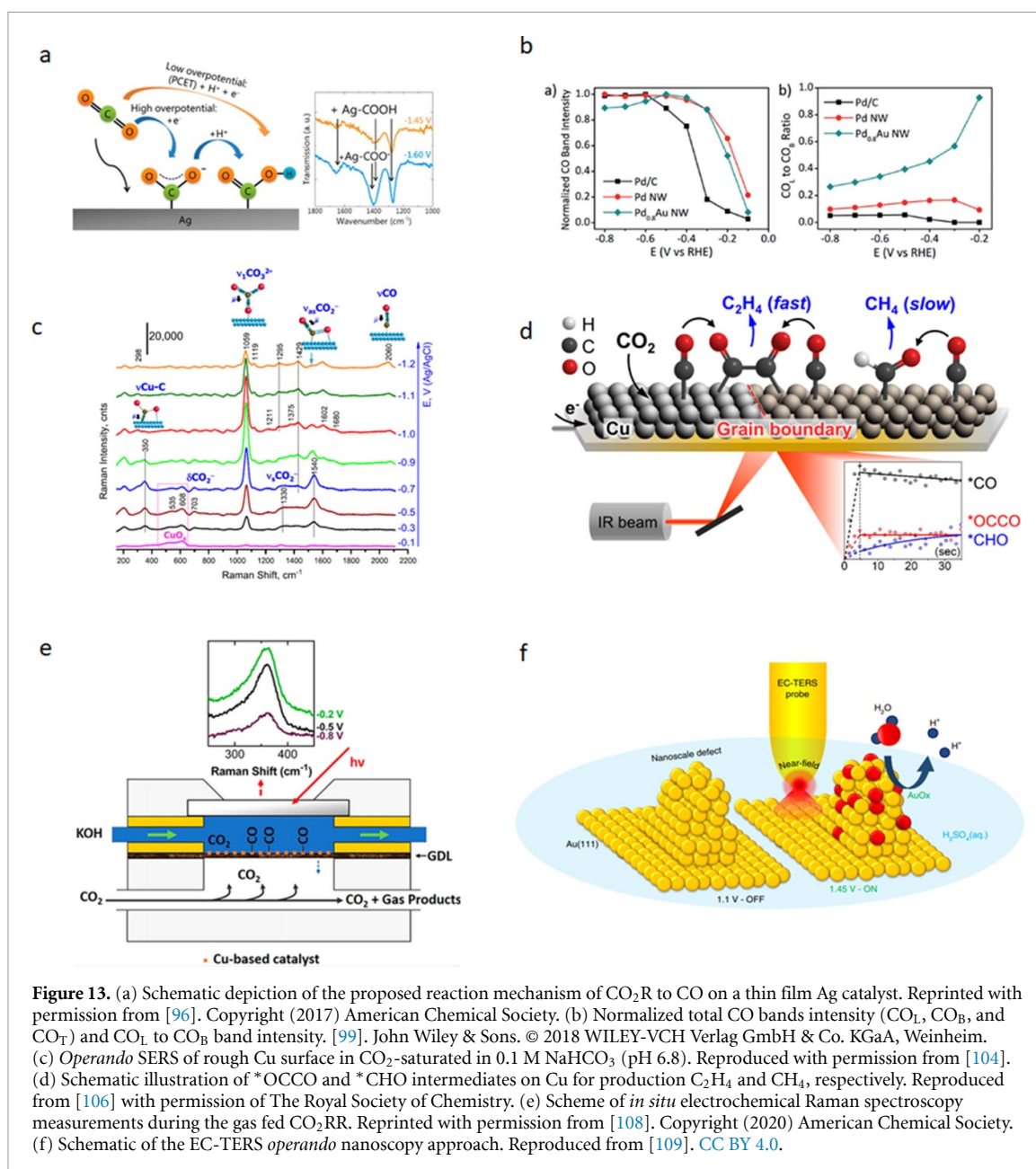
In electrochemical CO<sub>2</sub>RRs, investigation of adsorbed intermediates is critical to control reactions for products such as CO, HCOOH, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>, because of competitive pathways [93]. *In-situ/operando* spectroscopy provides experimental understanding of the intermediates, in addition to theoretical study. To clarify the transiently present intermediates, surface sensitive techniques, such as surface enhanced Raman spectroscopy (SERS), and attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) have been applied. SERS significantly enhances the signals on the specific metal surfaces, such as Ag, Au, and Cu, and low Raman scattering of water allows the *in-situ* measurement in an aqueous electrolyte. ATR amplifies the infrared (IR) vibrational signal by utilizing internal total reflection and is applied to various CO<sub>2</sub>RR catalysts on the prism [94].

*In situ* spectroscopy studies enrich mechanism and active site information depending on the catalyst conditions such as material, potential or environment. Ag, Au or metal–N–C catalyst demonstrates COO<sup>−</sup>\* and CO\* as the key intermediates of each electron reduction step for CO<sub>2</sub>RR to CO production. The first electron transfer followed by protonation proposes the COO<sup>−</sup>\* intermediate [95], and ATR-SEIRAS on Ag surface obtained both COO<sup>−</sup>\* and COOH\* intermediates at high overpotentials (i.e. −1.6 V vs Ag/AgCl), while a proton–electron coupled intermediate (COOH\*) was observed at a moderate overpotential (figure 13(a)) [96]. The surface-enhanced IR measurement strategies allow crucial \*CO signal observation on Ag in addition to CO<sub>2</sub>, HCO<sub>3</sub><sup>−</sup>, CO<sub>3</sub><sup>2−</sup>, and water related peaks [97]. SERS band shifts of \*CO inform changes in the adsorption sites from the bridge to the atop-bound on a Ag surface, influenced by an additional molecule [98]. ATR-SEIRAS also revealed linearly bonded CO (weak adsorbed) exhibited a higher proportion than bridge bonded CO (strong adsorbed) from Pd–Au when Au or defect was incorporated, indicating favorable kinetics for facile CO desorption (figure 13(b)) [99]. *In-situ* IR study combined with DFT simulation proposed the Fe–N<sub>4</sub> moiety with the defective graphitic layer as the active site of a Fe–N–C catalyst instead of the Fe center in the complete graphite due to their balanced \*COOH and \*CO binding strength [100]. In addition, insightful mechanism governing formate production supports the role of oxide states on p-block metals. The *operando* ATR-IR results firstly showed carbonate intermediates via Sn oxyhydroxide [101], and SERS support A<sub>1g</sub> Raman shift of SnO<sub>2</sub> [102].

Furthermore, Cu is more focused for observing intermediates toward hydrocarbons due to its suitable \*CO binding [103]. In addition to \*CO, the *operando* SERS on Cu showed multiple adsorbates associated with \*CO<sub>3</sub><sup>2−</sup> and \*CO<sub>2</sub><sup>−</sup> and proposed a carboxylate intermediate ( $\eta^2(\text{C},\text{O})\text{-CO}_2$ ) initiate CO<sub>2</sub>RR to formate (figure 13(c)) [104]. ART-SEIRAS proposes the key intermediate, \*CO on the Cu surface [105], is further reduced to hydrogenation (\*CHO) and C–C coupling (\*OCCO(H)) intermediates for CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> production, respectively [106]. Meanwhile, Cu(OH)<sub>2</sub> derived catalyst exhibited a rapid decrease of \*CO and an increase of \*OCCO(H), indicating favorable CO consumption for CO–CO coupling contributes to the selective C<sub>2</sub>H<sub>4</sub> production over wide potential ranges (figure 13(d)). In addition, positive Cu oxidation states were suggested to stabilize ethoxy intermediates (\*OCH<sub>2</sub>CH<sub>3</sub>) and contribute enhanced C<sub>2</sub>H<sub>6</sub> selectivity on the halide-derived active copper catalyst [107]. Through these recent progresses on probing the intermediates, design of catalysts are rapidly evolving.

### Current and future challenges

Main challenges remain in detecting additional intermediates for the oxygenated products and operating under realistic CO<sub>2</sub>RR conditions. Multi-carbon intermediates, whose signals are weak and indistinguishable from electrolytes, are more difficult to observe than the \*CO intermediates. While most of the Cu catalysts produce ethylene and ethanol simultaneously, the point at which these reaction pathways diverge remains unknown. Probing the intermediates for diverse products including ethanol, acetate, and C<sub>3+</sub> products is highly desired to develop controllable catalysts and find new catalytic reactions. Intermediates for oxygenate or C<sub>3+</sub> product are undetectable at this stage due to low selectivity of the catalysts. Observing the multi-carbon intermediates can, therefore, provide critical insights into new coupling reactions.



**Figure 13.** (a) Schematic depiction of the proposed reaction mechanism of CO<sub>2</sub>R to CO on a thin film Ag catalyst. Reprinted with permission from [96]. Copyright (2017) American Chemical Society. (b) Normalized total CO bands intensity (CO<sub>L</sub>, CO<sub>B</sub>, and CO<sub>T</sub>) and CO<sub>L</sub> to CO<sub>B</sub> band intensity. [99]. John Wiley & Sons. © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) *Operando* SERS of rough Cu surface in CO<sub>2</sub>-saturated in 0.1 M NaHCO<sub>3</sub> (pH 6.8). Reproduced with permission from [104]. (d) Schematic illustration of \*OCCO and \*CHO intermediates on Cu for production C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub>, respectively. Reproduced from [106] with permission of The Royal Society of Chemistry. (e) Scheme of *in situ* electrochemical Raman spectroscopy measurements during the gas fed CO<sub>2</sub>RR. Reprinted with permission from [108]. Copyright (2020) American Chemical Society. (f) Schematic of the EC-TERS *operando* nanoscopy approach. Reproduced from [109]. CC BY 4.0.

Next, for *in-situ* spectroscopy, the electrochemical cell is specially designed to allow light paths, and thus the intermediates are observed under controlled conditions. Environmental variables such as cell dimensions, CO<sub>2</sub> flow rate and electrolyte agitation can strongly influence on the mass transport and consequential product distribution of CO<sub>2</sub>RR. Direct CO<sub>2</sub> gas-fed electrolyzers have been recently applied to achieve high current densities (CDs) of hundreds mA cm<sup>-2</sup> for practical applications, and the reaction environments are significantly different from most of the *in-situ* spectroscopic cell where CO<sub>2</sub> is dissolved in the electrolyte. A spectroscopic electrochemical cell supplied with CO<sub>2</sub> gas must be developed to observe the real intermediates. Gewirth's group demonstrated *operando* SERS using a GDE flow cell under 1 M KOH with CO<sub>2</sub> gas-fed (figure 13(e)) [108]. The observed spectra of Cu-polyamine showed a strong peak of Cu-CO binding, promoting C-C coupling [110]. Since the flow cell has a catholyte, the next challenge is to observe the intermediates in a catholyte-free membrane-electrode-assembly electrolyzer, advantageous for stackable large scale application.

Increasing the measurement resolution is still challenging but important to reveal unknown transient information of the intermediates especially for time-resolved and space-resolved spectroscopy. Kim *et al* highlighted time-resolved observation of CO<sub>2</sub>RR intermediates in elucidating the origin of selectivity [106]. They observed that \*CO on high-frequency binding sites of Cu with grain boundaries declines rapidly with increasing \*OCCO(H), implying defective site-bound \*CO contributes to fast \*CO dimerization. Slow formation of \*CHO regardless of \*OCCO(H) formation suggests kinetically independent intermediates.

Further kinetic information can be observable with enhanced time resolution to  $\mu\text{s}$  or ns. Meanwhile, heterogeneous catalysts possess various surface sites including plane, step, and other defects, but the intermediate bindings have been estimated from the ensemble catalysts. Thus, future efforts should focus on the space-resolved spectroscopy by adapting nanoscale mapping technology to identify the site-specific intermediates. For example, tip-enhanced Raman spectroscopy can provide the mapping of active sites with a spatial precision of 10 nm during electrochemical reactions (figure 13(f)) [109].

### Advances in science and technology to meet challenges

IR and Raman vibrational spectroscopies are complimentary and particularly useful for probing the bonding nature of the adsorbates. Both techniques have been advanced for the *in-situ* electrochemical spectroscopy studies with the assistance of the electrochemical cell design and catalyst development. Although ATR-SEIRAS and SERS techniques have been developed rapidly in recent years, the sensitivity of detecting reaction intermediates in real CO<sub>2</sub>RR operations still needs to be improved due to weak signal of intermediates and interferences from the reactants, products and the electrolyte. To enhance resolution for Raman spectroscopy and diversify the applicable CO<sub>2</sub>RR catalysts beyond Au, Ag, and Cu, design of the catalyst substrate should be developed. The specialized electrode substrates should be further developed to prove limited signal of the intermediates. Technical development should focus on decoupling the intermediate signal from the aqueous electrolyte signal. To monitor intermediates with further clarity, detection capability of the instruments should be advanced by upgrading sensitivity of detector, power and laser source, and a new prism design. Synchrotron-based Fourier transform-IR spectroscopy can be a considerable approach due to large brightness and broadband spectrum, but thermal stresses induced by strong radiation should be counted. Synchrotron IR source significantly enhance spectral as well as spatio-temporal resolution. Faster time-resolved spectroscopic scans provide information about the life-time, kinetics and temporal behavior of the intermediates. The enhanced spatial resolution of vibrational spectroscopy conjugated with advanced mapping technology may reveal not only intermediates but also reaction pathways and activity specific to the active site type. These difficulties, therefore, raise the needs for a more advanced electrochemical cell and electrode substrate that support the detection of intermediates. Furthermore, to accommodate recent CO<sub>2</sub>RR technology, a specialized electrochemical cell design that has been optimized for gas-phase CO<sub>2</sub>RR is required, while maintaining resolution for the vibrational spectroscopy. The ATR prisms configuration that enable CO<sub>2</sub> gas supply in the electrochemical cell would be great challenge. Instead, external reflection-absorption infrared spectroscopy could be applied, in which the beam passes through a thin electrolyte layer before being reflected from the electrode surface.

### Concluding remarks

It is no doubt that observing the adsorbed intermediates by *in-situ/operando* vibrational spectroscopy is the key to understanding the CO<sub>2</sub>RR mechanism and designing effective catalysts in addition to DFT calculation. Combining the *in-situ/operando* spectroscopy with a custom-designed electrochemical cell can be a powerful tool to unveil key intermediates species, active sites, and reaction pathways for a wide variety of catalysts similar to the real CO<sub>2</sub>RR condition. Especially, CO<sub>2</sub>RR competes with multiple electron transfer pathways, some of which are shared for other products, and HER is a considerable side reaction. We have to consider that the intermediate should be measured as close to the actual reaction environment as possible because CO<sub>2</sub>RR performance is sensitively influenced by both of intrinsic and extrinsic properties. The intermediates (i.e. \*COOH, \*CO, \*CHO, \*OCCOH, etc) detected during CO<sub>2</sub>RR are complementary evidence to give feedback to the DFT simulations, thereby accomplishing more reliable mechanisms. A fundamental understanding of CO<sub>2</sub>RR will guide the development of advanced catalysts for high efficiency and the discovery of new chemical reactions with a variety of valuable products.

### Acknowledgments

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## 10. What can electrochemical mass spectrometry (EMS) tell us about reaction pathways in CO<sub>2</sub> reduction (CO<sub>2</sub>R)?

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### Status

Power-to-X technologies that efficiently convert renewable electricity, water, and carbon dioxide captured from air into sustainable chemicals and fuels such as CO, ethylene or ethanol remain one of the grand challenges of our times. Obtaining an accurate picture about the complex CO<sub>2</sub> electroreduction reaction (CO<sub>2</sub>RR) mechanism is paramount for the successful design of active, abundant and stable electrocatalysts, as well as suitable electrolyte-systems for producing preferably a single value-added chemical.

Generally, EMS offers the possibility to record the kinetics of parallel and serial elementary electrochemical reactions at an electrode-electrolyte interface. EMS can detect multiple chemical molecules with a high sensitivity, chemical selectivity at electrode-to-detector time-resolution in the (sub)second range. This has enabled scientists to follow interfacial electrochemical reactions, including the quantitative tracking of reactants, intermediates and products.

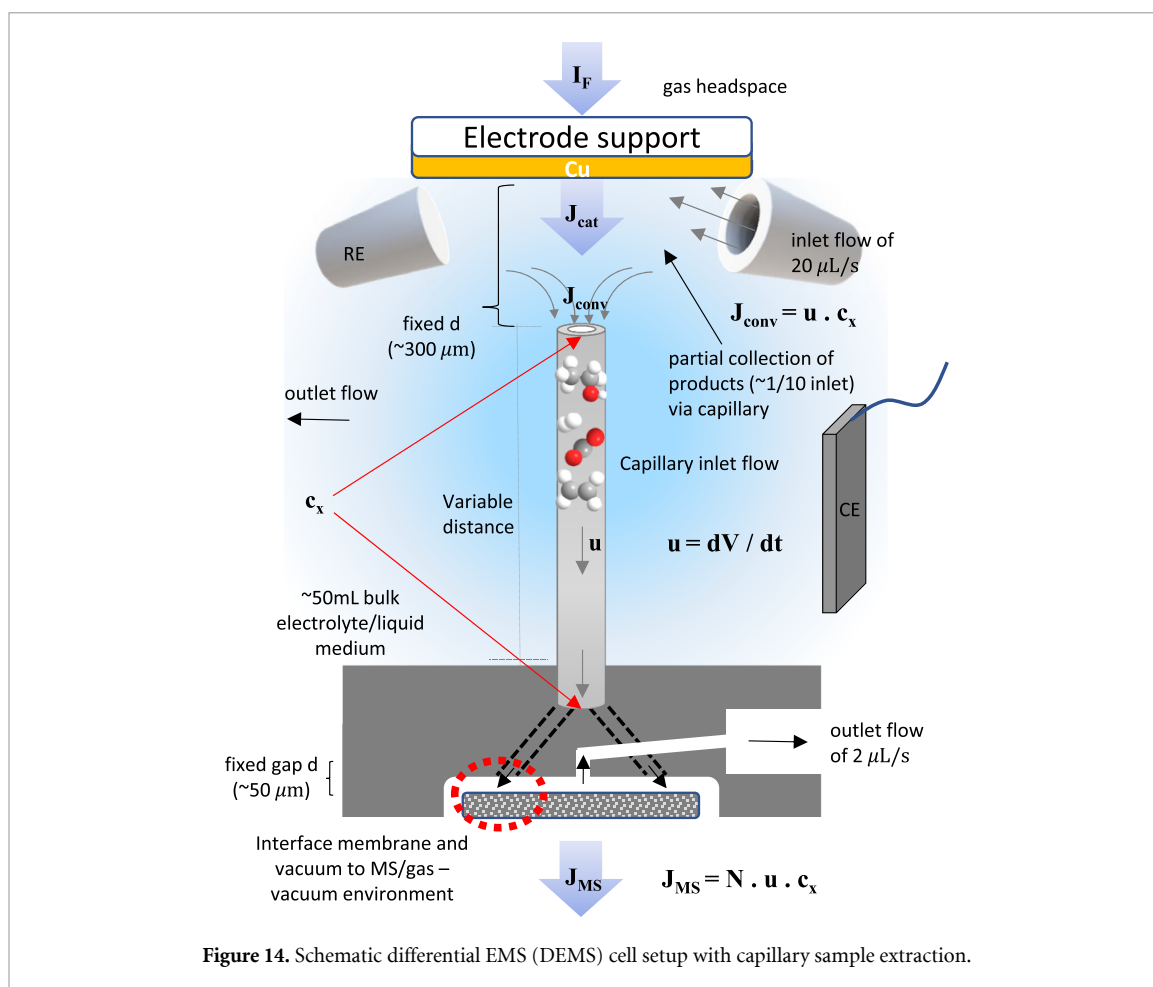
To experimentally track the kinetics of electrocatalytic reactions occurring at solid-liquid interfaces using EMS, a number of science and engineering challenges need to be met. These primarily refer to the design of the interface between the electrified solid catalyst-liquid electrolyte region, where electrochemical reactions occur and reactants/products are consumed/accumulated, and the evacuated reduced-pressure region, where the mass-spectrometric detection of species occurs. Additional challenges concern new design solutions for well-controlled fluid dynamics to ensure low MS ion current backgrounds and reproducible sample transfer from the electrified interface into the MS ionization region.

The earliest EMS interface solution, focused on studying reactions such as hydrogen or oxygen evolution, was a non-porous, relatively thick membrane inlet for detection of gas products [111, 112]. This approach suffered from rather slow response times, which made an alignment between the EMS ion currents and the applied corresponding electrochemical potentials difficult. Subsequent improvements involved the use of porous membranes and differential pumping stages [113] that enabled the use of stagnant thin layer, later flow-through (dual) thin layer cells with faster response times, differential detection mode, and near-total product collection efficiency. Limitations of these cell designs included relatively low operating CD and temporal misalignments in compound detection due to varying diffusivities. Improved EMS cell design solutions were needed yet again, when the focus shifted to the mechanistically complex electrochemical CO<sub>2</sub>RR to liquid, less volatile products, and to operation at high (>100 mA cm<sup>-2</sup>) CD, generating a wide array of chemically distinct reaction products.

### Progress in electrochemical mass spectrometry (EMS)

In an effort to address the above-mentioned shortcomings for the complex CO<sub>2</sub>RR, novel EMS designs emerged. Pioneering CO<sub>2</sub>RR studies combined an on-line electrochemical MS (OLEMS) with a RDE [114] to improve mass-transfer to and from the catalyst layer, or included a membrane covered pin-hole to sample in  $\mu\text{m}$  proximity of electrode surface [115], thus minimizing the distance and time for analytes to diffuse. OLEMS setups were used to systematically study the mechanism of the CO<sub>2</sub>RR on copper electrodes by separately following the reduction of likely intermediates along distinct pathways [4]. Although this method lacked in MS-signal sensitivity and accuracy of detected kinetic onset potentials, the experimental data confirmed the existence of specific reaction pathways delivering plausible hypothesis about carbon-carbon coupling mechanism [4]. Still, the on-line EMS analysis proved insufficient to fully resolve the mechanistic details about gas and liquid volatile products. Real-time EMS detection of accurate product onset potentials was needed. The value of EMS-derived trends in kinetic product onset potentials during voltammetric potential scans consists in their possible link to the corresponding position of products along the reaction coordinate, and, as such, computationally derived limiting (onset) potentials where the formation of product proceeds nearly barrierless. Accurate onset potentials require fast EMS response times and precise time alignment for gas and liquid compounds.

Advances to meet these challenges for gaseous CO<sub>2</sub>RR products have been put forward in form of novel electrolyte-vacuum interface based on microfluidic membrane chip design with a working electrolyte volume in the microliter-range. Major advantages include a 100% collection efficiency, high sensitivity and quantitative data analysis for highly volatile products [116]. Yet, liquid-phase products with lower volatility and diffusivity, such as alcohols or aldehydes, take significantly longer to reach the detector, compromising



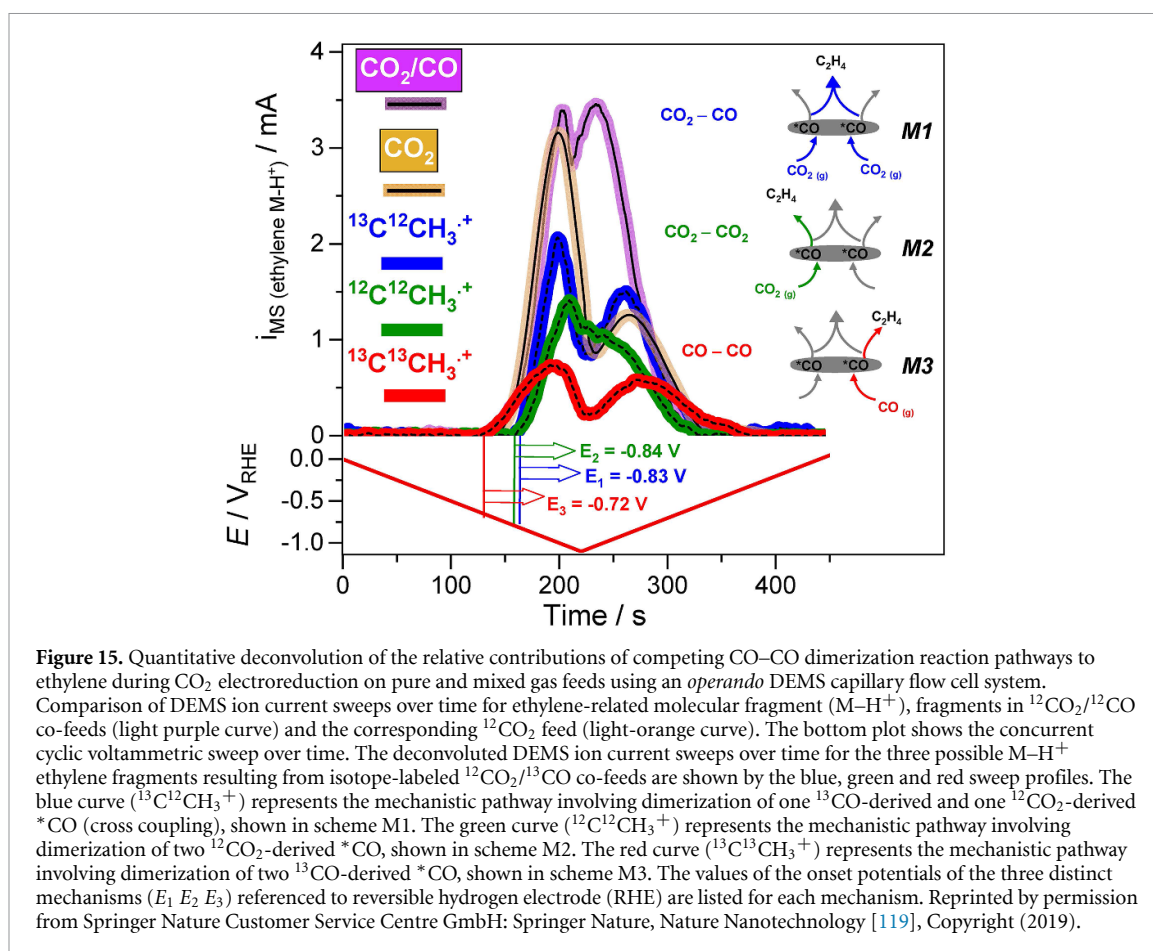
real-time analyses and accurate onset potentials. Combined with limitations in the maximum operating currents, the extraction of mechanistic information on liquid intermediates and products remained difficult. In another innovative EMS approach, selective reagent ionization was combined with time-of-flight mass spectrometry. This EMS technique obtained impressive real-time and quantitative data, providing access to selectivity and the formation rates for a wide array of relevant CO<sub>2</sub>RR products on copper electrodes [117]. Similarly, a modified dual thin layer electrolyte cell scheme with transfer capillaries achieved the qualitative detection of liquid products such as ethanol and propanol [118]. Ethylene, methane as well as the alcoholic liquid products reported, however, exhibited very similar onset electrode potentials, which appeared at variance with current mechanistic models.

### Meeting the ‘liquids challenge’ in electrochemical mass spectrometry (EMS)

A recently proposed EMS capillary flow cell design (figure 14) combines continuous convective electrolyte flow toward the electrified interface with fast capillary sampling flow toward the liquid–vacuum interface. A thin electrolyte layer at the electrified interface is replaced by a large bulk electrolyte volume to enable high currents and hence improved product sensitivities. While the capillary sampling lowers the collection efficiency, it is not affected by gas bubble formation. Also, the capillary flow extraction approach ensured high-speed plug-flow conditions, ultra-low response times combined with more precise alignment for all volatile products.

The capillary electrochemical flow cell design in figure 14 [119] allows for independent control of relevant design parameters, necessary for reliable temporal recording of product formation kinetics. Unlike in thin-layer electrolyte designs, inside this flow cell, the CO<sub>2</sub>-saturated electrolyte streams over the electrode surface at moderate 10 s of  $\mu\text{l s}^{-1}$ . The sampling capillary, located at controlled distances from the electrode surface, injects an optimal sampling volume to a spatially separated porous interface, delivering products in plug-flow for analysis at an adjustable collection efficiency. This design delivers excellent temporal alignment and resolution of gas and liquid volatile products. Stable MS baselines and high faradaic currents guarantee high signal-to-noise ratios.

Practical usefulness of the capillary MS cell design was recently shown in a mechanistic CO<sub>2</sub>RR study that focused on the dominant mechanistic pathways of mixed CO<sub>2</sub> and CO feeds toward ethylene [119]. The



capillary DEMS setup employed complex mixed reactant gas mixtures, partial pressures, as well as isotope-labeled <sup>13</sup>CO/<sup>12</sup>CO<sub>2</sub> co-feeds. The DEMS experiments yielded new important mechanistic insight into the reactive cross-coupling of CO<sub>2</sub> and CO on the Cu catalyst. Accurate experimental onset potentials could be extracted (figure 15) [119]. The capillary cell design is compatible with a variety of catalyst and electrode shapes and formats, tolerates wide applied potential or currents ranges, elevated pressures and wide variety of analytes.

### Concluding remarks

EMS has become an invaluable mechanistic tool to interrogate the reactivity of volatile species in complex multi-electron transfer reactions, such as the CO<sub>2</sub>RR. No EMS design to date was able to satisfy all requirements to full satisfaction. Although the real-time analysis has progressed significantly over past years, there is plenty of room for improvements for sensitive, fast and quantitative product detection. A deeper understanding and possible reengineering of how to control the fluid dynamics of the entire system appears necessary to obtain a balance between robustness by minimal system complexity, yet maximum application versatility.

Recently emerging EMS designs offer new and sometimes complementary features to elucidate subtle chemical reaction pathways in CO<sub>2</sub>RR. Fundamental mechanistic insights call for maximum product onset potential resolution capabilities, while practical process evaluation of FEs places more emphasis on quantitative capabilities. Key challenges for future EMS schemes include the combined monitoring of experimental product selectivity (FEs), absolute product formation rates and accurate onset potentials. In collaboration with theoreticians we need to gain a better understanding of the conceptual link of experimental onset potentials to microkinetic parameters, thereby enhancing their mutual predictive and diagnostic power in terms of chemical reaction mechanisms and new catalysts.

### Acknowledgments

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## 11. What is the potential of metal doped carbon for CO<sub>2</sub>R?

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### Status

Carbon-based materials doped with transition metals have emerged as efficient and low-cost catalysts for the CO<sub>2</sub> electrochemical reduction (CO<sub>2</sub>R) given their ability of selectively reducing CO<sub>2</sub> into CO, with CO partial CDs up to hundreds of mA cm<sup>-2</sup>. In these materials, the metal centers are incorporated into a carbon support via coordination with a heteroatom, commonly N, to form a class of materials that we will refer to as MNCs. The metal centers in MNCs form active sites similar to those on metal macrocycles which are known to be efficient catalysts for the CO<sub>2</sub>R [120].

An important advantage of these materials is that they can be prepared using simple methods and inexpensive precursors, which can be easily scaled up. Most commonly, the synthesis involves heat treatment of mixtures of inorganic salts, high surface area carbon and one or more N-containing precursors. During the heat treatment, a variety of functionalities are incorporated into the carbon structure, resulting in multiple sites that can be involved in the catalytic process (figure 16(a)).

Both experimental and theoretical studies have shown that the nature of the metal center is key in determining the performance of metal doped carbons (figure 16(b)), as it controls the binding energy towards different intermediates [121]. Ni has been shown to be one of the most interesting metal centers, reducing CO<sub>2</sub> into CO with FEs close to 100%. The overpotential however, is considerably larger than that of state-of-the-art Ag catalysts. By contrast, FeNC materials reduce CO<sub>2</sub> into CO at lower overpotentials with CO FEs up to 80%, in addition CH<sub>4</sub> has been reported as a minor product of the CO<sub>2</sub>R on FeNC [121]. Another commonly studied metal is cobalt, since Co complexes have reported excellent performance in the reduction of CO<sub>2</sub> into CO. Nevertheless, while some CoNC catalysts form CO with high selectivity, others produce H<sub>2</sub> as a main product, suggesting that the reactivity of a given metal center is also influenced by its chemical environment.

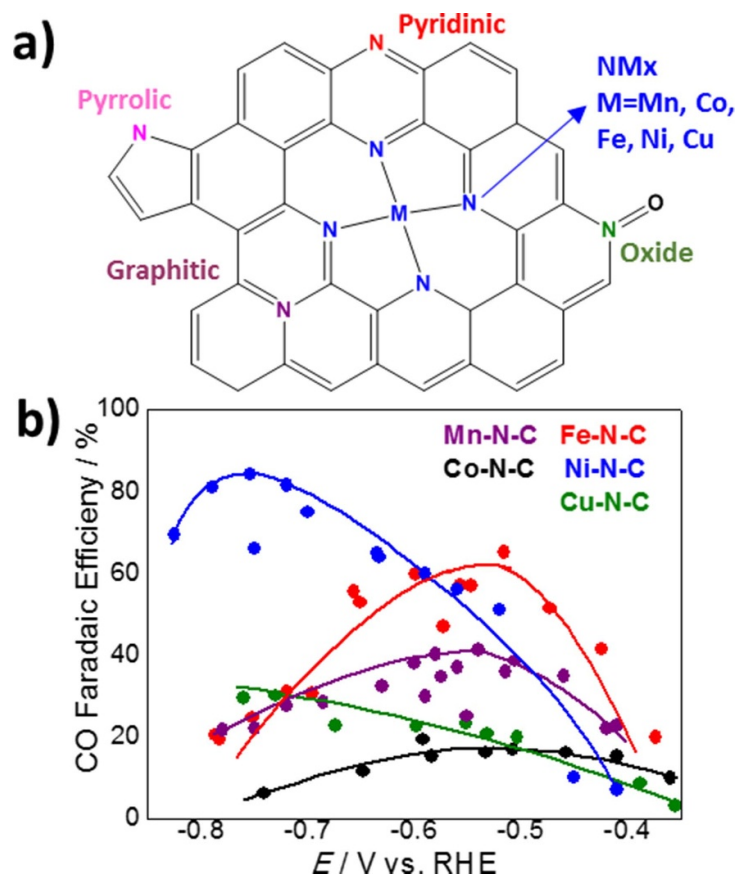
### Current and future challenges

Most of the studies on metal doped carbon have focused on CO production, which is a product of interest, given its use as a precursor for several synthetic processes. Nevertheless, the highly desired direct reduction of CO<sub>2</sub> into more reduced compounds or multi-carbon products is limited on MNCs materials. While the high binding energy between CO and the iron centers of FeNC allows the reduction of CO into CH<sub>4</sub>, the selectivity remains extremely low [122]. Methane has also been reported as a product of the CO<sub>2</sub>R on ZnNC catalyst [123], while other ZnNC materials form CO as the main product. More interesting products, such as ethanol and acetone, have been reported on CuNC materials [124]. The product distribution, however, varies greatly between different works which could be attributed to the heterogeneity of MNCs materials which tend to have different distribution of possible active sites. In addition, remaining metallic particles can participate in the catalytic process, and therefore it is crucial that the material is free from metal or oxide nanoparticles to ensure the observed catalytic performance is due to isolated metal centers.

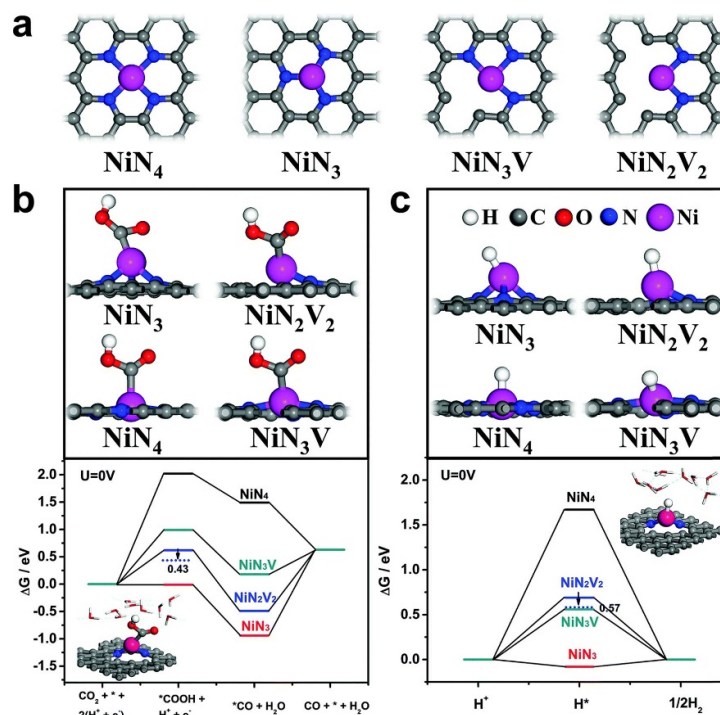
While it is clear that the metal plays an important role in the catalytic performance of MNC materials, the exact structure of the active site is still under debate. In fact, different MN<sub>x</sub> and free nitrogen sites are involved in the catalytic process. Despite the contribution of the nitrogen functionalities to the activity, for analogous materials, the catalytic current is dramatically enhanced by the presence of a metal center, suggesting a major contribution of the metal during the CO<sub>2</sub>R [122]. The coordination environment of the metal center and its oxidation state, however, is also affecting the catalytic performance of MNC materials. For instance in the case of NiNC materials, NiN<sub>4</sub> sites were initially proposed as the active site [125]. Later, a combined experimental and theoretical study suggested that the presence of vacancies enhances the binding energy towards the \*COOH facilitating CO formation, suggesting that undercoordinated sites will result in a higher activity towards CO<sub>2</sub>R (figure 17) [126]. While these results highlight the importance of the coordination number in controlling the catalytic performance of MNC materials, it is challenging to establish the predominant active site. Furthermore, the optimal metal configuration is likely to be specific for each metal.

### Advances in science and technology to meet challenges

Studies using both DFT calculations and spectroscopy techniques are needed to bring more insight into the nature of the active sites and to understand how their structure affects product distribution. Once the optimal catalytic sites are identified a key challenge will be the development of new and affordable synthetic methods to incorporate as many of the desired active sites into the carbon structure as possible.



**Figure 16.** (a) Scheme of the different N functionalities of MNC materials. (b) Effect of metal center on the selectivity of MNCs during CO<sub>2</sub> electrolysis carried out at constant potential in 0.1 M KHCO<sub>3</sub>. Reproduced from [121]. CC BY 4.0.



**Figure 17.** Effect of the coordination environment. (a) Different Ni<sub>x</sub> structures: Ni<sub>4</sub>, Ni<sub>3</sub>, Ni<sub>3</sub>V and Ni<sub>2</sub>V<sub>2</sub>. (b) DFT calculated free energy diagram for the CO<sub>2</sub>RR at 0 V (c) DFT calculated free energy diagram for the HER at 0 V (the white, gray, red, blue, and purple balls represent H, C, O, N, and Ni atoms, respectively). Reproduced from [126] with permission of The Royal Society of Chemistry.



For industrial applications, these materials will have to be selective and stable under high CDs, which can easily be obtained on gas diffusion electrolyzers (GDEs). Studies using NiNC catalysts in GDEs have yielded promising results, reaching CO selectivities higher than 80% at  $200 \text{ mA cm}^{-2}$  [127]. While the selectivity decreased slightly during CO<sub>2</sub> electrolysis, the cell voltage of 4.65 V was stable during the 20 h test. Despite the good performance observed on this NiNC catalyst, there are still improvements needed. On one hand, the product distribution needs to be stable for longer periods and therefore *operando* studies to understand the reason for deactivation will be crucial. In addition, it would be desired to lower the cell voltage and thus it is necessary to develop catalysts with high activities at low overpotentials.

Further improvement on the catalytic performance of carbon-based materials doped with transition metals could be achieved by incorporating different active sites. For instance, the use of other heteroatoms (P, F, S and B) should be explored in more detail. The coordination of the metal center to other heteroatoms can be used to modify the electronic properties of the active site and tune its catalytic activity [128].

More interestingly will be the use of a catalyst containing more than one metal to enhance catalytic activity. One approach is to have different active sites to create a tandem catalyst, on which the first reaction steps take place on one site and the reaction is completed on another. For instance, the metal center on MNCs reduces CO<sub>2</sub> to CO which is later reduced on copper nanoparticles into hydrocarbons [129]. Alternatively, both metals can be forming dual active sites on which the reaction's energy barriers are lowered reducing the reaction's overpotentials [130]. In addition, such dual sites present an opportunity to design catalysts to favor the formation of C<sub>2</sub> products.

### Concluding remarks

Carbon-based materials doped with transition metals are cost effective catalysts with encouraging activity towards CO<sub>2</sub>R. Nevertheless, more fundamental insight on the different parameters that influence the catalytic performance is still needed. Furthermore, in most cases CO<sub>2</sub> is only reduced into CO and the formation of other valuable products is limited. Therefore, DFT calculations and spectroscopy techniques will be useful tools to get the fundamental knowledge needed to develop novel catalysts with improved activity, selectivity and stability. Determining the optimal active site to ensure a high concentration of such sites on the carbon support would be beneficial to the catalytic performance of MNC materials. In addition, the use of catalysts with other heteroatoms and containing dual sites are strategies to be considered to improve catalytic activity of these carbon-based materials and to developed catalysts capable of reducing CO<sub>2</sub> into other valuable products such as ethylene.

### Acknowledgment

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## 12. What is the potential for molecular catalysts for CO<sub>2</sub>R?

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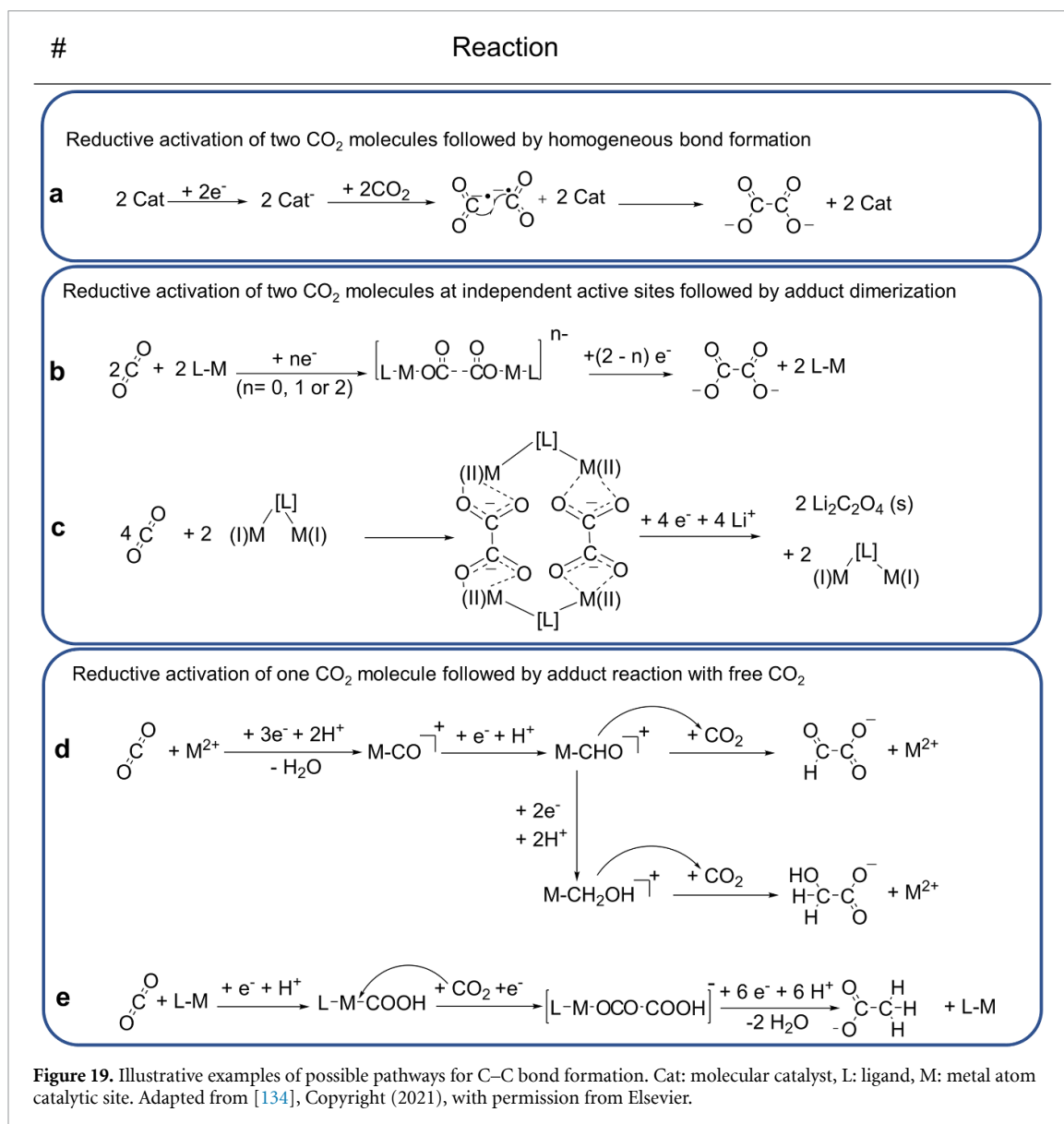
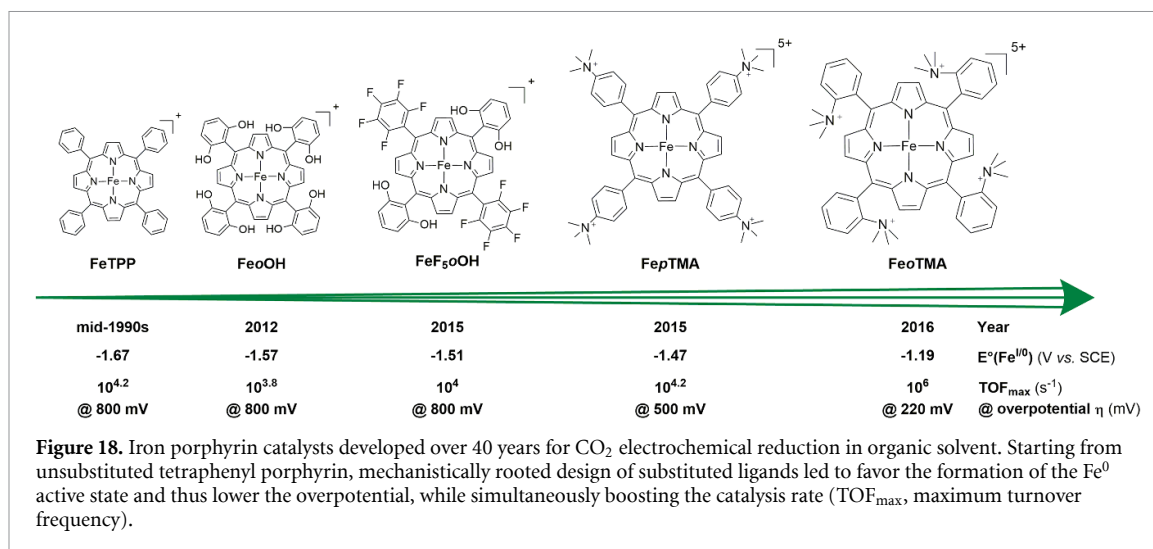
### Status

Molecular catalysts have the decisive advantage to display well define active sites configuration. Given their unique standard redox potential and spectroscopic signature, they offer the possibility to perform thorough mechanistic studies, through combining analytical electrochemistry, *in situ* and *operando* spectroscopies [131]. Likewise, such characteristics restrict the CO<sub>2</sub>RR and its competing HER reaction to a few possible pathways, hence leading to highly selective processes, provided the former ousts the latter. An additional asset of molecular species over solid-state catalysts lies in the infinite possibilities for precisely tuning the active site through synthesis design. Rooted in mechanistic investigation, molecular catalyst structure can be tuned so as to decrease the overpotential and to increase the intrinsic activity for CO<sub>2</sub>RR at the expense of the competing HER. Such rational optimization has been achieved within the family of tetraphenyl iron porphyrins (figure 18). First investigated in the 70s [132], these catalysts can be electro-reduced in an organic solvent to the formally Fe(0) state, a powerful nucleophilic species that binds and activate CO<sub>2</sub> through the formation of a Fe–CO<sub>2</sub> adduct. Introduction of electron withdrawing groups on the ligand core enabled to reduce the overpotential for generating the active Fe(0), but at the expense of a less active (nucleophilic) catalyst toward CO<sub>2</sub>. The rate determining step has been found to be the formation of the Fe–CO<sub>2</sub> adduct in typical experimental conditions. Its stabilization can be facilitated with hydrogen bonding and/or electrostatic effects with positively charged substituents (through space effects). Such effects were combined to inductive electronic (through structure) effect in the same catalyst and led to an overall optimized activity (faster rate and reduced overpotential, as illustrated on figure 18) [131]. Interestingly, when the deactivation of the catalyst occurs upon reduction of the ligand, addition of donating groups can extend its lifetime (stability). The high selectivity for CO<sub>2</sub>-to-CO conversion was transposed in water and molecular catalysts have been inserted into flow cells, matching the activity of nanomaterials [133].

The field is currently evolving toward reduction of CO<sub>2</sub> beyond two electrons. Selective processes have yet to be identified (as is the case for solid-state catalysts), but the combination of mechanistic studies together with relevant catalytic site design can open new perspectives.

### Current and future challenges

One challenge is to selectively reduce CO<sub>2</sub> to the full range of C<sub>1</sub> products with 4, 6 and 8 electrons (leading to formaldehyde, methanol and methane, respectively) and optimize the corresponding catalysts. To do so, in-depth understanding of the mechanism underpinning the few preliminary examples reported so far is necessary [134]. A second challenge is to catalyze C–C bond formation. In that case too, rare preliminary reports need first to be mechanistically re-investigated. All these processes require many electron and proton transfer steps, with several intermediate species on the route, it is thus questionable whether molecular catalysts would still convey a high selectivity. A way to tackle this issue relies on developing a cascade strategy with optimized catalyst for each 2e<sup>-</sup>/2H<sup>+</sup> step process (e.g. from CO to HCHO, from HCHO to methanol, etc). The formation of C–C bond (figure 19) may also be catalyzed at a specific molecular catalyst site, as it is the case, e.g. for electrocarboxylation. The latter illustrates that a mixture of several substrates may be necessary while a single one may be sufficient for producing symmetrical molecules (CO<sub>2</sub>R to oxalate or CO reduction to ethylene for example). An issue and a challenge towards upscaling systems including molecular catalysts at an industrial scale is related to their fragility, as compared to solid-state catalysts, and their synthetic cost. In this regard, attachment of molecular catalysts onto a solid support is a way to decrease the loading to low level and to maintain very high activity, providing the catalysts are properly dispersed [135]. Interestingly, such systems show extended durability. In order to maintain controlled selectivity, implementation of molecular catalysts into periodic structures such as MOF or covalent organic framework is certainly as a promising route (in electro- and photoelectrochemical contexts) [136]. Finally, the support may not be limited to a supporting role and could act as a co-catalyst. It points towards a challenging perspective where complex structures including molecular catalysts would combine complementary roles (light harvesting, CO<sub>2</sub> capture, proton channeling, substrate activation, etc), in line with historical developments that systematically took inspiration from nature (notably enzymes) for their ability to optimize complex functions.



### Advances in science and technology to meet challenges

To make progress in the understanding of catalytic mechanisms, including those going beyond  $2e^-$  processes and/or including C–C bond formation (figure 19), advances in the field of DFT could provide insights on the key intermediates and competing pathways. From an experimental point of view, the development of *operando* (x-ray absorption, x-ray photoelectron spectroscopy, electron microscopy) and (ultrafast) spectroscopy techniques and their coupling should also enable the identification of key intermediates such as transient species or specific molecular configurations preceding the reduction of a CO adduct or the formation of a C–C bond for example. Such techniques may allow investigating, at an atomic scale, interactions between the molecular catalysts and the support to reveal possible synergy (dispersion, steric hindrance, conjugation effect, local hydride formation, etc). Upon adsorption, molecular orbitals of a catalyst may partially or fully merge with the band structure of the support (e.g. with graphene-like materials) [137]. Ultimately, the formerly established distinction between molecular and solid-state nature vanishes. Even if scarce, the few already reported examples of CO reduction and of C–C bond formation at a molecular catalytic site represent the most natural front door towards a better understanding. It includes the dimerization of CO<sub>2</sub> radical anion to oxalate [138] and formation of more complex molecules (glyoxylate and hydroxy acetate) in the case of a Ru based catalyst (figure 19(b)) [139]. In parallel, a reassessment of previous molecular catalysts might be necessary with the objective to reduce CO, a substrate with a completely different reactivity than CO<sub>2</sub> and which may be activated by catalysts inactive toward CO<sub>2</sub> [134]. Going further, exploration of molecular catalyst with CO substrate should be completed with studies including mixture of substrates (CO<sub>2</sub>/CO, CO/HCHO, etc) as it is likely that C–C bond formation may involve carbon atoms with different oxidation state. Another approach is to develop hetero-multimetallic complexes able to act in synergy or in parallel to reduce CO<sub>2</sub> or a partially reduced substrate (e.g. CO). Ultimately, advances in the field of molecular CO<sub>2</sub> capture could have significant impact on molecular CO<sub>2</sub>R as multi-molecular entities able to electroreduce dilute CO<sub>2</sub> gas stream would be reachable, as already demonstrated in photochemical conditions [140]. Inventing an integrated (photo)electrochemical system combining CO<sub>2</sub> DAC and selective catalysis to a highly reduced product would illustrate achieving such challenges.

### Concluding remarks

Molecular electrocatalysts have been developed with remarkable creativity over decades, leading to highly efficient conversion of CO<sub>2</sub> into two electron reduction products. Their ability to drive  $2e^-/2H^+$  catalytic processes with exquisite selectivity is a firm basis to develop cascade reactions in which CO<sub>2</sub> will be transformed into more reduced products, including C<sub>1</sub> and multi-carbon products. Towards this goal, the ability to pursue historical strategy with detailed mechanistic studies upon combining theoretical tools, analytical electrochemical methods and high resolution spectroscopic techniques is a decisive asset of molecular based catalytic systems. Such approach finally bridges molecular and heterogeneous catalysis. It also opens a door toward multi-component, complex hybrid systems (electrodes, photoelectrodes, cells) that would integrate and synchronize all the functions to drive the CO<sub>2</sub> capture and reduction with ultimate selectivity and rate.

### Acknowledgments

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### 13. How does the nitrogenase enzyme enable C–C coupling?

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#### Status

Nitrogenases constitute the only known class of enzymes able to reduce the stable triple bond of the N<sub>2</sub> molecule to render the element nitrogen accessible for assimilation into biological macromolecules [141]. At ambient conditions and driven by adenosine triphosphate (ATP) hydrolysis, nitrogenases have long been studied to unravel their basic mechanism, but also as inspiration for novel catalysts for the reduction of inert substrates [142]. The most common class of nitrogenases utilizes an iron–sulfur cluster at its active site that additionally contains molybdenum at its apical position [143]. Under conditions of limited availability of Mo, many organisms resort to an alternative nitrogenase that replaces the heterometal with vanadium (figure 20) [144], or to a third ortholog that is based solely on iron [145]. While these alternative enzymes are less efficient in reducing N<sub>2</sub>, they catalyze distinct reactions that are not mediated by Mo nitrogenase. V nitrogenase reduces CO [146], a non-competitive inhibitor for all substrates other than protons (which lead to H<sub>2</sub> formation), while the solely iron-dependent nitrogenase reduces CO<sub>2</sub> [147]. Interestingly, the main product of the latter reaction is methane, CH<sub>4</sub>, but in the reduction of CO by V-nitrogenase more than 93% of the product are not the fully reduced compound, but rather ethylene (C<sub>2</sub>H<sub>4</sub>), with small amounts of ethane (C<sub>2</sub>H<sub>6</sub>) [148]. Whereas the finding that an enzyme evolved to reduce N<sub>2</sub> can also metabolize the isoelectronic but slightly less stable CO is less of a surprise, the formation of a C–C bond during this reaction is quite remarkable. From a technical perspective, all nitrogenases catalyze a Haber–Bosch-like reaction at ambient conditions, and V-nitrogenase has additionally mastered the Fischer–Tropsch reaction, while Fe-nitrogenase engages in Sabatier chemistry. It remains under debate whether these alternative reductions have a physiological significance, but the value of studying their mechanisms for understanding nitrogenase catalysis is broadly recognized today.

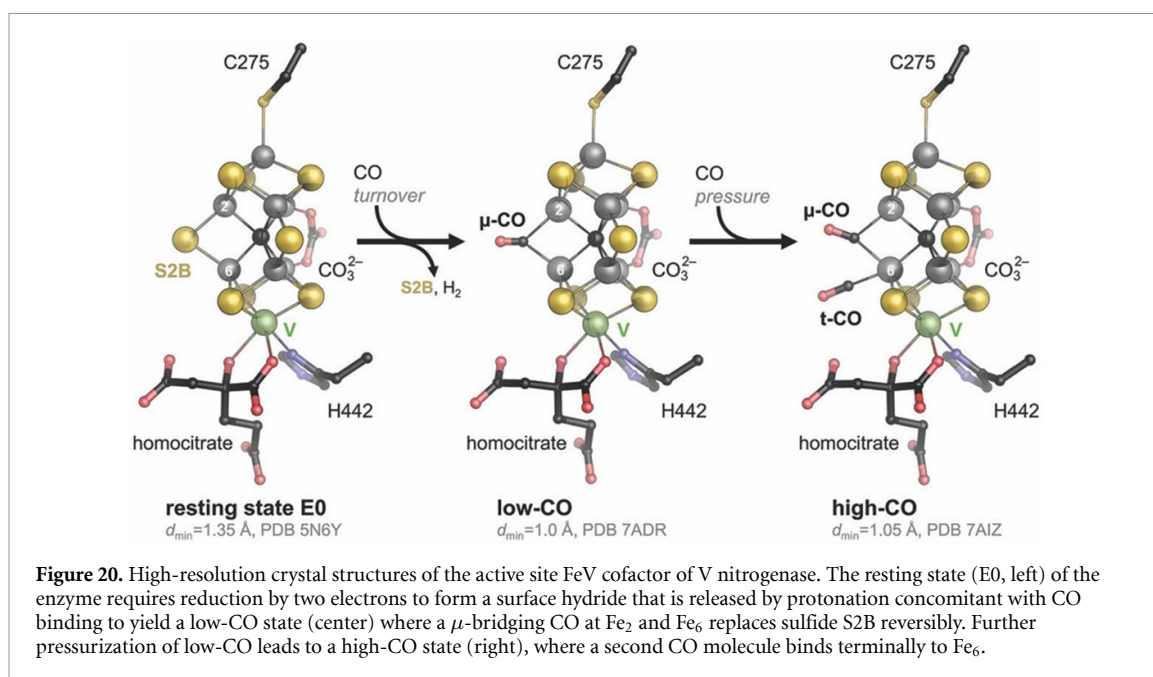
#### Current and future challenges

As the most strongly reducing enzyme known to date, nitrogenase must generate a reducing potential that falls quite clearly outside the classical water window, implying that water must be excluded from the active site where the reducing species is formed. Extensive kinetic studies in the 1980s have revealed that nitrogenase itself must accumulate four electrons sequentially before N<sub>2</sub> can be bound and activated [149]. These electrons cannot be stored in the already highly reduced active site cofactor but form a pair of bridging hydrides at its surface [150]. The electron donor for nitrogenase only transfers a single electron to the cluster at a time, but the presence of two surface hydrides now allows for the reductive elimination (re) of H<sub>2</sub>, leaving the enzyme in a highly reactive, two-electron-reduced state [151, 152]. Other than in Haber–Bosch chemistry, H<sub>2</sub> thus is a by-product, not a substrate of the nitrogenase reaction. The accumulation of electrons, on the other hand, cannot be facilitated by elevated temperature and pressure, so that this step represents the major challenge for the enzyme. The reduction of CO is less demanding than that of N<sub>2</sub>. V-nitrogenase does not readily react with the gas, but a reduction by only one or two electrons is sufficient for activation and a re of H<sub>2</sub> is not required. Mössbauer, electron paramagnetic resonance (EPR)/electron-nuclear double resonance, Fourier-transformed infrared (FTIR), XAS [153] and x-ray diffraction studies have shown how one (low-CO) [154, 155] or two (high-CO) molecules of CO bind specifically to the nitrogenase cofactors [156, 157], occupying a  $\mu$ -bridging (low-CO) position that is complemented with a vicinal terminal position (high-CO) at high pCO (figure 20). In the activation of small molecules, the first reduction step that reduces the substrates bond order is the most difficult. Consecutive reduction steps are more facile, and it constitutes a major challenge to populate the various intermediates of these reactions for subsequent analysis. Cryo-annealing has been applied successfully for spectroscopic studies [158], while crystallography has benefitted from the strong inhibitory effect of CO that renders adducts quite stable in the absence of a reductant.

In light of downstream applications the study of CO binding to Mo and V nitrogenase has provided multiple interesting leads, but has also highlighted that such complex enzymes are fully integrated systems that gain their catalytic abilities only through the combination of a dedicated, sequential electron transfer and activation machinery and a specialized protein environment that precisely positions and synchronizes electron and proton transfer from different directions to the active site cofactor.

#### Advances in science and technology to meet challenges

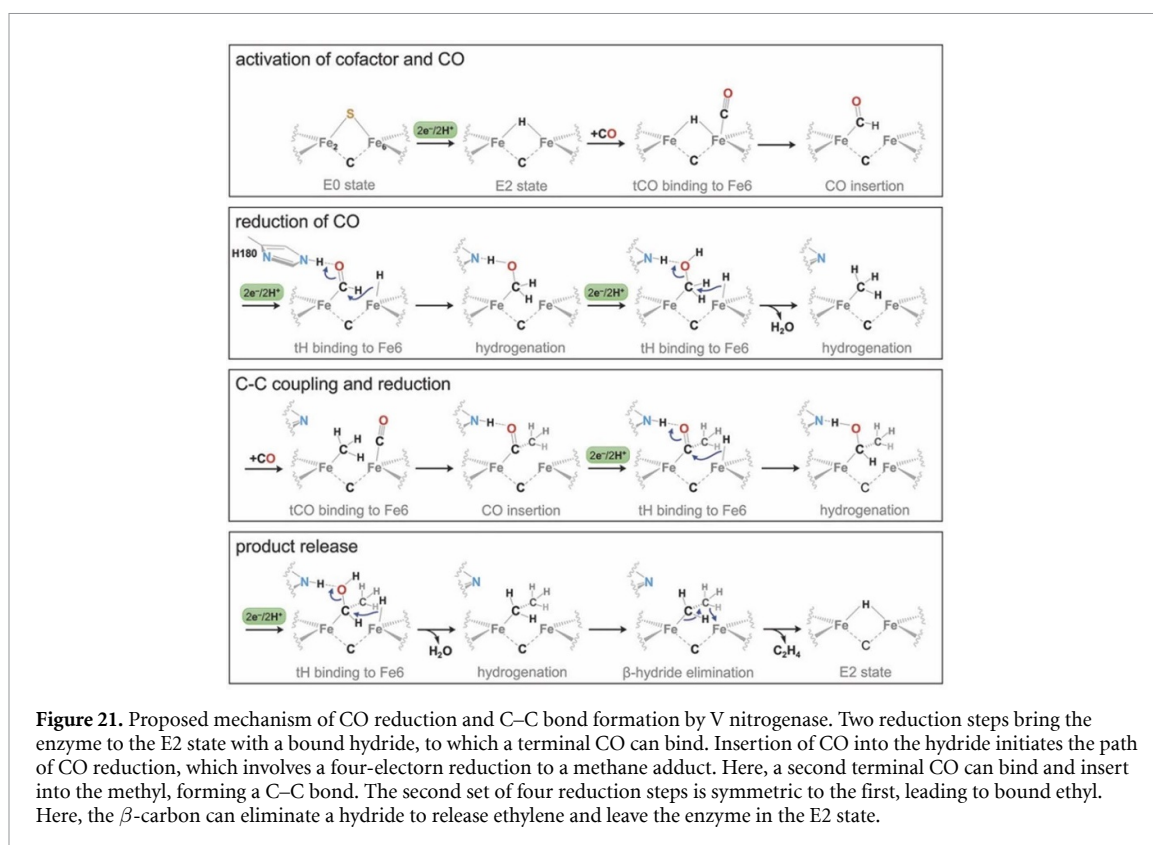
Recent years have seen tremendous advances and new experimental and theoretical studies of nitrogenases have outlined a catalytic mechanism that accounts for many of the intriguing findings from decades of



research [159]. Key to its function is the accumulation of reducing equivalents, driven by ATP hydrolysis, on an already highly reduced cofactor. The transfer of two electrons gives rise to the formation of a terminal hydride if a single proton is added, and over time this hydride will relax into a more stable, bridging conformation at two Fe sites, or be lost as unproductive H<sub>2</sub> if another protonation occurs first [160]. We have realized that the alternative substrate CO shares many features with hydrides: both are strong-field ligands with similar bond distances and can attain bridging or terminal binding modes at a multinuclear site. Based on the high-CO state structure of V nitrogenase, we have proposed that iron Fe<sub>6</sub> is the site that accepts a first electron (state E1) and subsequently forms a terminal hydride upon further reduction [160]. This H<sup>-</sup> displaces a bridging sulfide (S2B) and migrates into a bridging position at Fe<sub>2</sub> and Fe<sub>6</sub> to reach state E2 (figure 21) [156]. Repeating this process would lead to E4, while the unwanted protonation of the hydride in E2 leads back to E0, releasing H<sub>2</sub>. For CO we find the same binding modes: in the high-CO structure, a bridging  $\mu$ -CO is bound stably to Fe<sub>2</sub> and Fe<sub>6</sub>, while a labile *t*-CO is a terminal ligand to the now pentacoordinate Fe<sub>6</sub> [156, 157]. Electronically, both the low- and high-CO adducts represent an E0 state and are inhibited, unreactive forms of the enzyme.

To reduce CO, V nitrogenase must utilize the reducing power of the E2 state and avoid the loss of its electrons as H<sub>2</sub>. This is possible if the *t*-CO, rather than replacing it, can *insert* into the bound H<sup>-</sup>, leading to a direct two-electron reduction of the substrate and the generation of a formyl adduct (figure 21) [159]. At this point, the triple bond of CO is broken, and the subsequent steps follow swiftly: in two further cycles of hydride accumulation and insertion, the substrate is reduced to a bound methyl group, but the final protonation and release of methane are not favored under the high pCO required to drive the reaction. Instead, another *t*-CO will bind at Fe<sub>6</sub>, and instead of inserting into a bound hydride, it now inserts into the methyl, forming a C–C bond to yield an acetyl adduct. The enzyme then re-iterates its elementary cycle of reduction, hydride formation and hydrogenation to reduce the C<sub>2</sub> product via the aldehyde to an ethyl group. Once more the dissociation of ethane is not favored, and in principle the binding of a further *t*-CO can lead back to the formation of a C<sub>3</sub> product or even longer hydrocarbon chains that have indeed been observed experimentally. Alternatively, ethylene or longer-chain adducts offer a way out: a bound C<sub>2</sub> product can undergo a  $\beta$ -hydride elimination, replacing the bound product with a hydride and releasing an unsaturated species, ethylene (figure 21).

Several mechanistic proposals for nitrogenases have emerged over time, but the novel aspect of current models is that the dissociation of sulfide S2B opens a dinuclear iron site that is strongly reduced and enables a  $\mu$ -bridging binding of hydrides and ligands. Synthetic inorganic chemistry has yet to embrace this concept and meet the challenge of establishing a rigid framework with largely invariant Fe–Fe distances. However, the finding that only a single edge of the cofactor (figure 20) is active in the interaction with substrates provides the perspective that efficient homogeneous or even heterogeneous catalysts can be designed to incorporate these features, combined with an electrode for electron supply.



### Concluding remarks

The reduction of CO is only a side reaction of an enzyme that provides reactive nitrogen from atmospheric  $N_2$  for the entire biosphere. At first glance both reactions differ strongly: CO binding requires far less reducing power to be accumulated on the enzyme, at its reduction involves a C–C bond formation but does not proceed to completion. The underlying principle of both reactions, however, is a repetitive formation of a terminal hydride by accumulation of two electrons and a proton that can then insert into a stably bound reaction intermediate. For the reduction of  $N_2$ , an even stronger reductant is required that is formed by re of  $H_2$  from the E4 state. With only these two modes of operation, the enzyme functions as the most potent reductase in nature, and the astonishing diversity of its substrates may well be rationalized with a single mechanistic principle.

### Acknowledgments

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## 14. What is the future of single crystal studies in CO<sub>2</sub> reduction (CO<sub>2</sub>R)?

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### Status

Single crystalline electrode surfaces are atomically-flat, well-defined surfaces with an ordered two-dimensional arrangement of atoms. They are model surfaces to understand the structure-property relations in electrocatalysis, and thus to design scalable, optimized nanostructured catalysts for enhanced electrocatalysis. The pioneering work by Hori *et al* on single crystalline electrodes during the 80s–90s, showed that the efficiency for the CO<sub>2</sub>R was highly dependent on the surface structure [161]. Model studies carried out on single-crystalline Au, Ag and Cu electrodes show that, while <110> facets of Au and Ag are highly active and selective towards the formation of CO, Cu stands out as the only pure metal capable to convert CO<sub>2</sub> beyond CO to produce a variety of interesting products. Several studies have shown that the <100> facet is selective towards the production of ethylene. In addition, the introduction of steps and under-coordinated sites in combination with <100> terraces is more effective in producing C<sub>2</sub> products, such as ethylene and ethanol [54, 162].

The role, type and distribution of active sites with different coordination number on CO<sub>2</sub>R electrocatalysis is still under discussion [6]. This is due to different reasons, including: (a) the difficulty in controlling and testing the surface ordering before, after and under reaction conditions; (b) the lack of electrochemical methods to quantify the number of active sites, as well as the amount and creation of new defects and domains on Cu, under different electrochemical environments. Metallic surfaces are very dynamic and undergo re-faceting and transformation with time under different reduction potentials, which complicates finding the real relations between structure and catalytic performance [163].

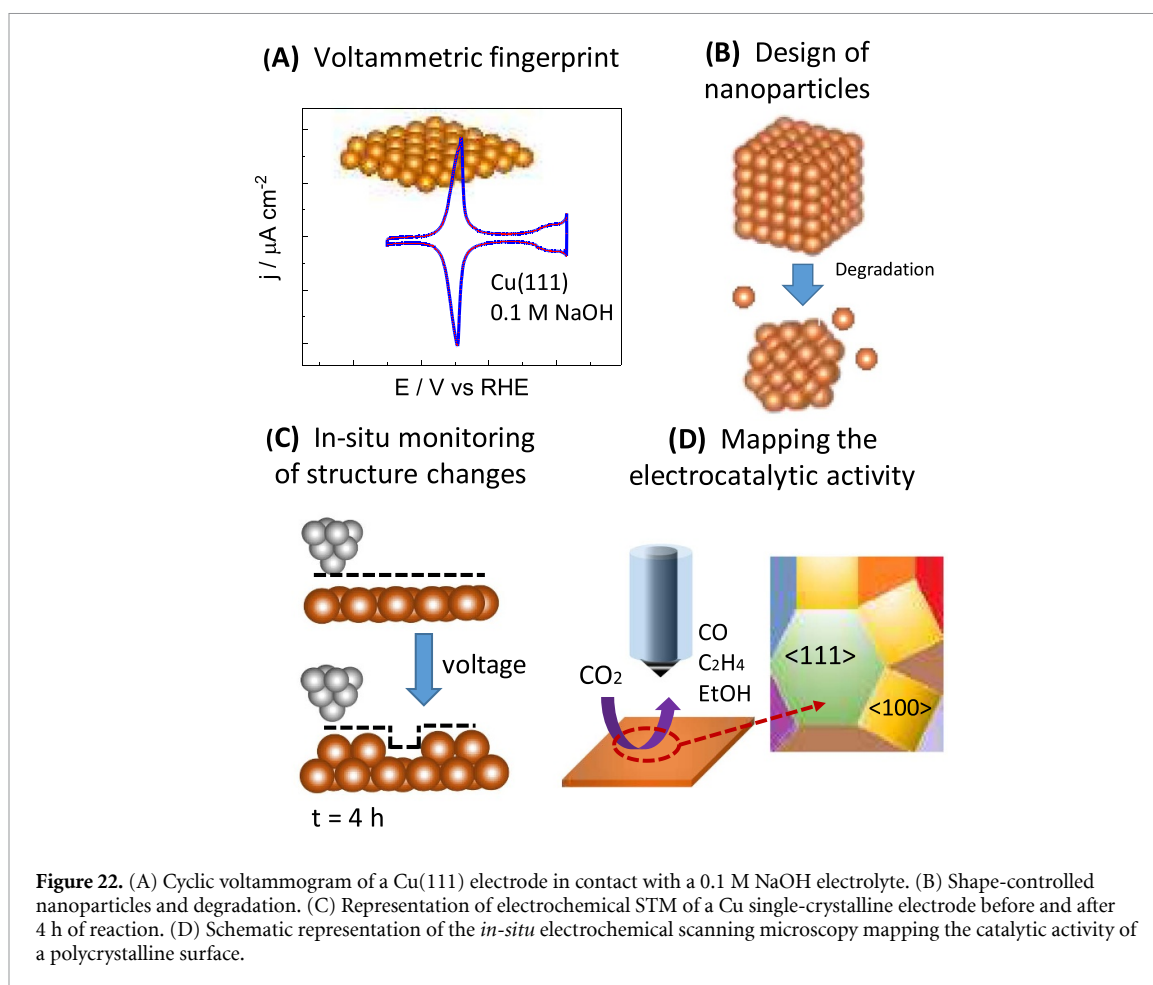
To fill these experimental gaps and rationally describe the structure-activity-selectivity relations for CO<sub>2</sub>R, it is key to combine electrochemical methods with surface-sensitive and atomic-scale *in-situ* characterization. This unique combination will be essential to elucidate the distribution of domains and changes in the surface structure under potential conditions, providing a detailed picture of the electrochemical interface [6]. These studies will also provide an in-depth understanding of the role of the electrolyte on the changes of the electrified interface structure under reaction conditions. Ultimately, the knowledge from well-controlled studies on single crystals will be key to engineer more stable, active and selective electrode–electrolyte interfaces and fabricate scalable catalysts operating at long time periods at devices such as GDEs [164].

### Current and future challenges

Cyclic voltammograms on single crystalline electrodes provide the electrochemical fingerprint of the electrode–electrolyte interface (figure 22(A)). Recent experiments on Cu(100) and Cu(111) showed that voltammetric profiles in alkaline media presented clear signs of contamination and an unknown amount of defects-sites. This suggested a lack of control of the real surface ordering and cleanness under reaction conditions in experiments [165]. Consequently, experimental work on CO<sub>2</sub>R on Cu single-crystalline surfaces needs to be revisited. In contrast to <111> and <100> flat facets, defect-rich and polycrystalline Cu surfaces present low intense voltammetric features, offering scarce information of the surface structure. In particular, there is a lack of electrochemical tools for reliable quantification of the electrochemically active surface area (ECSA) and the contribution of different crystallographic domains on Cu-based electrodes. Studies on Cu single facets have shown that voltammetric underpotential deposition (UPD) of a submonolayer of a lesser-noble metal on Cu, such as Pb, provides intense and distinguishable peaks which shape and potential are facet-dependent [166]. Thus, metal UPD is a promising tool to elucidate the distribution of electrocatalytically active sites as well as the ECSA, of paramount importance to assess the CO<sub>2</sub>R activity.

Many metals undergo surface re-faceting. Interestingly, Cu reconstruction is both time and potential dependent, which affects the distribution of products [163]. Additionally, tuning the electrolyte composition substantially changes the product selectivity, and electrolyte effects on the CO<sub>2</sub>R are facet-dependent. However, the effect of the electrolyte on the surface transformations of Cu single crystalline electrodes over time requires further analysis. What drives the reconstruction on Cu is still under discussion and requires future analysis. Not only the surface–electrolyte interactions and the adsorption of the intermediates of the CO<sub>2</sub>R will influence the surface reconstruction mechanism, but also the subsurface hydrogen at potentials close to the hydrogen evolution [167–169]. These studies will be also key to investigate the



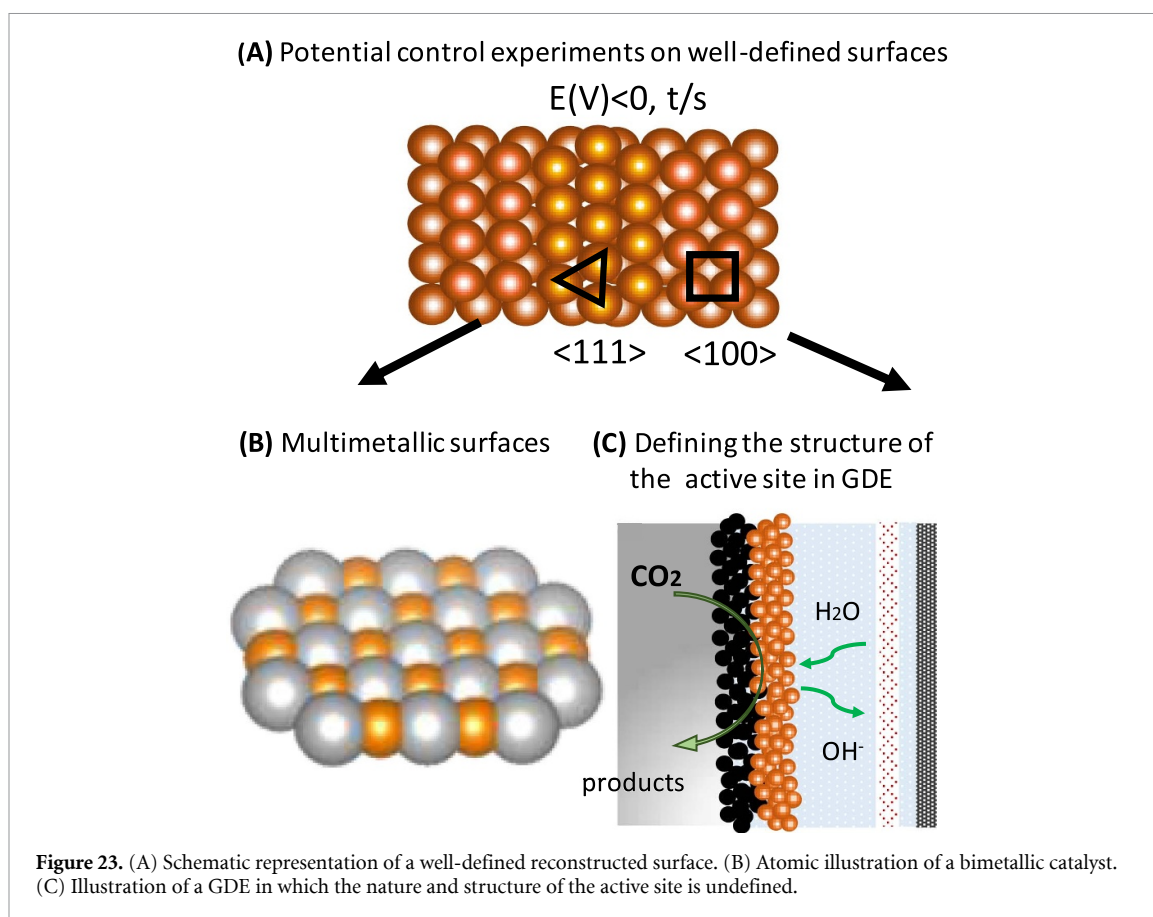


potential-dependence of the degradation mechanism on shape-controlled nanoparticles (figure 22(B)) under reaction conditions.

Controlled electrochemical experiments have shown that the catalytic performance on Cu is highly dependent on the potential limit conditions. Pulsing the applied potential from a reductive value to a higher value modifies the product distribution on Cu single crystalline electrodes, which has been ascribed to the generation of Cu motifs along with the formation of Cu(I) oxide [6]. It has been also claimed that defect-sites are essential to promote the formation of C<sub>2</sub> carbon products such as ethylene and ethanol [6]. However, the difficulty to quantify the different domains on the entire Cu surface along with the surface dynamics makes it challenging to rationalize which structural parameters govern the catalytic performance of Cu-based catalysts for CO<sub>2</sub>R.

### Advances in science and technology to meet challenges

*In situ* elucidation and quantification of both the atomic-scale structure of well-defined interfaces and the distinct crystallographic domains on the electrode surface is vital to understand the structure-performance relations. *In-situ* surface-sensitive characterization techniques, such as electrochemical AFM [80] and STM [167], are essential to elucidate the structure of the electrocatalytically active site at the atomic scale (figure 22(C)). Combination of (spectro)electrochemical methods and *in-situ/operando* characterization techniques with high time and spatial resolution will provide information on the electrified interface structure. Interestingly, we can investigate the solvent ordering and surface electric field—two key parameters of electrochemical interfaces [170] that affect electrocatalytic reactions—by means of techniques such as the laser-induced temperature jump method. These techniques can be also an attractive approach to investigate the electrochemical properties of surfaces which have been selectively modified by adatoms, or by the specifically adsorbed electrolyte species. Another promising technique is *in-situ* electrochemical scanning microscopy [171], which allows for in-depth analysis of the electrified interface composition affecting the activity on specific crystallographic domains of a polycrystalline electrode (figure 22(D)). A challenge of this



technique remains on the development of probe tips to differentiate between different carbon products beyond CO.

The use of *in-situ* and *operando* techniques in combination with electrochemical methods will be required to describe bimetallic and multimetallic electrodes, for which the synergetic combination of several metals modifies the electrocatalytic CO<sub>2</sub>R [54]. Here, the fabrication of well-defined surfaces combining two or more metals in an alloy, forming adlayers, atomic ensembles or single atom catalysts, could shed lights into the geometric and electronic effects of multimetallic materials on the CO<sub>2</sub>R (figures 23(A) and (B)). We anticipate that reconstruction under different potential and time conditions will not only affect the atomic ordering, but also the surface chemical composition, influencing the CO<sub>2</sub>R performance.

Potential-controlled experiments used to analyze the structural aspects of well-defined electrode | electrolyte interfaces could be used to engineer GDE configurations (figure 23(C)), in which lesser rationalization of the active site positions has been performed. Methods for the determination of the real active surface area as well as the crystallinity of the particles, under different reaction environments, are necessary to understand which factors control the CO<sub>2</sub>RR at higher rates and lower mass transport limitations on GDEs [164]. This would open the door for the rational design of industrial electrocatalysts with surface structures capable to maintain high selectivity and activities during longer times.

### Concluding remarks

Controlled studies on single crystalline electrodes are necessary to describe the structural changes at the electrified interface affecting the CO<sub>2</sub>RR performance. Assessment of electrolyte effects on the surface reconstruction is key to rationally design and tune the surface dynamics of CO<sub>2</sub>R catalysts over time. Future studies investigating how to selectively tailor specific active sites positions on well-defined surfaces will be essential to understand and tailor engineered active site structures. In addition, electrochemical methods combined with *in-situ/operando* surface-sensitive and atomic-scale characterization techniques will allow to elucidate the catalytic performance on specific active site positions. These studies will be also key for the rationalization and design of more active, selective and stable nanostructured surfaces to be used in e.g. GDEs. Lastly, we highlight that future studies in single crystals should be extended to multimetallic surfaces in which the surface re-faceting and metallic segregation will highly affect CO<sub>2</sub> electroreduction.

## Acknowledgments

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## 15. What are the open questions in the mechanistic understanding of CO<sub>2</sub> reduction (CO<sub>2</sub>R)?

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### Status

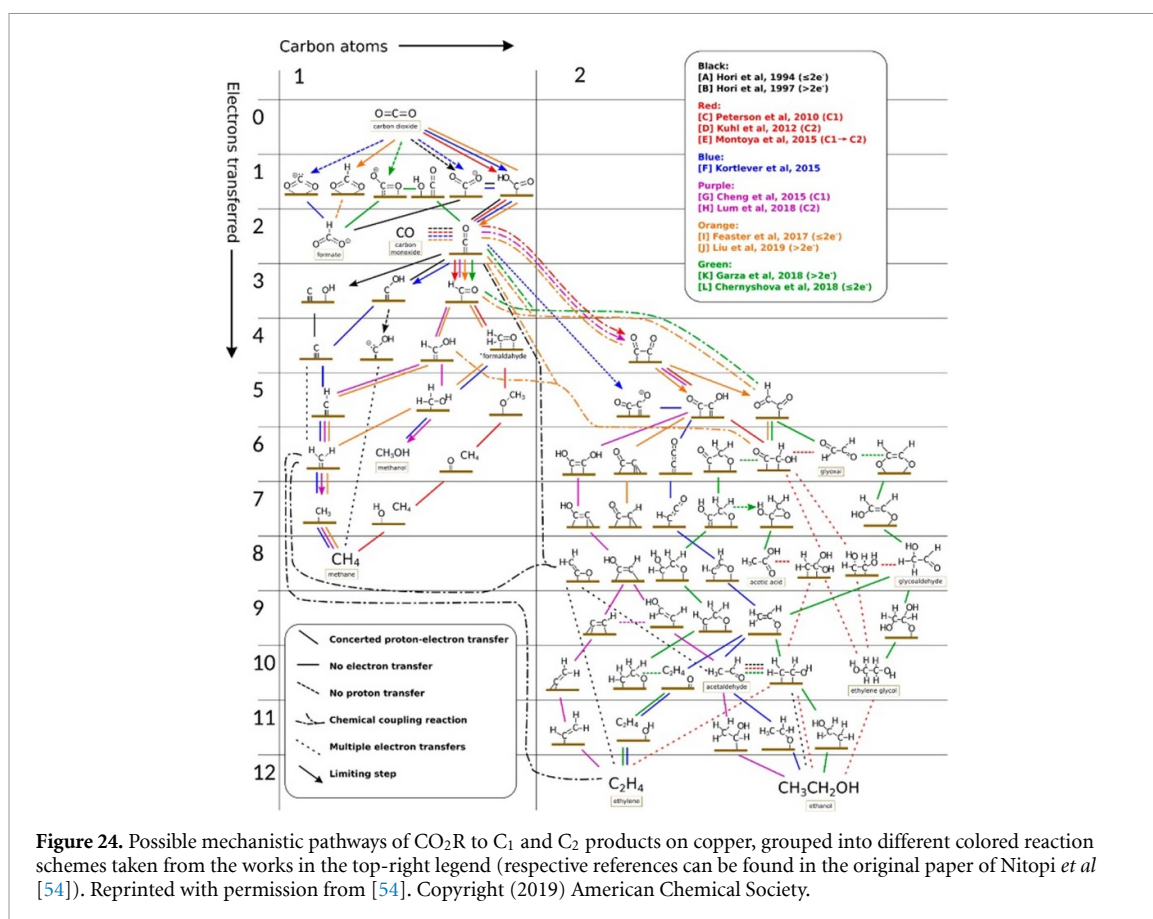
The mechanistic understanding of the electrochemical CO<sub>2</sub>R has been studied since the first report by Hori *et al* [1]. The current status of our understanding is roughly correlated to the number of carbons: as the number of carbons in the products increase, our knowledge about the reaction mechanism becomes less detailed. For the C<sub>1</sub> and C<sub>2</sub> products, several advances and important findings have been achieved by different groups over the years. Still, many disagreements about the exact pathways on Cu electrodes remain, as discussed by Nitopi *et al* [54], and as summarized in figure 24. For C<sub>1</sub> compounds, the intermediates \*COOH and \*OCHO are considered to produce CO and HCOOH, respectively. The formation of CH<sub>4</sub> and CH<sub>3</sub>OH is typically assumed to have CO as an intermediate that is further reduced [172]. For the synthesis of C<sub>2</sub> products, OC–CO dimerization is the most accepted pathway for the C–C bond formation, as predicted by DFT calculations [173, 174] and experimentally detected by FTIR [105], although there is still some debate about whether the coupling takes place between two CO adsorbates or between CHO and CO adsorbates. Besides the C–C bond formation, it is not yet known what makes the C<sub>2</sub> intermediates to be driven to a specific product (e.g. ethylene vs ethanol, or why ethane, glycolaldehyde, and ethylene glycol are not produced in significant amounts). Although OC–CO dimerization and HOC–CO coupling are accepted as C–C bond formation pathways for C<sub>2</sub> products, it is less clear how the additional C–C bond is made for the synthesis of propanol and other C<sub>3</sub> compounds. Recent work suggests carbonyl coupling as the most likely pathway [35, 175] but more research is needed to exclude potential alternatives. Formation of butanol and C<sub>4+</sub> compounds are never reported with FEs better than 1% and therefore there are not many studies about the reaction mechanism for C<sub>4+</sub> compounds. The most mature understanding of the formation of butanol consists of an aldol condensation of acetaldehyde to produce crotonaldehyde, followed by its electroreduction to butanal, and then to 1-butanol [176]. Future mechanistic work will likely focus on mechanisms for carbon-chain growth and to understand how and why these mechanisms are different from other mechanisms, such as those applicable for e.g. Fischer–Tropsch synthesis.

### Current and future challenges

Apart from the open questions regarding the nature of carbon-chain growth mechanism, as discussed in the previous paragraph, there remain important open questions about the nature of the initial activation of CO<sub>2</sub>, and how it depends on catalyst and electrolyte environment. More insights are necessary into how the electrode and/or the electrolyte stabilize the first intermediate CO<sub>2</sub>\*<sup>-</sup> so that the required potential to make this intermediate (–1.9 V vs normal hydrogen electrode) is drastically reduced; interaction with catalyst and electrolyte cation appear to be important factors in this [171]. Also, there appear to be multiple mechanisms for formate/formic acid formation: a hydride-mediated mechanism, a mechanism in which CO<sub>2</sub> interacts with the catalyst via the oxygen, and a mechanism in which the CO<sub>2</sub>\*<sup>-</sup> radical intermediate is formed at very negative potential, and subsequently reacts with water. Insights are needed into which mechanism dominates under which conditions. Among the more reduced C<sub>1</sub> products, methanol is the most intriguing product as it is hardly ever observed as a product on Cu electrodes at standard conditions. Although several advances have been achieved for selective methanol synthesis on bimetallic materials [172], the challenge is to understand how to guide the intermediate from CO selectively to CH<sub>2</sub>O, and then to methanol [4]. It has become clear in recent years that many electrocatalytic pathways are highly sensitive to the electrolyte composition (pH, presence of cations). It is known that the nature of the local environment influences the activity and selectivity of CO<sub>2</sub>R, but the detailed effect of the local DL composition (local pH, local cation/anion identity and concentration) remains incompletely understood and one of the important challenges consists in how to measure these effects both locally and individually. This observation of the importance of the electrolyte may partially explain the differences observed in the reaction mechanisms in electrocatalysis from those observed in thermocatalysis. Related to this, there is a lack of detailed work in the literature regarding the reaction mechanism in non-aqueous (organic) electrolytes and if those environments can guide the reaction towards different intermediates and products. Electrode modifications by organic layers have been shown to give rise to significant activity and selectivity effects, which also remain incompletely understood.

### Advances in science and technology to meet challenges

Further fundamental work is needed using well-defined electrode structures under well-defined electrolyte and mass transport conditions, combining electrochemistry experiments, *in situ* spectroscopy



(see sections 7–9), and high-level simulations (see section 5). Future computational work should address the complexity of the interface, not only at the quantum-chemical molecular level in terms of calculating barriers and detailed electrolyte effects, but also at the multi-scale level where kinetics couple with mass transport and complex nanoscale electrode architectures. Also, we believe that are fundamental opportunities in high-temperature and high-pressure experiments. Such ‘new’ conditions would allow us to gain more knowledge about the mechanisms as new pathways may open up or current pathways appear applicable to new catalysts, such as for example  $\text{C}_2+$  formation on Ag at high pressure [175]. Moreover, high-pressure and high-temperature experiments can bridge towards thermocatalytic  $\text{CO}_2\text{R}$ , and may elucidate certain mechanisms that remain elusive in electrochemical  $\text{CO}_2\text{R}$ , such as methanol synthesis.

Given the importance of the (local) electrolyte composition, instrumental advances are needed in measuring local properties, such as the local pH. Various *operando* studies have been dedicated to measuring the local concentrations near the electrode surface [176], but we are still far from reaching the required spatial and temporal resolution under relevant mass-transport conditions. Developments of *in-situ* techniques with high  $X$ – $Y$ – $Z$  resolution are still needed to image the 3D local concentration profiles within the diffusion layer, to further disentangle local effects in electrochemical  $\text{CO}_2\text{RR}$ , and to capture possible reaction intermediates as well. Infrared and Raman spectroscopy are recognized to be promising tools for local concentration measurements, although the  $XY$  resolution is limited and  $Z$  resolution is typically fixed in these experiments. Coupling electrochemistry with well-known 3D resolution scanning probe microscopy technique using ultramicroelectrodes is also a promising alternative. Finally, the well-defined diffusion-convection properties of the ‘good-old’ rotation-ring-disk-electrode make it an unparalleled technique to study local concentration gradient effects under mass transport-controlled conditions, and clever extensions of this methodology may further contribute to a detailed quantitative picture. In general, this is definitely an area where important instrumental advances in electrochemistry are required to make further progress in understanding the interplay between local reactivity, mass transport, and nanoscale architecture.

### Concluding remarks

The mechanistic understanding of the electrocatalytic  $\text{CO}_2\text{R}$  still has many open questions. Controlling the distribution of  $\text{C}_1$  products is still a challenge, especially for methanol synthesis. Selective synthesis of a

specific C<sub>2</sub> compound is also far from being fully understood, and the selective synthesis of C<sub>3</sub> and C<sub>4+</sub> products is at a very early stage. Future fundamental work must address the role of the electrode and electrolyte at various length scales, including the effect of mass transport and nanoscale architecture. This will require the development of new measurement techniques with 3D resolution, as well as the formulation and testing of multi-scale models. Furthermore, we believe there are opportunities in performing fundamental CO<sub>2</sub>R experiments under less conventional conditions, such as the development of electrochemical reactors at high pressure and high temperature, and the usage of non-aqueous solvents. High-pressure and high-temperature electrochemistry may also link naturally to thermocatalytic CO<sub>2</sub> hydrogenation, and may help in gaining a better fundamental understanding of the relation between electrocatalysis and high-temperature heterogeneous catalysis.

### Acknowledgments

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## 16. How to engineer surfaces to tailor reactivity?

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### Status

Electrosynthesis targeting high-value chemicals such as ethylene, ethanol, CO and formic acid has been suggested as a suitable market-entry strategy potentially able to displace existing petrochemical processes [54, 177]. Despite the increasing urgency, cost-competitiveness with our already established infrastructure remains a crucial hurdle posing demanding requirements on catalyst design to produce these chemicals with higher energy conversion efficiency, product selectivity and operational durability.

Catalyst design is driven by the development of a detailed understanding of the underlying reaction mechanisms while mechanistic pathways can only be corroborated by high quality experiments. A vivid example of this symbiosis are the works on the classification of metal electrocatalysts for the CO<sub>2</sub>RR. Hori *et al* (and others to that time) observed that several hydrocarbons (methane, ethylene) and alcohols (ethanol and propanol) can be obtained in significant quantities on copper electrocatalysts while other transition metal and p-block elements predominantly and sometimes exclusively form H<sub>2</sub> (Ni, Fe, Pt, Ti, Ga), CO (Au, Ag, Zn) or HCOO<sup>-</sup> (Pb, Hg, In, Sn, Cd, Tl) [57]. Thanks to the care in electrolyte purification (via pre-electrolysis), electrode preparation (mechanical and electropolishing) and the breadth of the experiments on a series of metals, these trends have been reproducible and reliable for the development of our current understanding of the reaction mechanism.

To explain reactivity of these pure metal surfaces, binding energies of key intermediates have been identified as useful descriptors that evaluate catalytic reaction steps based on the degree of orbital overlap with the adsorbate and the degree of filling of antibonding states on adsorption [178]. Using these reactivity descriptors, it is now well known that the above-mentioned classification can be explained based on the binding energies for \*CO and \*H as described in section 5 [58]. Amongst all pure metals, only Cu is able to produce hydrocarbons and alcohols due to its intermediate \*CO and weak \*H binding energies. However, it requires a significant overpotential to drive CO<sub>2</sub>RR and typically produces a variety of products. Improved catalyst design could result in more selective and efficient catalysts, greatly improving the economic viability of electrochemical CO<sub>2</sub>R.

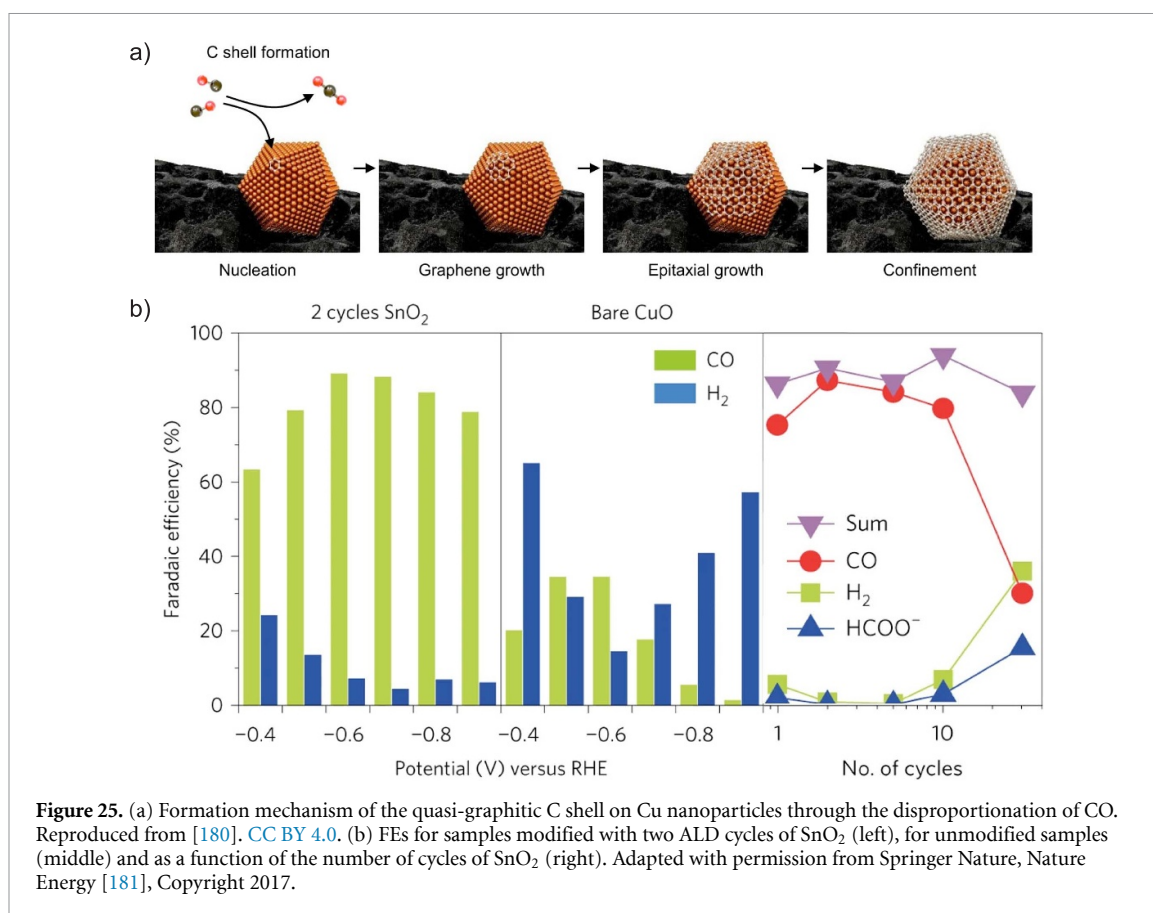
### Current and future challenges

Careful design of experiments is needed to extract information on **reactivity descriptors towards high value C<sub>2+</sub> products**. Surface engineering approaches such as nanostructuring, facet engineering, alloying, defect engineering or surface modifications (overlayers, small molecules, polymers) in combination with catalyst testing, thorough *operando* and post testing material characterization and computational work offer countless opportunities to explore structure-function relationships that can uncover key reactivity descriptors. One major challenge is to **design well-defined surfaces** that give insight on the active site and remain stable—even at commercially viable current densities (CDs). Clever experiment design is needed to assess the active site and understand if it becomes e.g. bimetallic with an altered binding energy for key intermediates or if two separate sites work in tandem. Furthermore, **secondary stabilization effects** of intermediates by **defects or non-metallic heteroatoms** (B, N, halides and others) located for example at steps adjacent to the active site atom are still not well explored or understood.

### Advances in science and technology to meet challenges

In order to relate the activity of an electrocatalyst to our understanding of CO<sub>2</sub> electroreduction on an atomic scale, it is necessary to **control metal facets also in nanostructured catalysts**. It is known from studies on Cu single crystals that ethylene formation is enhanced on **Cu(100) terraces** with further enhancement through **(111) or (110) steps** on those terraces [2, 6]. Targeting this basal plane in nanoparticle synthesis is hence a promising approach that has shown to yield high C<sub>2+</sub> FEs while achieving high CDs [179]. In the latter study, **surface reconstruction** has been intentionally used for catalyst synthesis such that the **(100) facets** were favored during the material synthesis under CO<sub>2</sub>R conditions and were less expressed when the synthesis was carried out under hydrogen evolution. This is a rare example of controlled surface reconstruction.

Several studies have reported on catalyst reconstruction affecting not only morphology and structure but also surface composition and oxidation state. The latter has been shown to be important in tailoring selectivity toward ethanol via coexisting **Cu(I) and Cu(0) species** [6]. Thus, **strategies are needed to restrict**



**Figure 25.** (a) Formation mechanism of the quasi-graphitic C shell on Cu nanoparticles through the disproportionation of CO. Reproduced from [180]. **CC BY 4.0.** (b) FEs for samples modified with two ALD cycles of SnO<sub>2</sub> (left), for unmodified samples (middle) and as a function of the number of cycles of SnO<sub>2</sub> (right). Adapted with permission from Springer Nature, Nature Energy [181], Copyright 2017.

**surface reconstruction** where not intended. One such strategy is the use of **overlayers**. A recent study used graphene to stabilize catalytic activity towards C<sub>2+</sub> products over a testing period of 180 h (figure 25(a)) [180]. Interestingly, the ‘quasi-graphitic’ surface overlayer seemed to be permeable for the incorporation of heteroatoms such as nitrogen and boron which needs further understanding. The authors demonstrated FEs for C<sub>2+</sub> products reaching about 80% at  $-0.7 V_{\text{RHE}}$  and  $400 \text{ mA cm}^{-2}$  with nitrogen-doped copper core catalysts which were protected with the quasi-graphitic shell.

**Semi-permeable overlayers of non-reducible oxides, chalcogenides, phosphides, and nitrides** could potentially achieve similar effects of restricting surface reconstruction and, in addition, impact selectivity. Here, atomic layer deposition can prove powerful due to its layer-by-layer growth mechanism. For example, it has been shown that the selectivity towards CO of a CuO nanowire electrode could be switched from <20% to more than 70% with a single cycle of SnO<sub>2</sub> (less than a monolayer) [181]. The selectivity was maintained between 80% and 85% for 2–10 cycles of SnO<sub>2</sub> (corresponding to <1.5 nm) before dropping sharply to 30% for 30 cycles (when a dense pinhole-free film of SnO<sub>2</sub> begins to form [182]) concomitant with increased production of formate and hydrogen (figure 25(b)). Such precision in surface modification is difficult to achieve with other techniques and has recently led to increased selectivity towards ethanol [183].

The **role of non-metal heteroatoms** has to be better understood. In addition to the study mentioned above, several works reported enhanced selectivity to C<sub>2+</sub> products with the implementation of nonmetallic heteroatoms (B, C, N, P) into the surface [184, 185]. The drivers behind the change in reactivity are yet to be understood. In a recent work on halide-doped copper, the authors argued that electronegativity might be the driving force varying the charge density on copper, enhancing CO adsorption and promoting the formation of a \*CHO intermediate that can undergo C–C coupling [186]. They also suggested that halides can promote water dissociation supplying \*H for the hydrogenation of \*CO. As is true for many surface modifications, it seems that one minor change in the surface composition induces several effects on the reaction mechanism that need to be decoupled. As such, surfaces need to be even better defined. Here, the **study of alternative non-metallic catalysts** (e.g. semiconducting, single atom catalysts/alloys, molecular catalysts such as Fe- or Mn-porphyrins [187]) could shed more light on the reaction mechanism beyond \*CO due to more defined density of states in these materials such that the function of heteroatoms can be further elucidated. Activity of such catalysts might be compromised for selectivity but a better understanding from the viewpoint of bonding between the density of states of surfaces with the adsorbate orbitals might bring valuable intuitive insight that can then be translated back to the design of more active catalysts.



### Concluding remarks

It remains challenging to design new electrocatalysts with tailored reactivity towards high-value chemicals at the CDs and selectivities required for them to be cost-competitive green alternatives to current fossil-fuel derived products. In the lab this challenge translates to the requirement to engineer, characterize and understand catalyst surfaces on the atomic scale to improve their performance.

Solution-based material synthesis techniques under the catalytic reaction conditions have shown to be able to produce nanostructured catalysts with high surface areas and desired facets that are less prone to undergo further surface reconstruction. On the other hand, surface engineering techniques hold great promise to also restrict undesired surface reconstruction and further the understanding of heteroatoms and overlayers on nanostructured catalyst surfaces. It has to be noted though, that special care should be taken to avoid surface contamination as every so little unwanted impurity can be detrimental to catalyst reactivity (e.g. common traces of Fe in electrolytes can lead to all selectivity to  $C_{2+}$  products being entirely lost).

Finally, it remains worrying that, despite tremendous efforts in catalyst design, the barrier for electrosynthesized chemicals and fuels to enter the market (including green hydrogen) might remain too high for too long without bolder policy incentives [188]. Instead of relying on established technologies to ensure energy security when supply from photovoltaics and wind is low, stronger incentives could pave the way for electrosynthesis of fuels and chemicals to be increasingly seen as an economic opportunity and not only as a potent decarbonization strategy.

### Acknowledgments

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## 17. How can we nanostructure Cu towards optimal CO<sub>2</sub>RR selectivity?

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### Status

A variety of nanostructured copper electrodes has been investigated to determine those structural features which direct selectivity in CO<sub>2</sub>RR. These catalysts include 3D electrodes and supported nanoparticles.

Three-dimensional nanostructured electrodes have been synthesized via different treatments of Cu and copper oxide, such as thermal annealing or *in-situ* potential cycling [54, 189, 190]. These electrodes have provided interesting information; for example, the importance of grain boundaries for the reduction of CO to ethanol [189]. However, the ill-defined nature of these catalysts leaves doubts on whether the surface roughness only or other intrinsic structural features of the catalysts (i.e. specific surface sites, facet orientation, size and shape of the pores, etc) account for their behavior. Actually, the comparison among 3D Cu prepared via different routes has suggested that the enhancement towards C<sub>2+</sub> products is mostly related to the increased geometric surface area [54, 190]. The latter allows to reach higher current densities and, therefore, to enter into a mass transport limited regime at lower overpotentials compared to planar electrodes [54, 190].

Well-defined Cu nanoparticles are emerging as extremely valuable model systems to uncover a diverse range of phenomena which contribute to increase the selectivity towards certain products. For example, a size-dependent study on Cu nanospheres has revealed that particles smaller than 5 nm promote the competing HER versus CO<sub>2</sub>RR, which suggested a high number of undercoordinated sites to be deleterious for CO<sub>2</sub>RR [191]. Different studies afterwards have found a similar trend also in shaped particles, with smaller particles promoting HER [192, 193]. At the same time, particle loading has also emerged as an important parameter. Indeed, it can tune the product distribution based on mass transfer effects and product reabsorption [54]. Furthermore, it can also impact the sintering behavior of nanoparticles. For example, 8 nm Cu nanospheres were shown to evolve into nanocubes at high loading density, thus becoming selective towards ethylene [194].

Shape-controlled Cu nanocrystals (NCs) have contributed not only to translate findings from single crystals to studies under more realistic conditions but also to reveal structure properties relations which would be difficult to assess otherwise. Cu nano-cubes have been the most studied system in this category. In addition to confirm the preferential formation of ethylene on Cu(100) surfaces, size dependent studies have revealed how an optimal ratio between (100) terraces and (110) steps must be sought after to increase selectivity towards ethylene [192]. One study on Cu nano-octahedra has shown a similar relationship for optimal (111)/(110) ratio for methane production [193]. More recently, these well-defined Cu NCs coupled with CO-producing Ag nanospheres have also aided to identify that the formation pathway towards ethanol shares common intermediates with methane rather than ethylene, therefore revealing a valuable design principle to increase selectivity towards alcohols [195].

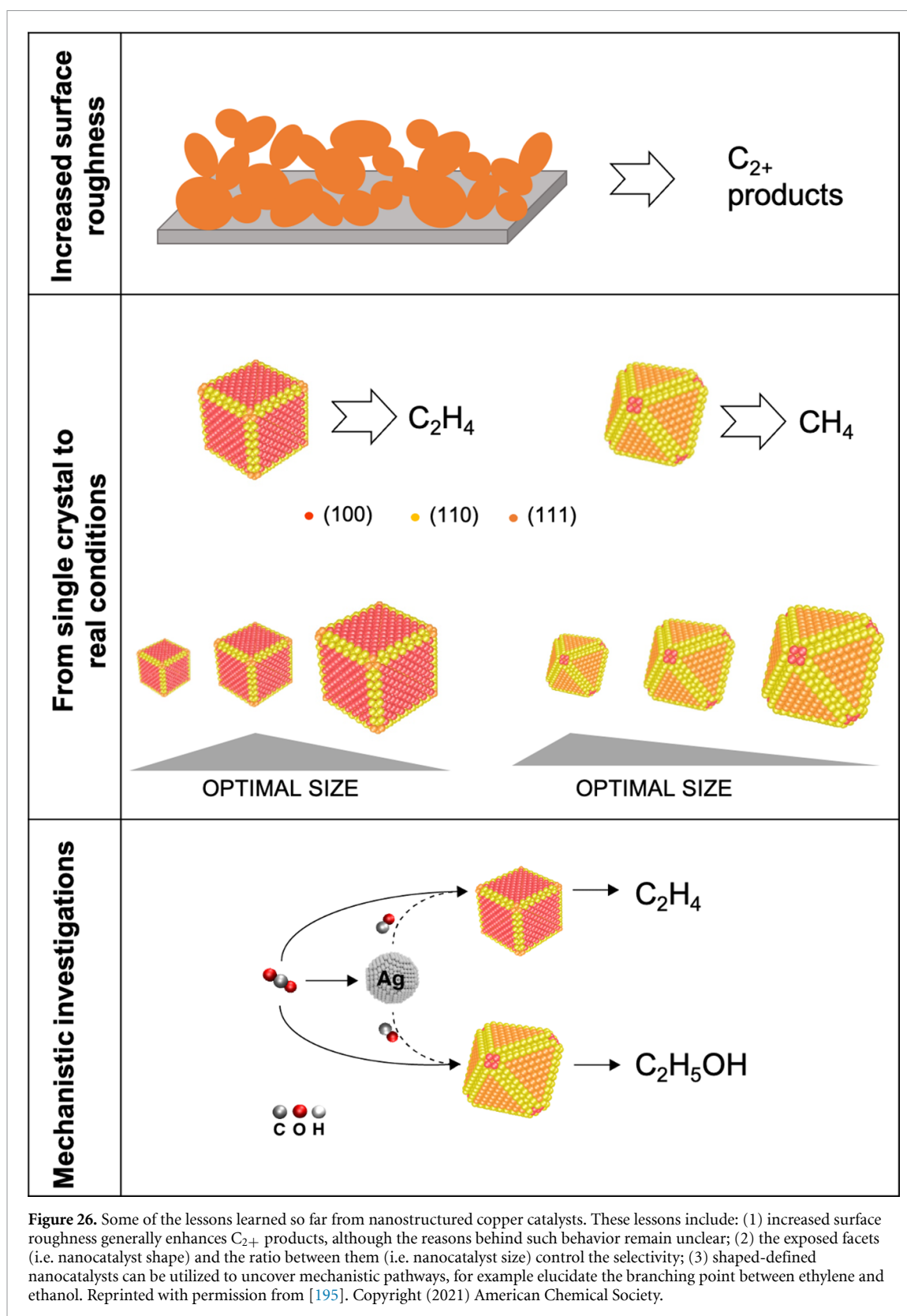
Figure 26 summarizes the major points discussed above.

### Current and future challenges

Figure 27 identified the major challenges ahead. As mentioned above, the 3D nanostructured Cu electrodes are ill-defined. One future challenge is to prepare them with controlled porosity (i.e. inverse opals), uniform grain size and orientation, tunable structural features. Only such approach will shed light on the specific morphological features regulating the product distribution.

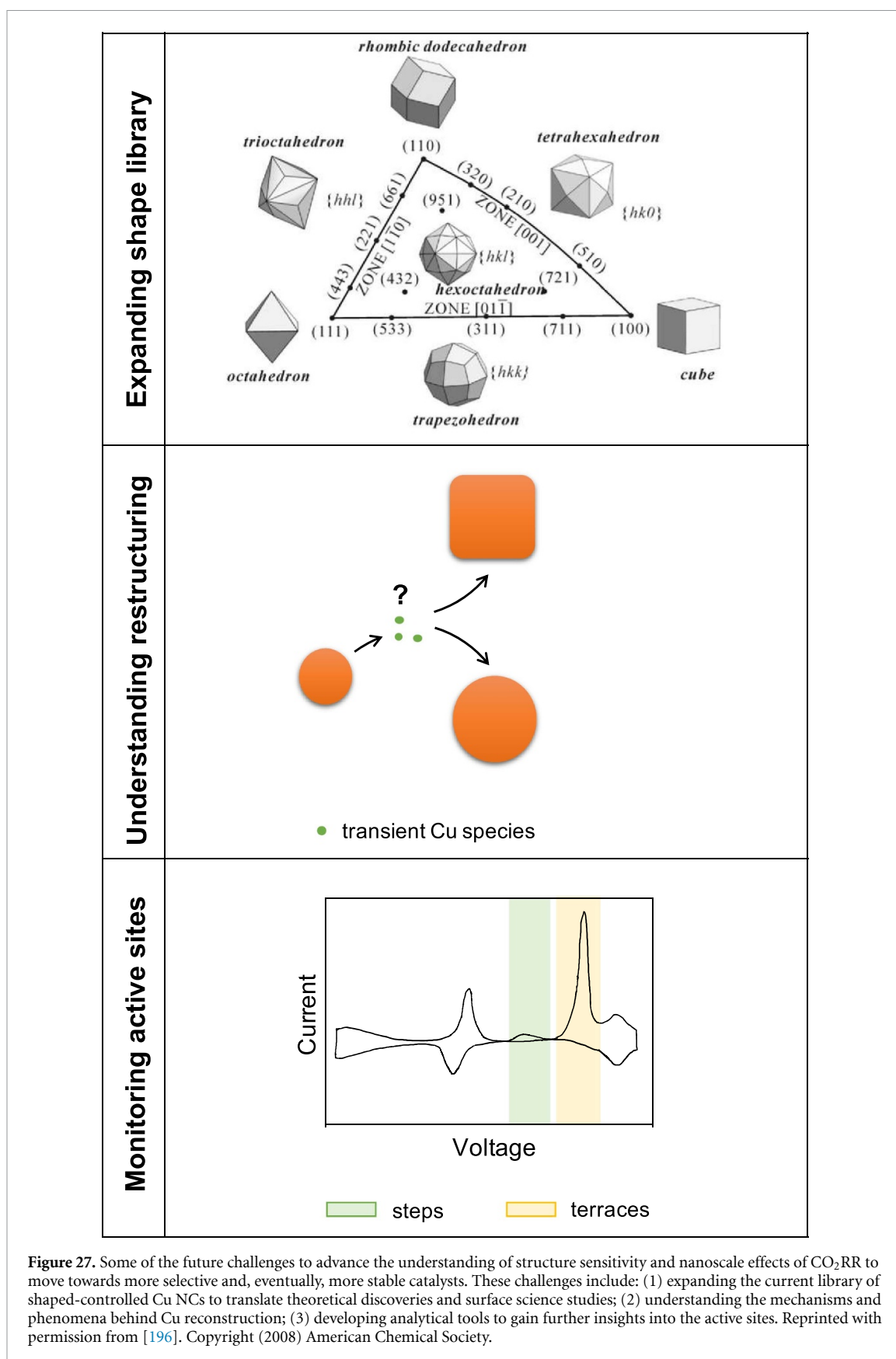
On the other side, well-defined Cu NCs have already started to have potential as model system to reveal selectivity rules in CO<sub>2</sub>RR. Nevertheless, the variety of shapes attainable with the current synthetic methods is still limited. Only spheres, cubes, octahedra, nanorods have been studied so far. To obtain NCs exposing high index facets is still a challenge, yet highly desirable to understand reaction pathway towards products different than ethylene by taking inspiration from calculations and other single crystal studies [196]. To cite one example, it would be interesting to obtain cubic nanocages to assess the role of steps independently from terraces.

While the presence of high index facets is desirable, they are expected to be metastable. Therefore, it will be important to assess if and how they change during operation, especially to identify the chemical nature of the copper intermediate species behind their eventual reconstruction. Indeed, such knowledge might open



opportunities to modulate the NC shape during operation and to direct it toward the most stable and selective form.

It is also still a challenge to characterize the surface sites active during  $CO_2RR$ . While this is not trivial due to the heterogeneity of NC surfaces, to identify their nature will be important moving forward to gain further insights into the impact of structural effects on reaction mechanisms.



Finally, unsupported nanoparticles are ideal for integration into different electrochemical devices, including the vapor-fed systems which are those enabling to achieve commercially relevant current densities. Only a few studies have explored this direction so far and more efforts should be undertaken to understand how the reaction microenvironment can aid to direct selectivity. In addition to providing knowledge about

translating catalyst design principles from model devices, to integrate well-defined Cu NCs in vapor-fed electrolyzers might also provide insight into their technological relevance. The scale up of their synthesis should then be tackled as the next challenge.

### Advances in science and technology to meet challenges

To expand the library of accessible shapes of Cu NCs, their material chemistry must be further developed. Colloidal chemistry is the most powerful approach to produce well-defined NCs which also come as inks, thus facilitating their integration in different types of electrolyzers. The rich diversity of noble metal nanoparticles with different shapes (e.g. Au, Ag, Pt, Pd) corroborates such a statement. However, the knowledge behind the formation of non-noble metal nanoparticles, including Cu, is lacking behind. Their tendency to oxidize requires the development of synthetic methodologies in organic solvent, instead of the aqueous environment used for noble metals. To gain mechanistic insight into nucleation and growth will be crucial to develop a more rational approach to synthesis.

To study reconstruction processes, combining the ongoing development in *in-situ* and *operando* electron microscopy with analytical tools which enable the identification of the chemical nature of the intermediates involved in the process would be extremely beneficial. To develop protocols for electrochemical adsorption experiments on Cu nanoparticles would represent a valuable addition to the current state-of-the-art. CO stripping has been interestingly used to gain information on electrocatalytic behavior of Pt nanoparticles [197]. To perform similar studies on shape-controlled Cu NCs coupled with differential EMS (DEMS) for product detection would be important to gain additional fundamental insight into the structural sensitivity of the CO<sub>2</sub>RR selectivity. Figure 27 summarizes the major points discussed above.

Finally, calculations aiming at building Wulff constructions and compositional phase diagrams, which integrate size and shape dependence as well as voltage and solvent effects would be desirable to complement synthesis and reconstruction studies under operation as well as possibly becoming predictive about their outcome.

### Concluding remarks

Nanostructuring of electrocatalysts is a powerful tool to achieve high ECSAs, thus high geometric CDs at lower overpotentials, as well as to enable translation of single crystal studies under more realistic conditions, including vapors-fed devices, in the case of nanoparticles with well-defined size and shape. The latter provide also opportunities to interrogate reaction pathways by exploiting their facet-dependent selectivity. Future development to increase the accessible shapes of Cu NCs along with fundamental understanding of their surfaces and their reconstruction during catalysis is expected to guide even further catalyst design to improve CO<sub>2</sub>RR selectivity towards the desired target products.

### Acknowledgments

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## 18. How to optimize GDEs for CO<sub>2</sub> reduction (CO<sub>2</sub>R)?

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### Status

To deploy CO<sub>2</sub> electrolyzers at scale as CO<sub>2</sub> utilization technologies, electrochemical CO<sub>2</sub>R must be operated at practical conversion rates to minimize capital costs. However, at such CDs (the electrolyzer current attributable to CO<sub>2</sub>R normalized by electrode area), the CO<sub>2</sub>R cathode may suffer from reactant starvation, leading to a poor energetic efficiency and a limited CD for CO<sub>2</sub>R. Vapor-fed CO<sub>2</sub>R, can solve the issue by improving CO<sub>2</sub> transport to the active catalyst. In practice, this can be accomplished with a GDE design, which allows for rapid transport of vapor fed CO<sub>2</sub> through a GDL comprised of a porous conductive material (e.g. carbon paper) coated with a well-dispersed catalyst layer; simultaneously enabling good CO<sub>2</sub> mass transport and ionic/electronic conduction between the current collector and electrolyte (figure 28(a)).

A typical CO<sub>2</sub>R GDE is fabricated by depositing a catalyst layer directly onto a GDL, typically a commercially available carbon-based substrate with hydrophobic treatment. However, poor electrode stability (<100 h) with electrolyte saturation (flooding) is a persistent issue, typically attributed to salt penetration into the GDL that compromises the hydrophobic property [198]. On a case-by-case basis, alternative GDL substrates [51], porous fillers for the catalyst layer [199], and functionalized polymeric binders [53] have all been employed to optimize GDE properties (figure 28(b)). Still, basic principles to rationally optimize any given GDE based on the used electrolyte remain elusive. Moreover, only a handful of reports come close to a stable performance on the order of 10 000 h and energetic efficiencies necessary for an economically feasible CO<sub>2</sub>R process [200]. Uncovering the relationship between GDE performance with other electrolyzer components (e.g. electrolyte) via characterization and modeling efforts can accelerate the discovery of materials and methods to achieve target GDE performance and stability criteria for deployment as a CO<sub>2</sub> utilization technology.

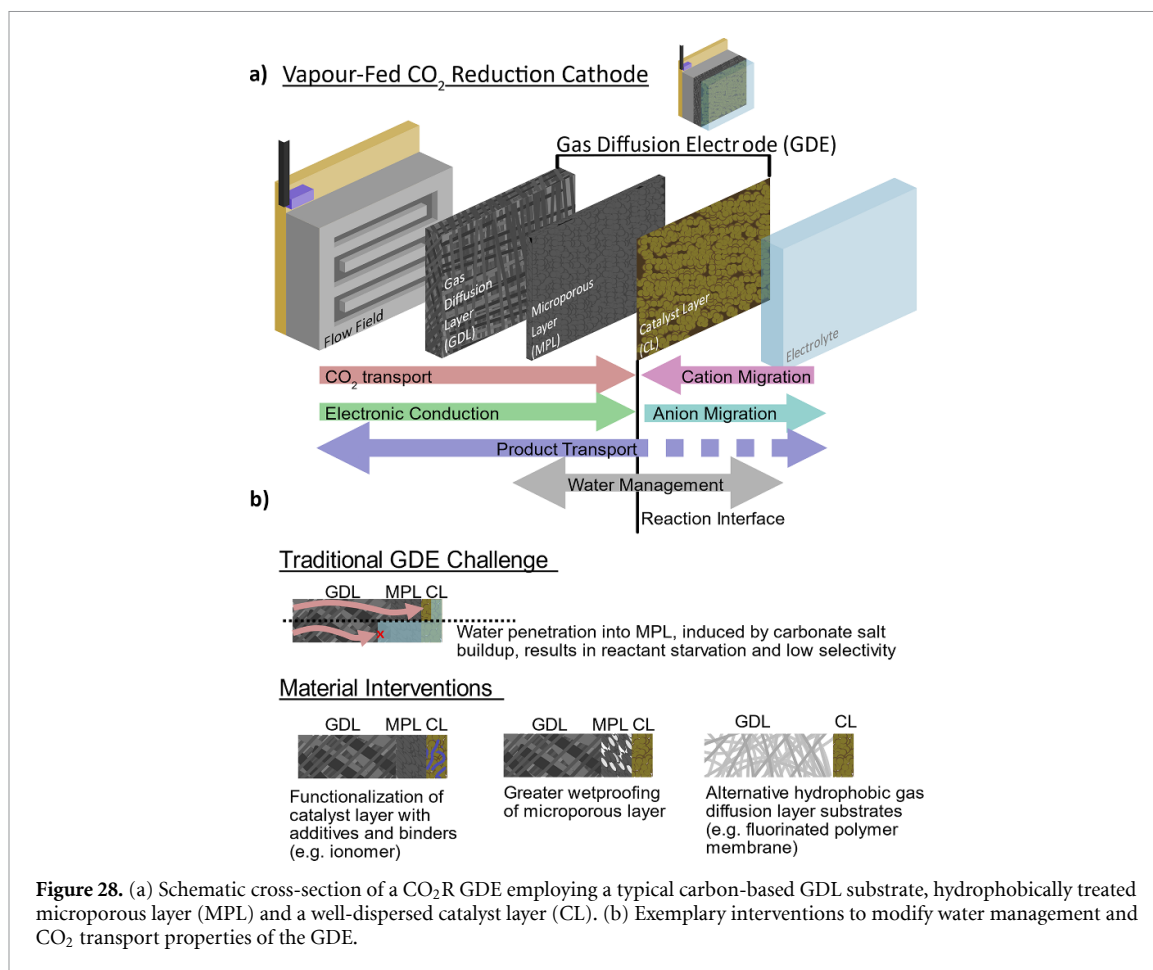
### Current and future challenges

The focal issue for designing optimal GDEs for CO<sub>2</sub>R lies in reliably achieving stable selectivity and efficiency at high CDs. Minor changes in material (e.g. ion conductive membrane), additives to the GDE, humidification of the CO<sub>2</sub> feed have all been shown to have potentially governing effects on the overall GDE performance [200, 201]. Some studies have sought to explain these differences as the presence of a liquid electrolyte (or lack thereof) and modes of ionic conduction between the cathode and anode in the electrolyzer changing local conditions regarding water, pH, salt, and product management [201]. For context, we illustrate how one crucial design factor, local water management, can change with CD and electrolyzer configuration (table 2). Therefore, GDEs optimized for one specific configuration may not translate well in another due to a mismatch in the GDE design and existing factors. It is well-known for other electrochemical reactions, such as oxygen reduction reaction, that substantial discrepancies exist between performance in a rotating disc setup versus in a membrane-electrode assembly (MEA) configuration [202]. Therefore, fundamental catalyst studies that may have stellar performance with a particular GDE in an *ex-situ* three-electrode configuration need be confirmed with tests in high-CD configurations where GDE design can alter catalyst performance.

A similar issue exists with many CO<sub>2</sub>R cathode catalyst studies that seek to show the best cathode energetic efficiency with an alkaline electrolyte. While employing an alkaline liquid electrolyte improves cathode performance, the cost associated with carbonated electrolyte regeneration is untenable despite superior cathode performance [203]. Demonstrating catalyst performance in electrolyzer configurations that address the carbonation issue then begets a new set of challenges to redesign the binders, fillers, and GDL substrate to control the local environment, be it pH, hydration, and salt concentrations to get optimal CO<sub>2</sub>R GDE performance.

### Advances in science and technology to meet challenges

To address the technical challenges for CO<sub>2</sub>R GDEs, techniques to elucidate what makes for the most stable and optimal GDE/catalyst/electrolyte interface at working conditions for various electrolyzer configurations, active component materials are essential. For attractive electrolyzer configurations like an MEA, there are still opportunities to leverage experience from developing diagnostic tools for other electrochemical devices. For instance, advanced impedance techniques can provide *in operando* snapshots of GDE dynamics of different timescales (ionic/electronic conduction, charge transfer, and mass transport). Moreover, even without a



**Table 2.** Cathode stoichiometric water balance (H<sub>2</sub>O per electron) for electrochemical generation of vapor phase products.

Mode of ionic conduction	HCO <sub>3</sub> <sup>-</sup> /OH <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	H <sup>+</sup>
Product			
Carbon monoxide	-0.50	0	+0.50
$\text{CO}_2 + 2\text{e}^- + \text{H}_2\text{O} \rightarrow \text{CO} + 2\text{OH}^-$			
$\text{CO}_2 + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{CO} + \text{H}_2\text{O}$			
Ethylene	-0.67	-0.17	+0.33
$2\text{CO}_2 + 12\text{e}^- + 8\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4 + 12\text{OH}^-$			
$2\text{CO}_2 + 12\text{e}^- + 12\text{H}^+ \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$			
Hydrogen (byproduct)	-1	-0.50	0
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$			
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$			
Bicarbonate buffer reactions	Water content of a humidified gas stream (4 sccm dry gas per cm <sup>2</sup> of electrode at 1 atm)		
$\text{CO}_2 \xrightarrow{+\text{OH}^-} \text{HCO}_3^- \xrightarrow{+\text{OH}^-} \text{CO}_3^{2-} + \text{H}_2\text{O}$	<i>T</i> <sub>dew</sub> (°C)	H <sub>2</sub> O flowrate (μmol H <sub>2</sub> O s <sup>-1</sup> )	H <sub>2</sub> O per electron (At 500 mA cm <sup>-2</sup> )
$\text{CO}_3^{2-} \xrightarrow{+\text{H}^+} \text{HCO}_3^- \xrightarrow{+\text{H}^+} \text{CO}_2 + \text{H}_2\text{O}$	20	0.07	0.01
	50	0.42	0.08
	80	2.65	0.51

The water content of humidified vapor streams is provided to contextualize how much water can be supplied by (or lost to) the cathode vapor stream. Other important factors for water balance at the GDE include electro-osmotic drag (on the order of ±1 H<sub>2</sub>O per electron) and water diffusion through a membrane. As a first approximation, water diffusion through membranes is of the order of 42.5 μmol cm<sup>-2</sup> s<sup>-1</sup> or approximately 1 H<sub>2</sub>O per electron at 4 A cm<sup>-2</sup> (based on literature for Nafion 212 water diffusion with an activity gradient of 0.5 [205]).

liquid electrolyte, a reference electrode can still measure an isolated cathode potential against a known potential [204]. Techniques to determine local humidity, chemical concentrations, pH, and post-mortem characterization also have key roles in fully understanding the GDE at working conditions. The enhanced resolution from diagnostic tools can reduce the effort required to generate initially good GDE designs and operating strategies and increase confidence in catalyst screenings and system-level models, thereby accelerating progress in the field.

Robust methods for accelerated stability testing are also necessary to extrapolate the stable performance of high-performance GDE design candidates. It is not practical to test all potential GDE designs at the time scale of 10 000 h. Existing accelerated stability testing protocols, such as well-established protocols for fuel cells, can provide a foundation to build upon [53]. The relative significance of CD, single-pass conversion, temperature, and concentration of liquid products (i.e. ethanol and acetate), all economically significant factors, on stability is not well understood. Robust protocols should provide the means to collect empirical evidence for developing theories of how these critical factors impact the lifetime of a GDE.

### **Concluding remarks**

The ideal (or benchmark) electrolyzer configuration and components for scaling up CO<sub>2</sub>R is still an open question. Consequently, there is a need for GDE design guidelines that account for the wide span of different electrolyzer configurations. The current standard case-by-case practice for optimizing the CO<sub>2</sub>R GDE based on measurements of hydrophobicity and selectivity towards CO<sub>2</sub>R products can be greatly accelerated with a toolbox of characterization tools and models. Finally, the development of accelerated stability testing protocols will greatly reduce the amount of time to examine the long-term stability of GDE designs, a critical factor for commercial applications.

### **Acknowledgment**

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## 19. What are the challenges to achieving steady state high CO<sub>2</sub> utilization?

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### Status

For low temperature (<100 °C) CO<sub>2</sub> electrolysis devices to be commercially viable, an effective separator needs to be used that prevents product crossover. However, the cathodic CO<sub>2</sub>R produces OH<sup>-</sup> as a byproduct, and OH<sup>-</sup> quickly equilibrates with CO<sub>2</sub> to form HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup> (CO<sub>2</sub>EQ), thus providing a highly undesirable loss mechanism that consumes no less than 50% of all CO<sub>2</sub> reacted near the catalyst [206, 207]. While one can try to engineer around the captured CO<sub>2</sub> forming HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup>, CO<sub>2</sub> electrolysis also both needs an alkaline environment to promote catalytic activity [54] and needs to minimize the thickness of any electrolyte layer between the catalyst and membrane to reduce ohmic losses.

Typically, AEMs are used in CO<sub>2</sub> electrolysis for a variety of beneficial reasons [10]. However, since AEMs transfer negatively charged ions, carbonates from CO<sub>2</sub>EQ are the dominant species transferred through the membrane after reaching steady state. This carbonate transfer not only reduces conductivity of the whole system (carbonate anions have low ion mobility), but once at the anode, the carbonate re-equilibrates (i.e. reacts) with the anodically produced protons from O<sub>2</sub> evolution (figure 29(a)). The end result is that the carbonate is subsequently released as gaseous CO<sub>2</sub> along with O<sub>2</sub> stream at a CO<sub>2</sub>:O<sub>2</sub> ratio of ~2 [206].

Cation exchange membranes (CEMs) prevents carbonate crossover, however they have other issues. While it is unclear why a MEA (i.e. zero gap) typically leads to H<sub>2</sub> selectivity over CO<sub>2</sub> reduced products with CEM [209, 210], the current approach is to have a liquid film between the cathode and membrane, which greatly increases ion transport losses and also makes maintaining cation balancing challenging. With the CEM conducting cations (figure 29(b)) from anode to cathode, this may lead to 'salting out' at the cathode. In addition, a rapid drop of conductivity at the anode side will occur if there is an electrolyte layer between the anode and membrane and the cation serves as the main charge-carrier [208].

BPMs resolve both carbonate and cation issues (figure 29(c)) [208], but BPMs have a high membrane potential due to a sudden jump in the concentrations of H<sup>+</sup> and OH<sup>-</sup> at the membrane/electrolyte interface [211].

### Current and future challenges

The unavoidable formation of carbonates near the cathodic GDE during CO<sub>2</sub> electrolysis provides an incredible engineering challenge. As noted in figure 30, there are many paths, all with their own challenges. In general, the challenge is how effectively can we re-equilibrate carbonate back to CO<sub>2</sub> while mitigating additional losses/issues.

For AEM, the challenge will be effectively separating the mixed CO<sub>2</sub> and O<sub>2</sub> stream to allow CO<sub>2</sub> to be recycled rather than vented to the atmosphere. Beside O<sub>2</sub> evolution, however, a more valuable anodic reaction such as Cl<sub>2</sub> evolution may potentially reduce costs in recycling the CO<sub>2</sub>. If an anodic liquid product would be produced, separations would be even easier. Thus, the challenge is to find high-value anodic products that could scale to match the demand for CO<sub>2</sub> electrolysis products.

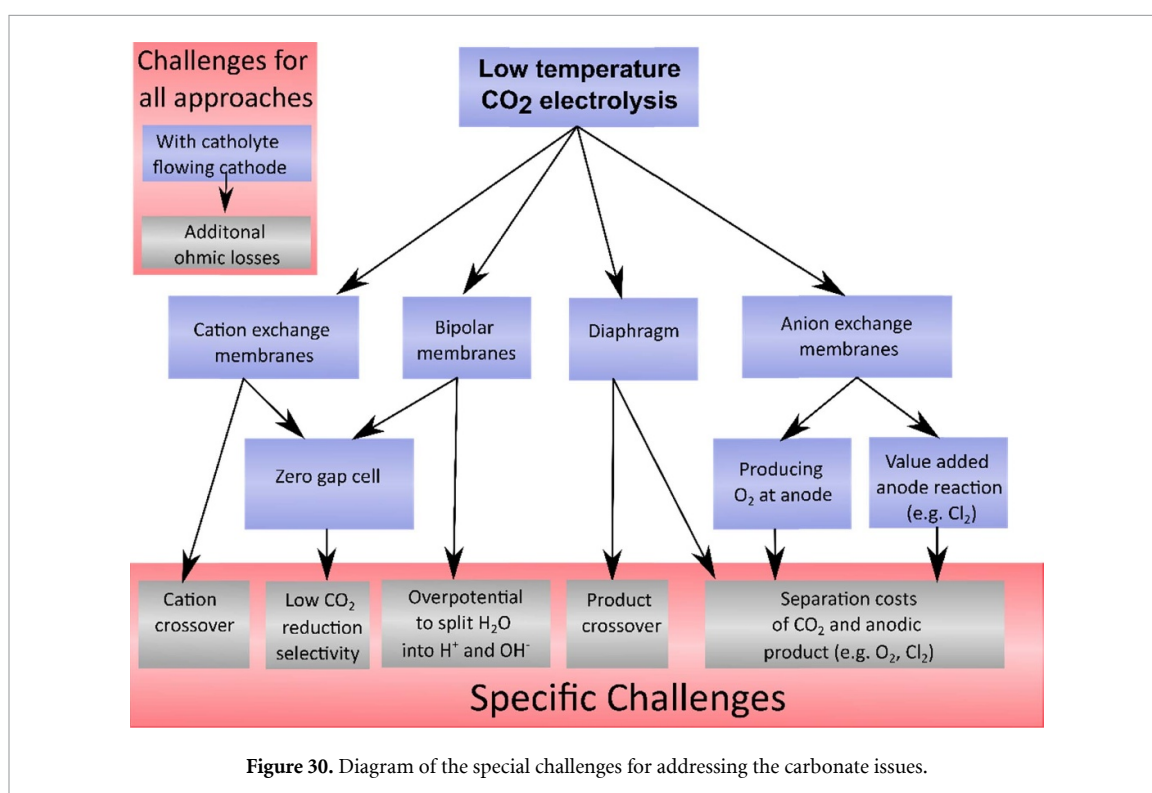
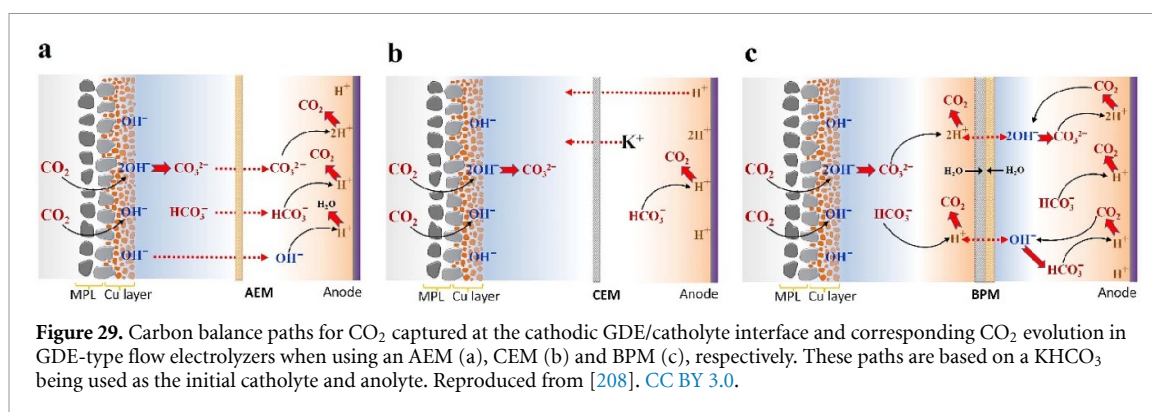
For CEM and BPM, a major challenge will be to balance the cation concentration at the cathode for zero gap approaches. Excess cations at the cathode can lead to oversaturation and the cations salting out that may block gas flow, but electrolyte cations (e.g. K<sup>+</sup>, Cs<sup>+</sup>) are essential to create a strong electric field for effective catalysis [54]. This problem becomes magnified for zero gap approaches with extremely low or no cation concentration (with H<sup>+</sup> being the dominant ion transfer mechanism), leading to high H<sub>2</sub> selectivity.

BPM easily allows for the carbonate to be converted back to CO<sub>2</sub> at the cathode side, allowing *in situ* recycling of the CO<sub>2</sub>, however the required high potential for BPM will diminish EE of the overall electrolyzer [208].

With diaphragms allowing all charged species to penetrate, this can reduce issues related to anodic CO<sub>2</sub> evolution and salting out at the cathode. However, product crossover is a major concern, especially for liquid products. With minimal work done with diaphragms, there could be additional unforeseen challenges (or benefits).

### Advances in science and technology to meet challenges

For addressing the CO<sub>2</sub> utilization related challenges, the necessary advances in science technology are discussed below.



**AEM:** Improvements in CO<sub>2</sub>/O<sub>2</sub> separation techniques will help advance this approach, and creativity in varying anodic reactions such as Cl<sub>2</sub> or Br<sub>2</sub> evolution, H<sub>2</sub> oxidation, etc could either potentially lower costs for recycling CO<sub>2</sub> or simplify anodic separation and improve overall process efficiency. From a techno-economic perspective, analyzing separation techniques is essential to find potentially synergistic processes to work with AEM based CO<sub>2</sub> electrolysis.

**Zero gap electrolyzer with CEM:** This approach needs to understand why H<sub>2</sub> selectivity dominates over CO<sub>2</sub>R, and resolve this problem. With the pH and electric field effect both strongly affecting selectivity, mass transfer modeling of local conditions is essential to address this issue. Optimal conditions need to be found to maintain a high (but undersaturated) steady state cation concentration just at the cathode.

**BPM:** The major advance needed for this approach is to reduce the overpotential for driving water dissociation inside the BPM (figure 30). Recent breakthroughs for decreasing membrane potentials have been reported [212], thus showing promise in this field. Due to their complexity, long term durability of BPM is also a concern to date.

**Diaphragm:** Detailed diaphragm design and proper parametrization is required for greatly reducing product crossover while mitigating losses of ion transport through the diaphragm.

**A two-step cascade process:** CO<sub>2</sub> upconversion to CO can be achieved via biomass pyrolysis, hydrogen electrolysis with reverse water-gas shift, or solid oxide based CO<sub>2</sub> electrolysis with none of these approaches having carbonate issues. Since CO is the first intermediate in CO<sub>2</sub> electrolysis, we could use an alternative approach with no carbonate issues to produce CO initially from CO<sub>2</sub>, and then just employ CO electrolysis

instead of CO<sub>2</sub> electrolysis. CO electroreduction does not produce carbonates, which resolves the major challenge with AEM, thus making this cascaded process a highly appealing approach.

### Concluding remarks

There are many forks in the road to finding a successful approach towards commercially viable low-temperature CO<sub>2</sub> electrolysis (figure 30). A major issue with all approaches is that there has been a lack of modeling of a full chemical plant with separations and a complete techno-economic analysis. Thereby, we are relatively blind to the degree to which process needs to advance scientifically to be economically viable. It should be noted that both biomass conversion and electrolysis based hydrogen followed by thermal processes with CO<sub>2</sub> can also provide most of the same products as CO<sub>2</sub> electrolysis. With these competitive processes on the horizon, this short perspective entails there is an urgent need for the CO<sub>2</sub> electrolysis field to filter out non-viable paths and make the necessary breakthroughs for developing a commercially competitive approach towards hydrocarbons and organic species.

### Acknowledgments

The authors would like to acknowledge funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 85144, (SELECTCO<sub>2</sub>) as well as the ECOEthylene project from Innovation Fund Denmark (Grant #8057-00018B). Authors also acknowledge National Natural Science Foundation of China (22179105).

## 20. How might bipolar membranes (BPMs) optimize CO<sub>2</sub>R electrolyzer efficiency?

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### Status

CO<sub>2</sub> electrolysis offers the prospect of using CO<sub>2</sub> captured from exhaust gas, the atmosphere, or the ocean as a precursor to high-value hydrocarbons or fuels [177]. Recent advances applying fuel-cell and electrolyzer technology concepts have led to CO<sub>2</sub> electrolyzers running at >1 A cm<sup>-2</sup>, albeit with large voltages and thus low energy efficiency (EE) <30% [51]. The high current density (CD), however, is important because higher product production rates are needed to offset capital expenditures, similar to water-electrolyzer technology.

CO<sub>2</sub> electrolyzers usually use proton- or hydroxide-conducting ion-selective membranes, a cathode electrocatalyst supported on a GDE, a soluble supporting electrolyte at neutral to basic pH, and a porous anode electrocatalyst for oxygen evolution (figure 31) [10]. While the liquid electrolytes conduct the ionic current from the GDE to the ionomer membrane, and control the anode and cathode pH, they are not strictly needed. Designs which use only solid-ionomer electrolytes, similar to PEM water electrolyzers, will be ultimately preferred because of reduced shunt currents (through the electrolyte flow paths) [213] and thus simpler stack construction using bipolar plates.

Thermochemical CO<sub>2</sub> hydrogenation (with renewable H<sub>2</sub> and electrical heat) directly competes with electrochemical processes. Thermochemistry has the advantages of known reactor engineering and scaling, as well as fast kinetics at high temperatures. Routes are evident to commercially viable fuels and chemicals if CO<sub>2</sub> streams and renewable H<sub>2</sub> at ~\$2 kg<sup>-1</sup> are available [214]. In order for low-temperature CO<sub>2</sub> electrolysis to compete, high efficiency and selectivity, low capital expense, and high durability are essential. Here we discuss how new BPMs may help in meeting this challenge.

### Current and future challenges

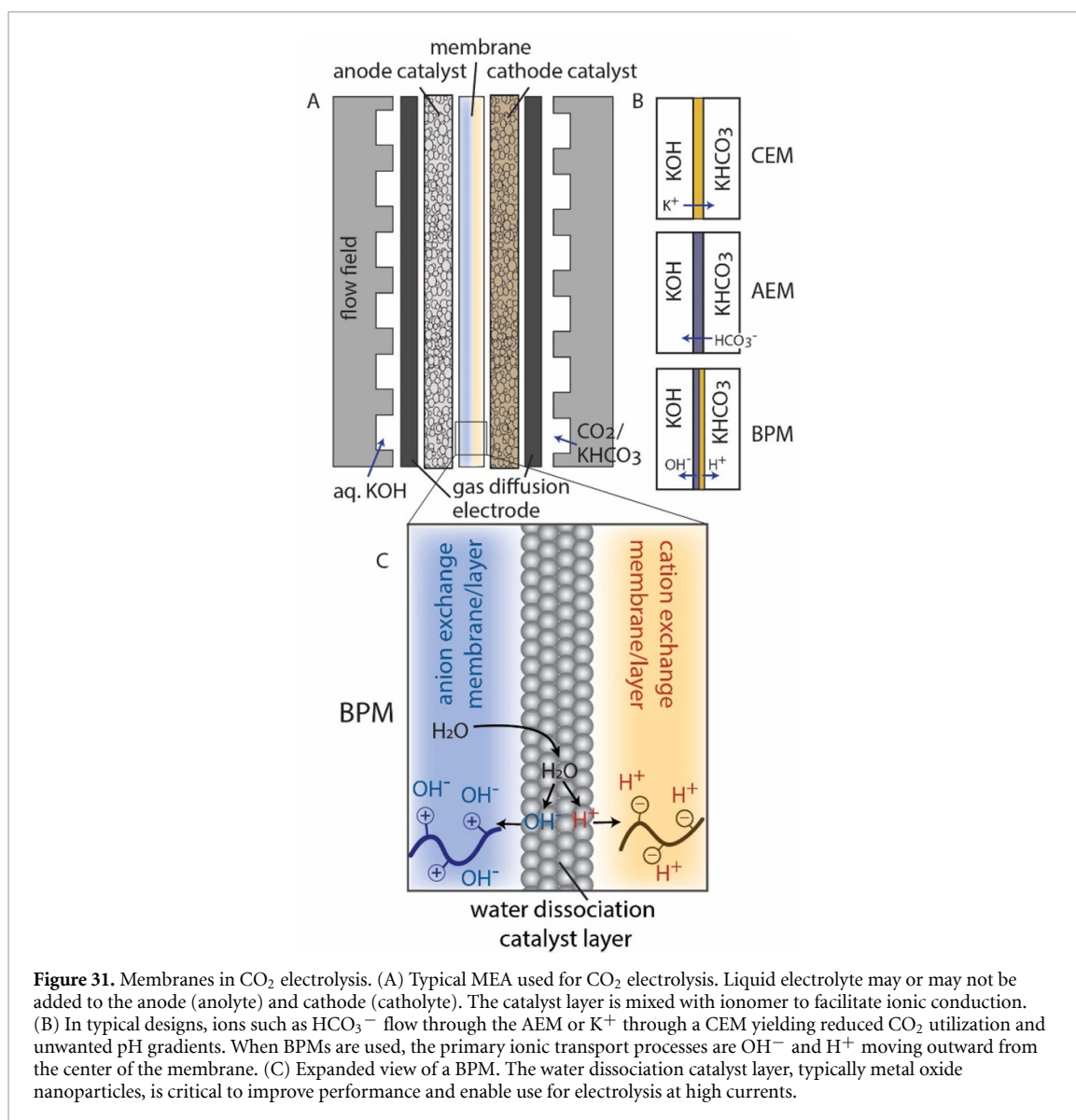
Serious challenges facing hydrocarbon electrosynthesis technology include improving the voltage, current and FEs, as well as the lifetime, selectivity, and CD (rate) of the electrolyzer. The voltage efficiency of a CO<sub>2</sub> electrolyzer is primarily controlled by: (a) the kinetic overpotentials at the anode and cathode, (b) ohmic losses due to ion transport through the device, and (c) concentration overpotentials associated with [CO<sub>2</sub>] and pH gradients [11]. The selectivity is governed by the catalyst and local pH at the cathode.

The type of ionomer membrane used is a critical factor determining many performance metrics. Conventionally there are two membrane types, acidic CEMs, such as Nafion, and basic AEMs (now widely commercially available, but less well developed). At the cathode GDE, basic conditions are needed to suppress the HER kinetics relative to the CO<sub>2</sub>RR on the electrocatalyst. Therefore many studies use AEMs to separate a basic catholyte, such as KOH, from the anode [51]. CO<sub>2</sub>, however, reacts with hydroxide to form carbonates which accumulate in the catholyte. At steady state and without the continuous consumption KOH, the pH of the catholyte decreases and (bi)carbonate eventually carries a substantial portion of the current, leading not only to a loss of CO<sub>2</sub> with the O<sub>2</sub> products but also the formation of a pH gradient across the device that induces a concentration (Nernst) overpotential [11].

One way to reduce cross-over of (bi)carbonate is use a CEM [215]. At the anode, this requires precious-metal water-oxidation catalysts, like IrO<sub>2</sub>, that are stable in a locally acidic environment. The cathode electrocatalyst, however, must be separated spatially from the acidic membrane. This is because at low pH, the HER dominates over the CO<sub>2</sub>RR. A pH = 1 phosphate catholyte was recently used in conjunction with a CEM [215]. When 3 M KCl was added to the catholyte, the FE for CO<sub>2</sub>RR over HER increased, especially at high CD. The addition of non-buffering electrolyte likely increases the catholyte pH gradient, leading to a more-basic cathode environment that preferences the CO<sub>2</sub>RR. Relying on concentration polarization to control local pH, however, impacts the EE, adding ~60 mV unit of ΔpH in the supporting electrolyte [11].

### Advances in science and technology to meet challenges

BPMs offer a new way for CO<sub>2</sub> electrolyzers to manage pH and reduce crossover of (bi)carbonate, neutral products, and other species [10, 216]. A BPM consists of an anion-exchange layer (AEL) and a cation exchange layer (CEL) with a water-dissociation (WD) catalyst in between the two (figure 31(C)). Under bias, water is dissociated, H<sub>2</sub>O → H<sup>+</sup> + OH<sup>-</sup>, at the junction between the AEL and CEL and the generated ions are driven by a gradient in electrochemical potential out from the center of the BPM in opposite directions [212]. Historically, significant overpotentials were needed to drive WD in BPMs and they were limited to ~100 mA cm<sup>-2</sup>; too low for electrolysis. Innovations in WD catalysis have changed this, with research BPMs



**Figure 31.** Membranes in CO<sub>2</sub> electrolysis. (A) Typical MEA used for CO<sub>2</sub> electrolysis. Liquid electrolyte may or may not be added to the anode (anolyte) and cathode (catholyte). The catalyst layer is mixed with ionomer to facilitate ionic conduction. (B) In typical designs, ions such as HCO<sub>3</sub><sup>-</sup> flow through the AEM or K<sup>+</sup> through a CEM yielding reduced CO<sub>2</sub> utilization and unwanted pH gradients. When BPMs are used, the primary ionic transport processes are OH<sup>-</sup> and H<sup>+</sup> moving outward from the center of the membrane. (C) Expanded view of a BPM. The water dissociation catalyst layer, typically metal oxide nanoparticles, is critical to improve performance and enable use for electrolysis at high currents.

operating at  $3 \text{ A cm}^{-2}$  while maintaining a locally basic anode and acidic cathode [217]. At  $0.5 \text{ A cm}^{-2}$  the loss due to water dissociation is only 100–200 mV.

The use of the BPMs dramatically prohibits unwanted crossover of (bi)carbonate to the anode because of the high outward flux of H<sup>+</sup> and OH<sup>-</sup>, and provides basic conditions for water oxidation allowing the use of earth-abundant catalysts. However, at the cathode, the H<sup>+</sup> flux leaving the acidic membrane leads to a preference for HER over CO<sub>2</sub>RR. The cathode GDE must thus be separated from the membrane with an intervening neutral-to-basic electrolyte layer, leading to a pH gradient from the strong-acid CEL, across the electrolyte layer, to the cathode. This gradient induces a concentration overpotential loss. Recently, thin weak-acid CELs layers have been added to a Nafion CEL in a BPM as another strategy to increase the pH at the cathode, perhaps with less of a voltage penalty [218].

There remains a tremendous need to better understand through modeling, experiment, and new precise BPM fabrication, the detailed interplay between the formation of pH gradients, electric-field gradients, ion selectivity, ion transport in the concentrated limit, and the steady-state operational voltage of BPM-based CO<sub>2</sub> electrolyzers. Specific opportunities include:

- tailoring of the local anode/cathode environment with ionomers with different pKa ranges (providing different internal pH values)
- building more-complex ionomer multilayers to effectively control ion transport and local pH leveraging the design of water dissociation and recombination layers

- understanding rigorously what the fundamental performance limits are and whether, with sufficient ionic conductivity and WD/water-recombination catalysis, the performance can approach the thermodynamic limit as is the case for PEM water electrolysis
- quantifying the role of coupled ion transport in ionomers in the relevant concentrated limit where, for example, outward flux of one ion (e.g.  $H^+$  or  $OH^-$ ) can retard inward flux of a minority ion even in the presence of a large driving force
- precise measurements of the electric field and ion concentration distributions in BPM electrolyzers at equilibrium and approaching steady state, showing where gradients in the electrochemical potential of  $H^+$  and  $OH^-$  develop (and thus where the supplied free energy is consumed) [212], comparing with models, and guiding development
- a detailed understanding of the steady-state concentration profiles of supporting electrolyte and (bi)carbonate ions both in static and flow cells and how this influences the rate at which electrolytes must be replenished (which affects EE)
- a fundamental understanding of the chemistry and physics of WD and water-recombination catalysis in the BPM junction.

### Concluding remarks

BPMs and related more-complex membrane architectures offer unique strategies to manage  $H^+$ ,  $OH^-$  and other ions in electrochemical systems. These properties have been exploited for decades in the electro dialysis field and now, with improved BPM voltage performance and currents, are allowing their use in electrolysis at practical CDs. Low-temperature  $CO_2$  electrolysis provides one area where BPMs may be critical in controlling ion cross over and managing local pH.

### Acknowledgments

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## 21. What is the promise of multi cell stacks for CO<sub>2</sub> reduction (CO<sub>2</sub>R)?

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### Status

As outlined in this Roadmap, electrochemical CO<sub>2</sub>R is gaining momentum not only in the research arena, but also on the industrial scene. High temperature CO<sub>2</sub> electrolysis technologies (such as solid oxide CO<sub>2</sub> electrolyzer cells) are excluded from our scope; since they are approaching maturity, with pilot scale devices installed worldwide [219]. Low temperature electrolyzer cells typically operate at temperatures below 100 °C, which allows the use of less expensive materials. Furthermore, their integration with renewable energy sources looks more straightforward, compared to their high-temperature counterparts. As detailed in section 19, many different cell configurations can be envisioned, and each of them faces different challenges with respect to scale-up. Constructing large size and multi-layer stacks is a common practice in both the fuel cell and water electrolysis fields; nonetheless, implementation of this concept to CO<sub>2</sub> electrolyzers is in its infancy. At the same time, we are convinced that building stacks is the only viable option to scale up electrochemical CO<sub>2</sub>R to an industrially relevant level.

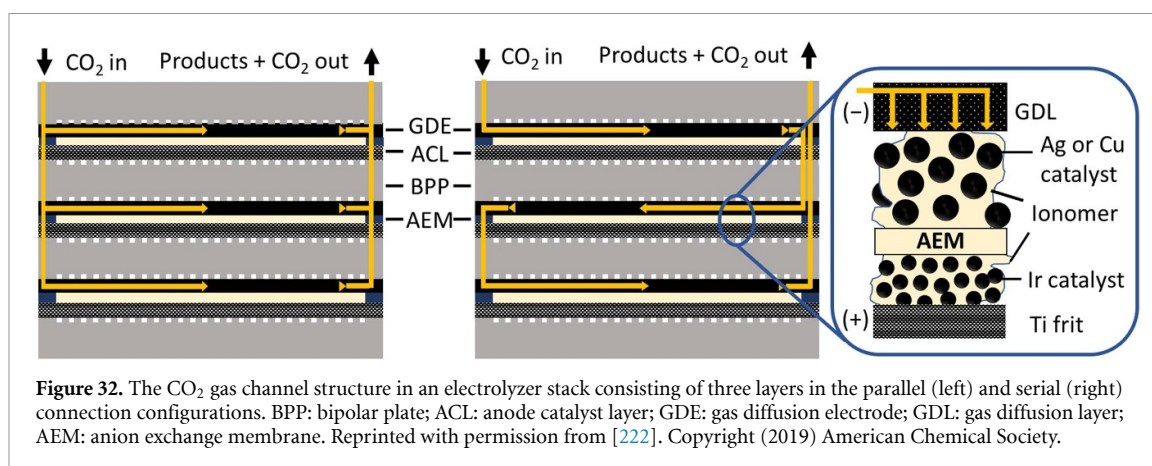
The first multi cell stack was shown for systems employing liquid catholyte, focusing on formic acid as product [220]. A similar system was reported with 1000 cm<sup>2</sup> size recently, with notable solar-to-chemical conversion efficiency, but very low CD [221]. Our group was the first to publish a zero-gap CO<sub>2</sub> electrolyzer stack, which can operate with a pressurized CO<sub>2</sub> gas feed, without the need for any liquid catholyte [222]. The flexibility of the presented design allows different connections between the cells regarding the distribution of the reactant CO<sub>2</sub> gas (i.e. serial or parallel gas feed), see figure 32.

The layers are connected in series electrically, and therefore the stack voltage scales with the number of the cells. The FE and the CO<sub>2</sub> conversion is calculated similarly to single-cell electrolyzers, by quantifying the formed products and applying Faraday's law. Calculating the EE (or more simply the voltage efficiency,  $E^{\circ}_{\text{product}}/E_{\text{cell}}$  for a single cell electrolyzer) of the electrolyzer stack is more complex, as would require measuring the individual cell voltages, and analyzing the formed products of each cell separately. We propose that a good estimate for the EE of the electrolyzer cells (for both the parallel and serial gas connections) is derived by using the overall product composition and the average cell voltage (stack voltage divided by the number of the electrolyzer cells).

As there is no liquid layer between the electrodes, the cell stack resistance is minimized. The components being in intimate connection with each other is also the largest bottleneck of these devices. If any of the components (e.g. electrode, catalyst, membrane, cell framework) underperforms, that will limit the efficiency of the whole cell, as no buffering electrolyte solution is present. In our follow-up studies we have shown that such cell stacks can operate with pure water anolyte and *simultaneously* provides high partial CD (over 600 mA cm<sup>-2</sup>), low cell voltage (−3.0 V), high conversion efficiency (up to 40%), and high selectivity for CO production (over 90%) [201]. A similar concept was shown for ethylene production, with a FE of 78.7% for C<sub>2</sub> products at a CD of 281 mA cm<sup>-2</sup> [223]. Different academic and industrial actors have been also working with stacked designs recently, but the details of their setups have not been published yet [224–226].

### Current and future challenges

To drive CO<sub>2</sub>R in an economically feasible way, electrolyzer cell stacks must be developed, which operate at high (a) conversion rate, (b) EE, (c) selectivity, and (d) conversion efficiency. Notably, even though these four parameters together describe the overall performance of an electrolyzer cell, very seldom are all of these reported in the scientific literature. Ensuring similar performance (in terms of all metrics) for each cell within the stack is also demanding. To reach the MW power regime (this translates to thousands t CO<sub>2</sub>/year processing capability), scale-up efforts need to continue, both in terms of the size of a single cell, as well as the number of cells in the stacks. This exercise however, will bring new challenges related to fluid (both CO<sub>2</sub> gas and water (vapor)) and heat management. In such electrolyzer stacks the temperature control is provided by the tempered anolyte, that must be evenly distributed within the stack, and within the electrolyzer cells despite the continuous bubble formation due to anodic OER. Introducing CO<sub>2</sub> to large electrolyzer cells at one peripheral point results in a large concentration gradient within the cells (especially in the case of large conversion rates), that might lead to increased HER at certain areas of the cell. These processes also affect durability, especially related to precipitate formation in the cathode GDE and flooding [227]. Gas and liquid flow channel engineering and rational GDE design are both necessary to mitigate these issues. The lack of



long-term studies, and standardized test protocols hinder the comparison among the different published data.

Furthermore, cost reduction will be also critical for the successful industrialization. This concerns all components of the electrolyzer stack, ranging from the catalyst (e.g. how to replace Ir anode catalyst), through the MEA (e.g. new membranes and porous layers) to the structural components (e.g. bipolar plates). In addition to novel materials, mass production methods (e.g. roll-to-roll processing of CCMs or metal stamping of bipolar plates) need to replace the current manufacturing processes (e.g. spray coating and Computer Numerical Control milling). Finally, when moving beyond the  $2e^-$  reduction products (i.e. CO and HCOOH), it looks difficult to achieve selective formation of either gas or liquid phase products. Forming product mixtures will further complicate the internal design of both the GDE and the bipolar plates. CO<sub>2</sub> is available as an industrial waste in large quantities in different gas mixtures. Feeding the electrolyzer cells/stacks with such gases will bring further technological challenges.

### Advances in science and technology to meet challenges

Multi-physics modeling has been proven powerful for designing efficient fuel cells and PEM water electrolyzers. Similar studies are ongoing for CO<sub>2</sub> electrolyzers that are expected to support technological developments. Furthermore, modeling the operation of complete electrolysis systems helps to identify the optimal process conditions, and to choose proper stack- and balance of plants components. The outcome of modeling has to be validated by experiments, where the community would certainly benefit from unified accelerated stress test protocols (similarly to the fuel cell and H<sub>2</sub> generation fields). Considering the complexity of the test environments (i.e. the need for temperature, anode and cathode pressure, gas and liquid flow rates, cell voltage control as well as online product analysis), commercial test stations could also accelerate the development process, by allowing interlaboratory data comparison. With the continuously accumulating large amount of experimental data, machine learning will be increasingly implemented. Novel bipolar plate structures will allow better heat and fluid management. Composite materials will be increasingly used, along with polymer processing technologies. After understanding the role of *materials properties and operational conditions on degradation effects will provide real-life feedback to the R&D community.*

### Concluding remarks

In our opinion, the parallel development of large electrolyzer stacks and fundamental studies on the activity/stability of the cell components is necessary for the industrialization of CO<sub>2</sub>R technologies. We envision a relatively straightforward path for HCOOH and CO generation (with and without using liquid catholyte, respectively). At the same time, synthesis of multicarbon products is challenging not only from the catalyst perspective (see section 17), but also from an engineering standpoint. Furthermore, alternative anode processes (resulting in high-value products) might also gain their foothold in the CO<sub>2</sub>R field [228], which again will necessitate extensive R&D on the applicable cell stacks. Finally, all key performance metrics need to be improved holistically, to successfully compete with the indirect CO<sub>2</sub> valorization technologies (such as catalytic CO<sub>2</sub> hydrogenation).



## Acknowledgments

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## 22. What is the future of electrochemical C–N bond formation?

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### Status

As CO<sub>2</sub> is the cheapest source of carbon, one can think of an endless list of substrates to react it with for the synthesis of high-value chemicals. Combining CO<sub>2</sub> electrochemical reduction (CO<sub>2</sub>RR) with nitrogen-containing compounds (such as N<sub>2</sub>, nitrate, nitrite, or amines) is an extremely attractive to achieve C–N bonds and obtain green amides, such as urea. An additional benefit being that the proposed process make use of two abundant and cheap and, in some cases, waste substrates. In this section, I will briefly describe progress in this nascent field, where there is much ground to be gained from adjacent developments in electrochemical CO<sub>2</sub>R.

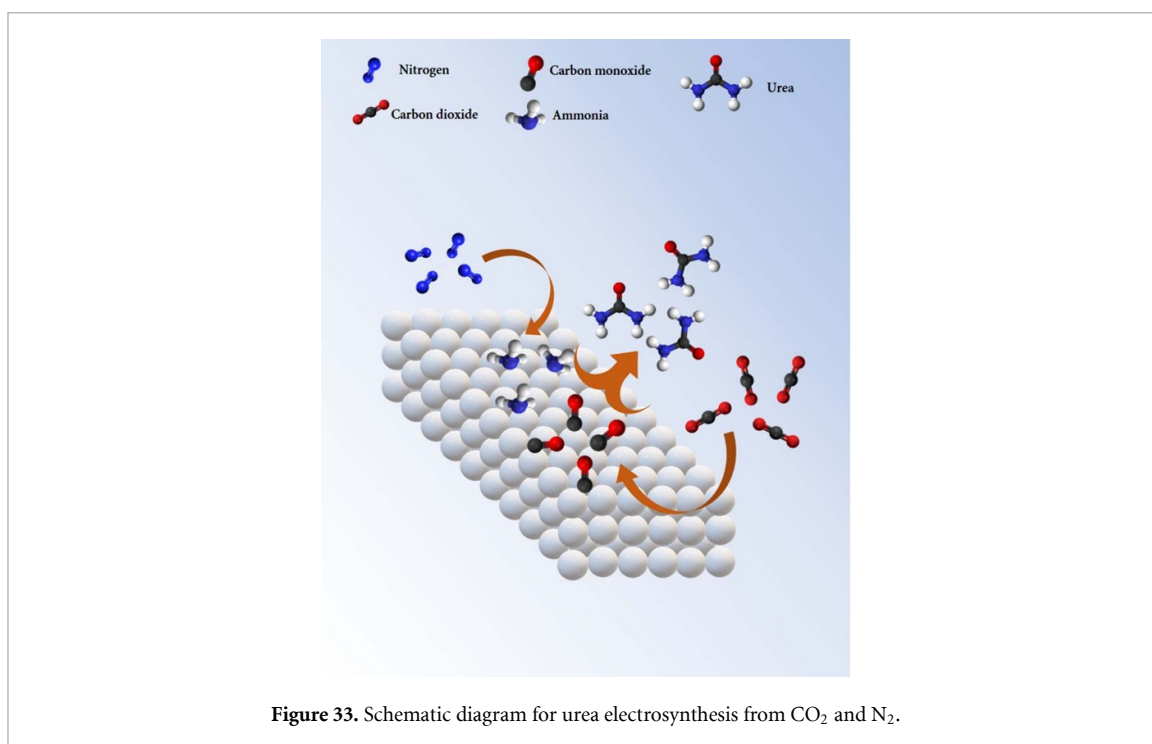
Urea is an important fertilizer for agricultural production of food crop and due to the increasing world population, its production is expected to increase in the coming years. Currently, urea is synthesized through the reaction of NH<sub>3</sub> and CO<sub>2</sub> at elevated temperatures and pressures (150 °C–200 °C, 150–250 bar) and it is responsible for the usage of 80% of the global NH<sub>3</sub>. By its turn, NH<sub>3</sub> is obtained via the Haber–Bosh process that consumes 2% of the annual world energy and has a carbon footprint of 1.5 tons of CO<sub>2</sub> per ton of NH<sub>3</sub> [229]. This makes the synthesis of urea a high energy demanding and ‘very far from green’ industrial process. In this context, the synthesis of urea via a direct electrochemical process from CO<sub>2</sub> and nitrogen-containing compounds would be a game-changer (figure 33). It would not only valorize waste products but would also benefit from all the energy savings and environmental advantages of electrochemical technologies, such as ambient reaction conditions, easy scalability and most importantly, direct use of renewable electricity. Moreover, developments in the efficiency and selectivity of this reaction will also contribute to the understanding of C–N bond formation. This will open a new opportunity to enlarge the landscape of amides and carbamates that can be synthesized from CO<sub>2</sub> and amine derivatives/nitrogen sources (nitrate, nitrite, NO, or many amines or their derivatives) [230].

### Current and future challenges

For the successful industrial electrocatalytic conversion of CO<sub>2</sub> and N<sub>2</sub> to urea we need to favor and optimize the formation of C–N bonds. The first barrier for the reaction is the high dissociation energies for N≡N (941 kJ mol<sup>-1</sup>) and the very stable C=O bond (806 kJ mol<sup>-1</sup>). These demanding energies make the activation of these molecules on the electrode surface very difficult, leading to high overpotentials and low efficiencies. Nitrogen electrochemical reduction reaction (NRR) has only been reported with promising FEs of around ~78% in non-aqueous media via lithium mediated nitrogen reduction [231]. In aqueous media, two major problems are observed: the reported FE are low and most of these studies lack of reliability [232]. The highest FE values reported so far do not go above 10% at –0.25 V (vs RHE) [233]. Despite the challenges in N<sub>2</sub> activation and quantification, the scientific community has been devoting some efforts to the development of measurement protocols that avoid false positives due to ammonia/ammonium from other sources than N<sub>2</sub> [234].

The situation is not very different for the electrochemical reduction of N<sub>2</sub> and CO<sub>2</sub> to urea. The reported FE are far from what would be desirable on a process with potential industrial applications, where CDs of at least 100 mA cm<sup>-2</sup> are mandatory. Another challenge is to direct both CO<sub>2</sub> and N<sub>2</sub> towards a C–N bond, instead of preceding with separate reactions to NH<sub>3</sub> and other C<sub>n+</sub> products. Moreover, the difficulties of accessing the origin of the NH<sub>x</sub> intermediates make it difficult to attribute the origin of the C–N bond to N<sub>2</sub>.

Yet, we have observed in the last decades how fast research can advance in unraveling electrocatalytic reactions and electrode properties. The increased power of physical characterization techniques such as imaging and spectroscopic methods that are now very commonly available *in situ*, allows us to gather essential information about the reactions at the electrode surface. This information can often be translated into the design of more active, stable and cheap catalytic materials. Hence, the biggest challenge for the electrochemical C–N bond formation is to unravel its mechanism, know important intermediates, and understand its dependence on surface orientation and composition. From the electrocatalytic perspective, the C–N bond has just started to receive attention. The pathway for development is still in its beginning and fundamental knowledge needs to be gathered.



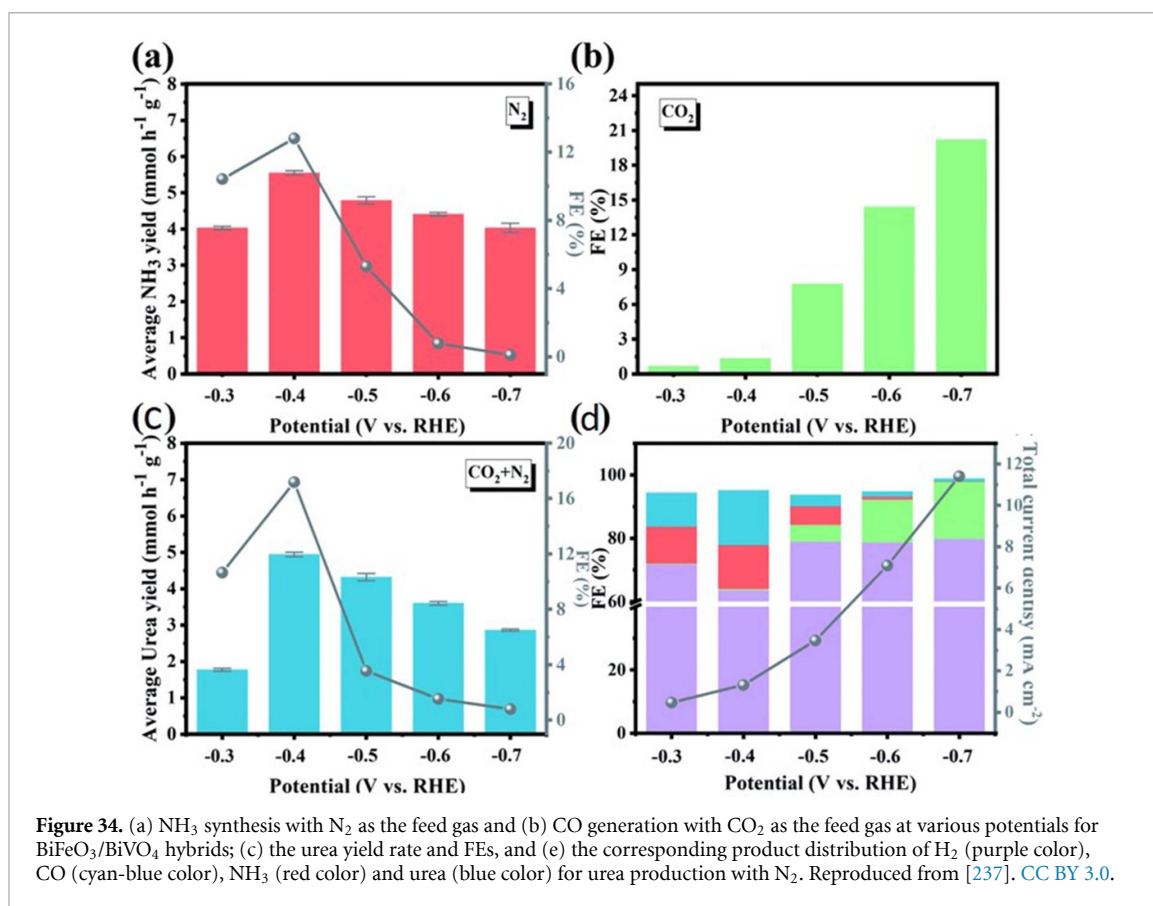
### Advances in science and technology to meet challenges

Although C–N bond formation from the electrochemical conversion of CO<sub>2</sub> and N<sub>2</sub> has just started to attract the attention of the scientific community, some interesting advances have been made in the last couple of years.

One of the first attempts has been made by Chen *et al* [235]. By using PdCu alloy nanoparticles supported on TiO<sub>2</sub> nanosheets the authors obtained urea at a formation rate of 3.36 mmol g<sup>-1</sup> h<sup>-1</sup> and a corresponding FE of 8.92% at -0.4 V vs RHE. It was shown that the efficiency is dependent on the metallic ratio between Pd and Cu, the support, and even the supporting electrolyte. By using in *operando* Synchrotron radiation FTIR and DFT the authors suggest that the presence of adsorbed N<sub>2</sub> (\*N<sub>2</sub>) can facilitate CO<sub>2</sub>R, and the reduced CO can further react with \*N<sub>2</sub> to form urea. The generation of intermediates (\*NCON\*) via activating N<sub>2</sub> is thermodynamically and kinetically feasible, acting as the key factor for effective urea production. The high yield rate of urea is mainly derived from the mutual promotion between the NRR and the CO<sub>2</sub>RR and both optimized reaction pathways. Furthermore, the amount of CO needs to be well controlled, since the excessive formation of CO will occupy excessive adsorption sites and will, to some extent, inhibit the activation of N<sub>2</sub> and CO<sub>2</sub> [235]. Moreover, the authors report isotopic labeling and control experiments to evaluate the possibility of ammonia contaminations in the system. Both show that the formation of urea occurs in a surface confined reaction involving N<sub>2</sub> and CO<sub>2</sub> and it does not result from ammonia contaminants.

Mott–Schottky heterostructural Bi–BiVO<sub>4</sub> hybrids (5.91 mmol h<sup>-1</sup> g<sup>-1</sup> with a FE of 12.55% at @0.4 V vs RHE) [236] and a BiFeO<sub>3</sub>/BiVO<sub>4</sub> heterojunctions (4.94 mmol h<sup>-1</sup> g<sup>-1</sup> and FE of 17.18% at -0.4 V vs RHE) [237]—figure 34—have also been reported as electrocatalysts for the synthesis of urea from N<sub>2</sub> and CO<sub>2</sub>. For these catalysts the authors have suggested that the adsorbed \*N<sub>2</sub> can promote CO<sub>2</sub>R to form CO, and then the generated CO will further react with \*N<sub>2</sub> to produce the desirable \*NCON\* intermediate via thermodynamically feasible electrochemical C–N coupling reaction. Despite the promising FE for urea, the authors do not show evidences that the experimentally observed NH<sub>3</sub> is originated from N<sub>2</sub> activation. In reports concerning C–N bonds formation from N<sub>2</sub> activation, similar protocols as reported by Iriawan *et al* [234] should be followed to avoid false negatives.

An interesting alternative to the use of N<sub>2</sub> as a source of N is the use of nitrates and nitrites. Nitrates and nitrites are well-known contaminants of surface water and present lower dissociation energies and higher solubilities in water than N<sub>2</sub>. These properties make these compounds attractive candidates for use in the synthesis of urea with CO<sub>2</sub> co-electrolysis. Materials such as TiO<sub>2</sub>/Nafion films [238] and oxygen vacancy-rich ZnO (ZnO-V) porous nanosheets [239] have been tested with encouraging FEs (40% and 26%, respectively). The reaction mechanism for urea electrosynthesis from nitrite seems to differ from the mechanism proposed when N<sub>2</sub> is the nitrogen source. For the ZnO-V, it is suggested that the reaction proceeds via coupling of \*NH<sub>2</sub> and COOH\* originated from (nitrite and CO<sub>2</sub>, respectively).



**Figure 34.** (a)  $\text{NH}_3$  synthesis with  $\text{N}_2$  as the feed gas and (b)  $\text{CO}$  generation with  $\text{CO}_2$  as the feed gas at various potentials for  $\text{BiFeO}_3/\text{BiVO}_4$  hybrids; (c) the urea yield rate and FEs, and (e) the corresponding product distribution of  $\text{H}_2$  (purple color),  $\text{CO}$  (cyan-blue color),  $\text{NH}_3$  (red color) and urea (blue color) for urea production with  $\text{N}_2$ . Reproduced from [237]. CC BY 3.0.

### Concluding remarks

The formation of C–N bond containing compounds from the electroreduction of  $\text{CO}_2$  and  $\text{N}_2$  (or other nitrogen-containing molecules) is still at its early stage. Nevertheless, the developments in the last couple of years are impressive: we went from a shy 8% FE to a more promising 20%–40%, depending on the starting nitrogen source. Further efforts should be devoted to a better understanding of the electrocatalytic formation of C–N bonds, as well as their dependence on surface sites, surface composition, reaction conditions, etc and avoid the existence of false positives. This might be challenging as we need to combine two complex reactions— $\text{CO}_2\text{RR}$  and  $\text{NRR}$ . However, this knowledge is crucial for the development of new and green production technologies for urea and other amines, that can have a significant impact on the transition to more sustainable chemical industry.

### 23. How can we systematically discover new materials for CO<sub>2</sub> reduction (CO<sub>2</sub>R)?

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#### Status

The electroreduction of carbon dioxide (CO<sub>2</sub>RR) to value-added chemicals and fuels provides an attractive route to store intermittent renewable energy sources. CO<sub>2</sub>RR systems include cathodes, anodes, membranes, reactant streams, and electrolytes, making up an electrolyzer [240]. To evaluate the economic feasibility of a CO<sub>2</sub>RR system, one must simultaneously consider product selectivity, CD, EE, stability, and the separation of product streams. The cathodic catalyst is a key factor determining product selectivity, overpotential, CD, and stability in a CO<sub>2</sub>RR system [241].

A wide range of products ranging from C<sub>1</sub> to C<sub>3</sub>—such as carbon monoxide (CO), formate, methane, methanol, ethylene, ethanol, acetate, and n-propanol—are produced in CO<sub>2</sub>RR. These are determined by the cathodic catalysts, taken together with conditions of electrolyte and applied reducing potential. In pioneering studies, Hori identified four distinct classes of metal electrodes for CO<sub>2</sub>RR: those producing C<sub>1</sub>–C<sub>3</sub> products (Cu), producing mainly formate (Pd, Hg, Tl, In, Sn, and Cd), producing mainly CO (Au, Ag, Zn, Pd, and Ga); and producing mainly H<sub>2</sub> (Ni, Fe, Pt, and Ti) [242]. Over the past decade, new classes of CO<sub>2</sub>RR catalysts continue to be discovered, including metal oxide derived catalysts, alloys, metal/carbon-based materials, MOFs, single-atom catalysts, and molecular catalysts [240, 241].

Much effort has been invested of late to explore new CO<sub>2</sub>RR catalysts, and progress has been made in promoting the FE, CD, EE, and stability to the various desired products of CO<sub>2</sub>RR [177]. To bring CO<sub>2</sub>RR technology closer to practical relevance will require new catalysts that do even better against these performance metrics taken together [12].

#### Current and future challenges

Today, in implementing the challenging series of multiple sequential reductive steps along CO<sub>2</sub>RR pathways, one incurs a high overpotential, corresponding to a low EE [240]. This has driven the field to seek to decrease overpotential, including by operating in extremely alkaline conditions. For instance, the onset potential for reducing CO<sub>2</sub> to ethylene decreased by 0.3 V when the electrolyte was switched from 1 M KOH to 10 M KOH [243]. However, highly concentrated alkaline electrolyte leads much CO<sub>2</sub> to turn to carbonate, resulting in a low CO<sub>2</sub> utilization efficiency [215]. New approaches to reducing CO<sub>2</sub> under low overpotential (e.g. <0.2 V) are required.

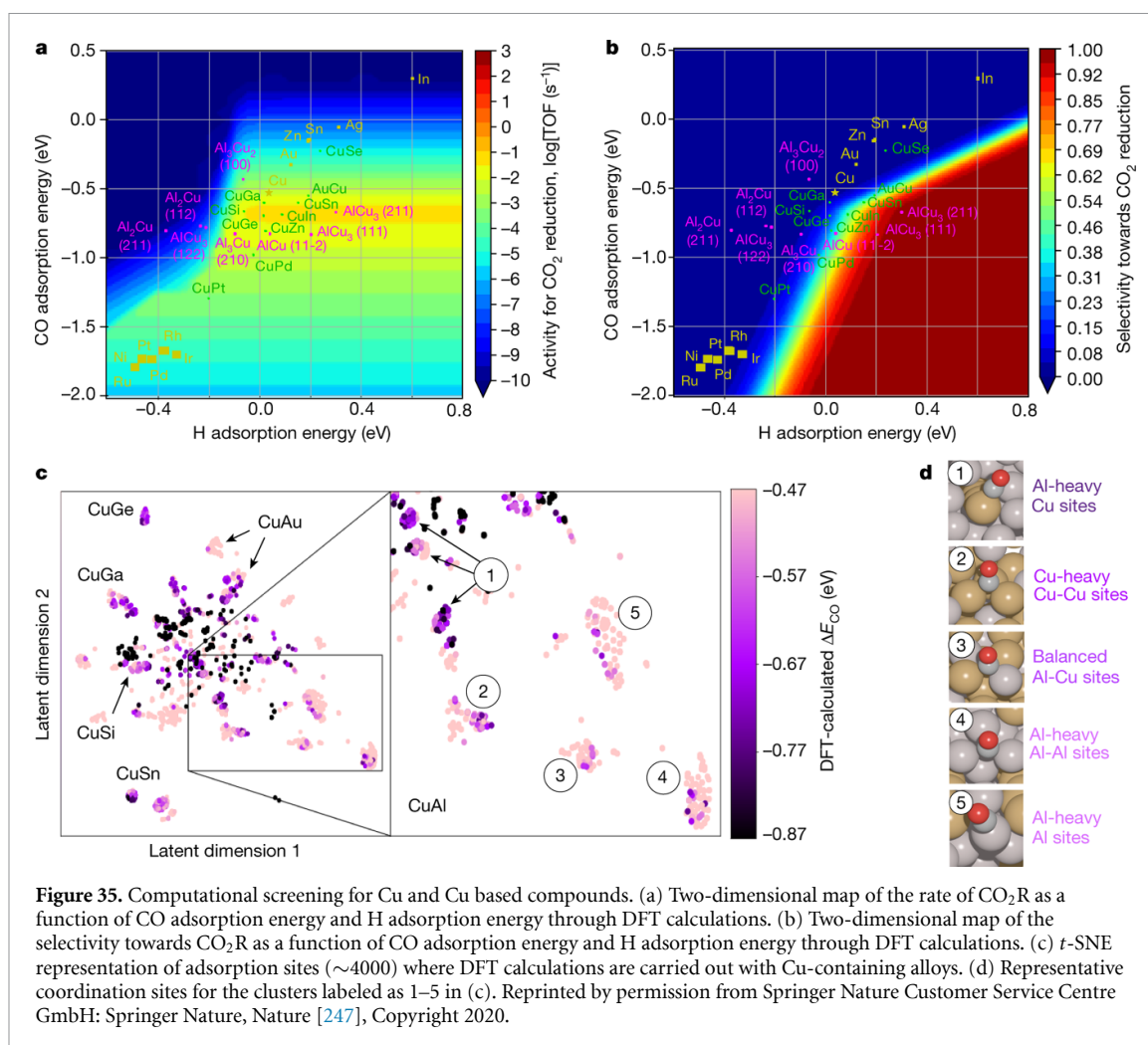
Theoretical studies have put focus onto pathways and key intermediates toward C<sub>1</sub> and C<sub>2</sub> products [240, 244]. The pathways/intermediates are many, and this increases the complexity of mechanistic investigations. There remains debate over detailed C<sub>2</sub> routes and in general a lack of clarity on the path to C<sub>3</sub>. This curtails the rational design of new CO<sub>2</sub> materials that are highly selective to specific C<sub>2+</sub> products.

The important direction is to seek high FE to one specific CO<sub>2</sub>RR product, combined simultaneously with high CD. Since proton is involved in the CO<sub>2</sub>R process to generate C<sub>1</sub>–C<sub>3</sub> products, the HER is a competing reaction. The wide spectrum of C<sub>1</sub>–C<sub>3</sub> products also compete with one another in CO<sub>2</sub>RR [240]. Nevertheless, experimentally, recent progress has been seen: the FE to certain CO<sub>2</sub>RR products at commercially relevant CDs (>100 mA cm<sup>-2</sup>) have registered impressive advances, such as CO (FE > 90%), formate (FE > 80%), ethylene (FE > 80%), and methane (FE > 80%) [245–248]. Taking this the rest of the way to CO<sub>2</sub>RR catalysts that generate a *single* specific C<sub>2+</sub> product with high FE (e.g. >80%) at high reaction rate (e.g. >100 mA cm<sup>-2</sup>) remains a challenge, but the field is progressing in this direction.

Stability is simultaneously an imperative metric for CO<sub>2</sub>RR electrocatalysts. To maintain performance under long-term operation, this will require catalysts whose structure and composition reach a stable configuration over the course of tens of thousands of hours operating under CO<sub>2</sub>RR. To date, CO<sub>2</sub> to CO has achieved 1000 h stability, maintaining a stable FE above 90% at 200 mA cm<sup>-2</sup> [245]. For other CO<sub>2</sub>RR products, new CO<sub>2</sub>RR materials need to be developed to achieve consistently high performing operation.

#### Advances in science and technology to meet CO<sub>2</sub>RR challenges

As noted above, the rational design of new CO<sub>2</sub>RR materials highly selective to specific C<sub>2+</sub> products will rely on ever-deepening physicochemical understanding of reaction mechanism. *Operando* and *in situ* characterization techniques facilitate investigations of reaction mechanisms in CO<sub>2</sub>RR. *Operando* x-ray absorption near edge fine structure and x-ray absorption fine structure spectroscopies probe valence states and the coordination environment of catalysts during CO<sub>2</sub>RR [34]. *Operando* Raman and infrared spectroscopy enable one to follow intermediates and increase mechanistic understanding of CO<sub>2</sub>RR [34, 249].



**Figure 35.** Computational screening for Cu and Cu based compounds. (a) Two-dimensional map of the rate of CO<sub>2</sub>R as a function of CO adsorption energy and H adsorption energy through DFT calculations. (b) Two-dimensional map of the selectivity towards CO<sub>2</sub>R as a function of CO adsorption energy and H adsorption energy through DFT calculations. (c) *t*-SNE representation of adsorption sites (~4000) where DFT calculations are carried out with Cu-containing alloys. (d) Representative coordination sites for the clusters labeled as 1–5 in (c). Reprinted by permission from Springer Nature Customer Service Centre GmbH: Springer Nature, Nature [247], Copyright 2020.

Computational approaches enable systematic exploration of possible pathways and the key intermediates on the path to C<sub>2+</sub> products. Uniting DFT with machine learning offers to accelerate CO<sub>2</sub>RR material screening *ab initio* for specific desired products (figure 35) [247]. The recent exploitation of high throughput experimental methods may promote efficient screening for CO<sub>2</sub>RR [250, 251].

### Concluding remarks

Discovering new CO<sub>2</sub>RR materials needs to meet the simultaneous requirements of promoting FE, CD, EE, and stability towards practical application, an effort that will rely on ever-improving fundamental understanding of reaction mechanism in CO<sub>2</sub>RR. Advances in computational approaches and *operando* techniques facilitate mechanistic picture development jointly from theory and experiment, helping to further the rational design of CO<sub>2</sub>RR materials. All this must be united with understanding of the role of electrolytes, anodes, membranes, and the electrolyzer system.

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### Data availability statement

No new data were created or analyzed in this study.

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