Ultra-high-rate CO$_2$ reduction reactions to multicarbon products with a current density of 1.7 A/cm$^2$ in neutral electrolytes

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Abstract

CO₂ electrolysis to value-added products is a promising technology to close the carbon cycle and sequester anthropogenic CO₂ into chemical feedstocks; an increase of the current density for multicarbon products is one of the requirements for practical implementation. We have successfully increased the partial current density for gaseous CO₂ reduction reactions to multicarbon products (C₂+) over Cu nanoparticles on gas diffusion electrodes in neutral electrolytes to a record value of 1.7 A/cm². The faradaic efficiency for multicarbon products increased with the current density and reached 76% at a total current density of 1.6 A/cm². The turnover frequency for the production of C₂+ per Cu atoms exceeded 2.8 s⁻¹. The optimal porosity and thickness of the catalyst layer are confirmed as factors that elicit the high-turnover frequency of Cu atoms, resulting in the record partial current density for C₂+. 
Introduction

The electrochemical carbon dioxide reduction reaction (CO$_2$RR) has attracted considerable attention as a promising strategy for the conversion of anthropogenic CO$_2$ into value-added products.$^{1-8}$ One advantage of this method is that this greenhouse gas can be reduced under mild conditions (close to ambient temperature and pressure).$^9$ However, the operative efficiency, product selectivity and rate must be improved for practical implementation.$^{10, 11}$ In particular, it has been reported that the current density for the production of high value-added products is directly correlated to the capital cost of the electrodes employed.$^{12}$ Therefore, improvement of the current density would significantly affect the feasibility of this technology.

The use of gas diffusion electrodes (GDEs) that allow the CO$_2$RR to occur at the solid-catalyst/liquid-electrolyte/gaseous-CO$_2$ interface, effectively accelerate the CO$_2$RR by solving the problem of the mass transport limitation due to the inherently low diffusion and solubility of CO$_2$ in water.$^{13, 14}$ A catalyst layer (CL) composed of metal Cu particles and ionomers on carbon-based microporous layers has been widely studied as the standard cathode for gaseous CO$_2$RR to produce C$_2+$ organics, such as C$_2$H$_4$, C$_2$H$_5$OH, C$_3$H$_7$OH and CH$_3$COOH.$^{15-18}$ Although the partial current density for C$_2+$ ($j_{C2+}$) has still remained below 500 mA/cm$^2$ in many studies,$^{15, 18-25}$ a few studies have developed novel
cathode assemblies or components toward an ultra-high-rate (UHR-) CO₂RR with over $j_{C_2^+} = 1 \text{ A/cm}^2$. Sargent et al. successfully achieved a $j_{C_2^+}$ over 1.2 A/cm² in 7 M KOH using an electrode fabricated by dropping Cu nanoparticles on a sputtered Cu film/porous polytetrafluoroethylene (PTFE).²⁶ Additionally, in this work, the bulk heterojunction of catalysts and ionomers decoupled the pathways for gases, electrons and ions, which resulted in a $j_{C_2^+}$ over 1 A/cm². Wang and coauthors reported that a fluorine-modified copper catalyst deposited on GDEs exhibited a total current density ($J_{\text{total}}$) of 1.6 A/cm² with a faradaic efficiency for C₂⁺ (FE$_{C_2^+}$) of over 80% (i.e., $j_{C_2^+} = 1.2 \text{ A/cm}^2$) in 0.75 M KOH.²⁷

In these reports, UHR-CO₂RR has been achieved using high alkaline solutions to suppress H₂ evolution, which competes with the CO₂RR. However, in addition to the toxicity and corrosivity, alkaline solutions quickly absorb CO₂ and convert it to electrochemically inert (bi)carbonate.²⁸⁻³¹ Based on these drawbacks, UHR electrolysis in neutral electrolytes is thus required from a practical viewpoint. Furthermore, these previous studies succeeded in achieving UHR-CO₂RR by developing novel components in the three-phase interfaces (i.e. catalysts or electrodes). However, the obtainable maximum $j_{C_2^+}$ value is still unknown when optimizing the standard assembly and components; Cu nanoparticle catalysts (CuNPs) and carbon-based gas diffusion layers.
An electrochemical system that can elicit the maximum $j_{C2+}$ using only standard components will become the primary platform for future studies to design materials and interfaces for UHR-CO$_2$RR. In other words, the design guidelines obtained from the UHR-CO$_2$RR with only ordinary materials would be quite general, and thus, they are expected to be widely applicable to novel materials and systems.

In the present work, we attempt to pursue a high partial current density for C$_2+$ ($j_{C2+}$) using neutral electrolytes by elaborating the standard components and assembly of the cathode. We investigated the relationship between current density ($J_{\text{total}}$) and FE$_{C2+}$ by variation of the loading method and the amount of Cu nanoparticles (CuNPs), and achieved a record current density of 1.7 A/cm$^2$ for multicarbon products in neutral electrolyte. Furthermore, we conducted systematic stability tests with respect to current densities of $J_{\text{total}} > 1$ A/cm$^2$ in neutral solutions for the first time.
Results and discussion

Physical and morphological characterization of CuNPs/GDEs

CuNP catalysts were synthesized by wet-chemical reduction using NaBH$_4$ as a reductant. Transmission electron microscopy (TEM) observations (Figures 1a and S1) show that the particle morphology and size is spherical and 20 nm, respectively. X-ray diffraction (XRD) patterns (Figure S2) indicate peaks at 35.5° and 38.7°, which are attributed to CuO(002) and CuO(111), respectively. This oxidation state of the as-prepared sample was also confirmed by narrow scan X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure (XANES), as shown in Figure S3 and S4, respectively. Note that the Cu(II) oxidation state was reduced to Cu(I)/Cu(0) during electrolysis (Figure S5 and S6).

Morphological characterization of the CuNPs/GDEs (Figure S7) was conducted using scanning electron microscopy (SEM). Figures 1b-d and S8 show top- and cross-sectional SEM images of CuNPs-1.7/GDE (where the loading amount of CuNPs is 1.7 mg/cm$^2$), respectively. CuNPs completely covered the electrode surface based on the top-view SEM images, and were deposited on the microporous layer (MPL) composed of carbon nanoparticles. The cross-sectional SEM images reveal that the thickness of the MPL and the CL were ca. 80 and 2 μm for CuNPs-1.7/GDE, respectively. When the loading amount
of CuNPs was varied to 0.34 mg/cm\(^2\) (Figure S9) and 3.1 mg/cm\(^2\) (Figure S10), the CL thicknesses changed to ca. 0.5 \(\mu\)m and 4 \(\mu\)m, respectively. The roughness of the CL was about 300 nm. From the top-view SEM observations, the surface morphology was almost the same among the three different loading amounts of CuNPs.

Figure 1 (a) Representative TEM image of the synthesized CuNPs. (b) Top-view and (c-d) cross-sectional SEM micrographs of CuNPs-1.7/GDE.

**UHR-CO\(_2\)RR using CuNPs over 1.7 A/cm\(^2\) for C\(_2\)+ products**

We measured the CO\(_2\)RR activity of the Cu-based GDE catalysts. An in-house-built three-compartment electrochemical cell was used for CO\(_2\)RR evaluation (Figure S11).\(^{32}\)\(^{33}\) \(J_{\text{total}}\) vs. potential \((U)\) curves were obtained in 1 M KCl under CO\(_2\) and argon conditions,
as shown in Figure S12. The onset potential of the cathodic current for bare and Cu-modified GDEs were -0.9 and -0.5 V vs. reversible hydrogen electrode (RHE, for the detail in IR compensation, see the experimental section) under CO₂, respectively. When the Cu amount was increased from CuNPs-0.34/GDE to CuNPs-3.1/GDE, the cathodic current under CO₂ gradually increased.

The CO₂RR products in outlet gas streams from the gas chamber and electrolytes from the catholyte room were analyzed using gas chromatography (Figure S13) and ¹H nuclear magnetic resonance (NMR) spectroscopy (Figure S14) after constant-current electrolysis, respectively. Figure 2a and 2b show the FE and partial current density of CO₂RR products against the applied potential for CuNPs-1.7/GDE in 1 M KCl, respectively. Under low current conditions ($J_{\text{total}} = 200 \text{ mA/cm}^2$) at -0.69 V vs. RHE, CO was the main product (FECO > 50%), and the FEC₂H₄ was below 20%. The FE for C₂+ products increased and reached 76% at -1.02 V vs. RHE ($J_{\text{total}} = 1.6 \text{ A/cm}^2$) when the applied potential was shifted to the negative side. In particular, the FEs for C₂H₄ and C₂H₅OH were 47% and 23% at -1.09 V vs. RHE, respectively. The partial current density for C₂+ products (C₂H₄, C₂H₅OH, C₃H₇OH, and CH₃COOH) was over $j_{\text{C2+}} = 1.7 \text{ A/cm}^2$ at -1.09 V vs. RHE. On the contrary, the FEs for C₁ products (CO, CH₄ and HCOOH) and H₂ were 8.4 and 15% at -1.09 V vs. RHE, respectively. Figure 2c and Table S1 show a comparison of $j_{\text{C2+}}$ and FEC₂⁺ in neutral
electrolytes among the reported values. The partial current density for C$_2^+$ production ($j_{C2^+} = \text{over 1.7 A/cm}^2$) is a record value, and the FE$_{C2^+}$ is also one of the highest. Therefore, the present study succeeded in eliciting the potential performance of an ordinary combination for UHR-CO$_2$RR (i.e., CuNPs and carbon-based GDEs). When the applied potential was changed to -1.12 V vs. RHE ($J_{\text{total}} = 2.8 \text{ A/cm}^2$), the FE for C$_2^+$ products suddenly decreased, and the FE for H$_2$ increased. The total FEs at -1.12 V vs. RHE did not reach 100% (ca. 80%) because the bubbles contained CO$_2$ substrate, CO$_2$RR products, and H$_2$ formed at the cathode surface and diffused into the catholyte chamber.

Even when using neutral solutions, the local pH at the surface of the catalyst should increase significantly during UHR-CO$_2$RR due to the consumption of protons with an increase in the CO$_2$RR current density. Therefore, the cathode reaction proceeded under alkaline environments for UHR-CO$_2$RR even with neutral solutions; therefore, the fabricated cathode was expected to be suitable for UHR-CO$_2$RR even in bulk alkaline solutions. Figure 2d shows the FEs of CO$_2$RR products against the applied potential for CuNPs-1.7/GDE in 1 M KOH alkaline electrolyte, and Figure 2e shows a comparison of the FEs of C$_2^+$ products for CuNPs-1.7/GDE in 1 M KCl and 1 M KOH solutions. The FEs for CO$_2$RR activity in alkaline and neutral solutions were almost the same in the range of $J_{\text{total}} = 200$-2400 mA/cm$^2$, which indicates that the local pH around the CL in 1
M KOH and 1 M KCl solutions was not dependent on the bulk pH during electrolysis at 200 mA/cm². The partial current density for C₂⁺ products in alkaline solutions reached $j_{C^2+} = 1.8$ A/cm², which is a record value in alkaline solution, as compared and listed in Figure 2f and Table S2 respectively, i.e., this electrode can exhibit a record $j_{C^2+}$ in both neutral and alkaline solutions.

Figure 2 (a) FEs of the CO₂RR products under various applied potentials on CuNPs-1.7/GDE in 1 M KCl. Reaction time: 30 min. (b) Partial current density for C₂⁺, C₁ and H₂ on CuNPs-1.7/GDE in 1 M KCl. (c) Comparison of $FEC_{2+}$ and $j_{C2+}$ for CuNPs-1.7/GDE with reported Cu-based catalysts in neutral solution (for the detailed references, see Table S1). (d) FEs for the CO₂RR products under various applied potentials on
CuNPs-1.7/GDE in 1 M KOH. Reaction time: 30 min. (e) Comparison of FE$_{C2+}$ in 1 M KOH and in 1 M KCl under various $J_{\text{total}}$ over CuNPs-1.7/GDE. (f) Comparison of FE$_{C2+}$ and $j_{C2+}$ for CuNPs-1.7/GDE with reported Cu-based catalysts in alkaline solution (for the detailed references, see Table S2).

**Current density dependence of CO$_2$RR selectivity**

The FE$_{C2+}$ increased with increasing current density in the present UHR-CO$_2$RR system, and thus, a trade-off relationship between rate and selectivity was exhibited, as shown in Figure 2a. Let us discuss the mechanism for the increase of FE$_{C2+}$ with the current density. The product selectivity can be explained from the viewpoint of current density: the effect of (1) CO partial pressure, (2) local pH, and (3) *in situ* formation of the three-phase interface.

The CO partial pressure in the CL became high with an increase in the current density, which facilitated CO dimerization. Jun Li et al. controlled local CO availability at the catalyst–electrolyte interface and demonstrated that a high concentration of CO accelerated CO dimerization, and caused a higher current density with C$_2+$ production.$^{34}$ Jing Li and coworkers reported that a high CO partial pressure suppresses H* adsorption, which leads to lowering of the hydrogen evolution reaction (HER).$^{35}$ It should also be
noted here that the FE for C$_2$H$_5$OH against C$_2$H$_4$ increased with increasing $J_{\text{total}}$ (Figure S15). It has been reported that high CO pressure on a Cu surface favors C$_2$H$_5$OH production over C$_2$H$_4$ because the *CHCHOH intermediate for C$_2$H$_5$OH becomes more stable than *CCH for C$_2$H$_4$ under high CO coverage.$^{34,36}$ This is because CCH* and *CHCHOH are adsorbed on Cu sites with side-on and end-on configurations, respectively, so that CCH* requires a larger occupied molecular area than *CHCHOH. This change in selectivity between C$_2$H$_4$ and C$_2$H$_5$OH supports that the CO local pressure depended on the current density. The increase in the local pH at the surface of the CL due to proton consumption by the CO$_2$RR suppressed HER (vide supra). The pH at the electrode surfaces is known to reach up to 11.9 under electrolysis at just 50 mA/cm$^2$ in neutral electrolytes.$^{14,37}$ Considering that the almost same product selectivity was obtained in neutral (1 M KCl) and alkaline (1 M KOH) solutions between 200-2400 mA/cm$^2$, the local pH in KCl solution became similar to that in KOH solution under electrolysis with $J_{\text{total}}$ of just 200 mA/cm$^2$. Further increase in the current density ($J_{\text{total}} > 1$ A/cm$^2$) would lead to a pH of over 15 at the surface of the catalyst.$^3$ Moreover, we propose that the \textit{in situ} formation of the gas-transport pathway depending on the current density occurs during electrolysis. Evolved gases, such as H$_2$, would migrate through gas-transport channels in the CL; therefore, the area of the CO$_2$RR active interface (three-phase
interfaces) could be expanded with an increase in the current density (see Figure S16).

**CO$_2$RR activity dependence on Cu-loading amount**

Then, we investigated the product distribution of the CO$_2$RR depending on the Cu content to figure out the following questions: (1) How large is the potential CO$_2$RR activity of a Cu surface? (2) Was the amount of Cu active surfaces in CuNPs-1.7/GDE suitable to obtain a high C$_2$+ current density?

The CO$_2$RR was investigated for CuNPs-3.1/GDE and CuNPs-0.34/GDE (detailed product selectivities are shown in Figures S17 and S18) and the standard CuNPs-1.7/GDE (see the FEs in Figure 2d) in 1 M KOH. The maximum $j_{C2+}$ for CuNPs-3.1/GDE was achieved at $J_{\text{total}} = 2.4$ A/cm$^2$, which was the same as that for CuNPs-1.7/GDE. The FEs for C$_2$+ over CuNPs-3.1/GDE were 7% lower than those over CuNPs-1.7/GDE, although there was a similar tendency of the potential dependence. The FE$_{H2}$ over CuNPs-3.1/GDE was higher than that over CuNPs-1.7/GDE for all current density regions. These results indicated that a lack of Cu active sites did not cause a decrease in FE$_{C2+}$ over $J_{\text{total}} = 2.4$ A/cm$^2$ for CuNPs-1.7/GDE. It was presumed that the Cu sites immersed in the electrolyte cannot serve as CO$_2$RR sites but only as HER sites, and thus, selectivity toward H$_2$ production increased with the amount of Cu (Figure 3d).
Next, the Cu amount on the GDE was decreased to 0.34 mg/cm$^2$. Although the FE$_{C2+}$ over CuNPs-0.34/GDE was greater than 70% at $J_{\text{total}} = 0.5$ and 1.0 A/cm$^2$, it decreased to below 60% at $J_{\text{total}} = 1.6$ A/cm$^2$. In contrast, when $J_{\text{total}}$ was varied from 1.0 A/cm$^2$ to 1.6 A/cm$^2$, the FEs for CH$_4$ and H$_2$ increased from 1.9% to 16%, and from 9.4% to 19%, respectively. This is because the lack of catalytic Cu sites would result in relative enhancement of the HER on carbon particles that compose the MPL. The significant increase in FE for CH$_4$ with an increase in current density would be due to the reduction of one CO molecule to CH$_4$ prior to the dimerization of two CO molecules due to the high reaction rate under relatively low CO pressure. This tendency for CH$_4$ was basically consistent with the reported potential dependence of the selectivity of the CO$_2$RR on Cu-based catalysts.$^{38-40}$

The turnover frequency (TOF) for C$_{2+}$ products was calculated with variation of the catalyst loading. Figures 3c and S19 show the mass activity for the CO$_2$RR and HER. With CuNPs-0.34/GDE, the C$_{2+}$ mass activity reached up to 2600 A/g at -0.84 V vs. RHE. If we considered all surfaces of the CuNPs were active for the CO$_2$RR, then the TOF for C$_{2+}$ products would exceed 2.8 s$^{-1}$ (i.e., the TOFs were underestimated; see the Supporting Information for details). The obtained TOF significantly exceeded the values that have been reported in most of the previous reports.$^{15, 18, 26}$
Figure 3. (a) $\text{FE}_{\text{C}_2^+}$ and (b) $\text{FE}_{\text{H}_2}$ against $J_{\text{total}}$ for various amounts of Cu loading (CuNPs-0.34, -1.7 and -3.1/GDE). (c) TOF for $\text{C}_2^+$ products as a function of the Cu loading amount. (d) Schematic image of the three-phase interfaces with various CL thicknesses.

**CO$_2$RR activity dependence on the morphology of the catalyst layers**

As shown in the previous section, the TOF for $\text{C}_2^+$ per Cu atoms in Cu metals reached up to 2.8 s$^{-1}$. The mass diffusion of CO$_2$ and products in the three-phase interfaces must be elaborated to elicit this potential performance. Therefore, the dependence of the CO$_2$RR activity on the morphology of the CLs under the UHR-CO$_2$RR was investigated next. A sputtered Cu layer with a thickness of 2 $\mu$m was fabricated, which was similar to CuNPs-1.7/GDE (see the cross-sectional SEM image in Figure S20). Figures S21 and S22 show the FEs for CO$_2$RR products over the sputtered-Cu/GDE. The $\text{FE}_{\text{C}_2^+}$ was the
highest at the lowest current density \((J_{\text{total}} = 200 \text{ mA/cm}^2)\) and monotonically decreased with an increase in the current density.

Compared with the cross-sectional SEM images of the CuNPs/GDEs, the sputtered-Cu/GDE had a relatively densely-packed CL. In contrast, the CL of CuNPs-1.7/GDE (Figure 1d) possessed a similar porosity with the MPL (ca. 300 nm), which was optimized for gaseous transportation. These results suggested that the optimal mass transportation in the CL for the CuNPs/GDEs was one of the factors to elicit the high TOF of Cu atoms.

**Analyses of three-phase interface with respect to current density**

It is important to identify the origin of the decrease in the CO\(_2\)RR activity by application of \(J_{\text{total}} = 2.8 \text{ A/cm}^2\) for CuNPs-1.7/GDE (Figure 2a) toward a further increase in the production rate. It was assumed that the three-phase interface was broken over \(J_{\text{total}} = 2.8 \text{ A/cm}^2\), which resulted in a severe decrease in the FE for C\(_2^+\) products. Figures 4 shows cross-sectional SEM images after application of \(J_{\text{total}} = 1.0, 2.0, \text{ and } 2.8 \text{ A/cm}^2\) (30 min), respectively. The particle size of the CuNPs in the CL did not essentially change after electrolysis, compared with that before electrolysis (Figure S23). Cross-sectional elemental energy dispersive X-ray spectroscopy (EDX) mapping show K\(^+\) derived from electrolytes entered the MPL layer. One-tenth and one-fourth of the MPL layers were
flooded after application of $J_{\text{total}} = 1.0 \text{ A/cm}^2$ and 2.0 A/cm$^2$, respectively. In contrast, after the degradation with application of $J_{\text{total}} = 2.8 \text{ A/cm}^2$ (30 min), the K$^+$ distribution was shown to reach half of the MPL layer (Figure 4e).

In addition, a residue of K$^+$ crystals (KHCO$_3$ and K$_2$CO$_3$, KCl and KOH) was observed throughout the MPL after application of $J_{\text{total}} = 2.8 \text{ A/cm}^2$. (Figures S24) Electrowetting effects, which decrease the solid–liquid interfacial tension and facilitate electrolyte penetration into the CL and MPL, are known to be emphasized under application of highly negative potentials.$^{41-43}$ Although the evolved gases may push out and expand the gas-transport pathways (as the in situ formation of the three-phase interface), flooding of the MPL due to electrowetting may exceed the rate of pushing out the electrolyte. The flooded CL (and MPL) produced only H$_2$ due to a lack of CO$_2$ transportation, and thus, H$_2$ production should become dominant at $J_{\text{total}} = 2.8 \text{ A/cm}^2$. This assumption is also supported by the diffusion of evolved gases into the catholyte chamber at $J_{\text{total}} = 2.8 \text{ A/cm}^2$ (vide supra).
Figure 4. (a,c,e) Cross-sectional SEM images of CuNPs-1.7/GDE and (b,d,f) K\(^+\) distribution (purple) obtained by EDX after application of (a,b) \(J_{\text{total}} = 1.0\) A/cm\(^2\), (c,d) \(J_{\text{total}} = 2.0\) A/cm\(^2\), and (e,f) \(J_{\text{total}} = 2.8\) A/cm\(^2\) for 30 min under CO\(_2\)RR conditions in 1 M KCl.

**Long-term stability dependence on current density**

Long-term stability might be a challenging issue in the practical implementation of UHR-CO\(_2\)RR. For example, in Ref. 27 the authors reported that the FE\(_{C2+}\) started to decrease within one hour at \(J_{\text{total}} = 1.2\) A/cm\(^2\) (\(j_{C2+} = 1\) A/cm\(^2\)) in 1 M KOH. In this time scale, the decrease in the CO\(_2\)RR activity on GDE is not due to the chemical degradation of components, but to the flooding of the CL and MPL. However, there is no systematic knowledge about the long-term stability of UHR-CO\(_2\)RR; especially, a durability test of UHR-CO\(_2\)RR in neutral solutions has not been conducted at all. Therefore we analyzed the change in the CO\(_2\)RR activity for long-term electrolysis under ultra-high-rate electrolysis conditions in neutral solutions.

Figures 5b and S25 show the FEs for CO\(_2\)RR products at \(J_{\text{total}} = 1.6\) A/cm\(^2\) in 1 M KCl as a function of the electrolysis time. The change in the FEs for CO\(_2\)RR products under electrolysis at \(J_{\text{total}} = 1.6\) A/cm\(^2\) was almost negligible for over 2 h. Although the FE for
C$_2$+ and H$_2$ then began to decrease and increase from 2 h, respectively, the FE$_{C2+}$ production remained over 75% for 2.5 h and 60 % for over 6 h. The electrode was analyzed after the decrease of FEs for C$_2$+ to clarify the origin of activity decrease. SEM observation (Figure S26) after electrolysis for 6 h at 1.6 A/cm$^2$ showed that the size and morphology of CLs did not significantly vary, and most of the MPL was flooded in a similar manner to that described in Ref. 44 and 45. The stability dependence on the applied current density was investigated next (Figures 5a-c and S25). The FE$_{C2+}$ of 70-80% almost unvaried for over 3 h and 1.5 h at $J_{\text{total}} = 1.0$ A/cm$^2$ and $J_{\text{total}} = 2.0$ A/cm$^2$, respectively. These results indicated a trade-off relationship between stability and current density; however, the decrease in FE$_{C2+}$ with a short timescale was due to flooding of the CL and MPLs. Therefore, we can expect the stability could be improved by the addition of hydrophobic materials and modulation of the porosity in the CL and MPL. The present electrochemical system and conditions will become one of the standard platforms toward these future studies.
Figure 5. FE\textsubscript{C2+} stability tests with respect to the current density over CuNPs-1.0/GDE in 1 M KCl under (a) $J_{total} = 1.0$ A/cm$^2$, (b) 1.6 A/cm$^2$ and (c) 2.0 A/cm$^2$.

**Conclusions**

In this work, our electrode exhibited the partial current densities for CO$_2$ reduction to C$_2$+ of 1.7 A/cm$^2$ in neutral solutions. When the total current density was increased, the FE$s$ for C$_2$+ increased monotonically. Therefore, the trade-off relationship between the reaction rate and selectivity was shown in the present UHR-CO$_2$RR. Although the cathode of this electrochemical system was composed of typical CuNPs, a carbon-based GDE, we successfully maximized the potential of the catalytic activity of the Cu surface by constructing a CL with optimal porosity and thickness. It is noteworthy that this electrode allowed us to achieve UHR-CO$_2$RR even in neutral solutions, which is more practical than alkaline solutions. The present system is expected to become one of the standards when pursuing high-current density for the CO$_2$RR by the design of novel components or
assemblies. Significantly, the obtained knowledge through the detailed analyses of our electrodes would be widely utilized to develop novel materials, such as catalysts and electrodes because our electrodes are composed of only standard components. Systematic stability tests were also conducted at over $j_{C_2^+} = 1 \text{ A/cm}^2$. Although the stability under ultra-high-current conditions was still far from a practical level, SEM observations revealed that flooding of the CL and MPL is a problem that occurs with the shortest time scale. The electrochemical conditions and systems in this study can serve as a platform for improvement of the stability of the UHR-CO$_2$RR.
Methods

Synthesis of CuNPs

CuNPs were synthesized via a wet-chemical reduction method. Briefly, 0.61 g of Cu(CH$_3$COO)$_2$·H$_2$O was dissolved in 250 mL of deionized water, and the resultant solution was stirred under Ar bubbling for 30 min to remove residual oxygen. 1.25 g of NaBH$_4$ in 20 mL of deionized water was dropped slowly into the copper(II) ion solutions. The synthesized CuNPs were rinsed with deionized water and ethanol.

Preparation of the electrodes

A homogeneous catalyst ink was prepared by sonication of 3.4 mg of CuNPs with 400 μL of isopropanol and 4.4 μL of a 5 wt% Nafion dispersion. The catalyst ink was drop-casted onto a conventional GDE (Sigracet 34BC) at 80 °C. A PTFE sheet with a hole (0.5 cm$^2$) was pasted on the GDE by hot pressing before catalyst coating to strictly fix the area of the electrode. The amount of CuNP loading was controlled according to the number of drops of the catalyst ink.

Characterization

Transmission electron microscopy (TEM) observation were conducted using a Hitachi H-
9000NAR microscope. X-ray diffraction (XRD patterns) were collected using a Miniflex diffractometer (Rigaku) equipped with a Cu Kα radiation source. X-ray photoelectron spectroscopy (XPS) analyses were conducted using an Axis Ultra spectrometer (Kratos Analytical) equipped with an Al Kα radiation source. Field-emission scanning electron microscopy (FESEM) images were obtained using a JEOL JSM-7800F microscope. Energy dispersive X-ray spectroscopy (EDX) elemental mappings were acquired using an Oxford Instruments X-MaxN spectrometer.

**Electrochemical experiments**

Electrochemical experiments were performed using electrochemical workstations (HAL3001A+HAL3001B10, Hokuto Denko and SI1287, Solartron). An in-house-built three-compartment electrochemical cell was used for all experiments (Figure S7). A proton-exchange membrane (Nafion 117) was used to separate the cathodic and anodic chambers. A Pt wire and a Ag/AgCl electrode with 3 M KCl solution were used as counter and reference electrodes, respectively. During the electrochemical experiments, CO₂ gas was supplied into the gas chamber at a rate of 15 sccm. Both catholyte and anolyte were flowed at a rate of 10 mL/min using peristaltic pumps. Gaseous and liquid products were quantified by online gas-chromatography and ¹H-NMR measurements, respectively.
It is difficult to accurately compensate applied potentials under high-rate electrolysis due to a significant IR drop and a large Nernstian potential loss associated with pH gradients.

In this work, we measured CVs using the current interruption technique\textsuperscript{46,47} for IR the compensation (Figure S12), and then, the relationship between $J_{\text{total}}$ vs. $U$ obtained in these CVs was utilized to evaluate applied potentials for the constant current measurements.
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