Polymer-Covered Copper Catalysts Alter the Reaction Pathway of the Electrochemical CO_2 Reduction Reaction

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ABSTRACT: The electrochemical CO_2 reduction reaction (CO_2RR) has attracted considerable attention recently due to the potential conversion of atmospheric CO_2 into useful organic products by utilizing electricity from renewable energy sources. However, the selective formation of desired products only via CO_2RR has been elusive due to the presence of a myriad of competing reaction pathways, thus calling for effective strategies controlling the reaction coordinates. The control of binding energies of the reaction intermediate, such as *CO, is pivotal to manipulating reaction pathways, and various attempts have been made to accomplish this goal. Herein, we introduce recent endeavors to increase the catalytic selectivity of Cu-based catalysts by surface modification with polymer coating, which can change the local pH, hydrophilicity/hydrophobicity, reaction concentration, etc. The polymer conjugation also contributed to the enhanced electrocatalytic stability of Cu-based catalysts during the CO_2RR. We also point to the remaining challenges and provide perspectives on the further development of Cu−polymer hybrid catalysts for the practical CO_2RR.
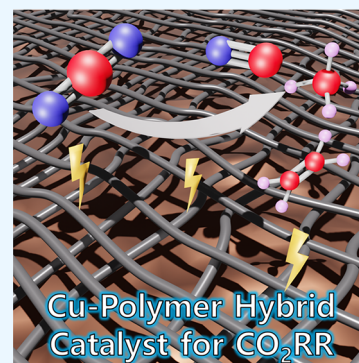
1. INTRODUCTION

The development of decarbonization technologies for reaching net zero CO_2 emission by 2050 is necessary to solve the problems of global warming and drastic climate change. Electrochemical storage of renewable energy (i.e., solar, tidal, and wind energy) as chemical energy in the form of various high-value chemical feedstocks is receiving considerable attention as a promising energy-conversion technology. Electrochemical CO_2 reduction (CO_2RR), in particular, has been regarded as a very useful strategy to convert renewable energy into chemical energy while reducing atmospheric CO_2 concentration.[1] However, low catalytic activity and poor product selectivity during electrocatalysis pose formidable obstacles to the practical application of CO_2RR. Reduction of undesired byproducts is also highly desired because it can reduce the additional separation cost after CO_2 electrolysis.[2]

Many efforts are being made to improve the selectivity of desired products during CO_2RR due to the existence of multiple competing reactions in addition to the most undesired hydrogen evolution reaction (HER).[3] As shown in Figure 1, reaction pathways other than HER lead to forming C_1 products, such as formate (HCOOH), methane (CH_4), and CO and C_2 products, such as ethylene (C_2H_4) and ethanol (C_2H_5OH).[4] The *CO dimerization step on the catalytic surface is a key step in determining whether the product of CO_2RR is C_1 or C_2. When the *CO dimerization step is promoted, the C_2 product selectivity increases, whereas in the absence of the *CO dimerization step, the C_1 product is
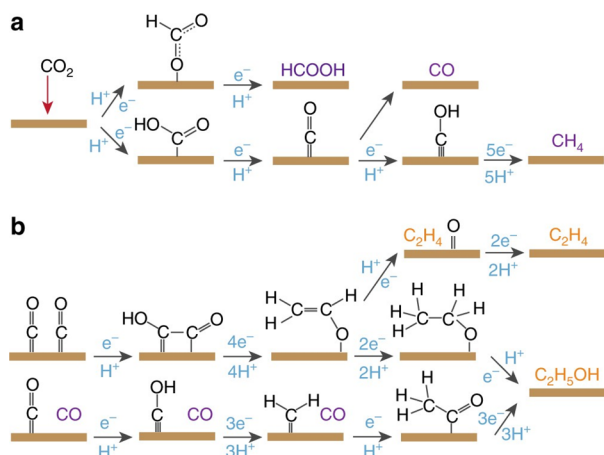

Figure 1. Proposed electrochemical CO_2RR mechanism for the formation of major (a) C_1 products (formate, carbon monoxide, and methane) and (b) C_2 products (ethylene and ethanol). Water molecules are not drawn, and the formation of C_2 products is drawn from CO intermediate. Reproduced with permission from ref 4. Copyright 2018 Springer Nature.
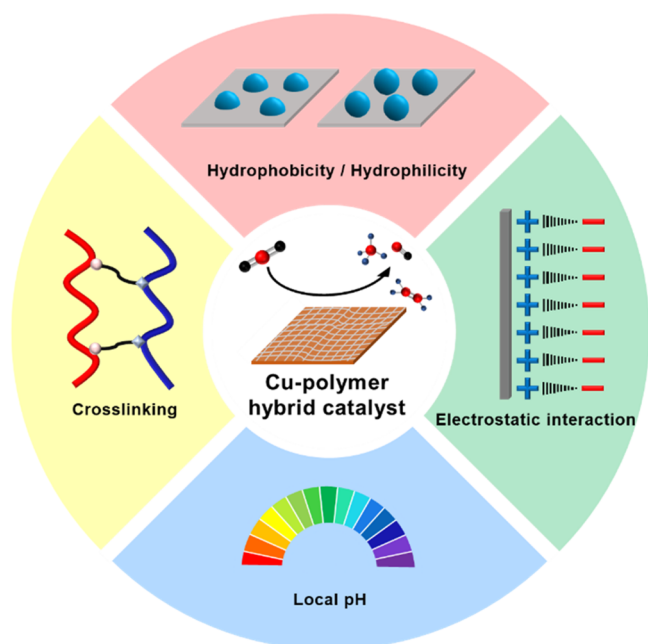
Figure 2. Summary of various factors that can improve the electrochemical CO_2RR performance in a Cu−polymer hybrid catalyst.

mainly produced. Among numerous metals, Cu, Au, Ag, Pd, and Zn have been mainly used in CO_2RR, and each metal produces different products due to the difference in their intrinsic surface energies. For example, metals such as Au, Ag, and Zn reduce CO_2 to CO selectively, and Cd, Sn, and Pb mainly produce formate.[5] Notably, Cu is the only metal that can form various C_1 and C_2 products by optimizing the binding energies of intermediates via surface structure modification. In particular, two main design concepts have emerged to enhance the product selectivity of Cu-based catalysts: (1) utilizing the Cu surface structural features (i.e., grain boundary and vacancy) or doping other metals[6,7] and (2) changing the catalytic interface where the reaction takes place by using organic ligands or forming the triple-phase boundary.[8,9]

Conjugation of Cu catalysts with polymers has been a very effective strategy to increase reaction selectivity by tailoring the local environment of Cu catalysts. Unlike the introduction of other elements, the introduction of a polymer does not provide new active sites for the CO_2RR, thus allowing the alteration of the local environment of the Cu surface without the formation of undesired products by additional active sites. Also, good adhesion of polymers on the electrode can prevent the change in the reaction pathway during the electrocatalytic reaction, thereby guaranteeing a consistent product composition.

As shown in Figure 2, multiple factors affect the electro-catalytic performance of Cu−polymer hybrid catalysts, thus regulating reaction pathways. In this mini-review, we introduce recent advances in Cu−polymer hybrid catalysts for the selective electrochemical CO_2RR. First, we discuss the catalytic activity and selectivity of pristine Cu catalysts. We then highlight the polymer-assisted change in the Cu surface property. Finally, we present an outlook to shed light on future research directions in this field.

2. ACTIVITY AND SELECTIVITY OF COPPER NANOCATALYSTS FOR THE CO_2RR

Various metals (i.e., Cu, Ag, Au, Pd, etc.) have been used as catalysts in the CO_2RR to produce valuable compounds.
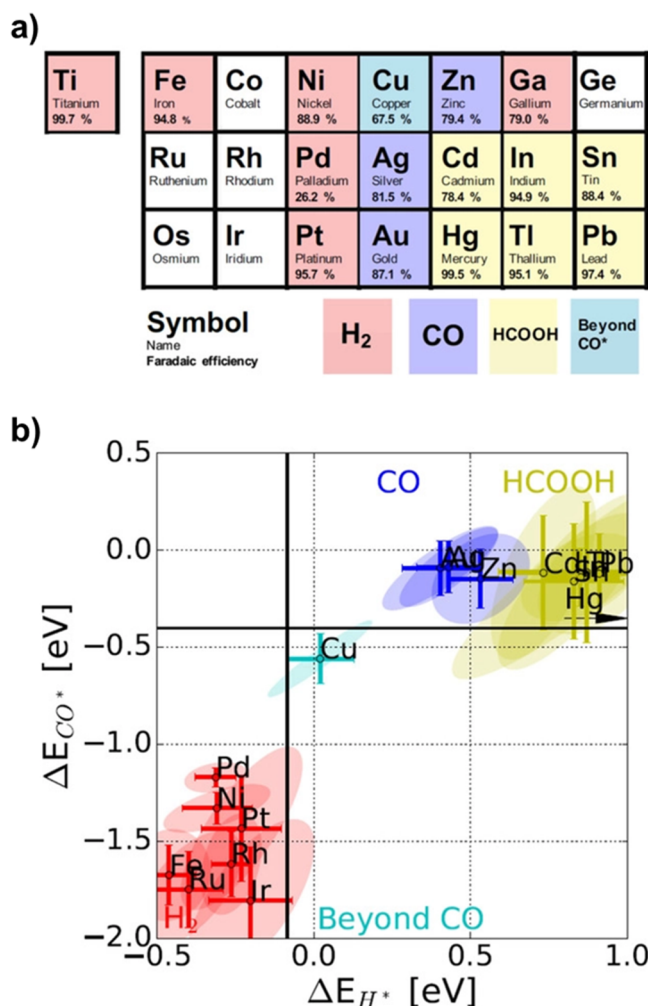

Figure 3. (a) Cropped periodic table of major product classification of metal catalysts for electroreduction of CO_2 with colors and major product faradaic efficiency. Four groups are identified with H_2 (red), CO (blue), HCOOH (yellow), and beyond *CO (cyan). (b) Binding energies of intermediates ΔE_{CO*} and ΔE_{H*}. The colors match the groups in (a). Reproduced with permission from ref 5. Copyright 2017 Wiley-VCH.

Among them, Cu is the only metal that can produce C_{2+} products (i.e., ethylene, ethanol, ethane, and 1-propanol). In the early stage of electrochemical CO_2 studies, Hori et al. examined the behaviors of several metal electrodes (Cu, Au, Ag, Pb, Hg, Ni, Fe, etc.) in an H-type cell with CO_2-saturated 0.1 M $KHCO_3$ electrolyte.[10] Based on the electrochemical measurement, metal elements can be classified into four groups by major products of the CO_2RR (H_2, CO, HCOOH, and beyond *CO), as shown in Figure 3a. To predict product distribution in the CO_2RR, Rossmeisl et al. suggested the binding energies of four intermediates (*H, *COOH, *CO, and *CH_3O) as descriptors because electrochemical CO_2RR has multiple different products while other electrochemical reactions such as HER, oxygen evolution reaction (OER), and oxygen reduction reaction (ORR) have a single product.[5]
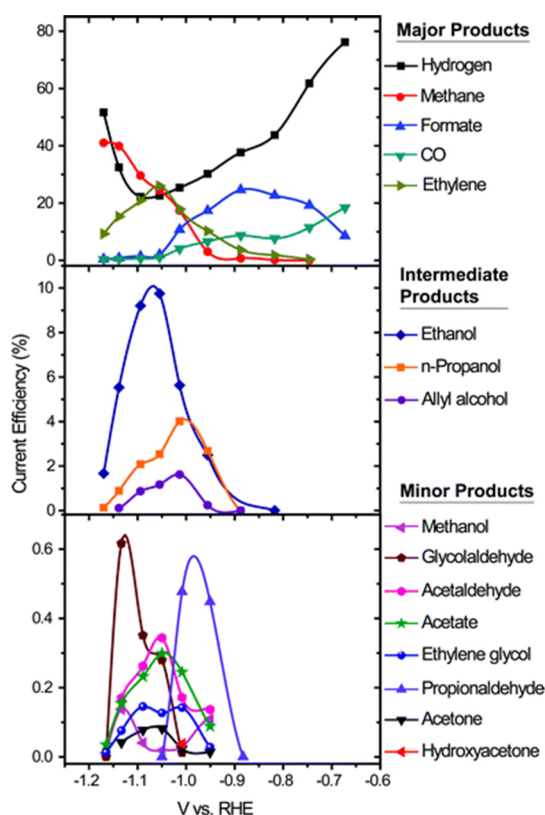
Figure 4. Current efficiency as a function of V vs RHE for CO_2 reduction products on metallic Cu surfaces. From top to bottom: major, intermediate, and minor products. Reproduced with permission from ref 11. Copyright 2012 The Royal Society of Chemistry.

Density functional theory (DFT) calculations were performed to compare the binding energies of intermediates on various metal surfaces (Figure 3b). In particular, *CO binding energy and *H binding energy act as crucial descriptors to explain why Cu is the only metal that can produce beyond *CO products (hydrocarbons and alcohols). When the adsorption energy of *H has a negative value (i.e., Pt, Ir, and Ni), the competitive reaction, HER, is promoted to produce hydrogen as a main product. On the other hand, most of the metal elements having positive adsorption energies of *H do not bind well to *CO intermediate and mainly generate CO or formate during the CO_2RR. Only Cu adsorbs *CO intermediates well while not adsorbing *H species, resulting in the conversion of CO_2 into beyond *CO products such as ethylene, methane, methanol, and ethanol.

To understand the unique abilities of Cu to generate products other than *CO, Jaramillo et al. designed and fabricated a new electrochemical reactor for CO_2 electrolysis to increase the sensitivity of product identification and quantification.[11] They detected a total of 16 products: hydrogen, methane, formate, CO, ethylene, ethanol, n-propanol, allyl alcohol, methanol, glycolaldehyde, acetaldehyde, acetate, ethylene glycol, propionaldehyde, acetone, and hydroxyacetone. As shown in Figure 4, the current efficiency of each product was plotted as a function of applied potential during the electrolysis, and the products were divided into three groups: major, intermediate, and minor products. When the low overpotential range below −0.8 V vs reversible hydrogen electrode (RHE) was applied, the Cu working

electrode mainly produced hydrogen, CO, and formate. As the overpotential increased, the current efficiencies of other products, such as ethylene and methane, were increased. However, since even the current efficiency of methane, which is the most generated product except hydrogen in the CO_2RR, is only about 40% on the Cu electrode, it is necessary to improve the product selectivity of the Cu-based catalyst. Therefore, various modification methods have been attempted to enhance the catalytic selectivity for the specific product on Cu-based catalysts.

3. TAILORING THE LOCAL ENVIRONMENT OF COPPER NANOCATALYSTS FOR THE CO_2RR BY THE INTRODUCTION OF POLYMER

In this section, we describe how the reaction pathway of the catalyst is modulated by the Cu−polymer hybrid catalysts. In
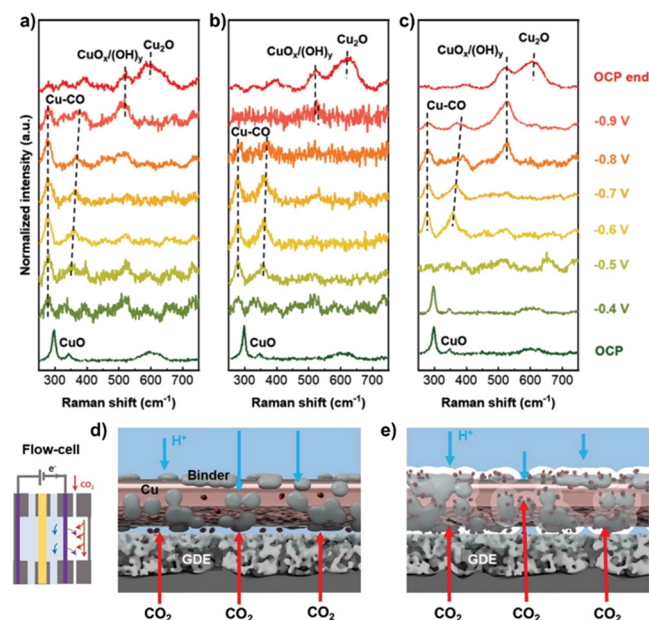

Figure 5. Operando Raman spectra of (a) Cu−FEP, (b) Cu−Nafion, and (c) Cu−PAA. From bottom to the top: initial OCP, −0.4 to −0.9 V vs RHE decreases to 0.1 V vs RHE, final OCP. Schematic illustration of the local reaction environment near the Cu surface with (d) hydrophilic and (e) hydrophobic polymer binders in the flow cell. Electrolyte (light blue), Cu (brownish red), polymer binder (gray), CO_2 pathway (red arrow), H^+ pathway (blue arrow), and trapped CO_2 in hydrophobic samples (white). Reproduced with permission from ref 15. Copyright 2022 Wiley-VCH.

the early stage of the Cu−polymer hybrid catalyst development, polymers were introduced to attain higher conductivity of metals and stabilization of electrodes during the CO_2RR. Jeong et al. introduced polyaniline (PANI), a conductive polymer, to Cu_2O to synthesize a catalyst with a band gap (1.92 eV) lower than that of bulk Cu_2O (2.3 eV).[12] The smaller band gap of PANI/Cu_2O catalyst improved the CO_2 reduction rate by facilitating electron transfer from the valence band to the conduction band. Poly(4-vinylpyridine) (P4VP) was also coated onto a Cu electrode to increase its catalytic stability.[13] In the Cu−P4VP hybrid catalyst, the Cu cations were coordinated with pyridyl groups of P4VP to prevent the loss of the Cu species during the CO_2RR, and the active sites
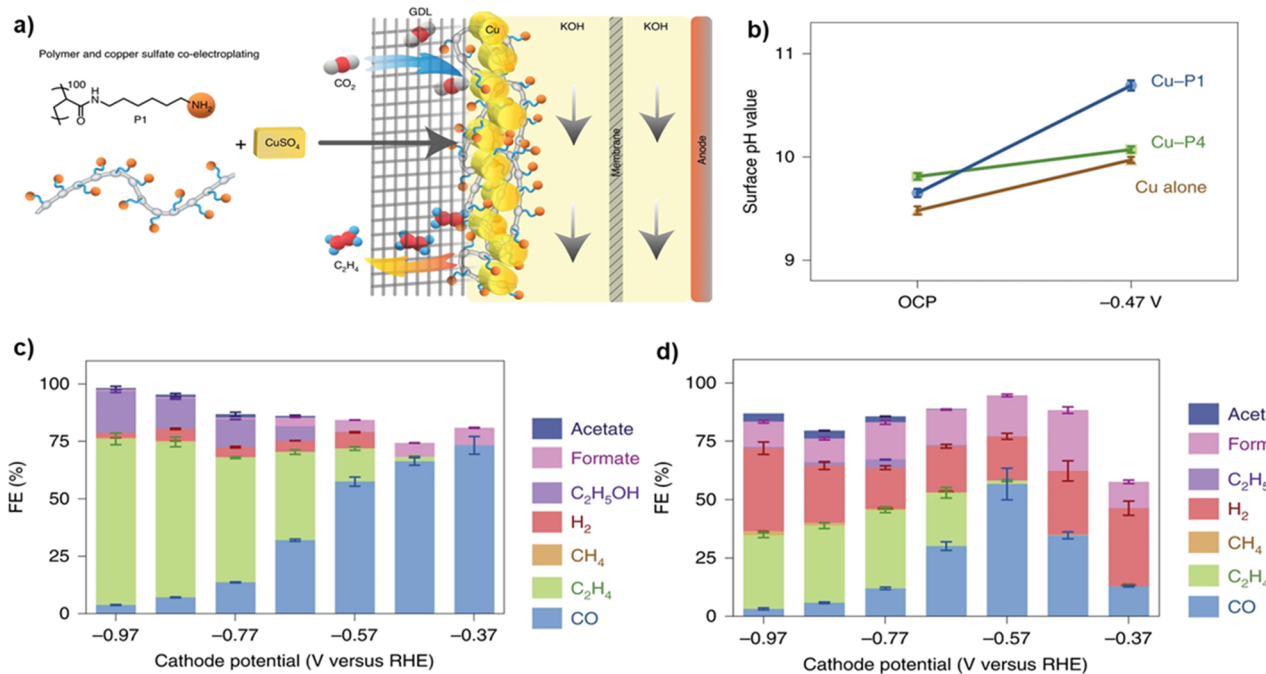
Figure 6. (a) Schematic illustration of poly-*N*-(6-aminohexyl) acrylamide (P1) and Cu coelectroplating on the gas diffusion layer (GDL). (b) Calculated surface pH on Cu-P1 (blue line), Cu-P4 (green line), and Cu alone (brown line) electrodes at OCP and −0.47 V by using the relative ratio of carbonate to bicarbonate peaks in the SERS spectra. Faradaic efficiencies for all products on (c) Cu-P1 and (d) Cu-P4 in 1 M KOH electrolyte. Reproduced with permission from ref 16. Copyright 2021 Springer Nature.

were stabilized by the bulky polymer coil, which increased the rigidity and insolubility of the catalyst.

Recently, the ability of the polymer to tune the reaction selectivity by affecting the intermediate concentration, not just improving the conductivity or stability of the catalyst, has gained the attention of the research community. For example, Chen et al. synthesized Cu−polymer hybrid catalysts using two polymers with similar structures but different functional groups: poly(acrylic acid) (PAA, −COOH group) with a hydrophilic functional group and polyvinylidene difluoride (PVDF, −CF$_2$ group) with a hydrophobic functional group.[14] The Cu−Nafion catalyst was also tested for comparison. The Cu−PVDF catalyst showed a faradaic efficiency (FE) of methane 1.6 times higher than that of Cu−PAA at −1.2 to 1.4 V vs RHE. Cu−PAA also exhibited a FE of formate at −1.2 to 1.4 V vs RHE 1.6 times higher than that of Cu−PVDF. There are two reasons behind this observation. First, the hydrophilic surface of Cu−PAA generated protons that served as reactants in the formation of formate at the potential over −0.9 V vs RHE. Second, hydrogen bonding between the −COOH group of Cu−PAA and the reaction intermediates led to binding energy stronger than that of Cu−PVDF and Cu−Nafion. DFT calculations also confirmed that different binding energies of reaction intermediates change the CO$_2$RR selectivity on the Cu surface.

Similarly, Luo et al. employed fluorinated ethylene propylene (FEP) as a binder for the Cu catalyst to inhibit the competing HER reaction in aqueous CO$_2$RR.[15] Nafion (with both hydrophilic and hydrophobic functional groups) and PAA (with hydrophilic functional groups) were also selected as binders to adjust the local environment of the Cu catalyst. The catalyst was prepared by dispersing both as-synthesized CuO particles and polymer in isopropyl alcohol and subsequent drop-casting on the electrode. In the flow-cell

system, Cu−FEP showed the highest FE of 77% for C$_{2+}$ products, followed by Cu−Nafion (about 60%) and Cu−PAA (about 30%) at −0.76 V. As shown in Figure 5a−c, the investigation of the catalyst surface through operando surface-enhanced Raman spectroscopy (SERS) indicated that CO molecules, the key intermediate of C$_{2+}$ products, were well formed during CO$_2$RR on all surfaces of Cu−FEP, Cu−Nafion, and Cu−PAA. Notably, the Raman spectra of Cu−FEP showed the CO adsorption peaks in a wider potential range compared to Cu−Nafion and Cu−PAA, confirming that Cu−FEP produces C$_{2+}$ products most efficiently in a wider potential range. Hydrophobic polymers as binders allowed CO$_2$ gas to easily access the catalyst surface at the triple-phase boundary between the electrolyte, Cu catalyst on the gas diffusion electrode (GDE), and the CO$_2$ gas in a flow cell system (Figure 5d,e). In addition, the hydrophobic polymer improved the stability of GDE by preventing the flooding of electrolytes.

In addition to hydrophilic/phobic modulation, polymers can enhance the selectivity of CO$_2$RR through local pH adjustment.[16] Gewirth et al. prepared electrodes by coelectroplating of poly-*N*-(6-aminohexyl)acrylamide (P1) and CuSO$_4$ on carbon-fiber-paper-based gas diffusion layer (GDL) substrates (Figure 6a). As a control group, the ratio of hydrogen atom substitution on the methyl group of amines was modulated through methylation of polymers (35%, 65%, and 100% methylated samples were denoted as Cu-P2, Cu-P3, and Cu-P4, respectively). At −0.97 V vs RHE, the FEs for C$_2$ products were 72% ethylene and 18% ethanol, while the competing reaction HER showed a low FE of less than 7%, and the total current density reached 433 mA cm$^{−2}$ in a flow cell (Figure 6c,d). On the other hand, under the same conditions (−0.97 V vs RHE), the unmodified Cu electrode exhibited an FE of 27% for ethylene with a total current density of 207 mA cm$^{−2}$.
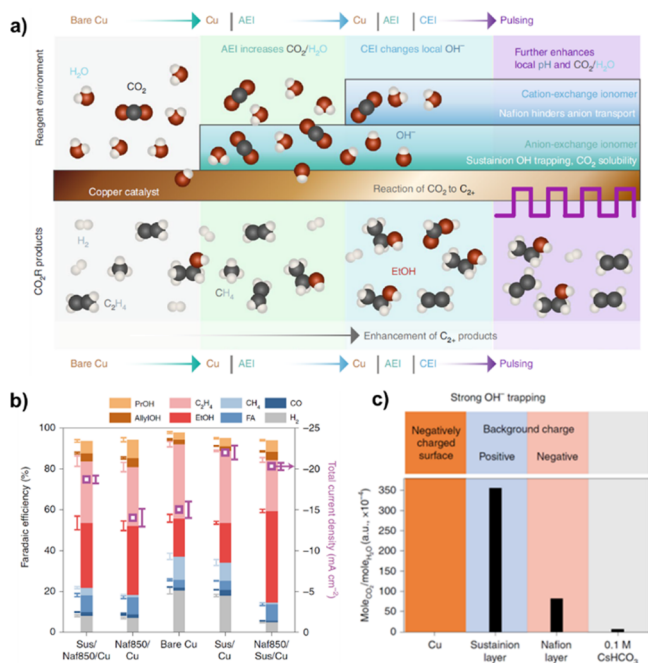
Figure 7. (a) Schematic illustration of enhanced CO_2RR performance using ionomers. Reference case where CO_2RR occurs in the presence of Cu catalyst (white area), the relative improvement in performance with the addition of an AEI layer (green area), with the addition of a CEI layer on AEI layer (blue area), and with the pulsed electrolysis (purple area) for enhancing the selectivity for C_{2+} products. (b) Catalytic performance of CO_2RR at −1.15 V vs RHE using stacked ionomer layers on Cu in 0.1 M $CsHCO_3$. (c) Local CO_2/H_2O ratio and spatial charge configuration of Naf850/Sus/Cu. Orange, blue, red, and gray areas correspond to Cu, Sustainion layer, Nafion layer, and 0.1 M $CsHCO_3$ solution (electrolyte solution), respectively. Reproduced with permission from ref 19. Copyright 2021 Springer Nature.
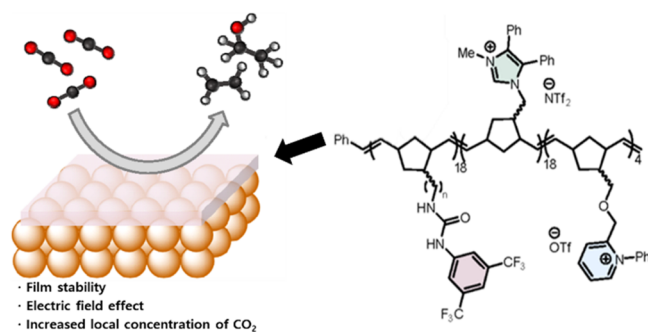

Figure 8. Tuning CO_2RR product distribution by using highly modular tricomponent copolymer modifiers. The blue group helps to stabilize the copolymer by acting as a cross-linker, the pink group helps to stabilize the intermediate by hydrogen bonding, and the green group helps to stabilize the intermediate by electrostatic interaction. Reproduced from ref 21. Copyright 2021 American Chemical Society.

Interestingly, FE for the ethylene was increased in the order of Cu-P2 (55%), Cu-P3 (43%), and Cu-P4 (32%), suggesting that the methylation of the functional group of polymers facilitated the HER and retarded CO_2RR kinetics.

To investigate the origin of different CO_2RR selectivity of samples, in situ SERS was conducted. Among the SERS spectra of Cu-P1, Cu-P4, and Cu electrodes, distinctive Cu−CO

binding peaks, evidence that CO intermediate was well generated on the catalyst, were observed only for the Cu-P1 electrode at −0.47 V vs RHE. Furthermore, in situ SERS spectra could provide information on the surface pH of electrodes during CO_2RR after calculating the relative concentration ratio of carbonate to bicarbonate (Figure 6b).[17] At the open circuit potential (OCP), the surface pH value of the Cu-P1 electrode (9.8) was higher than that of the Cu alone electrode (9.5) due to the presence of amino groups. When −0.47 V was applied, the surface pH values of the three electrodes (Cu-P1, Cu-P4, and Cu alone) increased. Among them, Cu-P1 exhibited the highest surface pH (10.7) due to the presence of protonated amines on the electrode. The acid−base reaction occurred on the surface of the Cu-P1 electrode according to the reaction formula below:

$$HCO_3^- + R\text{-}NH_2 \leftrightarrow CO_3^{2-} + R\text{-}NH_3^+$$
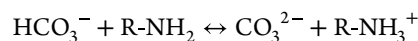
Since the increasing amount of R-NH_2 drives the reaction to the right when potential is applied, the concentration of CO_3^{2-} was increased, resulting in a high surface pH. In addition, the deprotonation of HCO_3^- was highly facilitated in Cu-P1 compared to Cu-P4 due to the presence of R-NH_2. As a result, the high surface pH derived from polyamine enhanced the selectivity for the C_2 product of the Cu catalyst during CO_2RR.[18]

By utilizing the multiple effects of polymers discussed above, Bell et al. suggested that a Cu catalyst coated with bilayer ionomers can control both the local pH and CO_2/H_2O ratio (Figure 7a).[19] The Cu electrode was prepared by sputtering Cu on the PTFE membrane to maximize the hydrophobicity, followed by a drop-cast of two ionomers: Nafion, a cation exchange ionomer (CEI), and Sustainion, an anion exchange ionomer (AEI). The product selectivity of the catalyst depended on the stacking order of ionomers on Cu, where Naf850/Sus/Cu (Naf850, Nafion with 850 g mol_{eq}^{-1} equivalent weight) showed excellent performances in producing C_{2+} products. When −1.15 V vs RHE was applied to Naf850/Sus/Cu catalyst in 0.1 M $CsHCO_3$, the FE of H_2 was at a low value of 5%, and the FE of C_{2+} was 80% with a total current density (TCD) of 20 mA cm^{-2} in a flow cell (Figure 7b). High selectivity and TCD of the prepared catalyst were feasible due to the following two reasons. First, the hydrophobicity of Sustainion enhanced the solubility of the CO_2, and thus the CO_2/H_2O ratio on the catalyst surface increased. Second, the outer Nafion layer, which has a negative background charge density, trapped the OH^- generated from CO_2RR due to the stronger Donnan exclusion, and thus the local pH of the catalyst surface was higher than that of the bulk electrolyte (Figure 7c).[20] To further increase C_{2+} product selectivity, a square wave potential pulse of −0.8 to −1.15 V was applied at intervals of 10 s. Such pulsed CO_2 electrolysis kept the FE for H_2 of Naf850/Sus/Cu catalyst below 4%, improving FE for C_{2+} products to 90%, with the TCD value of 12.1 mA cm^{-2}.

While it is possible to coat different types of polymers on Cu electrodes simultaneously, a tricomponent copolymer can be directly used to impart multiple functions to the polymer. Grubbs et al. prepared the electrodes by spin-coating various polymers onto the electropolished polycrystalline Cu foil (Figure 8).[21] Among the various catalysts, the Cu electrode coated with a copolymer incorporating three monomer components via ring-opening metathesis polymerization (ROMP) exhibited the best electrocatalytic performance.

Table 1. Comparison of the Faradaic Efficiency of Various Cu−Polymer Hybrid Catalysts toward CO2RR

strategy	catalyst	polymer	highlight products with FE	cell type	electrolyte	applied potential	electrode preparation method	ref
	Cu-PAA	poly(acrylic acid)	HCOOH (37.6%, −1.2 V)	H-type cell	0.1 M KHCO$_3$	−0.6 to −1.4 V	mixing commercial 20 wt % Cu NPs on carbon (particle size = 50 nm) with polymer binder and drop-casting on carbon paper	14
	Cu-PVDF	polyvinylidene difluoride	CH$_4$ (12.0%, −1.4 V)					
	Cu−Nafion[a]	Nafion	HCOOH (30.9%, −1.2 V), CH$_4$ (7.6%, −1.4 V)					
hydrophobic/philic modification	Cu-FEP	fluorinated ethylene propylene	C$_{2+}$ products (about 77%, −0.76 V)	flow cell	1.0 M KOH	−0.2 to −0.9 V	mixing homemade CuO with polymer binder and drop-casting on carbon paper	15
	Cu-PAA	poly(acrylic acid)	C$_{2+}$ products (about 30%, −0.76 V)					
	Cu−Nafion[a]	Nafion	C$_{2+}$ products (about 60%, −0.76 V)					
	Cu-FEP	fluorinated ethylene propylene	C$_{2+}$ products (about 53%, −1.1 V)	H-type cell	0.1 M KHCO$_3$	−0.6 to −1.2 V		
	Cu-PAA	poly(acrylic acid)	C$_{2+}$ products (about 43%, −1.1 V)					
	Cu−Nafion[a]	Nafion	C$_{2+}$ products (about 35%, −1.1 V)					
	Cu-P1	poly-N-(6-aminohexyl)acrylamide (methylation 0%)	C$_2$H$_4$ (72%, −0.97 V)	flow cell	1 M KOH	−0.37 to −0.97 V	coelectroplating of CuSO$_4$ and polymer on a carbon-fiber-paper-based gas diffusion layer	16
	Cu-P2	poly-N-(6-aminohexyl)acrylamide (methylation 35%)	C$_2$H$_4$ (55%, −0.97 V)					
	Cu-P3	poly-N-(6-aminohexyl)acrylamide (methylation 65%)	C$_2$H$_4$ (43%, −0.97 V)					
	Cu-P4	poly-N-(6-aminohexyl)acrylamide (methylation 100%)	C$_2$H$_4$ (32%, −0.97 V)					
	Cu alone[a]		C$_2$H$_4$ (27%, −0.97 V)					
reaction intermediate stabilization	Naf850/Sus/Cu	Nafion, Sustainion	C$_{2+}$ products (80%), C$_2$H$_4$ (23%), EtOH (47%)	flow cell	0.1 M CsHCO$_3$	−1.15 V	sputtering Cu onto a microporous (20 nm pore size) PTFE pervaporation membrane and drop-casting of polymer onto Cu/PTFE electrode	19
	Sus/Naf850/Cu	Nafion, Sustainion	C$_{2+}$ products (70%), C$_2$H$_4$ (31%), EtOH (30%)					
	Naf850/Cu	Nafion	C$_{2+}$ products (74%), C$_2$H$_4$ (30%), EtOH (32%)					
	Sus/Cu	Sustainion	C$_{2+}$ products (57%), C$_2$H$_4$ (36%), EtOH (18%)					
	bare Cu[a]		C$_{2+}$ products (57%), C$_2$H$_4$ (37%), EtOH (17%)					
	Cu-1	1-butyl-3-methylimidazolium	C$_2$H$_4$ (0%)	flow cell	0.1 M KHCO$_3$	−1.08 V	drop-casting of polymer on commercial Cu foil	21
	Cu-5	1-(3,5-bis(trifluoromethyl)phenyl)-3-methylurea	C$_2$H$_4$ (25.5%)					
	Cu-6	1-butyl-3-methylimidazolium, 1-(3,5-bis(trifluoromethyl)phenyl)-3-methylurea	C$_2$H$_4$ (30.4%)					
	Cu-block-8	1-butyl-3-methylimidazolium, 1-(3,5-bis(trifluoromethyl)phenyl)-3-methylurea, phenylpyridinium	C$_2$H$_4$ (34.5%)					

Table 1. continued

strategy	catalyst	polymer	highlight products with FE	cell type	electrolyte	applied potential	electrode preparation method	ref
	Cu-random-8	1-butyl-3-methylimidazolium, 1-(3,5-bis(trifluoromethyl)phenyl)-3-methylurea, phenylpyridinium	C$_2$H$_4$ (55.6%)					
	Cu[a]		C$_2$H$_4$ (22.3%)					

[a]Control group of the catalyst.

Based on the previous finding that ionic liquid enhances the selectivity for the CO$_2$RR,[22] the first monomer component, 1-butyl-3-methyl-4,5-diphenylimidazolium, was employed to stabilize the intermediates of CO$_2$RR by electrostatic interaction. The second monomer component, 1-(3,5-bis-(trifluoromethyl)phenyl)-3-methylurea, was introduced to increase the stability of the reaction intermediate on the catalytic surface through hydrogen bonding.[23] Finally, phenyl-pyridinium was added to enhance the contact stability between the copolymers and Cu foil catalysts during the electro-chemical CO$_2$RR as the phenylpyridinium moiety of the polymer strongly can interact with the Cu surface due to its role as a cross-linker.[24] The SEM results after the electro-catalysis confirmed that the catalytic surface became more robust when the phenylpyridinium moiety was included. Likewise, an atomic scale molecular dynamics (MD) simulation was performed to determine the CO$_2$ concentration in the inner Helmholtz plane (IHP) of each catalyst. The main catalyst composed of tricomponent copolymers and Cu foil showed a CO$_2$ concentration (0.86) 2.4 times higher than that of pristine Cu foil (0.36).

4. SUMMARY AND OUTLOOK

We have discussed recent advances in the polymer-assisted microenvironment modification strategies of Cu-based electro-catalysts to improve the electrochemical CO$_2$RR activity and selectivity. Table 1 presents the summarized performance of CO$_2$RR on various Cu−polymer hybrid catalysts. The surface modification of the Cu−polymer hybrid catalysts can lead to the following consequences. First, the hydrophilicity (or hydrophobicity) of the polymer near the catalyst surface dictates the local concentration of specific reactants, thereby changing the CO$_2$RR selectivity. Second, functional groups in the polymer can selectively stabilize certain reaction inter-mediates on the surface of the catalysts by changing the local pH or electrostatic interactions near the catalyst surface.

However, an in-depth understanding of the exact interaction mechanism between the catalyst surface and the functional polymers is still in its early stages. Only certain combinations between Cu nanoparticles and hydrophobic polymers (PTFE and PVDF), ionomeric binders (Nafion and PAA), or block copolymers have been thoroughly scrutinized. Therefore, systematic investigation and optimization of electrocatalyst−polymer interaction are utterly required. In situ/operando characterization techniques using X-ray photoelectron spec-troscopy (XPS), X-ray absorption spectroscopy (XAS), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, and mass spectroscopy (MS) allow for the observation of dynamic changes of catalyst, which reveals the reaction mechanisms, and thus would be very useful to understand the interaction between Cu catalysts and polymers.[25] Furthermore, it is well-known that the exposed facet of the Cu-based nanoparticles affects the binding energy of reaction intermediates considerably during the CO$_2$RR. Thus, the interaction between polymer-faceted Cu crystals might have to be carefully studied.

The exact molecular structures, including isomerism and molecular weights, should also be considered because their binding behavior on the surface of the electrocatalysts might also change depending on the exact polymer structure. Furthermore, the molecular structures of polymers affect their chain-folding behavior and local crystallite structure, which in turn can affect the local chemical environments, such

as hydrophilicity and gas permeability near the surface of the CO_2RR electrocatalysts.

In summary, many examples demonstrate clearly that surface functionalization of electrocatalysts by functional polymers can improve the overall activity and selectivity of the electrocatalysts toward the CO_2RR. Surface-binding polymers assist the catalytic performance in various aspects. The modified local pH or electrostatic interactions around the surface of the catalyst can change the proportion and energetics of surface-binding reaction intermediates. The polymers can also assist the material transport behaviors of the reactants (CO_2 gas and H_2O) and products, which would become one of the most critical issues in scaling up the reaction toward the A/cm^2 scale. The design concept of polymer–catalyst composites might also be applied to other electrochemical reactions, such as the electrochemical synthesis of ammonia and urea by using nitrogen and nitrate as N sources, particularly when the selectivity of the reaction is of great importance. We hope this mini-review will encourage further interest in polymer–catalyst composite electrocatalysts to realize the practical electrochemical synthesis of various valuable products.

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Taehyun Kwon obtained his Ph.D. degree (2021) in inorganic chemistry from Korea University. After working as a postdoctoral researcher at the Korea Institute of Science and Technology (KIST), he joined the Department of Chemistry at Incheon National University (INU) as an assistant professor. His current research interests include the design of nanostructured electrocatalysts and radical scavengers for electrochemical energy conversion devices.

Kwangyeol Lee obtained his Ph.D. degree (1997) in chemistry from the University of Illinois at Urbana—Champaign. After fulfilling his military obligation, he joined Korea University in 2003 as a chemistry faculty member before being appointed professor. His current research interests lie in the development of synthetic methods for catalytic nanoscale materials to support the environment by creating sustainable energy sources.

■ ACKNOWLEDGMENTS

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