Electrocatalytic CO_2 Reduction to Fuels – Progress and Opportunities

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Abstract

The electrochemical reduction of CO_2 remains an appealing option for storing renewable energy in a chemical form. Here, we assess progress in designing catalysts that convert CO_2 to high energy density products. We explain how reaction data can be reported to reflect the intrinsic properties of the catalyst. This analysis shows that limited advances have been made in improving the performance of Cu. We suggest that opportunities remain using bimetallic catalysts that are resistant to dealloying. While aqueous systems are instrumental to developing our understanding of this chemistry, gas-fed systems that operate at high current densities must be developed. Although obstacles remain for practical application of CO_2 reduction, advances in fundamental understanding made over the years give reason for optimism.

Copper catalysts for Electrochemical CO_2 reduction Electrochemical CO_2 reduction (CO_2R) provides a way to store energy from renewable sources of electricity in the form of chemical bonds.[1] Practical implementation of CO_2R is currently limited in large part by a lack of active and selective electrocatalysts to facilitate the reaction. Since the discovery that Cu electrodes are uniquely capable of catalyzing CO_2R to fuels and chemicals, many studies have focused on enhancing the catalytic performance of Cu.[2-5] The aim of this perspective is to evaluate the success of these catalyst discovery efforts and assess what further prospects and challenges await CO_2R. We begin by describing a way in which CO_2R rate measurements can be collected and reported to reflect the intrinsic behavior of a catalytic material. We use this methodology to determine whether various catalyst design strategies have been effective at enhancing the intrinsic activity of Cu and suggest new promising avenues. While our discussion centers on Cu catalysts in aqueous electrolytes, we suggest that gas-fed systems hold promise for practical applications. We hope that this assessment will help identify the areas for future research that will bring the prospect of practical electrochemical CO_2R closer to reality.

Important considerations when comparing CO_2R electrocatalysts

Metrics for evaluating catalyst performance

We begin by defining what is meant by catalyst performance for CO_2R and how it should be described most appropriately.[6] This will allow us to accurately assess the effectiveness of catalyst design strategies. A commonly used metric is the Faradaic efficiency (FE), which measures the fraction of the total current used to produce a specific product. An increase in the FE to a given product should not be used to suggest an increase in catalytic activity for forming that product without demonstrating that the rate, described by the partial current density to that product, has also increased.[6]

Another important point is that current density or partial current density to a given product is typically reported with respect to the geometric area of the electrode; however, this metric is dependent on catalyst loading and the specific surface area of the catalyst. If twice the number of catalytic sites are loaded onto a given electrode area, the geometric rate of reaction will

correspondingly double. Therefore, to understand the performance of a catalyst it is important to know its electrochemically active surface area (ECSA). While different methods for evaluating surface area or number of sites exist, each with its own strengths and limitations, most forms of normalization yield a much more satisfactory evaluation of activity than activity reported without any sort of normalization.[7, 8] Normalization of catalytic activity based on number of catalyst active sites is standard practice in thermal catalysis, and has been widely adopted for other electrocatalytic reactions such as the water electrolysis and fuel cell reactions.[9-12] Adopting these standard practices would greatly facilitate objective evaluation of CO_2R catalysts and aid in identification of promising new materials.

Mass transport limitations

Because the solubility of CO_2 and its mass transport coefficient in aqueous electrolytes are low, the CO_2R reaction becomes mass-transport limited even at relatively low current densities. [13, 14] Transport limitations also affect the measured product distribution, complicating the assessment of the intrinsic catalyst properties. Under conditions of moderate polarization, hydroxide ions produced at the cathode surface increase the near-surface pH. This change affects the product selectivity, since rates of CH_4 and C_2H_4 formation exhibit different dependencies on the electrolyte pH.[15-18] As electrolyte pH increases, the partial current density for CH_4 decreases whereas the C_2H_4 partial current density remains constant when the rates are compared on an SHE scale. By contrast, the CH_4 partial current density remains constant while the C_2H_4 partial current density increases as the electrolyte pH increases when the pH-dependent RHE scale is used. These trends are explained by the nature of the kinetically relevant step involved in forming the two products. The C-C bond formation step for forming C_2H_4 does not involve a proton transfer, thus C_2H_4 rates are independent of proton concentration on an absolute potential scale (SHE).[19-23] On the other hand, the formation of CH_4 involves a coupled proton-electron transfer (or alternatively, the transfer of a hydrogen atom via reaction of an electron with water) in the kinetically relevant CO hydrogenation step, and therefore, CH_4 formation rates depend on proton activity.[24] Under sufficiently high polarization, the CO_2 concentration at the cathode surface is depleted and the product distribution shifts toward hydrogen and methane. This is likely due to a reduced surface coverage of CO relative to H.[13, 17, 25] Therefore, the

distribution of products observed under conditions of significant mass transport limitations are a convolution of the intrinsic catalyst kinetics and the dynamics of mass transport. These factors indicate that research focused on identifying catalysts with higher intrinsic activity should be carried out at low current densities where transport limitations are negligible. Tests for the effects of external mass transport limitations can be conducted by varying the extent of mixing in the cell, to assure that catalyst activity is measured under kinetic control.[6, 26] Without these demonstrations, the possibility of mass transport limitations should always be considered along with their effect on measured performance.

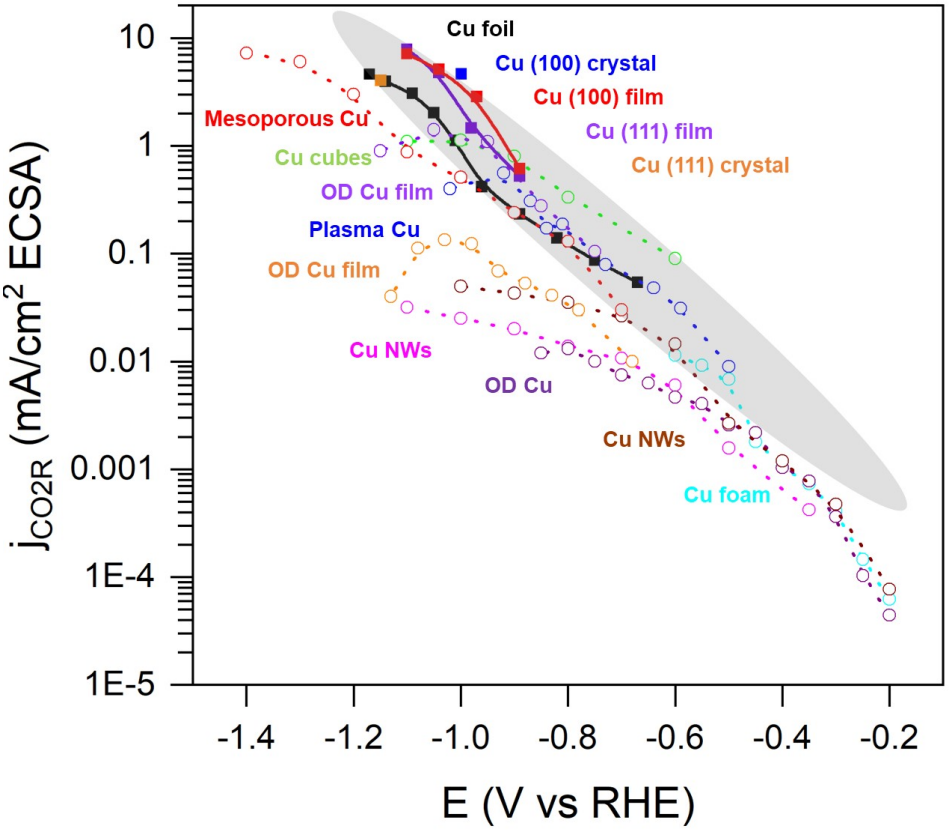

Figure 1: Effects of Cu facets and nanostructure on ECSA normalized activity for CO_2R. Comparison of overall CO_2R activity normalized to surface area for various nanostructured Cu electrocatalysts with Cu standards. The data were obtained from the following studies: Cu foil Kuhl et al. [27]; Cu (111) and (100) crystals Hori et al.[28]; Cu (111) and (100) films Hahn et al.[29]; Cu cubes Kwon et al.[30]; Plasma Cu Mistry et al.[31]; Cu foam Min et al.[32]; Cu NWs Ma et al.[33]; OD Cu Li et al.[34]; Cu NWs Raciti et al.[35]; OD Cu film Handoko et al.[36]; OD Cu film Ren et al.[37]; Mesoporous Cu Yang et al.[38]. The gray region indicates the approximate Tafel behavior of Cu standards and illustrates that no nanostructured catalyst shows significantly higher reactivity than these standards. Adapted with permission from Nitopi et al.[3].

Evaluating progress in improving the performance of Cu catalysts for aqueous CO_2 reduction

The preceding sections provide guidelines for how the intrinsic behavior of electrocatalysts for CO_2R can be assessed. Catalytic activity should be measured under conditions that mass transport limitations do not significantly affect rates and reported as partial current densities normalized by catalyst surface area or number of catalytic sites. Having established a method for clearly comparing catalytic performance, we now examine the effectiveness of common catalyst design strategies for improving the performance of Cu.

Modifying Activity and Selectivity of Cu Catalysts through Nanostructuring

Many investigators have examined the effects of surface faceting and roughening (referred to collectively as nanostructuring) on the activity and selectivity of Cu for CO_2R.[3, 27-42] The first question is whether surface roughening affects the intrinsic CO_2R activity of Cu. As noted above, surface roughness results in a higher geometric activity (i.e., current density normalized to the geometric surface area of the electrode) due to an increase in the catalyst surface area relative to that of a planar electrode. Figure 1 illustrates the ECSA-corrected current densities for CO_2R for a large number of Cu catalysts prepared in different ways.[3, 6] For cathode voltages below c.a. - 0.6 V vs RHE the Tafel slope is similar for different preparations of Cu, suggesting that the CO_2R activity of these catalysts is essentially the same. The deviation from Tafel-like behavior observed for each sample at higher applied potential reflects the effects of mass transport limitations. In all these cases, the FE for the HER rises relative to that for CO_2R. The rougher the surface, the lower the applied potential at which the onset of this effect occurs because the onset of transport limitations depends on the total current density and not the ECSA-based current density.[6] No nanostructured catalysts show significantly higher activity than Cu standards (single crystals, metal foils, and oriented thin films). Therefore, the lack of evidence for higher intrinsic activity of nanostructured catalysts suggests that modifying the surface topography of Cu is not a useful tool for significantly enhancing the intrinsic CO_2R activity of Cu. We note that the same conclusion has been reached by other authors.[3, 43]

While roughening Cu surfaces produces insignificant changes in the total CO_2R ESCA-based current density, it can affect the distribution of products formed. Figure 2 shows that increasing roughness of Cu surfaces, produced by electrochemical reduction of electropolished Cu pretreated in an Ar, O_2, or N_2 plasma or nitrided at high-temperature to form Cu_3N, increases the ratio of C_{2+} products and the ratio of oxygenated to hydrocarbon products. These changes are independent of the roughening procedure. This high selectivity can result from restructuring of the surface to present (100) terminations, as this crystal facet has been shown to be selective to C_2 products.[16, 28, 30, 40] Consistent with this, the ECSA normalized partial current density to C_2H_4 of a range of high surface area Cu catalysts is very similar to that of Cu (100) oriented films.[6] Selectivity increases to C_{2+} products with roughening are instead often the result of decreased TOFs to H_2 and CH_4, rather than increases in TOF to C_2 species.[6] Finally, under conditions where mass transport limitations are significant, local pH changes at the electrode-electrolyte interface can further increase the C_{2+}/C_1 selectivity.

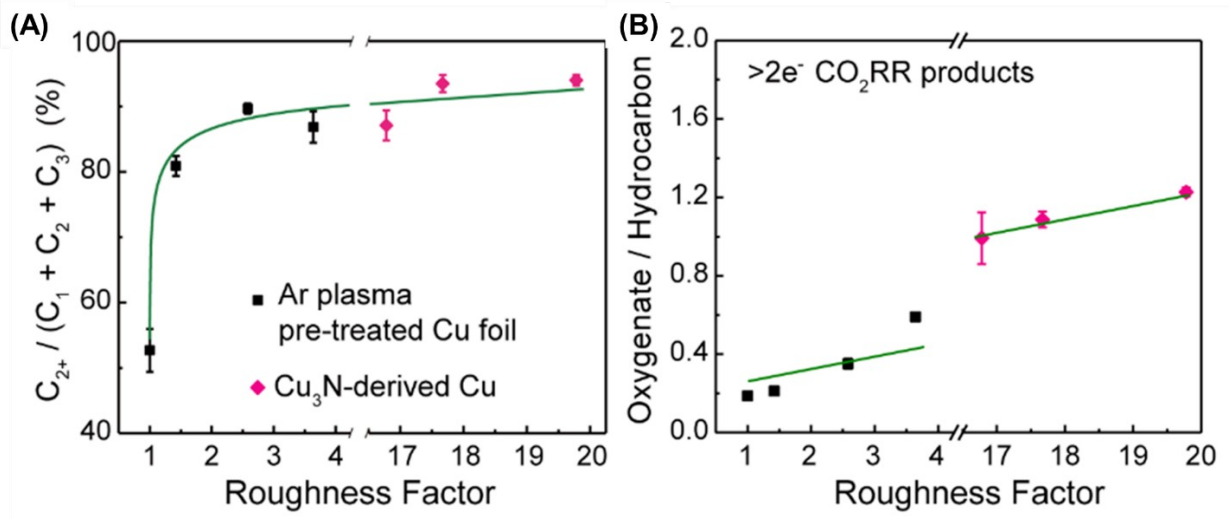

Figure 2: Effects of Cu roughening on CO_2R product distribution. (A) C_{2+} product selectivity and (B) Faradaic efficiency ratio of oxygenate versus hydrocarbon products for physically roughened Cu foils obtained by Ar-plasma pretreatment and Cu_3N-derived Cu electrodes prepared with different annealing times; all measurements were made at a cathode potential of – 1 V vs RHE, in 0.1 M CO_2-saturated $CsHCO_3$. Adapted with permission from Ebaid et al. [40]

Modifying reactivity of Cu catalysts through change in composition

Bimetallic catalysts

Research has been done to determine whether the CO_2R activity and selectivity of Cu can be modified by forming a bimetallic alloy. Combining Cu with a second metal can influence reactivity through both electronic and geometric effects.[44] Electronic effects result from modification of the electronic structure of Cu through interaction with the second metal. This in turn influences the interaction of Cu with adsorbates.[45] Modifications that reduce the electron density of Cu d-states near the Fermi level weaken the interactions of adsorbates with Cu, whereas an increase in populated d-states near the Fermi level leads to stronger interactions.[45] Electronic effects can be caused by charge transfer between the two metals (ligand effect) or a modification in the lattice constant of Cu upon addition of a second metal (strain effect).[46] Changes in the lattice constant result in differences in orbital overlap between metal atoms and thus the broadness of the density of electronic states of the metal. To maintain orbital occupancy constant, a change in the broadness of the metal d-band results in a shift in its position relative to the Fermi level, thereby modifying metal-adsorbate interactions.[47] Geometric effects include changes in the atomic arrangement of actives sites (ensemble effects) and the creation of bifunctional active sites where neighboring metals serve different catalytic roles. For instance, the addition of an oxophilic modifier to a Cu surface could potentially modify its activity by preferential stabilization of oxygenated intermediates through interaction of the oxygen functionality with this second metal.[48]

Similar to the case for nanostructured catalysts, previous studies have shown that the turnover frequency (catalytic rate per catalytic site per unit time) of Cu for both forming multicarbon products, and separately for forming $2e^-$ products (CO and $HCOO^-$), is not enhanced significantly by addition of a second metal (see Ref. 3 and references therein). Unfortunately, the small number of studies reporting electrochemically active surface areas for bimetallic Cu catalysts limits systematic comparison of the intrinsic activity of such catalysts.[49, 50]

It is interesting to consider why extensive studies of bimetallic catalysts have not yielded larger improvements in activity. A plausible explanation is that this is due to the difficulty in controlling bimetallic surface composition through synthesis, handling, and reaction testing. Cu forms relatively weak alloys with many transition metals. This means that the energetic benefit

for mixing a second metal with Cu is low. In contrast, the energetic benefit from adsorption of gas phase species onto these metal surfaces can be much higher. For example, if Cu is mixed with a more reactive metal (such as Ni, Fe, Pt) the energy gained by adsorbing CO, the most abundant reaction intermediate formed during CO_2R over Cu, onto the more reactive metal is much larger than the free energy of formation of the alloy. This suggests that CO formation will drive surface segregation of the more reactive metal and result in a surface composition that is different from the bulk composition. This has been observed for alloys of Cu under CO_2 hydrogenation conditions.[51, 52] Consistent with this proposition, most alloys of Cu with reactive metals have yielded product distributions much more representative of the reactive metal (i.e., high selectivity to HER) than the product distribution associated with Cu.[53] For Cu mixed with oxophilic metals (such as Zn, Sn, In) the enthalpy of formation of a monometallic oxide of the oxophilic metal is much larger than the alloy formation energy of the metals. Consequently, the alloy catalyst is likely terminated with a monometallic oxide layer after exposure to air and potentially the electrolyte. When a reducing potential is applied this metal oxide reduces, but it is unclear to what extent re-alloying of the two metals occurs under conditions of CO_2R. Again, the product distributions for this class of bimetallics have generally not been representative of Cu catalysts, with bimetallics showing high selectivity to $2e^-$ reduction products, CO and $HCOO^-$.[54-56] While probing these surface compositional changes under relevant conditions is difficult, as the presence of the electrolyte strongly attenuates the signal from most surface sensitive compositional probes, it appears from the reactivity of these catalysts that the surface compositions intended is not realized.

Non-metallic modifiers

In addition to modifying the composition of Cu through alloying with a second metal, many studies have explored the use of non-metal dopants (e.g. oxygen, sulfur, nitrogen).[34, 57-61] A number of authors have proposed that upon reduction of oxidized Cu, subsurface oxygen is retained, resulting in the creation of Cu sites that are particularly active for formation of C_{2+} products.[31, 61-66] However, both experimental and theoretical studies strongly suggest that subsurface oxygen is not retained under the aggressively reducing conditions used for CO_2R (e.g., cathode voltages of -1 V vs RHE).[67-69] Similar behavior has been shown for dopants

such as sulfur and nitrogen.[58, 59] Therefore, while dopants can be introduced into Cu, their impact on steady state catalytic performance is not significant.

Status of catalyst design efforts

We have shown that despite extensive efforts, catalyst design strategies aimed at improving the intrinsic catalytic activity of Cu for CO_2R have been largely ineffective. Given the wealth of studies on these materials we emphasize the importance of accurately assessing intrinsic catalytic behavior. New candidate catalysts should show enhanced activity (normalized to the number of catalytic sites) under conditions free of transport limitations before investigations of unique properties of the candidate catalyst are warranted. Given the challenges in enhancing the intrinsic activity of Cu, we now suggest remaining avenues to do so, and consider alternative methods for improving the overall performance of electrochemical CO_2R systems.

Opportunities for further improvements of the performance of Cu catalysts

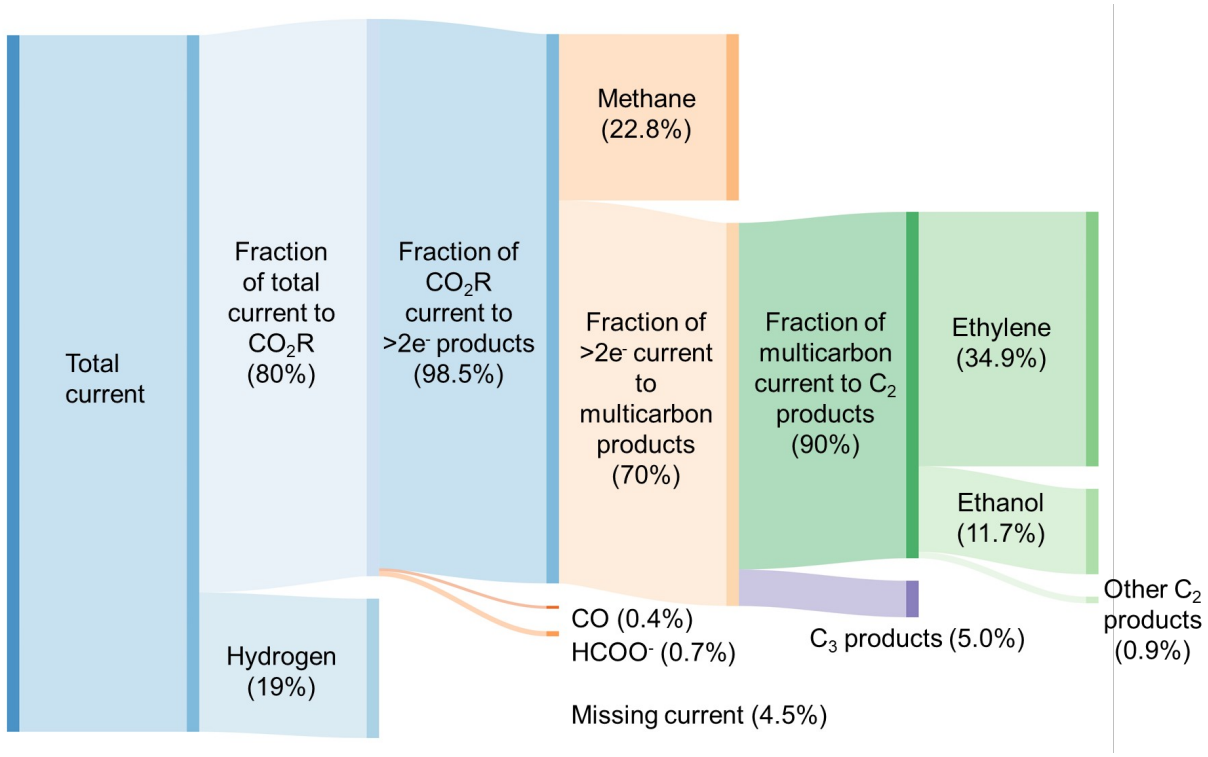

Figure 3: Understanding the product distribution of Cu for CO_2R. Sankey diagram showing the breakdown of current for Cu (100) at -1.04 V vs RHE. Note that fractions of current are distinct from

overall Faradaic efficiencies. Total current efficiency is 95.5%, and missing current is 4.5%. Adapted with permission from Hahn et al.[29]

The distribution of total current to different products formed over a Cu (100) surface at ~-1 V vs RHE, is shown in Figure 3. This plot helps us identify what improvements might be made in the performance of Cu-based catalysts.[29] The first deduction is that a significant fraction of the total current is lost to hydrogen evolution; thus, catalysts that inhibit the propensity of Cu to produce hydrogen are desirable. Secondly, while nearly all the CO produced at this potential is further reduced, a certain fraction is lost to methane, an undesired product due to its low cost and volumetric energy density. A significant fraction of current goes to C_{2+} products, primarily ethylene, ethanol, and a smaller proportion of propanol. While ethanol and propanol are useful as fuels, their separation from water is energy intensive.[70] Therefore, for systems with an aqueous electrolyte it would be desirable to achieve high selectivity to ethylene, the most abundant C_2 product formed over Cu. It would also be desirable to find catalyst compositions and structures that could produce higher alcohols and alkenes. Propylene and butene are valuable molecules, but no catalysts currently produce these products in measurable yields. The selective formation of butanol would also be attractive since this alcohol would phase separate from water at concentrations above 9%. To target specific multicarbon products, it is important to understand which elementary steps in the reaction network control the growth of C-C bonds and which bifurcate between different products (hydrocarbons and oxygenates). Few studies have examined the reaction mechanism after the first C-C coupling step.[22, 71] In summary, future effort on catalyst development should focus on lowering the kinetic overpotential for CO_2 reduction to CO and C-C coupling and enhancing the selectivity for CO_2R relative to that for HER. Tuning of the product selectivity towards specific multicarbon products will likely be difficult as these steps occur after the kinetically difficult first C-C coupling step, but further investigation of the reaction elementary steps past this point are needed. With these goals in mind, we discuss some possibilities for influencing the performance of CO_2R systems.

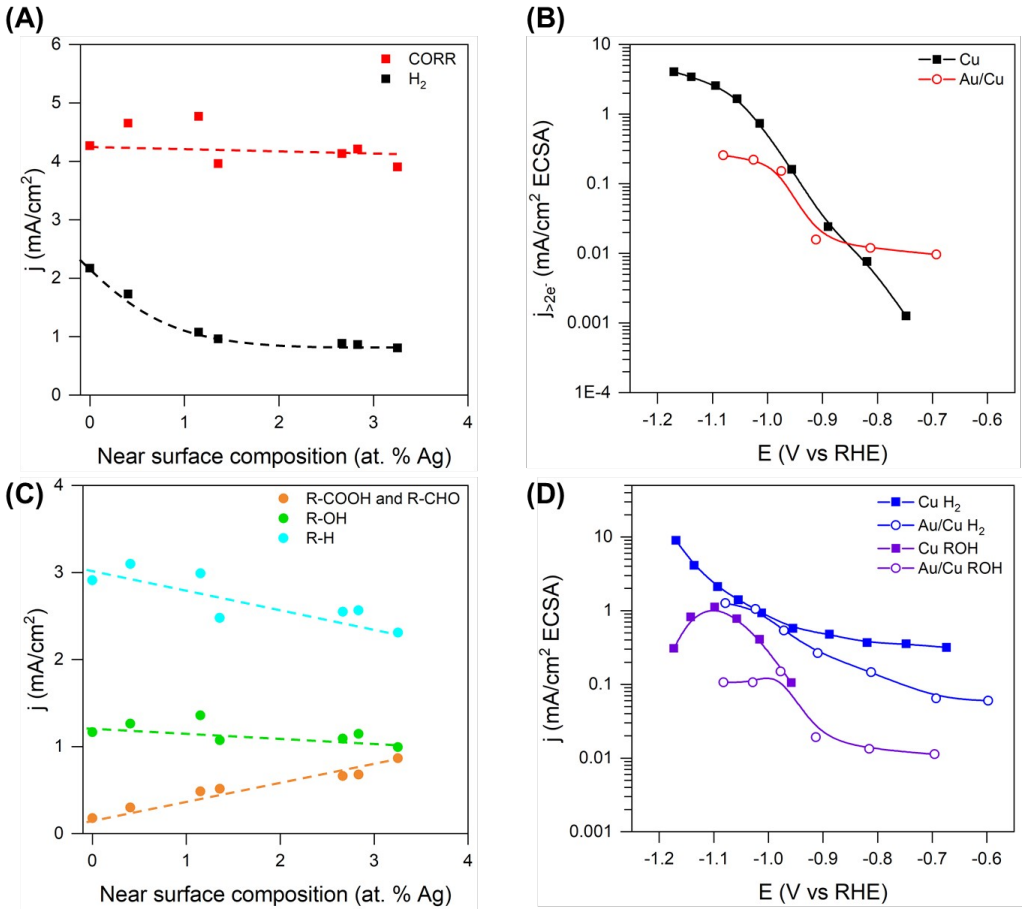

Figure 4: Effects of surface alloying on the product distribution of Cu catalysts. A) and C) show the effect of addition of Ag into the surface of a Cu(100) oriented thin film. While overall rates of >2e- products (CO reduction products) are relatively unaffected, rates of hydrogen evolution and hydrocarbon formation are reduced with Ag incorporation, while the rates of carbonyl and carboxylic acid formation are enhanced. B) and D) show the effect of Au addition to the product distribution of Cu. While the total activity to forming >2e- products is similar for all but the lowest potentials, the distribution of products is changed by Au addition, mainly due to lower rates of hydrogen evolution. Figures adapted with permission from Clark et al.[49] and Morales-Guio et al.[50].

Prospects for surface alloys

While demonstrable improvements in the overall activity of Cu catalysts through alloying are lacking, there are still opportunities for modifying the reactivity of Cu through the addition of a second metal. As mentioned above, bulk Cu alloys suffer from surface segregation, which result in a composition at the surface that is different from that in the bulk. One way to mitigate this issue is through the formation of a surface alloy, a catalyst in which the bulk is Cu and only the topmost layer of Cu contains a second metal. Since the second metal is not present in the bulk, adsorbates produced during reaction or pretreatment will not allow the formation of a shell of the

second metal. Few previous reports have studied the behavior of such materials for CO_2R. Notably, surface alloys of Cu and Ag have been shown to tune the product distribution over Cu without compromising overall activity.[49] The introduction of larger Ag atoms into the Cu lattice results in compressive strain. This strain leads to preferential destabilization of adsorbed hydrogen, resulting in a product distribution that favors oxygenates over more hydrocarbon products. Figure 4 illustrates similar shifts in product distribution towards alcohols and away from hydrocarbons for Au-promoted Cu.[50] In addition to this strain effect, these surface-modifying atoms can impact reactivity through electron transfer with Cu, ensemble effects, and by providing bifunctionality.[48] The fundamental properties of surface alloys of Cu have been studied in some detail in the context of so-called single atom alloys.[72-76] We suggest that this class of materials could yield interesting and enhanced performance for Cu catalysts.

Targeting other products of CO_2R

It is possible that the most efficient route for forming fuels and chemicals will not be via direct electrocatalytic reduction of CO_2. For example, selective production of CO from CO_2R and H_2 from water splitting can produce syngas that can be converted to a range of valuable products through well-established thermochemical routes. Figure 5 shows some possible pathways to produce fuels and chemicals from CO_2. It seems unlikely that direct production of syngas from CO_2R (i.e., unselective production of CO combined with HER) will be the most efficient approach, as the activity for HER under CO_2R conditions and catalysts is very low compared to the performance of conventional HER.[77] Preliminary assessments of the technoeconomic feasibility of obtaining different products from CO_2 have been reported by several authors.[78-80] While these analyses show that molecular building blocks which can be produced with high selectivity are most desirable, the conclusions are sensitive to both the model inputs and catalyst performance. Recent studies have also examined the possibility of coupling electrocatalytic CO_2R to biochemical processes to produce commodity chemicals and fuels that are currently inaccessible through direct CO_2R (e.g. isopropanol, butanol, 3-methyl-1-butanol).[81] Due to the uncertainty concerning which processes will be most impactful in practice, we suggest that the development of active, selective, and durable catalysts for producing different products of CO_2R (CO, $HCOO^-$, multicarbon products) should continue.

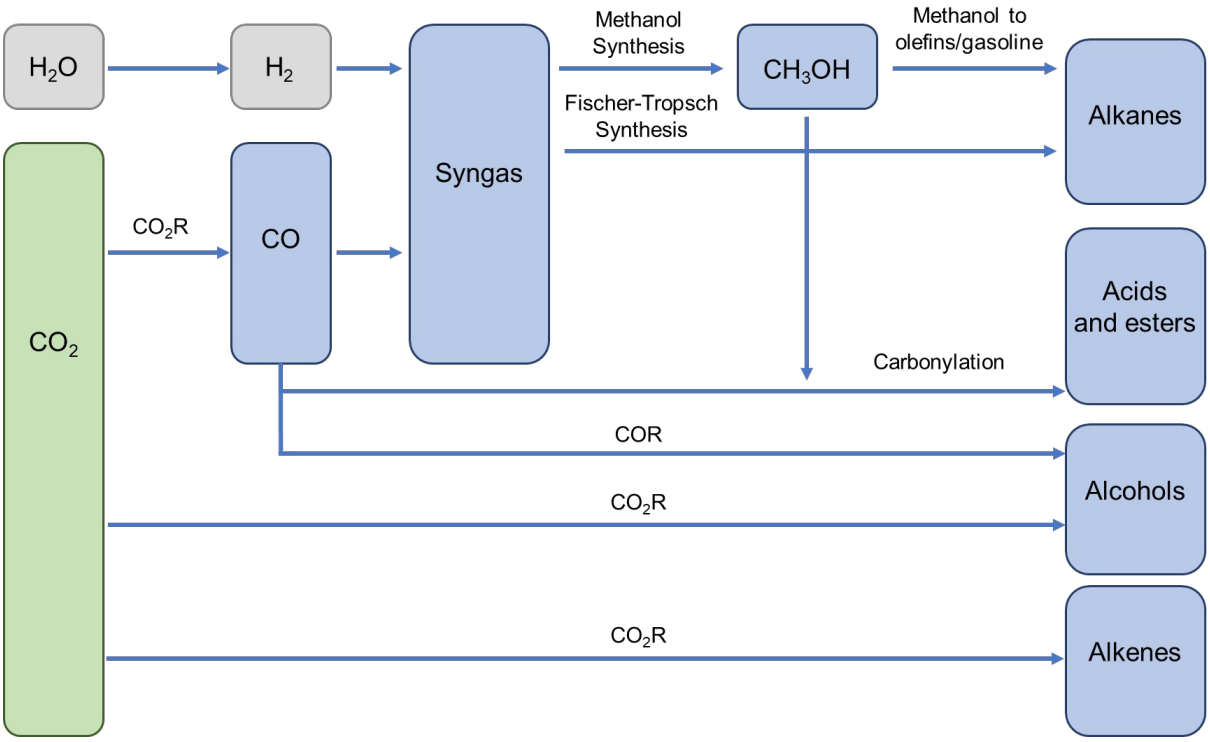

Figure 5: Possible routes to fuels and chemicals using CO_2R. Possible routes to renewable commodity chemicals driven by electrocatalysis from H_2O and CO_2 as feedstocks. Adapted with permission from De Luna et al.[78]

Enhancing the performance of CO_2 reduction beyond aqueous systems

Non-aqueous, liquid phase systems

The use of non-aqueous solvents to enhance the performance of CO_2R systems has been suggested.[82] The proposed benefits are often based on the higher solubility of CO_2 in solvents such as methanol or acetonitrile. While initially appealing, it is not clear that increased CO_2 solubility should fundamentally enhance CO_2R rates. The kinetic rate of CO_2R is dependent on the chemical potential of the reactant, dissolved CO_2, rather than its concentration.[83] As the solution is in phase equilibrium with the gas phase, the chemical potential of CO_2 in solution is equal to that of CO_2 in the gas phase. If the solvent is changed, the chemical potential of dissolved CO_2 remains fixed to the chemical potential of the gas it is in equilibrium with (i.e., 1 bar CO_2). Therefore, CO_2R kinetic rates should be independent of CO_2 solubility.

However, solvent composition can influence the kinetics of CO_2R.[84-86] The solvent may preferentially stabilize kinetically relevant transition states relative to their precursor state.[20,

87] If both reactant and transition states are similarly stabilized, the solvent will have no effect on activation barriers.[88] In cases where solvents influence measured rates, it is important to decouple the effects of solvent composition on intrinsic reaction kinetics from other effects. For example, water or a proton source is needed to yield hydrogenated products (i.e., products besides CO and oxalate) when aprotic solvents are used.[1] However, the addition of water makes it difficult to understand the electrode-electrolyte interface and what effects dominate observed reaction rates. More studies should be undertaken aimed at understanding the effects of solvent composition and how it can be used to tune activity and selectivity of Cu for CO_2R.

The promise of gas-fed reactor systems

While planar electrode assemblies (PEAs) are well suited for developing a deeper understanding of CO_2R and identifying promising electrocatalysts, they are not well suited for practical applications. The maximum current density attainable in a PEA is limited by mass transport through the electrolyte (< 10 mA/cm^2).[13] For CO_2R to be commercially viable, it is necessary to operate at current densities > 100 mA/cm^2.[80] This is achievable using gas-diffusion electrodes (GDEs), which exhibit significantly lower mass-transfer resistances for CO_2 and ion transport.[89-103] For practical application of CO_2R, it is also desirable to eliminate aqueous electrolytes, since at high current densities, the ohmic losses associated with the electrolyte contribute significantly to a loss of energy efficiency. This can be done using a membrane electrode assembly (MEA).[104, 105] In an MEA the catalyst layer (CL) is deposited onto a polymeric electrolyte or onto a gas diffusion layer (GDL) to form a GDE, which is then bonded to the electrolyte membrane. To provide pathways for ions to transit from the membrane to the CL in an MEA system, the nanoparticles of catalyst in the CL are coated with a thin layer of ionomer. Typically, this material has the same composition as the membrane. However, little is known about how the ionomer-catalyst interface influences the progress of reactions occurring on the catalyst surface. Understanding how ionomers influence catalytic activity could provide a means for controlling CO_2R through targeted modification of ionomer functionalities. These modifications could leverage recently developed understanding of how the reaction environment influences catalysis in the liquid phase.[17, 106, 107] There are additionally open questions in understanding mass transport and water management in these systems.[95, 104, 105, 108] We

anticipate that investigation of these questions will benefit from knowledge gained in the development of more mature electrochemical technologies, such as fuel cells and electrolyzers. It is also worth noting that high temperature CO_2R in solid-oxide electrolysis cells represents an alternative and promising approach to low temperature systems.[109]

Concluding remarks

Producing high-value fuels and chemicals in a sustainable way via electrochemical CO_2R coupled with a renewable source of electricity remains an attractive goal. In this perspective, we have summarized the state of catalyst design efforts for Cu catalysts capable of producing valuable products and future opportunities for enhanced performance.

While limited advances have been made in improving the intrinsic activity of Cu catalysts, opportunities still exist for the development of CO_2R systems. To improve the activity of Cu catalysts, bimetallic catalysts that mitigate the problems introduced by surface segregation should be investigated more thoroughly. Stable surface alloys of Cu should enable the formation of multicarbon products while modifying the selectivity and activity compared to pure Cu. While direct production of hydrocarbons or alcohols is particularly appealing, it is also possible that the most efficient systems may make use of tandem processes where CO_2 is first converted to CO, followed by further transformation.[110]

In parallel to the development of new active and selective catalysts, work should continue on the development of gas-fed CO_2R reactor systems capable of operation at high current densities. These systems have already shown promising performance. We expect that increased fundamental understanding of the transport processes in these reactors, and the nature of the environment surrounding catalytic active sites will help in the design of reactor components (catalysts, membranes, supports, electrolytes) and the choice of operating conditions.

While many challenges remain in the development of CO_2R systems with sufficient activity, selectivity, stability, and scalability for practical application, there is reason to remain optimistic. Significant progress has been made in developing fundamental understanding of this process, and we expect that with continued research, the electrochemical reduction of CO_2 will enable sustainable production of chemicals and fuel.

Outstanding questions

- Extensive efforts aimed at increasing the intrinsic catalytic activity of Cu catalysts for producing multicarbon products from CO_2 have been largely unsuccessful. How do we design stable and active catalysts that are selective for desired multicarbon products?
- The environment surrounding catalytic active sites can significantly affected measured performance. How can we develop experimental and computational tools for understanding effects of the electrochemical environment on catalysis, both in aqueous and non-aqueous systems?
- How can we leverage knowledge from fuel cell and electrolyzer technologies to rapidly develop highly efficient gas-fed CO_2 reduction systems?

Highlights

- Standard practices are necessary for accurate assessment of catalytic performance for CO_2 reduction
- Catalyst design efforts aimed at improving the activity of Cu for CO_2 reduction have been largely unsuccessful
- Opportunities remain for modifying Cu through formation of surface alloys
- For practical application of CO_2 reduction, transition to gas-fed systems is necessary
- Increasing fundamental understanding of surface chemistry will continue to aid the development of efficient CO_2 reduction systems

Glossary

Faradaic efficiency (FE): The fraction of total charge used in a specific Faradaic process (to produce a certain product).

Mass transport limitations: For reaction to occur, reactants must be transported to and products transported from the catalyst surface. When surface reaction rates become sufficiently high, overall measured rates will be influenced by these transport processes, masking the intrinsic kinetic behavior of the catalyst surface. Under conditions of mass transport limitations, the conditions in the electrolyte (pH, concentration of CO_2) near the catalyst surface will differ significantly from the bulk solution.

Tafel slope: Defined by the Tafel equation that relates applied potential and current density:
$\eta = a + b \log(j)$
Where η is the overpotential or the difference between the electrode potential and the standard potential, a is the exchange current density, b is the Tafel slope, and j is the current density. The Tafel slope quantifies the sensitivity of the current density to the applied potential. In principle,

experimentally observed Tafel slopes can be compared with theoretically derived slopes based on a microkinetic model.

Turnover frequency (TOF): The number of molecules of a specified product made per catalytic site per unit time. TOFs generally depend on electrode potential, reactant concentration, temperature, etc.

Conflict of interest statement: The authors declare no conflicts of interest.

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