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# Carbon Monoxide Reduction Reaction to Produce Multicarbon Products in Acidic Electrolytes Using Gas Diffusion Electrode Loaded with Copper Nanoparticles

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The synthesis of multi-carbon products ( $C_{2+}$ ) by electrochemical  $CO_2$  reduction reaction ( $CO_2RR$ ) is a promising technology that will contribute to the realization of a carbon-neutral society. In particular, efficient  $CO_2RR$  to produce  $C_{2+}$  in acidic electrolytes is desirable because the conversion of  $CO_2$  to inert (bi)carbonate can be suppressed under acidic conditions, thereby increasing the efficiency of substrate  $CO_2$  utilization. Herein, since  $C_{2+}$  products are produced via the dimerization of carbon monoxide, an intermediate in  $CO_2RR$ , the focus is on the carbon monoxide reduction reaction (CORR). A gas diffusion electrode loaded with copper nanoparticles is used in acidic electrolytes to investigate the conditions necessary for efficient  $C_{2+}$  production. The faradaic efficiency and partial current density for  $C_{2+}$  production attained 75% and  $280\text{ mA cm}^{-2}$  in a pH 2.0 solution, and they reached up to 66% and  $260\text{ mA cm}^{-2}$  even in a pH 1.0 solution. Numerical simulations showed that increasing the alkalinity of the electrode surface to greater than pH 7 by consuming protons is necessary to facilitate the production of  $C_{2+}$  during the CORR. When the desired level of alkalinity is achieved, the concentration and type of alkali cations present at the electrode surface have an impact on the selectivity for  $C_{2+}$  production.

the  $CO_2RR$ , it is necessary to improve energy efficiency, product selectivity, and production rate.<sup>[5–7]</sup> One essential criterion for the social implementation of this technology is the production of higher-value chemicals at a high reaction rate, including multi-carbon compounds ( $C_{2+}$ , (e.g., ethylene, ethanol, acetic acid, and *n*-propanol)). Although non-Cu electrocatalysts for generating  $C_{2+}$  compounds have recently begun to be successfully developed,<sup>[8,9]</sup> Cu-based electrocatalysts have been the most extensively studied to efficiently produce these multi-carbon compounds.<sup>[3,10–14]</sup>  $CO_2RR$  studies using Cu-based catalysts have generally been performed in neutral or alkaline electrolytes<sup>[15,16]</sup> because the competing  $H_2$  evolution reaction (HER) tends to become dominant in acidic solutions. However,  $CO_2$  is easily converted to inert (bi)carbonate, which migrates to the anode compartment or is discharged at the outlet of the anode compartment; thus, neutral or alkaline electrolytes are disadvantageous from the viewpoint of substrate utilization efficiency.<sup>[17–19]</sup> Therefore, an efficient  $CO_2RR$  that proceeds under acidic conditions is required.

## 1. Introduction

The electrochemical carbon dioxide ( $CO_2$ ) reduction reaction ( $CO_2RR$ ) has attracted much attention as a strategy to valorize anthropogenic  $CO_2$ .<sup>[1–4]</sup> For practical implementation of

viewpoint of substrate utilization efficiency.<sup>[17–19]</sup> Therefore, an efficient  $CO_2RR$  that proceeds under acidic conditions is required.

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The use of a gas diffusion electrode (GDE), which can overcome the problem of limited mass transport due to the low solubility of  $\text{CO}_2$ , has recently been reported to be an effective method to accelerate the  $\text{CO}_2$ RR.<sup>[20–22]</sup> For high-rate  $\text{CO}_2$ RR with GDEs, the local pH at the electrode surface increases with increasing cathodic current density, as both  $\text{CO}_2$ RR and HER consume protons. Therefore, the use of a GDE is expected to enable the  $\text{CO}_2$ RR to be conducted in acidic electrolytes. In fact, Huang et al. deposited a cation augmentation layer composed of cationic perfluorosulfonic acid ionomer onto the cathode surface; as a result, the  $\text{CO}_2$ RR was successfully conducted on a Cu catalyst at pH < 1 with a faradaic efficiency (FE) of 48% for multicarbon products at  $1200 \text{ mA cm}^{-2}$ .<sup>[23]</sup> Ma et al. reported that a high-alkalinity microenvironment was created when porous Cu nanosheets were used, resulting in an FE of 83.7% and a partial current density of  $560 \text{ mA cm}^{-2}$  for  $\text{C}_{2+}$ .<sup>[24]</sup> Our group also reported that Ni-doped covalent triazine frameworks (Ni-CTFs) on a GDE showed an FE greater than 90% for CO production from  $\text{CO}_2$  in a solution at pH 2.<sup>[25]</sup> By contrast, when a normal immersed electrode was used, the FE was only 1.2% in an electrolyte with the same pH.<sup>[25]</sup> Several other groups have reported efficient electrochemical  $\text{CO}_2$  reduction using acidic electrolytes.<sup>[18,26–34]</sup>

Although several studies have been conducted on the production of  $\text{C}_{2+}$  via  $\text{CO}_2$ RR in acidic solutions as mentioned above, the necessary conditions to improve its efficiency have not been fully elucidated, especially from a quantitative perspective. To obtain guidelines for enhancing  $\text{C}_{2+}$  production efficiency, we have turned our attention to the fact that the formation of  $\text{C}_{2+}$  products in the  $\text{CO}_2$ RR proceeds through the dimerization of the precursor, CO. To shed light on the factors contributing to the selective generation of  $\text{C}_{2+}$  in acidic solutions, studying CO electrolysis is more beneficial than studying  $\text{CO}_2$  electrolysis. This is because the direct study on CO electrolysis allows for a constant amount of CO to be supplied to the catalytic surfaces and eliminates local pH variations caused by the dissolution of  $\text{CO}_2$ , thereby providing a more suitable environment to investigate important factors for CO dimerization in acidic electrolytes. However, the CO reduction reaction (CORR) to produce  $\text{C}_{2+}$  in acidic electrolytes has not been studied. In the present work, we quantitatively investigate the CORR to form  $\text{C}_{2+}$  products in an acidic solution through experimental gaseous CO electrolysis and numerical simulation of the local pH with the aim of identifying the necessary conditions for  $\text{C}_{2+}$  production.

## 2. Results and Discussion

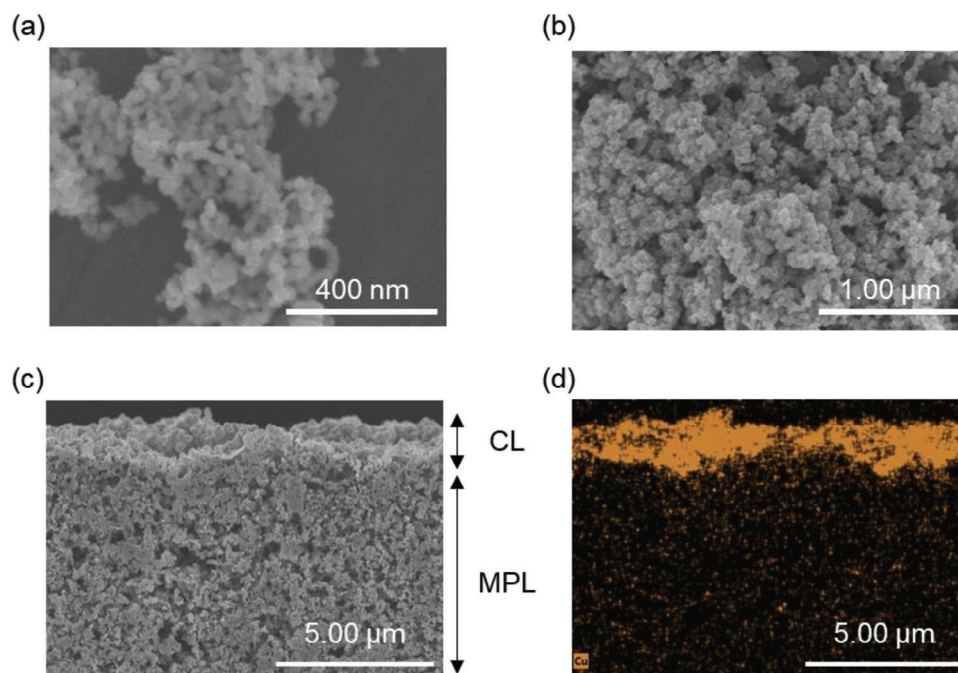
### 2.1. Synthesis and Characterization of Cu Nanoparticles and GDEs Carrying Them

Copper nanoparticles (CuNPs) catalysts were synthesized using a chemical reduction method with  $\text{NaBH}_4$  as the reductant (for details, refer to the Supporting Information). The crystal structures of the CuNPs were characterized by X-ray diffraction (XRD) analysis (Figure S1, Supporting Information). The XRD pattern shows peaks at  $35.5^\circ$  and  $38.7^\circ$ , which correspond to CuO(002) and CuO(111) planes. The Cu(II) oxidation state was also investigated by narrow-scan X-ray photoelec-

tron spectroscopy (XPS) and X-ray absorption near edge structure (XANES) (Figures S2 and S3, Supporting Information). The narrow-scan Cu 2p XPS spectrum shows that both the Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  peaks at bonding energies of  $\approx 933.8$  and  $\approx 953.7$  eV contain signals from Cu(II). These results indicate that the surface of the CuNPs was almost oxidized by ambient air after synthesis. Figure 1a shows an SEM image of the CuNPs. Figure 1b,c show top-view and cross-sectional SEM images, respectively, of the CuNPs/GDE. Figure 1d shows an EDX mapping image corresponding to Figure 1c for Cu (the mapping images for other elements are shown in Figure S4, Supporting Information). The thickness of the CuNPs catalyst layer was  $0.5\text{--}2 \mu\text{m}$ . The surface of the microporous layer (MPL) was almost fully covered by CuNPs.

### 2.2. CORR to Form $\text{C}_{2+}$ Products in Acidic Electrolytes

For the CORR measurements, we used a custom-made three-compartment electrochemical cell (Figure S5, Supporting Information).<sup>[35,36]</sup> We obtain the current density versus potential curves of our electrode solution in pH 1.0 and 2.0 under continuous Ar or CO delivery conditions (Figure S6, Supporting Information). For all four conditions, the onset potential of cathodic currents was  $\approx -0.8$  V versus Ag/AgCl. When Ar conditions were changed to CO conditions, the current values slightly decreased, which is likely due to the fact that adsorbed CO suppresses HER. The gaseous CORR products and liquid products were analyzed by gas chromatography and  $^1\text{H-NMR}$  spectroscopy, respectively, after constant-current electrolysis (Figures S7 and S8, Supporting Information, respectively). The CORR products were analyzed at pH 1.0–14 under constant-current-density conditions. The  $\text{K}^+$  concentration was fixed at  $2.0 \text{ M}$  in the series of experiments to eliminate the effect of alkali cations. The FEs for the CORR products in pH 2.0 solutions at different current densities are shown in Figure 2a. At the low current density of  $50 \text{ mA cm}^{-2}$ , the HER—the reaction that competes with the CORR—was dominant (FE<sub>H<sub>2</sub></sub> of 75%), whereas the FEs for  $\text{CH}_4$  and  $\text{C}_{2+}$  from the CORR were 15% and less than 5%, respectively. The FE<sub>C<sub>2+</sub></sub> increased with increasing current density in the electrolyte at pH 2.0, reaching 75% at  $200 \text{ mA cm}^{-2}$ , and the main products were  $\text{C}_2\text{H}_4$  (38%), ethanol (14%), acetic acid (17%), and *n*-propanol (6%) at  $200 \text{ mA cm}^{-2}$ . The FE<sub>C<sub>2+</sub></sub> did not substantially change even at  $400 \text{ mA cm}^{-2}$ . The partial current density for each product is shown in Figure 2b. The partial current density for  $\text{C}_{2+}$  production ( $j_{\text{C}_{2+}}$ ) increased monotonically to  $j_{\text{C}_{2+}} = 280 \text{ mA cm}^{-2}$  at  $J = 400 \text{ mA cm}^{-2}$ . Approximately the same tendency was observed when the pH 1.0 solution was used as the electrolyte (Figure 2c,d). This is the first demonstration of CO reduction reaction to  $\text{C}_{2+}$  products at industrial current densities in acidic electrolytes. However, when the pH was lowered to 0.5,  $\text{H}_2$  production became dominant even when the total current density was increased to  $200 \text{ mA cm}^{-2}$  (Figure 3a). The pH dependence of the CORR activity at  $200 \text{ mA cm}^{-2}$  (Figure 3a) revealed that although the increase was very slight above pH 7, the FE<sub>C<sub>2+</sub></sub> for CORR monotonically rises from pH 1.0 to pH 14. Although almost no FE<sub>C<sub>2+</sub></sub> was observed the HER was dominant at pH 0.5, and apparent  $\text{C}_{2+}$  formation (FE > 65%) occurred at pH 1.0–14.

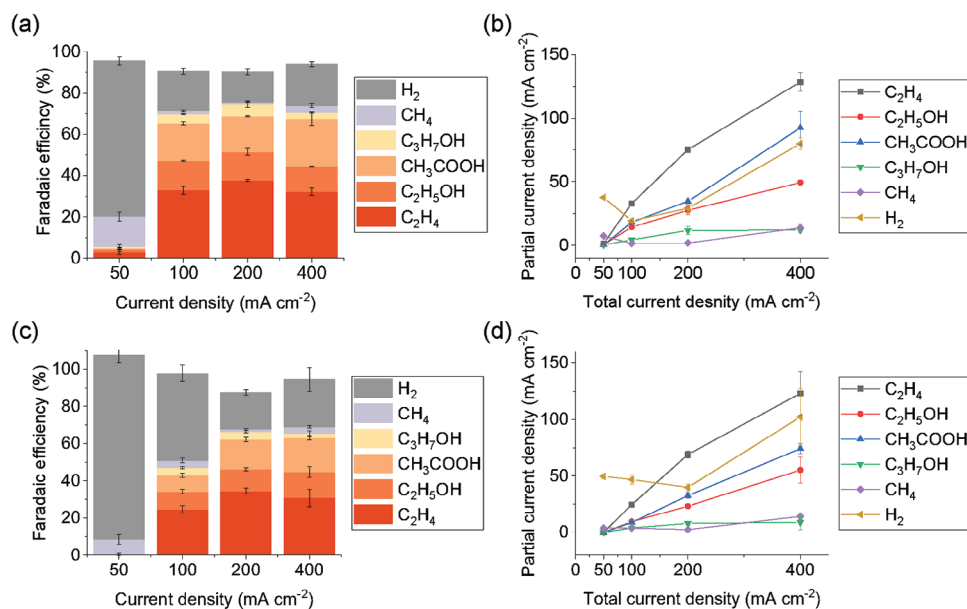


**Figure 1.** SEM image of a) CuNPs and b) CuNPs/GDE. c) Cross-sectional SEM image of CuNPs/GDE. d) The corresponding EDX mapping for Cu in the image (c).

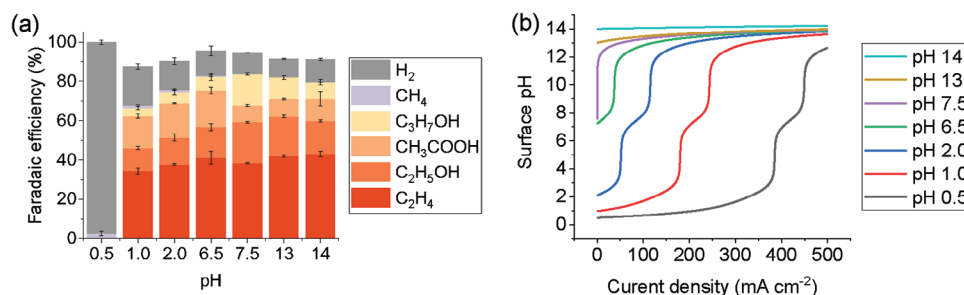
### 2.3. Surface pH Simulation in Acidic Electrolytes

Given that the apparent  $C_{2+}$  formation was observed over a wide pH range (pH 1.0–14), we assume that the pH value at the surface of the catalyst layer (CL) increased substantially and became highly alkaline even when acidic or neutral electrolytes were used under high-rate electrolysis con-

ditions. The alkalinity is attributed to both the CORR and HER being proton-consuming reactions. In addition, our group has shown that using a GDE enhances local proton depletion compared with the case where planar electrodes are used.<sup>[25]</sup> This assumption is also supported by the observation that the FE for  $C_{2+}$  increased with increasing current density.



**Figure 2.** a) Faradaic efficiency and b) partial current density in pH 2.0 solution (0.5 M  $H_3PO_4$  + 0.5 M  $KH_2PO_4$  + 1.5 M KCl) at different current densities. c) Faradaic efficiency and d) partial current density in pH 1.0 solution (1.0 M  $H_3PO_4$  + 2.0 M KCl) at different current densities.



**Figure 3.** a) Faradaic efficiency at  $200\ mA\ cm^{-2}$  in electrolytes at various pH levels. The composition of each electrolyte is listed in Table S3 (Supporting Information). b) Simulation results of the surface pH (distance to the cathode of  $0\ \mu m$ ). The current density was varied from 0 to  $500\ mA\ cm^{-2}$ . The electrolyte was the same as in the experiment in (a).

Thus, we next clarified the effect of local pH on the CORR under high-rate electrolysis using macro-scale theoretical simulations. The surface pH was simulated using the Reaction-Diffusion model.<sup>[37]</sup> A set of partial differential equations was solved using the finite element method implemented in the COMSOL Multiphysics environment. The thickness of the diffusion layer was set to  $100\ \mu m$  on the basis of previous reports.<sup>[18,31,38]</sup> For simplicity, we used a one-dimensional model with a point electrode and only considered the proton-consuming reaction, which can be rationalized because we can omit the pH alteration caused by  $CO_2$  dissolution. Further details are provided in the Supporting Information. Figure 3b shows the theoretical surface pH as a function of the current density for various bulk pH levels. As predicted, the surface pH increased sharply at the current density threshold as a function of the bulk pH. The surface pH for a solution with a bulk pH of 2.0 increased to 3.8 at  $50\ mA\ cm^{-2}$  (i.e., the conditions were still acidic). For reactions in bulk pH 2.0 solutions, the surface pH crossed 7 at  $70\ mA\ cm^{-2}$  and the solution became strongly alkaline (12.9) at  $200\ mA\ cm^{-2}$ . This simulation result is basically in agreement with the experimental CORR results corresponding to pH 2.0 (Figure 2a). Specifically, the FE for  $C_{2+}$  dramatically increased from 5% at 50 to 70% at  $100\ mA\ cm^{-2}$ , reaching a value of 75% at  $200\ mA\ cm^{-2}$ . At pH 0.5, the surface remained acidic at  $200\ mA\ cm^{-2}$  (with a simulated surface pH of 0.95), which is consistent with the almost negligible production of  $C_{2+}$ . With respect to the results at pH 1.0, the simulation results indicate that the first and second pH jumps occur at 180 and  $245\ mA\ cm^{-2}$ , respectively. Meanwhile, the FE of  $C_{2+}$  production is 47% and 66% at 100 and  $200\ mA\ cm^{-2}$  at pH 1.0, respectively. While these results are qualitatively accurate, there is a slight quantitative discrepancy. This difference could be attributed to the need for an additional consideration of the local pH within the microscopic three-phase interface. We continue to investigate this aspect in our research lab and plan to report our findings in subsequent publications.

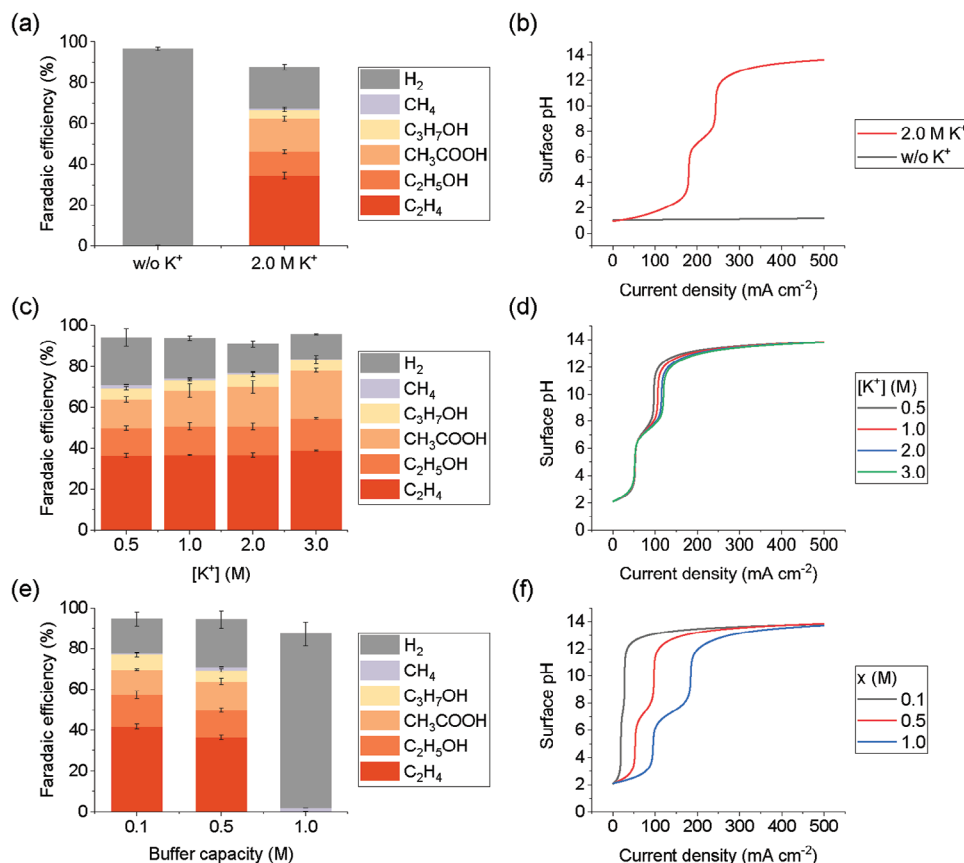
The simulated surface pH at  $200\ mA\ cm^{-2}$  was 0.9, 7.1, 13.0, 13.3, and 14.1 at bulk pH levels of 0.5, 1.0, 2.0, 6.5, and 14, respectively. These results are quantitatively consistent with the result that the HER dominates the CORR when the electrode surface is acidic. Thus, the change in surface pH is the most important factor for suppressing HER and for C–C bond formation.

## 2.4. Factors Affecting Surface Alkalization

As shown in the previous section, an increase in surface pH is critical for  $C_{2+}$  production by the CORR in acidic solutions. We next attempted to identify important factors for increasing the surface pH, focusing on the concentrations of alkali cations and on buffering effects. We first investigated the necessity of alkali cations for the CORR. Figure 4a shows the results for the CORR conducted in a pH 0.80 alkali cation-free electrolyte. In the absence of alkali cations, the predominant process observed was  $H_2$  evolution. The only CORR product generated under these conditions was methane, albeit in minuscule amounts ( $FE_{CH_4} = 0.2\%$ ); no  $C_{2+}$  products were detected. Figure 4b illustrates the simulation results reflecting the pH changes on the electrode surface while employing an electrolyte devoid of alkali cations. Irrespective of the increase in current density, the electrode surface maintains an acidic environment, suggesting that the system is unable to attain alkalinity because of a lack of counterbalancing positive charge against  $OH^-$ . Therefore, in the CORR processes involving acidic electrolytes, alkali cation species appear to facilitate local alkalization by serving as counter ions to the anions present on the electrode surface.

We then investigated the concentration dependence of the alkali cation species in the CORR. Figure 4c shows the FEs for CORR products at  $200\ mA\ cm^{-2}$  in pH 2.0 solutions in which the  $K^+$  concentration was varied from 0.5 to  $3.0\ M$  by the addition of KCl. The  $FE_{C_{2+}}$  exceeded 65% at all of the investigated  $K^+$  concentrations and increased slightly with increasing  $K^+$  concentration: from 69% at 0.5 to 83% at  $3.0\ M\ K^+$ . We used COMSOL to simulate the surface pH values in the presence of  $K^+$  ions at various concentrations (Figure 4d). Although we observed that the pH jump from neutral to alkaline shifted to a lower current density with decreasing  $K^+$  concentration, the concentration of  $K^+$  had little effect on the surface pH compared with the bulk pH and the current density. In particular, the surface pH reached 13 at  $200\ mA\ cm^{-2}$  (experimental conditions), which coincides with the  $FE_{C_{2+}}$  being consistently greater than 70% when the  $K^+$  concentration is in the range of 0.5– $3.0\ M$  (Figure 4c). Namely, the alkali cation concentration is not the primary factor contributing to the surface alkalization, despite the slight increase in  $FE_{C_{2+}}$  observed with an increase in  $K^+$  concentration. The implications of the slight increase in  $FE_{C_{2+}}$  with the increasing  $K^+$  concentration will be discussed in the following section.



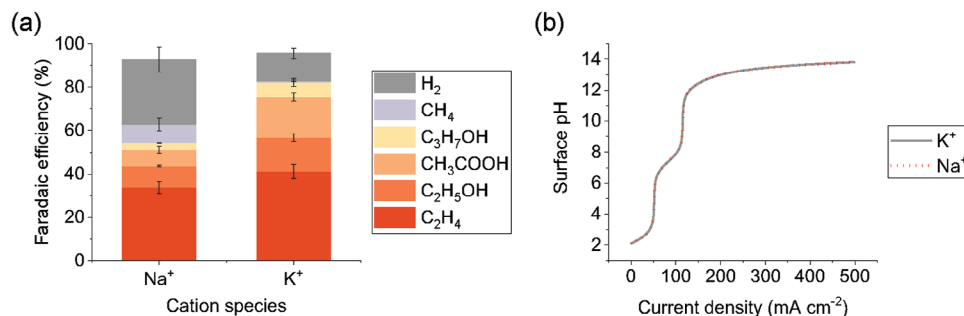


**Figure 4.** a) Faradaic efficiency in an alkali cation-free electrolyte (1.0 M  $\text{H}_3\text{PO}_4$ ) at  $200 \text{ mA cm}^{-2}$ . b) Simulation results of the surface pH in an alkali cation-free electrolyte (1.0 M  $\text{H}_3\text{PO}_4$ ). The results for a solution containing 2.0 M  $\text{K}^+$  ions are shown for comparison. c) Faradaic efficiency in pH 2.0 solution with different  $\text{K}^+$  concentrations (0.5 M  $\text{H}_3\text{PO}_4 + 0.5 \text{ M KH}_2\text{PO}_4 + x \text{ M KCl}$ ,  $x = 0, 0.5, 1.5, 2.5$ ) at  $200 \text{ mA cm}^{-2}$ . d) Simulation results for the surface pH. The electrolyte was the same as in the experiment in (c). e) Faradaic efficiency in pH 2.0 solution with different buffer capacities ( $x \text{ M H}_3\text{PO}_4 + x \text{ M KH}_2\text{PO}_4$ ,  $x = 0.1, 0.5, 1.0$ ) at  $200 \text{ mA cm}^{-2}$ . f) Simulation results for surface pH. The electrolyte was the same as in the experiment in (e).

Because the concentration of the buffer strongly affects local pH changes within the diffusion layer,<sup>[39,40]</sup> we next investigated the effect of a buffer on CORR activity by changing the phosphate species concentration. We prepared pH 2.0 solutions with 0.1, 0.5, and 1.0 M phosphates as electrolytes. Notably, although we also needed to change the  $\text{K}^+$  concentration to maintain the bulk pH as the phosphate buffer concentration was varied, the  $\text{K}^+$  concentration did not affect the CORR activity in this concentration range (Figure 4c). Figure 4e shows that the  $\text{FE}_{\text{C}_{2+}}$  for the CORR at  $200 \text{ mA cm}^{-2}$  was 77% and 69% in 0.1 and 0.5 M phosphate solutions, respectively. However, when the phosphate concentration was increased to 1.0 M, the HER became dominant and  $\text{C}_{2+}$  formation was scarcely observed. As the buffering capacity increased with increasing concentration of phosphate anions, the pH jump threshold shifted toward higher current density. Although the surface apparently became alkaline at  $200 \text{ mA cm}^{-2}$  in 0.1 and 0.5 M phosphate solutions (bulk pH 2.0), the current density of  $200 \text{ mA cm}^{-2}$  was just at the threshold for the pH jump in 1.0 M phosphate solutions (Figure 4f). These simulation results suggest that alkalization of the surface would not be sufficient for an effective CORR in 1.0 M phosphate solutions in the experiment, consistent with the experimental CORR results (Figure 4e).

## 2.5. Factors Affecting $\text{C}_{2+}$ Selectivity After Surface Alkalization

In the previous sections, alkalization of the electrode surface was shown to be required to suppress the HER and selectively generate  $\text{C}_{2+}$  products. Therefore, we next investigated the factors that further influence the selectivity for  $\text{C}_{2+}$  products when alkalized. As shown in Figure 4c, we observed a slight increase in  $\text{FE}_{\text{C}_{2+}}$  with a rising amount of  $\text{K}^+$ , even though the surface pH remained constant. We assumed that this slight increase in  $\text{FE}_{\text{C}_{2+}}$  is due to the stabilization effect of surface alkali cations on the adsorbed CO molecules. Previous theoretical and experimental studies have shown that adsorbed CO molecules are coordinated and stabilized by alkali cations, promoting CO dimerization.<sup>[32,41–43]</sup> (please see the next section) To investigate this hypothesis, we replaced  $\text{K}^+$  with  $\text{Na}^+$  ions in the electrolyte. Although the surface pH did not depend on the alkali cation species (Figure 5b), the  $\text{FE}_{\text{C}_{2+}}$  in  $\text{Na}^+$  solutions was much lower than that in  $\text{K}^+$  solutions (Figure 5a). We observed the apparent difference of FE among  $\text{K}^+$  and  $\text{Na}^+$  even when using 1.0 M  $\text{H}_3\text{PO}_4 + 1.3 \text{ M MCl} + 0.7 \text{ M MOH}$  (for the detail, see Figure S9, Supporting Information and its caption). In addition to the alkali cation species dependence of the CORR, given that the surface  $\text{K}^+$  concentration depends on the bulk  $\text{K}^+$



**Figure 5.** a) Faradaic efficiency in pH 2.0 solution containing different cation species (0.5 M H<sub>3</sub>PO<sub>4</sub> + 0.5 M H<sub>2</sub>PO<sub>4</sub> + 1.5 M MCl, M = Na<sup>+</sup>, K<sup>+</sup>) at 200 mA cm<sup>-2</sup>. b) Simulation results for surface pH. The electrolyte was the same as in the experiment in (a).

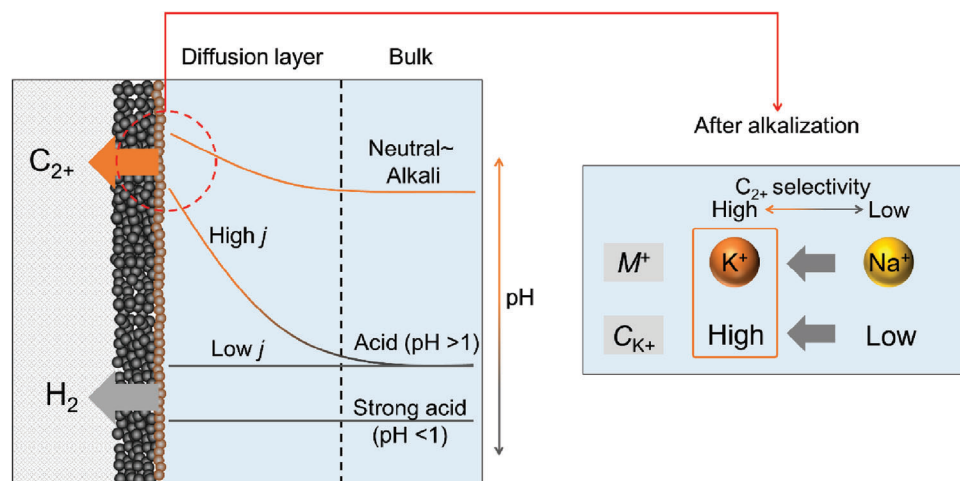
concentration (Figure S10, Supporting Information), the surface K<sup>+</sup> would facilitate CO dimerization, resulting in a slight increase in FE<sub>C<sub>2</sub>+</sub> with increasing bulk K<sup>+</sup> concentration.

## 2.6. Discussion About C<sub>2</sub><sup>+</sup> Formation in Acidic Electrolyte

Our CORR experiments and simulation results indicate that local alkalinity at pH levels greater than seven is an absolute requirement for selective C<sub>2</sub><sup>+</sup> formation (FE<sub>C<sub>2</sub>+</sub> > 60%). In addition, when local alkalinity is achieved, the concentration and species of alkali cations influence the selectivity for C<sub>2</sub><sup>+</sup> production (Figure 6, left). Here, let us consider the mechanism of these trends. First, we can explain the requirement of alkaline conditions for C<sub>2</sub><sup>+</sup> formation as follows. There are mainly two possible mechanisms by which C<sub>2</sub><sup>+</sup> formation is enhanced by the local alkaline environment. First, whereas the rate and theoretical potential for H<sub>2</sub> formation are clearly dependent on proton activity, the rate-determining step (RDS) for the reduction of CO or CO<sub>2</sub> to C<sub>2</sub><sup>+</sup> is suggested to be unrelated to proton addition. Despite also being a proton-consuming reaction, Wang and colleagues demonstrated that C<sub>2</sub><sup>+</sup> formation during CO<sub>2</sub>RR catalyzed by polycrystalline copper occurs independently of pH when measured on a standard hydrogen electrode (SHE) scale.<sup>[44]</sup>

Additionally, Kastlunger et al. showed that the dimerization of CO is an RDS based on the experimental results of CORR and constant-potential density functional theory.<sup>[45]</sup> Based on these studies, H<sub>2</sub> evolution would be selectively suppressed and C<sub>2</sub><sup>+</sup> formation would become relatively dominant under alkaline conditions. Another possible explanation is that hydroxide ions facilitate the formation of C<sub>2</sub><sup>+</sup>. For instance, the presence of OH<sup>-</sup> ions can reduce the activation energy required for C–C coupling, as indicated by DFT studies.<sup>[46,47]</sup> This effect is attributed to the increased charge imbalance between carbon atoms in the adsorbed OCCO species, leading to a more stable intermediate due to enhanced dipole attraction.<sup>[46]</sup> Furthermore, Sun et al. provided experimental evidence that electrodes with higher amounts of OH exhibit enhanced selectivity for C<sub>2</sub><sup>+</sup> by fabricating OH/Cu electrodes with varying amounts of OH adsorption.<sup>[48]</sup> As a future work, we would like to elucidate the detailed mechanism using both experimental and computational studies.

Next, we discuss the effect of the concentration and species of alkali cation on C<sub>2</sub><sup>+</sup> selectivity after surface alkalization (Figure 6, right). It has been reported that alkali cations have the effect of stabilizing the intermediate species for C<sub>2</sub><sup>+</sup>. For example, alkali cations have been shown to directly coordinate with the OCCO intermediate, as evidenced by ab initio molecular dynamics (AIMD).<sup>[41]</sup> The free energy for the dimerization of CO was



**Figure 6.** Schematic of electrode vicinity during electrochemical CO reduction. This figure shows the relationship between local pH and product selectivity.

reduced as the radius of the coordinating alkali cations increased. The other reported effect of alkali cations on the dimerization of CO is due to the modulation of the interfacial electric field. Resasco et al. observed an increase in the partial current density for  $C_{2+}$  (ethylene and ethanol) during  $CO_2$ RR on Cu electrodes with increasing the radius of alkali cations in electrolytes.<sup>[42]</sup> They attributed this effect to the stabilization of the intermediate by the interfacial electric field, which is dependent on the cation radius. Additionally, Ringe and colleagues, using an ab initio/continuum approach, reported that weakly hydrated cations such as  $K^+$  and  $Cs^+$  tend to accumulate at the outer Helmholtz plane.<sup>[43]</sup> Consequently, the presence of these cations in the electrolyte results in an increased surface positive charge density, leading to a stronger interfacial electric field. In this study as well, the effects exerted by these alkali cation species on the reaction intermediates likely modulated the  $C_{2+}$  production selectivity after surface alkalization.

### 3. Conclusion

In conclusion, we attained  $C_{2+}$  production through the CORR in highly acidic solutions with a pH of 1.0 or 2.0. The achievement of local alkalinity with a pH > 7 at the electrode surfaces, which is a result of electrochemical proton-consuming reactions (i.e., the CORR and HER), is a requirement for  $C_{2+}$  production ( $FE_{C_{2+}} > 60\%$ ). Through numerical calculations and CORR experiments, we found that the local pH is primarily influenced by the bulk pH and the current density. Once alkalinity was achieved, the concentration and species of alkali cations became the determining factors affecting the selectivity for  $C_{2+}$  production. Achieving efficient  $C_{2+}$  formation via the  $CO_2$ RR in an acidic electrolyte is beneficial from the viewpoints of carbon and energy efficiency because neutral and alkaline solutions absorb  $CO_2$  as (bi)carbonate, and substantial energy is required to convert (bi)carbonates back into  $CO_2$ . In addition, the practical implementation of  $CO_2$ RR requires a membrane electrode assembly (MEA)-type cell, similar to the implementation for water electrolysis. Currently, only systems equipped with anion-exchange membranes can generate  $C_{2+}$  in MEA-type  $CO_2$  electrolysis. Therefore, the use of a more robust and highly conductive acidic proton-exchange membrane to establish MEA-type  $CO_2$  electrolysis is desirable. The novel insights obtained in this study are expected to contribute to the development of an MEA-type  $CO_2$  electrolysis system equipped with proton-exchange membranes.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

acidic electrolyte,  $CO$  reduction reactions, gas-diffusion electrodes, high-rate electrolysis, numerical simulation

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