Polymer-Covered Copper Catalysts Alter the Reaction Pathway of the Electrochemical CO$_2$ Reduction Reaction

Minki Jun, Doyeop Kim, Minsu Kim, Minah Kim, Taehyun Kwon,* and Kwangyeol Lee*

ABSTRACT: The electrochemical CO$_2$ reduction reaction (CO$_2$RR) 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$_2$RR 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$_2$RR. We also point to the remaining challenges and provide perspectives on the further development of Cu−polymer hybrid catalysts for the practical CO$_2$RR.

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$_2$RR), 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$_2$RR. 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$_2$RR 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$_2$H$_4$) and ethanol (C$_2$H$_5$OH).$^4$ The *CO dimerization step on the catalytic surface is a key step in determining whether the product of CO$_2$RR 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$_2$RR 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.
mainly produced. Among numerous metals, Cu, Au, Ag, Pd, and Zn have been mainly used in CO$_2$RR, 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$_2$RR, 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 electrocatalytic 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$_2$RR. 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$_2$RR

Various metals (i.e., Cu, Ag, Au, Pd, etc.) have been used as catalysts in the CO$_2$RR to produce valuable compounds.

Among them, Cu is the only metal that can produce C$_n$ 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$_2$RR (H$_2$ (red), CO (blue), HCOOH (yellow), and beyond *CO (cyan)). (b) Binding energies of intermediates $\Delta E_{CO}$ and $\Delta E_{H}$. The colors match the groups in (a). Reproduced with permission from ref 5. Copyright 2017 Wiley-VCH.

\[\Delta E_{CO} \cdot [eV] \quad \Delta E_{H} \cdot [eV]\]

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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 CO₂RR. Only Cu adsorbs ∗CO intermediates well while not adsorbing ∗H species, resulting in the conversion of CO₂ 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 CO₂ electrolysis to increase the sensitivity of product identification and quantification.⁹ They detected a total of 16 products: hydrogen, methane, formate, CO, ethylene, CO₂, 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 CO₂RR, 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 CO₂RR 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 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 CO₂RR. Jeong et al. introduced polyaniline (PANI), a conductive polymer, to Cu₂O to synthesize a catalyst with a band gap (1.92 eV) lower than that of bulk Cu₂O (2.3 eV).⁹ The smaller band gap of PANI/Cu₂O catalyst improved the CO₂ 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. 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 CO₂RR, and the active sites...
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, −CF₂ group) with a hydrophobic functional group. The Cu–Nafion catalyst was also tested for comparison. The Cu–PVDF catalyst showed a faradaic efficiency (FE) of 77% for 

$\text{C}_2\text{O}_4^2-$ 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 (ERS) indicated that CO molecules, the key intermediate of 

$\text{C}_2\text{O}_4^2-$ products, were well formed during CO₂RR 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 

$\text{C}_2\text{O}_4^2-$ products most efficiently in a wider potential range. Hydrophobic polymers as binders allowed CO₂ 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 CO₂ 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 CO₂RR through local pH adjustment. Gewirth et al. prepared electrodes by coelectroplating of poly-N-(6-aminoethyl)acrylamide (P1) and CuSO₄ 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 FE for 

$\text{CO}_2$ was modified to 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. At −0.97 V vs RHE, the FE for 

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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\textsubscript{RR} kinetics.

To investigate the origin of different CO\textsubscript{RR} 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\textsubscript{RR} after calculating the relative concentration ratio of carbonate to bicarbonate (Figure 6b).\textsuperscript{13} 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:

\[
\text{HCO}_3^- + \text{R-NH}_2 \leftrightarrow \text{CO}_3^{2-} + \text{R-NH}_3^+ 
\]

Since the increasing amount of R-NH\textsubscript{2} drives the reaction to the right when potential is applied, the concentration of CO\textsubscript{3}\textsuperscript{2−} was increased, resulting in a high surface pH. In addition, the deprotonation of HCO\textsubscript{3}\textsuperscript{−} was highly facilitated in Cu-P1 compared to Cu-P4 due to the presence of R-NH\textsubscript{2}. As a result, the high surface pH derived from polyamine enhanced the selectivity for the C\textsubscript{2} product of the Cu catalyst during CO\textsubscript{RR}.

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\textsubscript{2}/H\textsubscript{2}O ratio (Figure 7a).\textsuperscript{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\textsuperscript{−1} equivalent weight) showed excellent performances in producing C\textsubscript{2} products. When −1.15 V vs RHE was applied to Naf850/Sus/Cu catalyst in 0.1 M CsHCO\textsubscript{3}, the FE of H\textsubscript{2} was at a low value of 5%, and the FE of C\textsubscript{2} was 80% with a total current density (TCD) of 20 mA cm\textsuperscript{−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\textsubscript{2} and thus the CO\textsubscript{2}/H\textsubscript{2}O ratio on the catalyst surface increased. Second, the outer Nafion layer, which has a negative background charge density, trapped the OH\textsuperscript{−} generated from CO\textsubscript{RR} 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).\textsuperscript{20} To further increase C\textsubscript{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\textsubscript{2} electrolysis kept the FE for H\textsubscript{2} of Naf850/Sus/Cu catalyst below 4%, improving FE for C\textsubscript{2}, products to 90%, with the TCD value of 12.1 mA cm\textsuperscript{−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).\textsuperscript{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.
| strategy | catalyst | polymer | highlight products with FE | cell type | electrolyte | applied potential | electrode preparation method and ref |
|----------|----------|---------|---------------------------|----------|------------|-------------------|-------------------------------------|
| Cu-PAA  | poly(acrylic acid) | HCOOH | H-type cell | 0.1 M KHCO₃ | −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 |
| Cu-PVF  | polynvinylidene difluoride | CH₄ (12.0%, −1.4 V) | HCOOH (30.9%, −1.2 V), CH₄ (7.6%, −1.4 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 |
| Cu-Nafion | Nafion | C₂H₄ products (77%, −0.76 V) | H-type cell | 0.1 M KHCO₃ | −0.6 to −1.2 V | mixing hydrophobic/philic modification |
| Cu-FEP  | fluorinated ethylene propylene | C₂H₄ products (60%, −0.76 V) | H-type cell | 0.1 M KHCO₃ | −0.6 to −1.2 V | mixing hydrophobic/philic modification |
| Cu-PAA  | poly(acrylic acid) | C₂H₄ products (30%, −0.76 V) | H-type cell | 0.1 M KHCO₃ | −0.6 to −1.2 V | mixing hydrophobic/philic modification |
| Cu-PVF  | polynvinylidene difluoride | C₂H₄ products (about 53%, −1.1 V) | H-type cell | 0.1 M KHCO₃ | −0.6 to −1.2 V | mixing hydrophobic/philic modification |
| Cu-Nafion | Nafion | C₂H₄ products (about 43%, −1.1 V) | H-type cell | 0.1 M KHCO₃ | −0.6 to −1.2 V | mixing hydrophobic/philic modification |
| Cu-P1   | poly-N-(6-aminohexyl)acrylamide (methylation 0%) | C₂H₄ (72%, −0.97 V) | flow cell | 1 M KOH | −0.37 to −0.97 V | coelectroplating of CuSO₄ and polymer on a carbon-fiber-paper-based gas diffusion layer |
| Cu-P2   | poly-N-(6-aminohexyl)acrylamide (methylation 35%) | C₂H₄ (55%, −0.97 V) | flow cell | 1 M KOH | −0.37 to −0.97 V | coelectroplating of CuSO₄ and polymer on a carbon-fiber-paper-based gas diffusion layer |
| Cu-P3   | poly-N-(6-aminohexyl)acrylamide (methylation 65%) | C₂H₄ (43%, −0.97 V) | flow cell | 1 M KOH | −0.37 to −0.97 V | coelectroplating of CuSO₄ and polymer on a carbon-fiber-paper-based gas diffusion layer |
| Cu-P4   | poly-N-(6-aminohexyl)acrylamide (methylation 100%) | C₂H₄ (32%, −0.97 V) | flow cell | 1 M KOH | −0.37 to −0.97 V | coelectroplating of CuSO₄ and polymer on a carbon-fiber-paper-based gas diffusion layer |
| Cu alone | | C₂H₄ products (about 35%, −1.1 V) | flow cell | 1 M KOH | −0.37 to −0.97 V | coelectroplating of CuSO₄ and polymer on a carbon-fiber-paper-based gas diffusion layer |
| NaB₈O/Sus/Cu | Nafion, Sustainion | C₂H₄ products (80%), C₂H₆ (33%), EOH (47%) | flow cell | 0.1 M CsHCO₃ | −1.15 V | sputtering Cu onto a microporous (20 nm pore size) PTFE pervaporation membrane and drop-casting of polymer onto Cu/PTFE electrode |
| Sus/Cu  | Nafion, Sustainion | C₂H₄ products (70%), C₂H₆ (31%), EOH (30%) | flow cell | 0.1 M CsHCO₃ | −1.15 V | sputtering Cu onto a microporous (20 nm pore size) PTFE pervaporation membrane and drop-casting of polymer onto Cu/PTFE electrode |
| Cu alone | | C₂H₄ products (74%), C₂H₆ (30%), EOH (32%) | flow cell | 0.1 M CsHCO₃ | −1.15 V | sputtering Cu onto a microporous (20 nm pore size) PTFE pervaporation membrane and drop-casting of polymer onto Cu/PTFE electrode |
| Cu-1    | 1-butyl-3-methylimidazolium | C₂H₄ (0%) | flow cell | 0.1 M KHCO₃ | −1.08 V | drop-casting of polymer on commercial Cu foil |
| Cu-5    | 1-(3,5-bis(trifluoromethyl)phenyl)-3-methylurea | C₂H₄ (20%) | flow cell | 0.1 M KHCO₃ | −1.08 V | drop-casting of polymer on commercial Cu foil |
| Cu-6    | 1-butyl-3-methylimidazolium, 1-(3,5-bis(trifluoromethyl)phenyl)-3-methylurea | C₂H₄ (30.4%) | flow cell | 0.1 M KHCO₃ | −1.08 V | drop-casting of polymer on commercial Cu foil |
| Cu-block-8 | 1-butyl-3-methylimidazolium, 1-(3,5-bis(trifluoromethyl)phenyl)-3-methylurea, phenylpyridinium | C₂H₄ (34.5%) | flow cell | 0.1 M KHCO₃ | −1.08 V | drop-casting of polymer on commercial Cu foil |
Based on the previous finding that ionic liquid enhances the selectivity for the CO$_2$RR, 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. Finally, phenylpyridinium was added to enhance the contact stability between the copolymers and Cu foil catalysts during the electrochemical 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. The SEM results after the electrocatalysis 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 electrocatalysts 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 intermediates 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 spectroscopy (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.

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$_2$RR 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$_2$RR. 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$_2$O) 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.

Author Contributions

Minki Jun — Department of Chemistry and Research Institute for Natural Sciences, Korea University, Seoul 02841, Republic of Korea; orcid.org/0000-0003-0575-7216; Email: kylee1@korea.ac.kr

Taehyun Kwon — Department of Chemistry and Research Institute for Basic Sciences, Incheon National University, Incheon 22012, Republic of Korea; orcid.org/0000-0002-7402-027X; Email: thyunkwon@inu.ac.kr

Authors

Minki Jun — Department of Chemistry and Research Institute for Natural Sciences, Korea University, Seoul 02841, Republic of Korea

Doyeop Kim — Department of Chemistry and Research Institute for Natural Sciences, Korea University, Seoul 02841, Republic of Korea

Minsu Kim — Department of Chemistry and Research Institute for Natural Sciences, Korea University, Seoul 02841, Republic of Korea

Minah Kim — Department of Chemistry and Research Institute for Natural Sciences, Korea University, Seoul 02841, Republic of Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c05920

Author Contributions

*M.J. and D.K. contributed equally.

Notes

The authors declare no competing financial interest.

Biographies

Minki Jun (B.S. 2017) is currently pursuing his Ph.D. degree in inorganic chemistry under the supervision of Prof. Kwangyeol Lee in the Department of Chemistry, Korea University. His current research interests include the development of nanomaterials as catalysts for hydrogen energy conversion and the synthesis of nanoparticles in the microfluidic system.

Doyeop Kim (B.S. 2022) is currently pursuing his Ph.D. degree in inorganic chemistry under the supervision of Prof. Kwangyeol Lee in the Department of Chemistry, Korea University. His current research interests are focused on the synthetic strategy of various nanostructured electrocatalysts and their application for fuel cells and water-splitting systems.

Minsu Kim (B.S. 2022) is currently pursuing his M.S. degree in inorganic chemistry under the supervision of Prof. Kwangyeol Lee in the Department of Chemistry, Korea University. His current research interests are in the improvement of oxygen evolution reaction performance in polymer electrolyte membrane water electrolysis by substrate effect.

Minah Kim (B.S. 2022) is currently pursuing her M.S. degree in inorganic chemistry under the supervision of Prof. Kwangyeol Lee in the Department of Chemistry, Korea University. Her current research interests are in the design of nanostructured electrocatalysts for carbon dioxide reduction reaction applications.

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.

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