

## 17. CO<sub>2</sub>RR catalysis: surface reactivity and products selectivity

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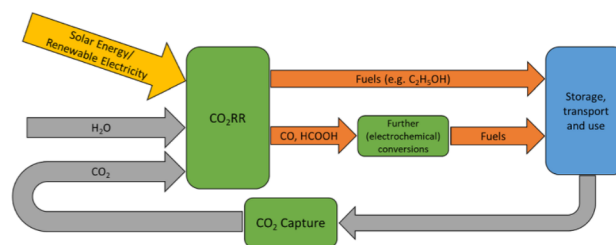
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### Status

Taking advantage of renewable energy sources to convert CO<sub>2</sub> to fuels and chemicals electrochemically has the potential to sustainably produce currently fossil-derived molecules artificially, using systems that mimic photosynthesis. The ultimate goal is solar fuels or ‘electrofuels’, and by developing the technology into an efficient and scalable one, a circular economy can be formed around CO<sub>2</sub>-neutral production and subsequent use of fuels, figure 30. In addition, it presents an avenue for efficient utilization of intermittent, renewable energy along with the vast, pre-existing infrastructure for storing and transporting these molecules. Nonetheless, considerable progress must still be made to achieve industrially relevant targets for the technology to be considered for large-scale implementation, as featured in a recent techno-economic and carbon emissions analysis [54].

At the heart of this development is the electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), which takes place on the surface of an electrocatalyst. Thus, it is vital to gain a fundamental understanding of how different parameters influence the selectivity and efficiency of the CO<sub>2</sub>RR. Over the past few years, considerable work has been done to gain mechanistic insight into various aspects of the electrocatalysis, such as the initial activation of CO<sub>2</sub>, the importance of stabilizing key intermediates, and their relation to the observed overpotentials [178]. The effect of the molecular nature or catalyst morphology (particle size, shape, roughness, defect density and composition) on CO<sub>2</sub>RR selectivity has also been examined [179, 180] in detail. More recently, attention has been given to (local) electrolyte effects and the role of mass transport [181] in relation to product selectivity. Finally, potential pulses leading to a change in the catalyst morphology, oxidation state and local pH have been featured as an additional avenue to tune the product selectivity [182]. Progress in understanding these fundamental aspects of the CO<sub>2</sub>RR will be crucial in developing both solar-driven and electricity-driven systems.

Currently, the best Faradaic efficiencies (FEs) have been reported for the two-electron products carbon monoxide (CO) and formic acid (HCOOH) as well as 12-electron product ethylene (C<sub>2</sub>H<sub>4</sub>). Electrochemical engineering efforts are progressing these best candidates towards commercial relevancy through innovations in gas diffusion electrodes, ion-exchange membranes, flow-cell architectures and process optimization. In order to enhance this progress and expand the range of favorable CO<sub>2</sub>RR products, further advancements must be made in understanding the electrocatalysis.



**Figure 30.** The role of the CO<sub>2</sub>RR in a circular economy for production of fuels from solar energy and renewable electricity.

### Current and future challenges

One of the core issues for the CO<sub>2</sub>RR is the competing hydrogen evolution reaction (HER) that limits the FE of desired (carbon containing) products, hindering the overall energy efficiency, especially at low potentials, and requires additional steps downstream for the H<sub>2</sub> gas [54]. Under alkaline conditions often used for aqueous CO<sub>2</sub>RR, the slow rate of water reduction helps to suppress the HER. However, alkaline conditions lead to the formation of carbonates that trap the CO<sub>2</sub> and cross the anion-exchange membrane used in those systems [183]. Strategies to overcome the challenges presented by the HER will be necessary as the technology progresses.

Since the pioneering work of Hori [184], Cu has been known as a promising catalyst for C–C bond formation, with computational calculations and experimental evidence showing that the mechanism proceeds through a CO-dimer [185]. Despite the remarkable ability of Cu to effectively catalyze the CO<sub>2</sub>RR towards C<sub>2</sub> products, high overpotentials are required. There are also issues with selectivity, with a large product distribution often observed [186]. The C<sub>2</sub> products formed with the highest FE are ethylene and ethanol, but it remains a challenge to direct the reaction towards a single target molecule to avoid additional separation steps. Furthermore, the surface of Cu has been shown to restructure under CO<sub>2</sub>RR conditions [187], limiting its durability and consequently commercial viability. For next generation catalyst design, Cu surfaces should be further tailored to facilitate C–C bond formation and improve their stability. Recently, it was shown that rather than targeting ideal surfaces with specifically oriented facets, selectivity tuning can be achieved through catalyst pre-treatments, leading to specific surface defects [187], the nature of which and their correlation to a specific selectivity trend is still to be unveiled.

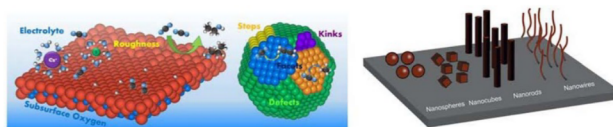
Efficient catalysis towards other valuable CO<sub>2</sub>RR products is another significant research challenge. This includes C<sub>1</sub> molecules methanol and methane, with a huge demand for a low-carbon production pathway, together with C<sub>2</sub>+ molecules of high value. Understanding the factors that govern the formation of these molecules, even as minor products, will aid the development of future catalysts. One such study outlines strategies for catalyst design for C<sub>2</sub>+ products whilst giving attention to the critical role of the electrolyte for these reactions [186]. Further insight into selective catalysts for methane

[188] and methanol [189] is also needed. Finally, real world industrial applications of this technology will likely involve hybrid processes where the CO<sub>2</sub>RR will be integrated within a catalytic system comprising steps to be carried out within a coupled thermal reactor.

### Advances in science and technology to meet challenges

Further advancements in CO<sub>2</sub> electrolysis will be necessary to reach a level similar to that of the more mature H<sub>2</sub>O electrolysis technology for ‘green hydrogen’ production. The selectivity, durability and rate of reaction of current state-of-the-art catalysts can be improved through the modification of surface morphology and composition to optimize the activity, figure 31. More detailed work on electrolyte effects will also be required to meet the ambitious goals for the technology. Another avenue to tune the selectivity towards C<sub>2</sub> products over Cu catalysts is to increase the CO surface coverage, with higher coverages favoring the C–C coupling [190]. This can be achieved by combining Cu with CO-making metals such as Ag, resulting in enhanced ethylene and ethanol production. Hybrid approaches, such as combinations of molecular and heterogeneous catalysts, may also be advantageous for future catalysts.

Further analysis of mass transport and pH effects on different catalysts will help to suppress the HER and thus improve the FE for desired products. For this purpose, pulsed electrochemistry approaches are also being considered [191], with the value of the anodic potential pulse drastically influencing the reaction selectivity through the associated changes in the morphology, adsorbate coverage and local pH [192]. As recent work has shown [193, 194], investigations into the CO<sub>2</sub>RR in acidic conditions with different electrolytes and mass transport control could alleviate some of the aforementioned HER issues. To improve the selectivity towards a single C<sub>2</sub> product on Cu, similar strategies should be employed, with a focus on achieving good selectivity to one molecule. For effective CO<sub>2</sub>RR to additional products of interest, other approaches may be considered, such as a tandem-electrolysis approach, where CO<sub>2</sub> is initially reduced to CO or COOH, then converted further to a higher value product.



**Figure 31.** Illustration of catalyst surface effects on the CO<sub>2</sub>RR activity and selectivity. Reproduced with permission from [178, 179].

Many experimental spectroscopic, microscopic and diffraction techniques that allow for detailed analysis of catalyst surface and bulk structures, chemical composition and reaction will require greater sensitivity and a more realistic operation environment. Detecting intermediates at very low coverage will enable more insights into reaction mechanisms as well as the effect of different surface structures. Finally, complimentary progress in theoretical methods is vital. Realistic models for electrolyte-electrolyte interfaces and mass transport effects, using explicit solvent and electrolyte ions, will progress the understanding of such effects at an atomic level. Machine learning approaches will become increasingly important for the evaluation of large microscopy or spectroscopy datasets experimentally generated under *operando* reaction conditions.

### Concluding remarks

Gaining a fundamental understanding of the electrocatalysed CO<sub>2</sub>RR will help to progress the technology towards commercialization, where it has the opportunity to play a significant role in the energy transition. Mechanistic understanding of the different reactions that occur on the catalyst surface will help to rationalize activity and selectivity, aiding both the optimization of current catalysts and design of next generation catalysts. Studying the effect of *in situ* conditions, including pH and mass transport effects, on the CO<sub>2</sub>RR will enable further progress to be made with catalyst performance. The catalyst morphology and degradation mechanisms must be understood in order to enhance the durability to the level required for large-scale implementation. To enable this progress to be made, *in silico* theoretical and *operando* experimental techniques must be further developed and utilized in tandem.