Controlled Substrate Transport to Electrocatalyst Active Sites for Enhanced Selectivity in the Carbon Dioxide Reduction Reaction

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The selective electrochemical reduction of CO_2 to value added products is a useful strategy for the local storage of intermittent energy sources as chemical fuels and the recycling of industrial CO_2 waste into industrial feedstocks. This review highlights some of the recent research focused specifically on modulating substrate delivery and local catalyst environment to enhance reaction and product selectivity in the CO_2 reduction reaction by both solid-state materials and discrete molecular systems. We discuss recent studies that focus on (1) using nanostructured and mesoporous solid-state electrocatalysts to modulate local pH and CO_2 concentrations near active sites, (2) coating electrocatalysts with porous overlayers to directly control substrate delivery to the electrocatalyst surface, and (3) using polymer encapsulation to modify the coordination environment surrounding molecular electrocatalysts to enhance activity and selectivity for CO_2 reduction. We believe that increased research in controlling substrate delivery to enhance reaction and product selectivity for the CO_2 reduction reaction is a promising strategy for designing new electrocatalytic systems for the selective and efficient conversion of CO_2 to value-added products.

Keywords: carbon dioxide reduction, electrocatalysis, proton transport, substrate transport, polymer encapsulation

1. Introduction

The *selective* electrochemical conversion of CO_2 in the carbon dioxide reduction reaction (CO_2RR) offers an intriguing approach for the local storage of intermittent energy sources as chemical fuels (e.g. solar fuels) and for the recycling of industrial CO_2 waste into useful chemical feedstocks.[1-12] However, developing electrocatalytic systems that show promising *reaction selectivity* for the CO_2RR over competitive side reactions like the hydrogen evolution reaction (HER) and show promising *product selectivity* for the formation of single C-containing products remains a fundamental challenge in CO_2 conversion technology. State-of-the-art polycrystalline Cu electrocatalysts show high activity for the CO_2RR but tend to operate with low selectivity, generating up to 16 different C-based products as well as H_2.[13-17] Planar Au and Ag catalysts are more selective for CO_2 reduction to CO, but this increased selectivity is potential dependent and the systems still suffer from the competitive HER.[14,18,19] The desire for enhanced reaction and product selectivity for the CO_2RR has been the focus of intense research over the past few decades as has been summarized in several reviews.[2,5-7,14,17,19-49]

Enzymatic systems such as NiFe carbon monoxide dehydrogenase (CODH) provide fundamental insight for the design of electrocatalytic systems that operate with high activity and product selectivity.[6,50] In these biological systems, fast catalytic activity and high product selectivity are achieved by carefully controlling the primary, secondary, and outer coordination spheres of the enzyme's active site. Of particular importance in enzymatic systems is the use of the outer-coordination sphere to exclude solvent (e.g. H_2O) from the active site, which is crucial for the stabilization of catalytic transition states[51,52] and for the controlled delivery of substrate.[6] For example, in the case of NiFe CODH, coordination of CO_2 to the 2 e^- reduced NiFe active site is thought to occur at the coordinatively-unsaturated Ni^I site, and the coordinated CO_2 is stabilized by H-bonding interactions with lysine and histidine moieties in the secondary coordination sphere (Figure 1).[6,53,54] Subsequent protonation and loss of water leads to the initial formation of a reduced CO_2 intermediate bridged by the Ni and Fe sites and the eventual cleavage of a C-O bond to form a $Ni^{II}CO$ species, which then releases CO.[6] Note that in this system, the active site resides in a hydrophobic core and H^+ delivery is carefully controlled through H^+ relays in the outer-coordination sphere. The control of primary, secondary, *and outer* coordination spheres in this system is essential for catalytic activity and selectivity.

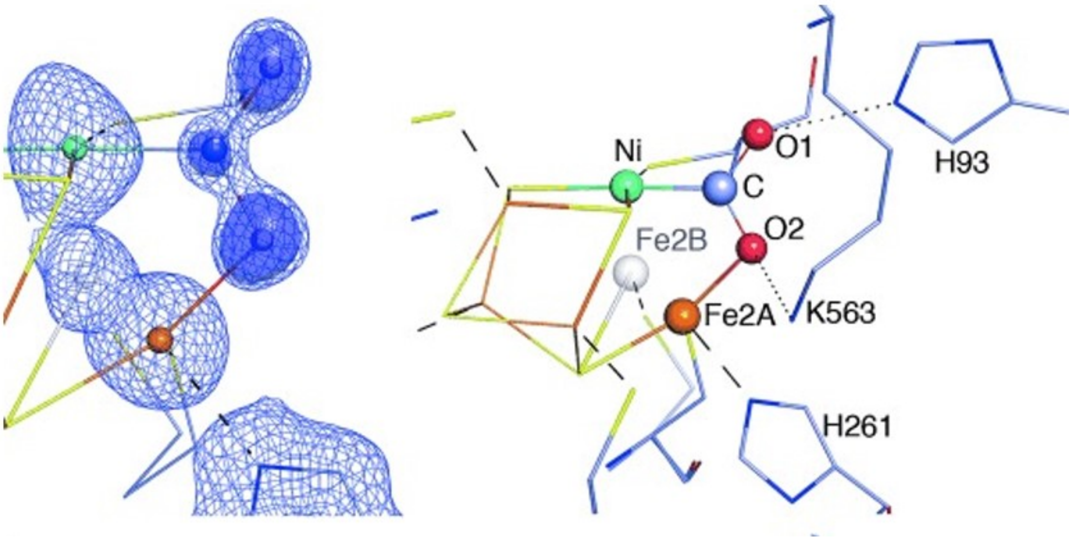

Figure 1. The proposed structure of coordinated CO_2 to the NiFe CODH active site. The CO_2 adduct is stabilized by H-bonding from histidine and lysine residues in the secondary coordination sphere. H^+ delivery to the active site is controlled through proton-relays in the protein structure. Adapted with permission from Ref. [54].

One way to increase product selectivity in the CO_2RR is to modulate the local concentration of CO_2 and H^+ near the electrocatalytic active sites in a manner similar to enzymatic systems. During electrolysis, depletion of electroactive species at the electrode surface gives rise to innate concentration gradients due to diffusion limited replenishment of both species (Figure 2). These gradients result in lower CO_2 concentration and higher pH near the electrode surface compared to bulk solution during the CO_2RR process. The extent of these gradients depends on numerous factors: bulk CO_2 concentration, solution pH, buffer concentration and composition, solution convection, etc. However, there has been a recent interest in the CO_2RR community to develop systems that purposely control the transport of CO_2 and H^+ to electrocatalyst active sites and/or control the coordination environment surrounding these electrocatalyst active sites as a means of enhancing CO_2RR selectivity.

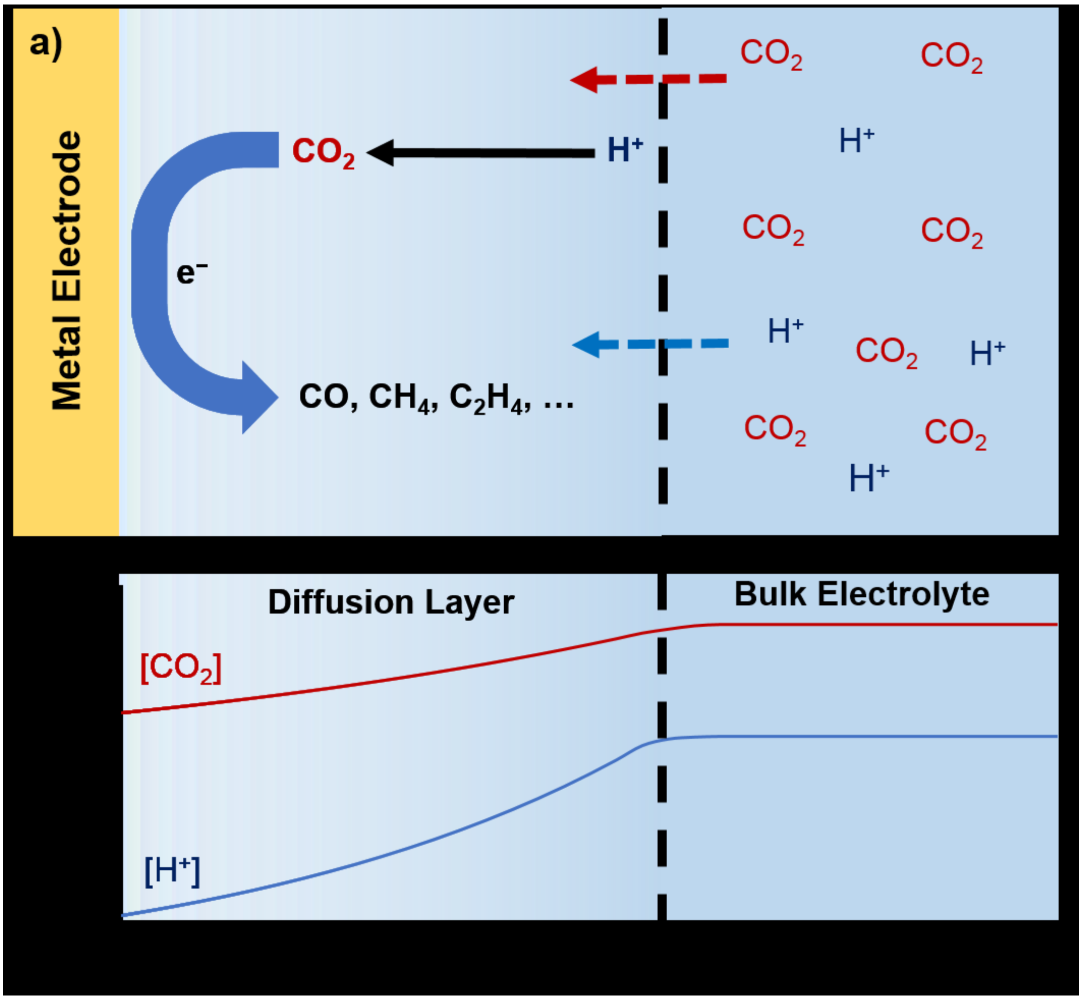

Figure 2. a) Schematic illustrating CO_2 and H^+ transport to and consumption at a metal electrode surface during the CO_2RR, and b) the resulting concentration gradients for CO_2 and H^+.

This review highlights some of the recent research focused specifically on modulating substrate delivery and local catalyst environment to enhance reaction and product selectivity in the CO_2RR by both solid-state materials and discrete molecular systems. We begin our discussion focusing on the importance of local H^+ concentration near the catalyst surface on reaction mechanism and product selectivity for C-containing products by solid-state metal electrocatalysts. We also the highlight recent studies in which porous oxide and polymer overlayers on metal electrodes are used to control substrate delivery and protect electrocatalyst surfaces from solution contamination and poisoning. Finally, we discuss new research using polymer-encapsulation of molecular electrocatalysts to directly control both substrate transport to and coordination environment surrounding catalyst active sites to promote increased activity and selectivity for the CO_2RR.

1. Effect of Local pH and Local CO_2 Concentration on CO_2RR Selectivity at Solid-State Metal Electrocatalysts

During the CO_2RR, H^+ are consumed in the formation of the various CO_2RR products as well as through the competitive hydrogen evolution reaction (HER). The consumption of H^+ results in increased local pH near the electrode surface[55-60] For unbuffered systems at intermediate bulk pH ($10 > pH > 4$), the effective local pH rapidly increases to above pH = 10 when consuming H^+ during the HER at 1 mA cm^{-2} current density.[55] The addition of a pH buffer into the system can mitigate this increase in local pH, with the extent of the mitigation depending on the buffer capacity.[55,61] Local pH is important not only in controlling the supply of H^+ to the catalyst active site, but also in determining the local concentration of dissolved CO_2 due to the pH dependence of CO_2 solubility and the CO_2/HCO_3^- equilibrium.[56,57,62] A recent study modeling CO_2 concentration and local pH at an electrode surface during CO_2RR in 0.1 M bicarbonate solution as a function of both current density (e.g. H^+/CO_2 consumption rate) and time (Figure 3) illustrates the effects of substrate consumption on local pH and local CO_2 concentration.[56] As the CO_2RR reaction proceeds, both H^+ and CO_2 are consumed, leading to increased local pH and decreased local CO_2 concentration. The extent of the change in local concentration depends on the current density and the duration of the reaction.

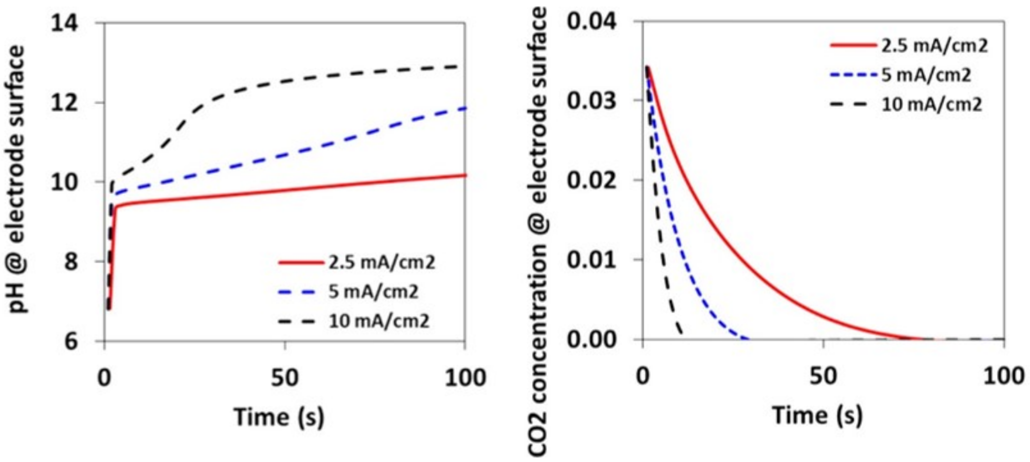

Figure 3. (left) Local pH and (right) local CO_2 concentration at the electrode surface as a function of time in a CO_2-saturated bicarbonate buffer at different operating current densities.[56] Adapted with permission from Billy, J. T.; Co, A. C. *ACS Catal.* **2017**, *7*, 8467-8479. Copyright 2017 American Chemical Society.

Several recent studies have focused on understanding the role of bulk pH and local pH near the electrode surface on the mechanism of the CO_2RR by Cu electrocatalysts. One such study investigated the effect of bulk pH on product distributions for the CO_2RR at Cu(111) and Cu(100) electrocatalysts in buffered and unbuffered solutions.[16] In particular, they showed that at intermediate bulk pH, the onset potential vs NHE of the 8 e^- reduction of CO_2 to CH_4 on Cu(100) and Cu(111) surface is pH dependent on both surfaces, whereas the onset potential vs NHE for the 12 e^- reduction of CO_2 to C_2H_4 on a Cu(100) surface is pH-independent.[16] This suggests that rate-limiting step for CO_2 reduction to CH_4 on Cu(100) and Cu(111) involves a proton transfer event (such as the formation of a CHO species), whereas CO_2 reduction to C_2H_4 on a Cu(100) surface operates via a pH-independent rate limiting step (such as the formation of a surface CO dimer) as shown in Figure 4.[16] CO_2 reduction to C_2H_4 on Cu(111) surfaces shows a pH dependence similar to that for CO_2 reduction to CH_4, suggesting there also exists a pH-dependent pathway for C_2H_4 formation on this crystal facet that shares a common intermediate with CH_4.[16] The proposed mechanisms from these pH-dependent studies are consistent with other experimental[63-66] and computational[67,68] mechanistic investigations.

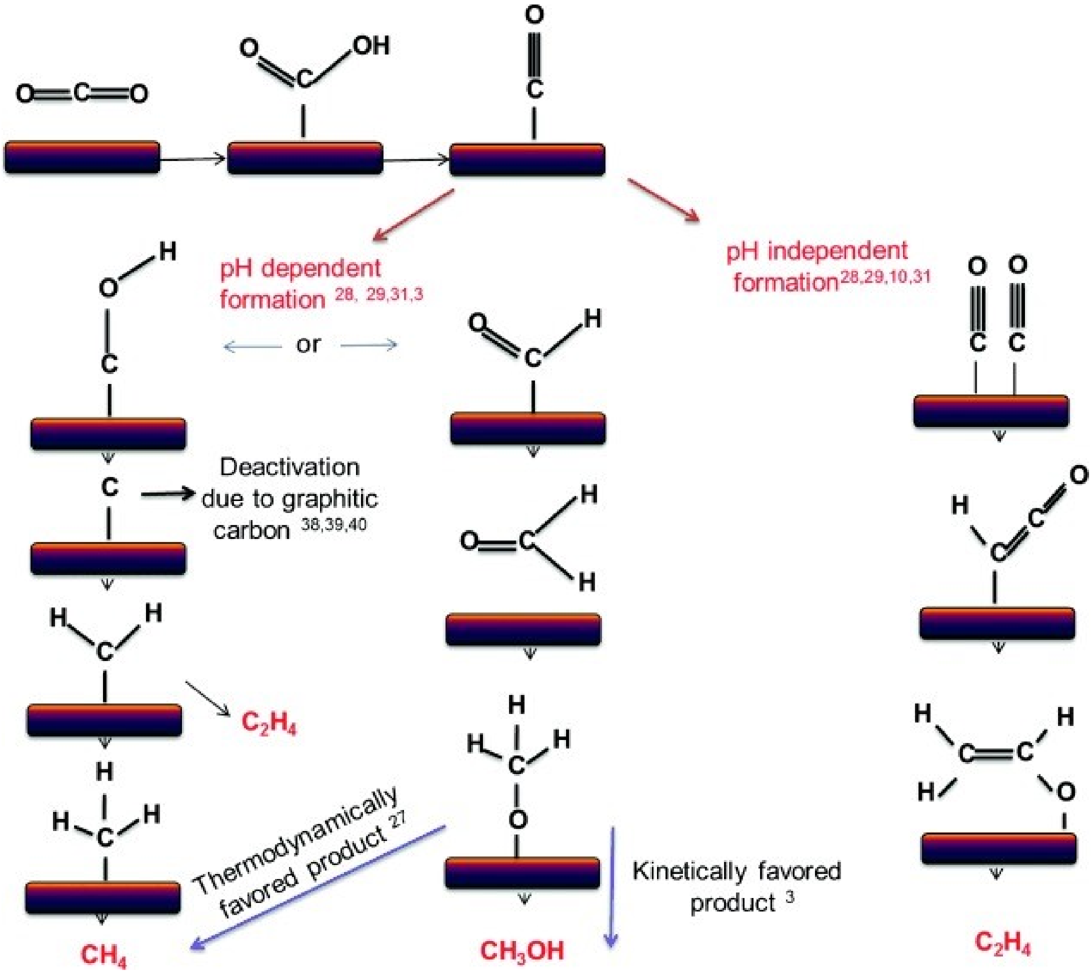

Figure 4. Proposed mechanisms for the CO_2RR to different products showing the pH-dependent pathways for the formation of CH_4, and CH_3OH, and the pH independent pathway for the formation of C_2H_4. Reprinted with permission from Reference [69].

The local pH and the extent of the change in local pH during CO_2RR predominantly depend on the buffer capacity of the electrolyte. Buffer capacity has significant effect on CO_2RR product distributions not only on planar Cu metals,[63,66] but also on other Cu-based catalysts. The change in production distribution using Cu nanoparticles was investigated in various concentrations, which dictate the buffer capacity, of bicarbonate buffers. They showed that as the bicarbonate concentration was increased from 0.1 M (weaker buffer capacity) to 0.5 M (stronger buffer capacity), there was a corresponding increase in CH_4 production and decrease in C_2H_4 production.[69] These results are consistent with the findings of several other studies including studies on CO reduction.[16,56,60,70] Although increasing bicarbonate concentration increases bulk pH, it also increases the buffering capacity of the solution which allows for fast replenishment of the consumed H^+ near the electrode surface. This means that at higher buffer capacity, the local pH near the electrode surface is closer to that of bulk, favoring the production of pH-dependent CH_4 and H_2, whereas at lower buffer concentrations the local pH near the electrode surface increases, leading to increased formation of pH-independent products such as C_2H_4 (Figure 5).[69] The authors also showed that increasing CO_2 pressure increases the Faradaic efficiency for C_2H_4 from the CO_2RR (Figure 5).[69] This observation is consistent with a rate-limiting CO dimerization step for the CO_2RR to C_2H_4—as the bulk CO_2 concentration increases, the relative coverage of *CO adducts on the surface also increases, leading to an increased probability of CO dimerization. Another recent study has suggested there is a competition between forming surface *CO and *H on Cu surfaces, and increased Faradaic efficiency for C_2H_4 production at increased CO_2 pressures is due to suppression of CH_4 and H_2 production rather than increased rate of C_2H_4 production. This is because at higher CO_2 pressures, there is a larger surface concentration of *CO adsorbed to Cu active sites resulting in a lower surface concentration of *H.[71] This led to a decrease in CH_4 and H_2 production which require surface *H, but there was no corresponding increase in C_2H_4 production rate.[71] This competition for active sites between CO_2RR and HER is consistent with studies that have shown HER is suppressed in the presence of CO_2, and that this suppression is enhanced with increased local concentration of CO_2. [72,73]

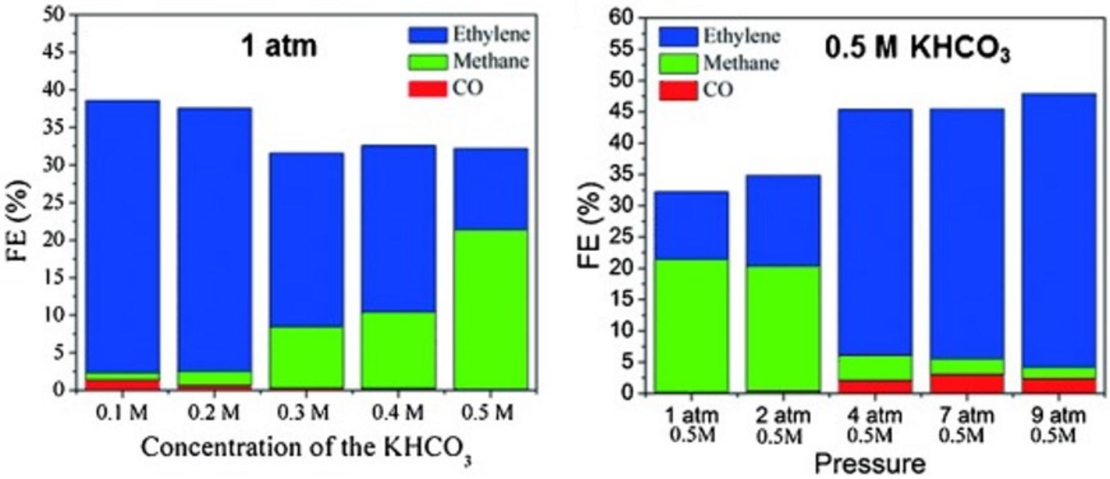

Figure 5. Product distributions for the CO_2RR on Cu nanoparticle catalysts as a function of (left) buffer concentration and (right) CO_2 pressure. Adapted with permission from Reference [69].

In another study, a rotating disk electrode assembly was used to control the transport of substrate to a Cu disk electrode in bicarbonate buffered solutions and studied the effects of rotation rate on CO_2RR product distributions.[74] As the rotation rate of the electrode increases, there is a corresponding decrease in the formation of CH_4 and an increase in the formation of CO and H_2.[74] The authors attribute this change in product distribution to changes in local pH and local CO_2 and CO concentrations. The increase in CO production with faster rotation rates is due to the weakly adsorbed *CO leaving the electrode surface before it is further reduced to other hydrocarbons. The increase in HER at faster rotation rates is attributed to the decrease in surface CO coverage, thus increasing the number of active sites for proton reduction.[74] Other studies using rotating disc voltammetry showed that the HER is inhibited by surface adsorbed CO, which blocks active sites for water reduction. This inhibition becomes more pronounced as transport of CO_2 is improved.[73] These studies once again highlight the importance of controlling mass transport in CO_2RR to improve reaction selectivity and product distribution.

The identity of the cation associated with the buffer system has also been observed to alter the product distribution during the CO_2RR on Cu surfaces,[14,75] and this may be partially due to local pH effects, although the exact mechanism is not clear. A recent study investigated the product distribution for CO_2RR on Ag and Cu surfaces in CO_2-saturated bicarbonate solutions as a function of cation size ($Li^+ \rightarrow Cs^+$).[76] An increase in CO production and decrease in competitive HER on Ag electrodes was observed when increasing the cation size from Li^+ to Cs^+. When exploring CO_2RR on Cu electrodes, the authors found that rate of production of highly-reduced C_2 products such as C_2H_4 and CH_3CH_2OH increase as cation size increases (Figure 6), although interestingly the rates of CO and H_2 production are unaffected.[76,77] One hypothesis provided by the authors to explain this observation is that larger cations have higher buffering capacity than smaller cations and are able to keep local pH sufficiently low to retain higher concentrations of CO_2 near the electrode and available for reduction.[76] Higher CO_2 concentrations near the electrode surface would account for increased CO production at Ag electrodes, and also for increased production of C_2 products at Cu electrodes. However, this argument disagrees with other mechanistic studies that suggest low local pH favors HER and CH_4 production because of a pH-dependent reaction mechanism.[16,63-68] An alternative explanation is that the interaction between solvated cations and adsorbed species on the electrode can stabilize intermediates such as $*CO_2$ and $*CO$, therefore increasing the product selectivity towards CO and hydrocarbons, and this is supported by DFT calculations.[77] Although the exact explanation is still unclear, cation identity had been experimentally shown to affect product distribution in CO_2RR.[76,77]

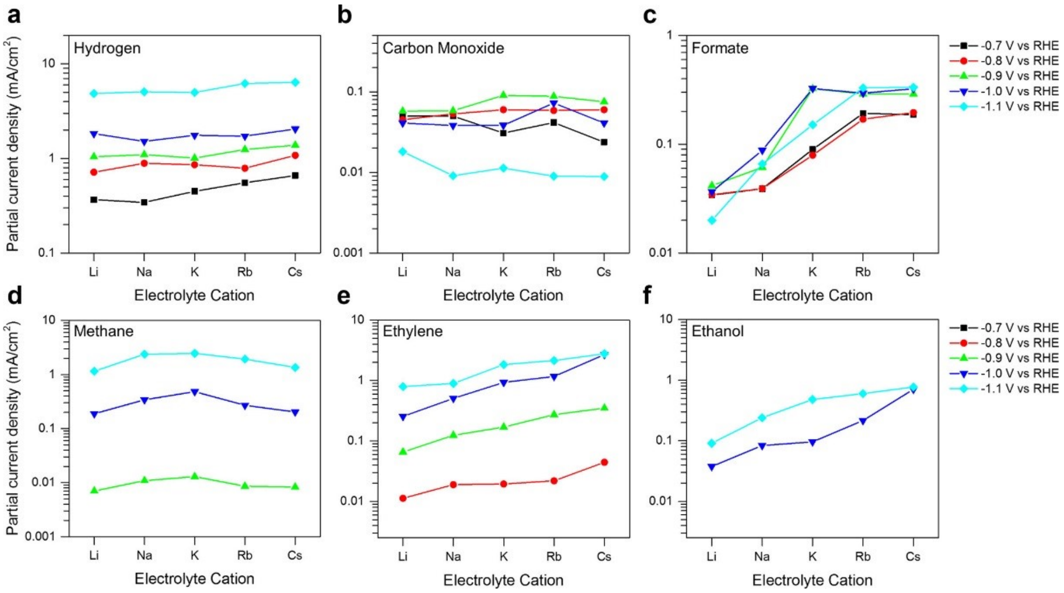

Figure 6. Partial current densities (e.g. rates of production) for various CO_2RR products as a function of electrolyte cations. As the size of the electrolyte cation increases, there is increased production of HCOOH and the C_2 products C_2H_4 and CH_3CH_2OH.[77] Reprinted wih permission from Resasco, J.; Chen, L. D.; Clark, E.; Tsai, C.; Hahn, C.; Jaramillo, T. F.; Chan, K.; Bell, A. T. *J Am. Chem. Soc.* **2017**, *139*, 11277-11287. Copyright 2017 American Chemical Society.

Researchers have also designed nanostructured and porous catalyst systems to better control local pH to increase CO_2RR product selectivity. In one series of studies, mesoporous Ag and Au catalysts have shown high selectivity for CO_2RR to CO over the competitive HER.[78,79] For instance, in the case of mesostructured Ag films, as the roughness factor is increased by growing thicker porous films, there is a corresponding increase in CO production from the CO_2RR and a decrease in competitive HER (Figure 7).[79] This reaction selectivity is attributed to increased local pH within the porous catalyst that suppresses HER and promotes CO_2 adsorption on the metal surfaces.[78,79] In another study, Cu nanoparticles deposited onto a high-surface area carbon paper support showed higher activity for C_2+ products than the same nanoparticles deposited at similar loadings onto a planar graphite plate.[80] The authors suggest the increased activity for C_2+ products for the Cu nanoparticles on the high-surface carbon paper may be due to increased local pH.[80] Likewise, studies of the effects of surface roughness on C_2H_4 production have shown a general increase in C_2+ products with increasing surface roughness, which has been attributed to an increase in local pH.[81,82] However, there was an optimal roughness beyond which the local pH was thought to increase too much, decreasing local CO_2 concentration, thus inhibiting CO_2RR.[82] It is important to note that other factors may contribute to increased activity for more highly-reduced products in porous and nanostructured materials including increasing numbers of defect sites or grain boundaries[83-87] and the mobility of reaction intermediates.[88]

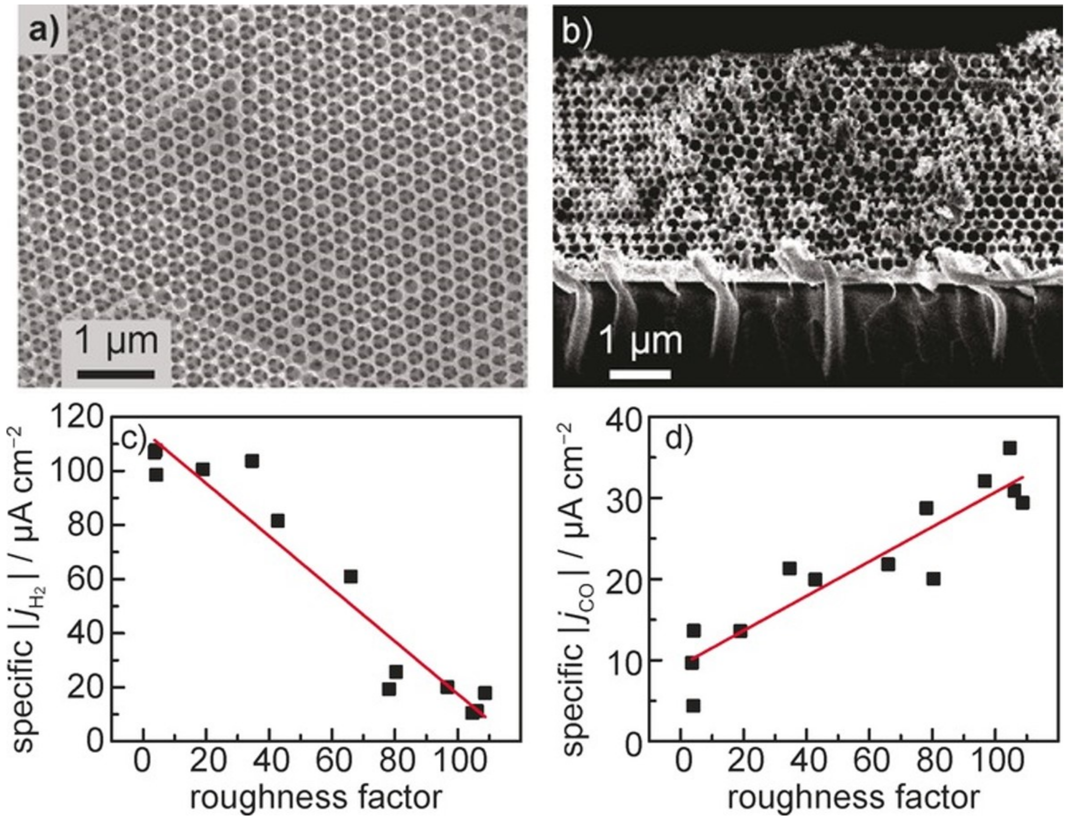

Figure 7. a) Top down and b) cross-sectional SEM images of a mesostructured Ag film with ~200 nm voids interconnected by ~50 nm diameter channels. c) H_2 production shown here as a specific current density j_{H2}, decreases with increasing roughness factor, and d) CO production increases with increasing roughness factor. Adapted with permission from Reference [79].

The effects of pH on product distributions are also evident on single-site catalyst systems. For instance, in the CO_2RR by Fe-N-C systems—porphyrin-like Fe-N_4 active sites embedded within extended graphite structures—the rate of formation of H_2 and CH_4 are both dependent on the solution pH. The rates decreases with increasing pH in a trend qualitatively similar to that observed on Cu surfaces.[59] In contrast, CO formation in this system was found to be independent of pH, suggesting CO is formed through decoupled electron-proton transfer process.[59]

3. Using Overlayer Films to Control Substrate Transport and Influence CO_2RR Selectivity

One approach to controlling local pH and CO_2 concentration near catalyst active sites is to coat solid-state electrocatalyst surfaces with porous overlayers that directly control substrate transport to the catalyst surface (Figure 8). Overlayers have been used extensively to control stability and efficiency for the electrocatalytic oxygen reduction reaction (ORR)[89-91] and the HER,[92,93] but are far less prevalent in the CO_2RR literature. However, overlayer-coated electrodes hold significance promise as electrocatalyst systems for enhanced CO_2RR reaction and product selectivity. For example, a recent DFT study on porous graphdiyne (GDY) coated Cu surface suggests that the GDY overlayer decreases reaction barriers and onset potential of CO_2RR intermediate steps, which enhances the performance of metal catalyst.[94] The GDY coating is thought to interact with CO_2 and increase local CO_2 concentration near the Cu surface. It may also stabilize *CO intermediates on the Cu surface favoring the subsequent reduction of *CO to CH_4.

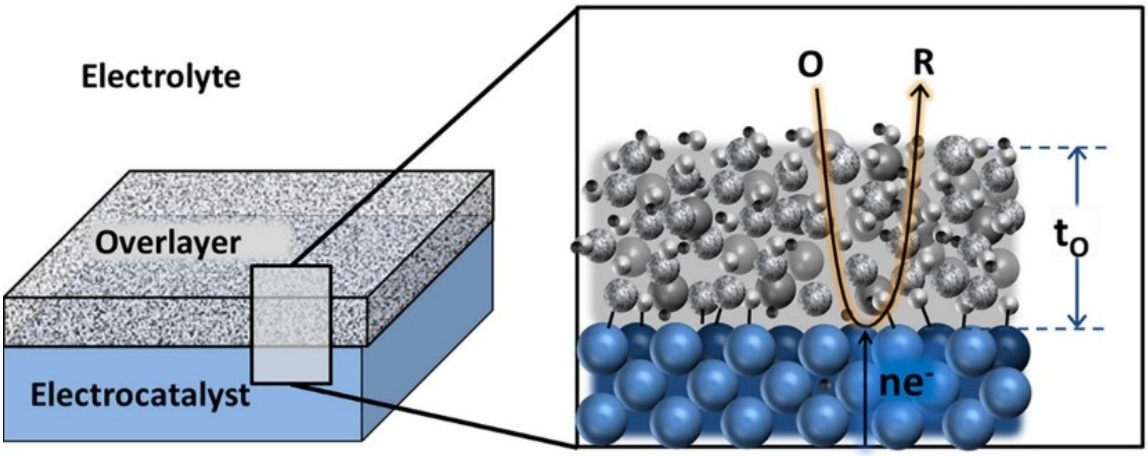

Figure 8. Illustration of an overlayer-coated electrode showing controlled substrate transport through the overlayer film to the electrocatalyst surface.[95] Adapted with permission from Esposito, D. V. *ACS Catal.* **2018**, *8*, 457-465. Copyright 2018 American Chemical Society

Polymer-coated catalysts are a specific subset of overlayer-coated electrodes which have been used to modulate the activity, product distribution, and stability of electrocatalysts for various electrocatalytic reactions including the CO_2RR.[96] The polymer films can impart significant benefits on the electrocatalysts by controlling substrate transport, stabilizing the reaction intermediate, and protecting against contaminants.[95,96] When polymer-coated catalysts are used to enhance the CO_2RR, the hydrophobicity of polymer films can increase local CO_2 concentration near catalytic active sites and limit the transport of protons, thus enhancing the CO_2RR and suppressing the competitive HER.

For example, studies of CO_2RR by Cu surfaces coated with electropolymerized polypyrrole (PPy) films show a shift in the product distribution of CO_2RR towards more highly-reduced hydrocarbons while suppressing H_2 production.[97] The authors propose that the polypyrrole films decreases the concentration of H^+ and causes a change in the mechanism of the CO_2RR to a surface hydrogenation of CO_2 intermediates rather than sequential electron and proton transfer events.[97] Similar enhancement of the CO_2RR and suppression of the HER have been shown for MoS_x nanoparticle incorporated within polyethylenimine (PEI)-modified reduced graphene oxide films.[98] PEI is thought to suppress the HER by inhibiting H_2 formation,[98] and also to stabilize reaction intermediates through secondary-coordination sphere effects.[98,99] In the case of the CO_2RR on poly-4-vinylpyrydine (P4VP) coated Cu electrodes, P4VP is postulated to coordinate with reduced Cu sites on the surfaces to form active Cu^{II}-P4VP complexes which strongly interact with CO_2. This polymer-coordination on the surface facilitates the formation of surface-CO_2 intermediates and limits the available sites for interactions with H^+, thus preferentially favoring the CO_2RR and suppressing the HER.[100]

Because of their hydrophobicity, polymer films can also increase local CO_2 concentration and stabilize reactive intermediates. For instance, it’s thought that polymers such as P4VP and PEI might stabilize the formation of $CO_2{\bullet}^-$ radical anions either through direct electrostatic interactions between $CO_2{\bullet}^-$ and protonated sites on the polymer,[98,99] or by forming a local non-aqueous environment which facilitates formation of the radical anion species.[100,101] In addition, polymer films may increase the lifetime of desorbed intermediates. For example, Re surfaces coated with electropolymerized PPy films show increased activity for CO_2RR to CH_4 compared to bare Re.[102] It has been postulated that this increased activity for CH_4 production may be due to trapping of desorbed CO within the PPy matrix which increases the probability of CO re-adsorption and subsequent reduction to CH_4.[102]

Coating electrode surfaces with porous overlayers can also play an important role in decreasing transport of contaminants to the electrode surface and thus preventing electrode poisoning and deactivation.[93,95,103] This is particularly important for CO_2RR at Cu surfaces which are extremely susceptible to surface poisoning,[14,104] especially by trace metal contaminants in the electrolyte solutions.[104-106] A recent study of CO_2RR by P4VP-coated Cu electrodes for the CO_2RR found that P4VP can act as a sink for heavy-metal contaminants in standard purity (99.7+ %) electrolytes, thereby decreasing the effect of the metal contaminants on the electrocatalytic activity and product distribution.[100]

4. Selective CO_2RR by Polymer-Catalyst Composite Films

In addition to serving as porous overlayers that control substrate transport to catalyst active sites, polymers can also be used to modulate the coordination environment of metal-macrocyclic complexes to increase their activity and selectivity for the CO_2RR. There are two common strategies for heterogenizing molecular catalysts within polymer films: 1) electropolymerization of metal complexes in which the molecular catalysts are directly incorporated into the polymer structure, and 2) polymer encapsulation in which the molecular catalyst is confined within a coordination polymer. The resulting polymer-catalyst composite films typically retain the main advantages of molecular electrocatalysts—including high selectivity for single products, single active sites, and tunable structures—while increasing effective charge transfer to the catalyst sites and increasing catalyst stability.

For electropolymerized catalyst-polymer composite films, 2-electron reduced products such as CO and HCOOH are the most common CO_2RR products in both aqueous and organic electrolyte solutions.[96,107-112] More highly-reduced products (e.g. CH_4, CH_3OH, and C_2H_6) have been achieved by some polymeric structures,[113-116] especially systems with bimetallic or multimetallic active centers that can stabilize CO_2RR intermediates and/or facilitate C-C coupling.[113,117,118] However, proton-delivery can also play an important role in these systems. For instance, electropolymerized films of Co-polyvinylterpyridine complexes show selective CO_2RR towards the 2-electron production of HCOOH in non-aqueous solutions (DMF and acetonitrile),[112,119] but these films reduce CO_2 by 4-electrons to formaldehyde in aqueous sodium perchlorate electrolytes.[120] It is postulated that the difference in the CO_2RR products in non-aqueous and aqueous electrolytes is due to proton-transport—when non-aqueous electrolytes are used, CO_2RR is limited by a lack of H^+ which results in release of HCOOH before it can be further reduced to HCHO.[120] It's also worth noting that the electrocatalytic activity per active site decreases with increasing film thickness, presumably due to poor electron transport through the non-conducting polymer films.[120]

Polymer-encapsulation of molecular catalysts is another way to promote selective CO_2RR by composite catalyst-polymer films. In this case, the polymers can influence the activity of the molecular catalysts through numerous effects including primary coordination sphere effects such as axial-coordination to the metal active sites, secondary-coordination effects such as H-bonding interactions, and outer-coordination sphere effects such as controlled delivery of H^+ and CO_2 to the active sites.[121-126] A polymer-encapsulated system of particular interest to our group is cobalt phthalocyanine (CoPc) immobilized within poly-4-vinylpyridine (P4VP) films (Figure 9). CoPc-P4VP composite films have been shown to have enhanced CO_2RR activity and selectivity compared to the parent CoPc.[122-124] It was postulated that the enhancement in CO_2RR activity and selectivity was due to three synergistic effects imbued by the P4VP polymer.

First, the pyridyl groups in P4VP can axially-coordinate to the Co metal center and facilitate CO_2 binding and reduction.[124] This is consistent with studies that show when σ-donating ligands such as pyridines or imidazoles are coordinated to metal porphyrin and phthalocyanine complexes, the resulting systems show an increase in catalytic activity for CO_2 reduction and O_2 reduction.[127-130] In addition, the polymer membrane can stabilize reduced CO_2 intermediates through H-bonding interactions with protonated pyridyl moieties. This proposed secondary-coordination sphere stabilization of reactive intermediates is analogous to that reported in several other studies of synthetic molecular catalysts.[131-135] Finally, the P4VP film can modulate H^+ transport to the active sites by using the pyridyl moieties as proton relays.

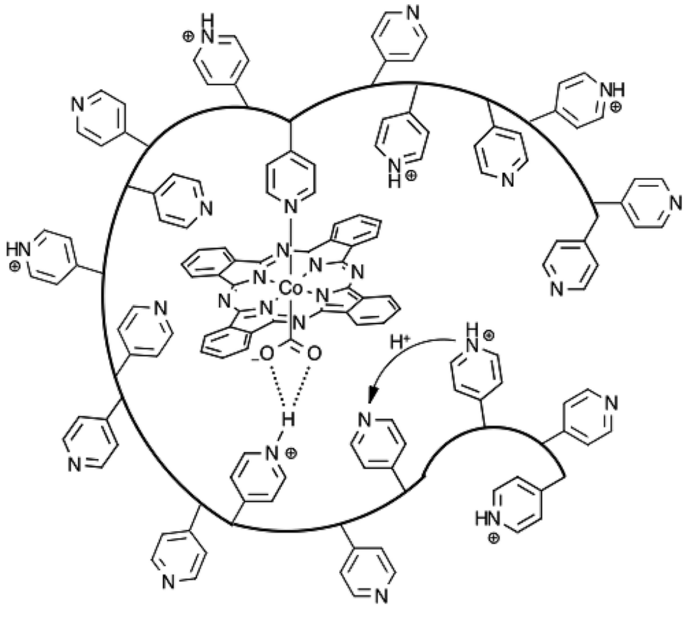

Figure 9. Cobalt phthalocyanine (CoPc) encapsulated within a poly-4-vinylpyridine (P4VP) film. The postulated primary coordination sphere effects (axial coordination of the pyridyl group to the CoPc), secondary coordination sphere effects (H-bonding stabilization of CO_2 intermediates), and outer coordination sphere effects (control of H^+-transport through a proton relay) are shown.[124] [W. W. Kramer and C. C. L. McCrory, Chem. Sci., 2016, 7, 2506] – Published by The Royal Society of Chemistry.

Our work has focused on distinguishing between the primary, secondary, and outer-coordination sphere effects in the polymer-encapsulated CoPc system and determining the extent to which each effect modulates the activity and selectivity for CO_2 reduction by CoPc. We systematically altered the polymer-encapsulated system to independently assess the role of each coordination sphere in the CO_2 reduction mechanism by the CoPc-P4VP system (**Figure 10**). In doing so, we determined the following effects: 1) axial coordination of pyridine to CoPc to form CoPc(py) leads to an increase in the CO_2 reduction activity and a moderate increase in selectivity; 2) immobilizing CoPc into poly-2-vinylpyridine (P2VP) to form CoPc-P2VP leads to an increase in the selectivity for CO production, but no change in the overall catalytic activity compared to the parent adsorbed CoPc. We propose that the steric congestion surrounding the P2VP pyridyl moieties prevents axial coordination to the Co metal center, and that inhibition of H_2 production in the CoPc-P2VP system is due to the limited transport of H^+ through the polymer film; and 3) immobilizing CoPc(py) into P2VP to form the CoPc(py)-P2VP system leads to dramatically increased activity and selectivity for CO_2 reduction compared to the parent CoPc system. We hypothesize that the increase in selectivity is due to a combination of both axial-coordination effects and the outer-coordination sphere effects.[124] Note that rigorous studies on the types of polymers have been shown that synergy between catalyst and polymer effects is required for increased activity and selectivity in polymer-encapsulated systems.[125]

[redacted]

Figure 10. CO_2-reduction activity (TOF_{CO}) and Faradaic efficiency for CO production (ε_{CO}) by CoPc-P4VP and related systems. CoPc and CoPc(py) are complexes directly adsorbed to carbon electrodes with no polymer, whereas CoPc-P4VP, CoPc-P2VP, and CoPc(py)-P2VP are catalyst-polymer composites in which the catalyst is encapsulated within the P4VP or P2VP polymer.[124] Adapted with permission from: [W. W. Kramer and C. C. L. McCrory, Chem. Sci., 2016, 7, 2506] – Published by The Royal Society of Chemistry.

In addition, we used kinetic isotope effect (KIE) measurements to probe the effect of axial coordination on the CO_2RR mechanism by CoPc-P4VP.[126] In particular, CoPc has a KIE ≈ 1 which suggests that the rate determining step does not involve a H^+-transfer event and is presumably instead the CO_2 binding step. However, CoPc(py) showed a KIE ≈ 3 which is indicative of H^+-transfer event in the rate-determining step. Thus, axial-coordination of a pyridyl-group to the CoPc facilitates CO_2 binding, consistent with our previous hypothesis, and changes the rate-determining step to a subsequent protonation event.[126] Using proton-inventory studies,[136-138] we were able to show that H^+-delivery to the CoPc active sites is controlled via a proton-relay mechanism through the polymer involving the partially-protonated pyridyl moieties (rather than H^+ diffusion through the polymer film),[126] supporting our hypothesis regarding the mechanism of H^+ delivery within our polymer-catalyst composite system. We postulate that the protonated pyridyl residues within the polymer are acidic enough to facilitate H^+ transport and stabilize reduced CO_2 intermediates at the CoPc active sites, but H^+ transport in the polymer is sluggish enough to suppress the competitive HER.

Developing a comprehensive understanding of the mechanism and rate of substrate and electron transport to electrocatalyst sites is crucial for rationally designing new polymer-catalyst composite films. Transport and activity in polymer-catalyst composite films can be described by a combination of five interdependent rates, expressed here as currents:[139-144] (1) i_A, the rate of transport of substrate through the electrolyte solution to the film, (2) i_S, the rate of transport of substrate within the polymer film to the catalyst, (3) i_P, the rate of substrate transport across the polymer/electrolyte interface, (4) i_E, the rate of electron transport through the film to the randomly-distributed catalysts, and (5) i_K, is the rate of the catalytic transformation and is not dependent on transport. Although exact relationship between these five rates and measured catalytic activity is complicated,[139-144] better understanding how each of these rates contributes to overall activity of polymer-composite electrocatalysts will inform the design of new, more active materials for the CO_2RR.

5. Conclusions

This review highlights some of the recent work focused on developing new electrocatalytic systems for selective CO_2RR by controlling H^+ and CO_2 delivery to catalyst materials. In the CO_2RR, controlling H^+ and CO_2 delivery to electrocatalyst active sites is essential to achieve high reaction selectivity (CO_2RR vs competitive HER) and high product selectivity (for specific carbon products). For solid-state electrocatalysts for the CO_2RR, local pH and CO_2 concentration influence both electrocatalytic mechanism and product distribution. In particular, high local pH and/or high CO_2 concentration near the electrocatalyst surface facilitates C-C coupling reactions and enhances production of C_2 products. To better control local substrate concentrations, researchers have developed new mesoporous and nanostructured catalyst that result in concentration gradients near interior active sites and modulate overall CO_2RR product distributions, and have designed overlayer-coated electrocatalysts in which substrate transport to the catalyst directly controlled by transport through the porous overlayer. In the case of CO_2RR by molecular catalysts, polymer-catalyst composite films, including polymer-encapsulated molecular catalysts, provide a unique strategy to not only control substrate delivery but also enhance reaction activity by modulating the catalyst's primary, secondary, and outer coordination spheres. We believe that the studies featured in this review demonstrate the promising strategy of controlling substrate delivery to enhance reaction and product selectivity for the CO_2RR and efficiently convert of CO_2 to value-added products.

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Disclosure Statement.

No potential conflict of interest is reported by the authors.

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