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Mixed Copper States in Anodized Cu Electrocatalyst for Stable and Selective Ethylene Production from CO₂ Reduction

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ABSTRACT: Oxygen-Cu (O-Cu) combination catalysts have recently achieved highly improved selectivity for ethylene production from the electrochemical CO₂ reduction reaction (CO₂RR). In this study, we developed anodized copper (AN-Cu) Cu(OH)₂ catalysts by a simple electrochemical synthesis method and achieved ~40% Faradaic efficiency for ethylene production, and high stability over 40 hours. Notably, the initial reduction conditions applied to AN-Cu were critical to achieving selective and stable ethylene production activity from the CO₂RR, as the initial reduction condition affects the structures and chemical states, crucial for highly selective and stable ethylene production over methane. A highly negative reduction potential produced a catalyst maintaining long term stability for the selective production of ethylene over methane, and a small amount of Cu(OH)₂ crystal structure and mixed states disappeared on the catalyst, becoming more favorable to methane production after few hours. These results show the selectivity of ethylene to methane in O-Cu combination catalysts is influenced by the electrochemical reduction environment related to the mixed valences. This will provide new strategies to improve durability of O-Cu combination catalysts for C-C coupling products from electrochemical CO₂ conversion.

Introduction

Recently, electrochemical CO₂ conversion has received a great deal of attention because of its potential to produce value-added chemicals while utilizing CO₂. In addition, the electrochemical conversion pathway is applicable as a future energy storage system (ESS), which is increasingly in demand due to the imbalanced supply of renewable energy sources.¹⁻² To achieve economic feasibility of the electrochemical CO₂ conversion technique, it is required to produce market valuable chemicals with efficient energy conversion from electricity to chemical energy, and the electrochemical system is strongly depends on catalyst performance.3 In the last few years, among various possible chemical products from the electrochemical CO₂ reduction reaction (CO₂ RR), focus has been concentrated on the production of C1 chemicals such as carbon monoxide (CO) or formate (HCOO⁻) due to their potentially large global usage.⁴⁻⁶ In addition, CO or formate can

be produced via a two-electron (2e⁻) reduction reaction, relatively simple compared with the reduction pathway of other products such as methane (CH₄) and ethylene (C,H₄), which are 8e⁻ and 12e⁻ reduced products, respectively.7 Even in the case of two-electron mediated reactions, selective CO₂ reduction is still challenging because of the highly competitive hydrogen evolution reaction (HER) from water splitting in the aqueous solution. Recent progress with nanostructured electrocatalysts based on metals such as Au, Ag, and Zn etc. have included reports that defective surface structures such as grain boundaries, or lower coordinated sites, can achieve high product selectivity for CO of over 95%, with decreased overpotential. This consequentially improves the energy conversion efficiency and opens up industrial applications.8-12

Meanwhile, to improve the economic feasibility of the electrochemical CO₂ reduction, diversifying the product s Environment

toward more valuable chemicals has been proposed. One of the promising candidates is ethylene, which is widely used in the production of polymer plastics. However, unlike CO or formate production, direct CO₂ conversion to ethylene has still low product selectivity, near 30~40 % of Faradaic efficiency (FE). Also, while copper is almost the only heterogeneous catalyst for producing ethylene, it can also catalyze other multiple-electron transfer reactions beyond CO, formate, hydrogen, and methane.^{4, 7} Therefore, understanding the copper catalyst states related with selective ethylene production¹³ becomes important to design efficient electrocatalysts for CO₂ reduction reaction.

Researchers have tried to increase the number of active sites on Cu-based electrocatalysts that have a high ethylene/methane production ratio,¹⁴⁻¹⁵ and great improvements in selective ethylene production has been accomplished using copper and oxygen combined electrocatalysts, such as oxide-derived Cu electrodes, and mixtures of Cu and copper oxides.^{14, 16} In addition, various strategies, such as using halide ions in the electrolyte, or inducing local pH deviation via control of surface morphology, have been also demonstrated to increase ethylene production activity on Cu electrodes.¹⁷⁻¹⁹

However, we find that the previously reported product distributions largely deviate among CO, formate, CH₄, C_2H_4 , and H_2 depending on the preparation methods of the oxides or oxide-derived Cu catalysts. For example, annealed Cu₂O electrodes exhibit high selectivity for C1 products, CO with ~ 40 % FE and formate with ~ 30 % FE.²⁰ Its high CO₂ reduction activity is attributed to grain boundary formation during the oxidation/reduction process.²¹⁻²² Meanwhile, D. Raciti et al. reported that the annealed copper oxide electrocatalysts have different product selectivity depending on the reduction conditions²³; a thermally reduced Cu electrode primarily produces H₂ hydrogen (60 \sim 80% FE) and formate (\sim 20% FE), whereas an electrochemically reduced one produces CO at up to 60 % FE. Unlike the annealed Cu-based electrocatalysts, electrodeposited Cu₂O has been reported to have high ethylene production up to ~ 40 % FE, and suppressed C1 chemical production have been reported.¹⁶

However, the origin of the large differences in product selectivity has not been fully understood yet, and the active species of the Cu-based electrocatalysts are also difficult to identify during the reduction reaction. Based on in-situ and theoretical studies with electrochemically prepared Cu-based samples, it has been proposed that defect structures, oxygen moieties in the copper, or copper oxidation states contribute to stabilize the intermediate and increase ethylene production by the CO₂ reduction reaction (CO₂ RR).²⁴⁻²⁷ Other researchers have reported that an oxygen-plasma-treated Cu electrode achieved one of the highest ethylene production selectivities (~60 %), and the residual Cu⁺ phase under a cathodic potential was proposed to play an important role in selective ethylene production.¹⁴ Therefore, better understanding of the changes of the Cu and O states in the oxidederived copper electrocatalyst is required to design selective and stable electrocatalysts.

In addition, stability is as important as selectivity, because the selectivity of CO₂ reduction in the Cu cathode can be easily deteriorated by long-term electrolysis. Hori et al. reported the deactivation phenomena on Cu electrodes due to temperature or impurity deposition,²⁸ while durability study of a Cu catalyst has been performed by utilizing foreign metal atoms.²⁹ However, more studies are still required to increase the durability of the CO2 reduction catalysts. In our study, we investigated anodized-Cu (AN-Cu) electrocatalysts for the CO₂RR, and the AN-Cu catalysts exhibited a two times improvement in ethylene selectivity compared to Cu-foil. Its selective ethylene production remained stable for 40 hours, one of the longest reported to date. In addition, the highly performing electrocatalyst was prepared using a simple electrochemical synthesis method which did not require a complex Cu precursor solution, as is the case with an electrodeposited copper oxide (Cu₂O) catalyst, or a lengthy annealing, as is the case with heat-treated oxide-derived Cu. We also found that the durability of the selective C_2H_4 production over CH4 was critically sensitive to the initial reduction environments applied to the AN-Cu electrode possibly affecting Cu oxidation states and structural changes. These changes in selectivity and surface state will be very important information for studying ethylene selectivity in future O-Cu combined catalyst studies.

Experimental

Cu Electrocatalyst Preparation

All Cu samples were prepared from 0.1 mm thick poly crystalline Cu foil (Alfa Aesar, 99.9999%). Anodized Cu electrodes were prepared by modifying a previous method.³⁰⁻³¹ Cu foil was electrochemically oxidized in 3 M KOH (Sigma-Aldrich) aqueous electrolyte at a constant current condition for 60 sec at 10 mA/cm² which formed Cu(OH)₂ nanowire arrays.

In an electrochemical cell, the Cu foil working electrode was kept positioned 2 cm away from a platinum plate counter electrode. The AN-Cu sample was rinsed with deionized water (18.2 M Ω) and consecutively dried with nitrogen gas flow. Then, the AN-Cu electrocatalysts were either used as-prepared, or after electrochemical reduction. The AN-Cu samples underwent electrochemical reduction in CO₂ (≥99.999%) saturated o.1M KHCO₃ (Sigma-Aldrich, 99.95%) electrolyte, and instantly proceeded to CO₂RR.

Two different types of Cu electrodes were prepared by changing the condition of this electrochemical reduction step prior to the CO2RR. A highly negative bias potential (- 4.0 V versus Ag/AgCl reference electrode) was applied for 10 min to reduce the anodized Cu electrode for a short time (denoted as HPR-Cu). For comparison, a lower reduction potential (-1.15 V versus an Ag/AgCl reference electrode) was applied for 100 min (denoted as LPR-Cu)

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for slow reduction. Except for the applied potential and the period of the time, other sample preparation environments and CO₂RR activity measurements were identical. In order to compare the catalytic activities of bare Cu foil electrodes, Cu foil samples were cleaned by electropolishing in phosphoric acid (Sigma-Aldrich, 85% in H₂O) at 4 V versus a platinum plater counter electrode for 300 sec.

Electrochemical CO₂ Reduction Reaction Measurements

All electrochemical measurements were conducted using an Ivium potentiostat (Iviumtechnology) in a twocompartment electrochemical cell made of polyether ether ketone (PEEK). A Selemion AMV anion exchange membrane was sandwiched between the separated cathode and anode compartment. A Cu sample working electrode, and an Ag/AgCl reference electrode (Basi, 3M NaCl) were placed in the cathode side, and a platinum counter electrode was placed in the other anode side. The geometrical surface areas of the Cu cathodes were controlled to be 0.5 cm² for easy comparison of their catalytic activities.

To compare CO₂RR activity, a fresh working electrode was replaced at each applied potential. For the long-term activity, CO₂RR measurement was also performed for 40 hours at a fixed potential. To compensate *iR* loss, solution resistance (R_s) was measured by electrochemical impedance spectroscopy (EIS) from 1000 to 0.1 Hz, and normal values of R_s were determined to be 75~80 Ω in CO₂ saturated 0.1M KHCO₃ whose pH was measured to be 6.8. The measured potential values were converted to reversible hydrogen electrode (RHE) by using the equation below.

 $E(vs RHE) = E(vs Ag/AgCl) + 0.209 V + 0.05916 \times pH$

Products Analysis of CO₂ Reduction Reaction

The produced gases at each fixed potential were quantitatively analyzed by Gas Chromatograph (GC; Younglin 6500 GC) which was on-line connected with the head space of the cathode side of the electrochemical cell, and the gas products were injected to the GC using a six-port valve system. High purity CO_2 gas (\geq 99.999%) was continuously flowed into the electrochemical cell during CO_2RR . The CO_2 gas flow rate was controlled with a mass flow meter, and its flow rate was adjusted to be 20 cc/min, as measured by a universal flow meter (Agilent AMD 2000) at the outlet of the electrochemical cell.

The GC system was equipped with two columns and two detectors to separate gas products from the CO₂RR. A HayeSep D (11ft, Agilent) packed column separated CO_2 , C_2H_4 , C_2H_6 , etc., while a Molecular Sieve 13X (6 ft, Restek^{*}) packed column separated small gaseous molecules such as H_2 , N_2 , O_2 , CO, and CH_4 . A thermal conductivity detector (TCD) and a flame ionization detector (FID) with a methanizer were installed. The former device detects hydrogen gas and the later one detects small hydrocarbon products (CO, CH_4 , C_2H_4 , and C_2H_6). A methanizer was utilized to increase the detection sensitivity of CO by FID. High purity Argon (Ar; 99.999%) was used as a carrier gas.

$$i_{x} = \frac{C_{x} \times q \times p}{RT} \times n_{x}F$$
(1)
F. E. (%) = $\frac{i_{x}}{i_{total}} \times 100$ (2)

The partial current (i_x) needed to produce each product $(x=H_2, CO, CH_4, C_2H_4, \text{ or } C_2H_6)$ was obtained from equation (1) in which C_x is the volumetric concentration of product *x* extracted from the GC calibration curve, and *q* is the gas flow rate. Here, *p* is the pressure, R is the ideal gas constant (8.314 m³·Pa/K·mol), and T is the temperature. n_x is the number of reduced electrons needed to produce *x* from CO₂ molecules, F is the Faradaic constant (96485 s·A/mol). Then, the Faradaic efficiency (F.E.) was derived from the following equation (2) in which i_{total} is the current density measured by the potentiostat during CO_2RR .

The accumulated liquid products in electrolyte was analyzed by proton nuclear magnetic resonance (NMR) spectroscopy (DD2 600 MHz FT NMR, Agilent). In case of the HCOO⁻, phenol was used for internal standard. But the other products were compared by internal standard, dimethyl sulfoxide (DMSO) chemical shift at 2.6 ppm.

Material Characterization

To observe the surface morphology of each electrode, field emission scanning electron microscopy (FE-SEM, FEI, Inspect F) was used. Each AN-Cu sample was characterized in detail by transmission electron microscopy (TEM, FEI Talos). The crystal structure information of the Cu electrode was obtained using high resolution TEM (HR-TEM) images and by grazing incidence X-ray diffraction (GI-XRD, Rigaku corporation, D/Max 2500), which had a Cu K α radiation wavelength of 0.15406 nm.

X-ray Spectroscopic Analysis of the Cu electrocatalysts

The element oxidation state changes were measured by X-ray photoelectron spectroscopy (XPS) pre- and post-CO₂RR. Immediately after the Cu samples were taken out of the electrolyte, they were thoroughly rinsed with DI water and then dried with N₂ gas flow. In order to prevent further contamination, the Cu electrodes were vacuumpacked and stored until X-ray measurement. The control experiments storing the post-CO2RR catalyst to the air ambient indicated the vacuum-package was effective to decrease the copper oxide formation on the surface during the sample transfer. High resolution XPS measurement was performed at the 8A2 beam-line of the Pohang accelerator laboratory (PAL) with an incident photon energy of 630 eV for higher surface sensitivity. The energy of the incident X-ray photons at 8A2 were calibrated with Au foil. In addition, we used an X-ray spectrometer equipped with a K-alpha model of Thermo U.K. that had an Al K α monochromater ($E_{photon} = 1486.7$ eV) to obtain Cu LMM Auger spectra, which can distinguish Cu[°], Cu⁺, and Cu²⁺ states better than Cu 2p spectra.

Additionally, the chemical state changes of each Cu electrode were further observed by using soft X-ray absorption near edge structure (XANES) in the 10D XAS KIST beam-line of PAL. Cu L-edge XANES was measured in the energy regions of 920~980 eV, respectively.

Results and Discussion



Figure 1. Cu-foil SEM image and AN-Cu synthesis confirmed a) Cu-foil SEM image, c) AN-Cu HR-TEM image, d) Cu-foil and AN-Cu GI-XRD pattern.

The nanowire arrays were obtained on the Cu foil after a short-time anodization process in a KOH condition as shown in the SEM images (Figure 1). The SEM image shows the polycrystalline Cu-foil has a flat surface (Figure 1a), while the AN-Cu is composed of bundles of nanowire arrays (Figure 1b), similar to other reports.³⁰⁻³¹ The length and the coverage of the nanowire arrays were varied by controlling the anodizing time, and we optimized the anodization condition to avoid delamination issues. In addition, the HR-TEM of a single nanowire and GI-XRD of the ensemble AN-Cu sample were measured, and both of them confirmed the prepared nanowire had a Cu(OH), crystal structure (Figure 1c and d). The obtained XRD patterns of the AN-Cu samples were all matched with Cu(OH), (JCPDS # 80-1916) and metallic Cu (JCPDS # 04-0836) because our anodization process synthesized Cu(OH), nanowire arrays on the Cu foil substrate.

Next, the electrochemical activity of the prepared AN-Cu was measured for CO₂ RR. Highly improved selectivity for C₂H₄ over CH₄ was achieved compared to the polycrystalline Cu flat surface (Figure 2). Our GC measurement can analyze H₂, and gas products up to C₃ chemicals such as CO, CH₄, C₂H₄, C₂H₆, C₃H₈, etc.. The main detected gas products were H₂, CH₄, C₂H₄, and negligible amounts of others at -1.08 V vs. RHE, where the highest C_2H_4 production selectivity was achieved (Figure 2a). Consistent with the previous study, flat Cu-foil preferentially resulted in CH₄ production. However, the AN-Cu achieved up to 38.1 % of Faradaic efficiency for C_2H_4 production, twice that of the Cu-foil, while CH₄ generation was notably suppressed to 1.3 % FE. This result means selective C_2H_4 production accounted for 50% of the total gaseous products. The other liquid products faradaic efficiency was shown in Figure S1, the total faradaic efficiency was closed to 100 %.

More notably, the AN-Cu catalysts showed significantly enhanced stability for C_2H_4 production compared to the Cu foil (Figure 2b-d). Short-term (i.e. 100 min) stability test showed that the Cu-foil started to have a significant drop in current density and C_2H_4 production selectivity after 60 min. For the much longer period of 40 hours, the AN-Cu maintained stable total current density and C_2H_4 selectivity, with close to 40 % of Faradaic efficiency (Figure 2d and Figure S2). There have been several Cu-based catalysts which reported C_2H_4 selectivity similar to our AN-Cu catalyst, but their reported stabilities were shorter than 10 hours (Table 1).

The changes in gas products for the flat Cu-foil and AN-Cu were also compared depending on the applied potentials, and the surface Cu states were analyzed pre- and post-CO₂RR (Figure 3). First, in terms of product variation, the Cu-foil always preferred CH₄ for all applied potential regions (-0.75 ~ -1.15 V vs. RHE), and the Faradaic efficiency changes are almost synchronized during CH₄ and C₂H₄ production, indicating the bare Cu foil has poorer activity for C-C bond coupling regardless of the applied potentials. On the other hand, the AN-Cu samples suppressed CH₄ and CO generation and selectively generated C₂H₄ suggesting C-C bond formation was activated even at low applied potentials (-0.9 V vs. RHE). In particular, extremely low CH₄ production for all applied potentials was noted.

The surface of the AN-Cu was characterized by XPS before and after CO₂RR (Figures 3c and d). Cu 2p XPS clearly showed that the as-prepared AN-Cu surface has Cu²⁺ states which were distinctively reduced to the lower binding energy associated with the Cu⁺ or Cu^o state after 100 minutes of reaction. Because the binding energies of the Cu⁺ and Cu^o states in the Cu 2p peak are similar,³²⁻³³ it is difficult to distinguish them, as seen in Figure 3c. Therefore, further surface state analysis was performed with a Cu LMM auger peak (Figure 3d). Previous studies have shown a Cu₂O (or Cu⁺) auger peak at 570.0 eV, Cu^{\circ} peaks at 567.7 to 567.9 eV, and Cu(OH)₂ auger peaks at 570.4 eV.³⁴⁻³⁷ Again, the feature around 570.4 eV confirms the formation of Cu(OH)₂ in the as-prepared AN-Cu sample. After the CO₂RR of the AN-Cu sample, both the Cu^o and Cu⁺ states were present.

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Catalyst	electrolyte	Experiment conditions	C ₂ H ₄ F.E. (%)	C ₂ H ₄ Partial J (mA/cm ²)	Stability (h)
AN-Cu (this work)	0.1 M KHCO ₃	-1.08 V vs RHE	38.1	7.3	40
Cu ₂ O film ¹⁶	0.1 M KHCO ₃	-0.99 V vs RHE	37.5	~12.9	1
3C-Cu ₂ O film ⁴⁴	0.1 M KHCO ₃	-1.1 V vs RHE	32.5	~ 12.5	5
Cu-mesocrystal ⁴⁵	0.1 M KHCO ₃	-0.99 V vs RHE	27.2	~ 6.8	6
Plasma-Cu* ¹⁴	0.1 M KHCO ₃	-0.9 V vs RHE	60*	~ 6.6	5
Nanoporous-Cu*46	1M KOH(GDE)	-o.60 V vs RHE	38.2	~ 90*	8*(only current)
Cu-foil ²⁷	0.3 M KHCO ₃	-1.4 V vs SHE	10	~ 0.5	1
Mesopore-Cu* ¹⁸	0.1 M KHCO ₃	-1.7 V vs NHE	38	~ 7.2	4*(only current)
Prism-Cu ⁴⁷	0.1 M KHCO ₃	-1.15 V vs RHE	30	~ 12	1.5
Amino-Cu ⁴⁸	0.1 M KHCO ₃	-1.9 V vs Ag/AgCl	13	~ 1.4	12
Cu nanocube ⁴⁹	0.25 M KHCO ₃	0.96 V vs RHE	32.5	~21	2.5
Cu Cube ⁵⁰	0.1 M KHCO ₃	1.0 V vs RHE	Not available	10 (Total J)	Not available
ERD Cu ²⁷	0.1 M KHCO ₃	1.2 V vs RHE	~ 38	~ 22	1

Plasma-Cu*: Faradaic selectivity (target product amount/total detected product amount) instead of faradaic efficiency. Nanoporous-Cu*: Gas diffusion electrode (GDE) flow cell was used and did not report C2H4 production stability. Mesopore-Cu*: Stability of C2H4 production and selectivity of HER and hydrocarbon were not accessible.

Here, it was confirmed that the initial $Cu(OH)_2$ phase was also reduced under the CO_2RR condition, and the reduced copper states irreversibly changed to the mixed states of metallic and oxidized coppers post CO₂RR. Although the oxidized copper states were evolved to reduced forms by the CO₂RR, the improved selectivity for C_2H_4 was stable for as long as 40 hours.

To understand the high stability and activity of the AN-Cu, additional surface spectroscopic analyses and catalytic activity measurements were performed with the AN-Cu and its modified samples (Figure 4). Two different types of electrocatalysts were prepared from the AN-Cu (Figure 4), by introducing an electrochemical reducing pre-treatment step prior to the CO₂RR. Their surface Cu states were scrutinized pre- and post-CO₂RR to further understand the relation of CO_2RR activity to the surface states. First, a highly negative potential reduction-Cu (HPR-Cu) was prepared by applying a very negative potential (-4.0 V vs. Ag/AgCl) to the as-prepared AN-Cu sample for 10 minutes. In the other case, a milder reduction condition was applied to AN-Cu with a small negative potential (-1.15 V vs Ag/AgCl) for 100 minutes to make a low negative potential reduction-Cu (LPR-Cu). The total charge passing through the AN-Cu during the HPR-Cu preparation was almost an order magnitude higher than that of LPR-Cu (Table S1), but the initial morphology of the Cu(OH)₂ nanowire arrays on the LPR-Cu were more severely collapsed during the pre-reduction steps (inserted images in Figures 4a and 4c).



Figure 2. AN-Cu and Cu-foil feature comparison a) HER and hydrocarbon selectivity, b) current density and stability, c) ethylene production stability, d) AN-Cu C₂H₄ production stability.



Figure 3. AN-Cu and Cu-foil feature comparison a) Cu-foil CO2RR selectivity, b) AN-Cu CO2 RR selectivity, c) AN-Cu pre-post Cu 2p XPS peak, d) AN-Cu pre-post Cu LMM auger peak.



Figure 4. Selectivity and stability of HPR-Cu and LPR-Cu a) HPR-Cu CO₂ RR product selectivity; the insert SEM is HPR-Cu as prepared, b) HPR-Cu 10h stability, c) LPR-Cu CO₂RR product selectivity; the insert SEM is LPR-Cu as prepared, d) LPR-Cu 10h stability.

Comparing the current density (i.e. conversion rate) of the AN-Cu and two other Cu samples derived therefrom (HPR-Cu and LPR-Cu), they had similar total current densities, which were two times higher than that of the Cu-foil (Figure S₃). In addition, the partial current densities of CH₄ and C₂H₄ depending on the applied potentials showed that the HPR-Cu had higher activity for C₂H₄ production than the other Cu samples, while the LPR-Cu showed exceptionally enhanced CH₄ production activity, which caused a higher C₂H₄ selectivity for the HPR-Cu. All of the Cu-based catalysts reached their highest C₂H₄ production selectivity near -1.05 ~ -1.1 V vs. RHE where hydrogen production was the smallest, suggesting that the surface active sites might be competing between HER and CO₂ to C₂H₄.

Interestingly, both the AN-Cu and HPR-Cu, the two active catalysts for selective C_2H_4 production, produced a small amount of C_2H_6 (Figures S4b and c). According to the proposed mechanism,³⁸⁻³⁹ C_2H_6 is produced through different reaction pathways than CH_4 . It is presumed that the AN-Cu and HPR-Cu catalysts are capable of reducing C_2H_4 to a more reduced product, C_2H_6 .Next, as shown in Figure 4, the CO_2RR activities of these two types of Cu samples were measured under various applied potentials, as well as at a fixed potential (-1.05 V vs. RHE) for a 10 hour reaction (also see Figure S5). The HPR-Cu showed almost similar selectivity for C_2H_4 (38 % of Faradaic efficiency) over CH_4 (< 1.0 % of Faradaic efficiency) compared to AN-Cu, and it also had highly stable C_2H_4 production activity for 10 hours at – 1.05 V vs. RHE (Figures 4a and 4b). On the other hand, the LPR-Cu showed increased amounts of CH_4 production (~ 7 % of Faradaic efficiency at – 1.05 V vs. RHE; Figure 4c). This became more pronounced with the longer reaction time, and larger than the C_2H_4 production after 6 hours (Figure 4d).

A local difference in pH induced by the surface morphology has been demonstrated to cause different preferences, to C_2H_4 versus CH_4 production. When SEM images were taken after 100 min of CO_2RR , however, the morphology of the HPR-Cu and LPR-Cu appeared to be similar, unlike their initial morphologies (Figure S6). This suggests their different activities in C_2H_4 and CH_4 selectivity may not be due to a difference in macro morphology. During the electrochemical modification, the different reduction potential conditions can affect the structural changes forming under-coordinated defective atoms known as active sites for ethylene production. Considering the significant

Figure 5. GI-XRD analysis a) pretreated sample XRD comparison, b) HPR-Cu time dependent ex-situ analysis, c)LPR-Cu time dependent ex-situ analysis.

difference in activity between HPR-Cu and LPR-Cu, it is hypothesized that the initial states of the catalysts before CO₂RR measurement are important for determining the long-term activity, although the surface oxidized copper reduces to metallic form during the CO₂RR.¹⁴⁻¹⁵

Next, various surface analysis measurements were performed on the HPR-Cu and LPR-Cu to characterize their surface states over the course of the CO₂ reduction reaction at - 1.05 V vs. RHE, initial, 100 min, and 10 hours later. First, GI-XRD patterns were compared, as shown in Figure 5. Again, our synthesized AN-Cu had a crystalline Cu(OH)₂ structure on a metallic Cu substrate. After electrochemical pre-treatment was applied to the AN-Cu, both the HPR-Cu and LPR-Cu had an evolution of new patterns at 36.5°, 42.6° and 61.5° (JCPS # 65-3288) associated with crystalline Cu₂O. However, interestingly, the HPR-Cu sample still had a small intensity of Cu(OH)₂ patterns at 16.7°, 23.9° and 34.2°, implying mixed states with Cu₂O , Cu, and Cu(OH)₂ were present on the HPR-Cu surface. Also, AN-Cu had a small amount of Cu(OH), signal even after 40 h bulk electrolysis (Figure S7). In Figure 5b, Cu(OH)₂ can be noticeably observed on the HPR-Cu even after 100 min of CO₂RR, and the Cu₂O peaks became stronger after 10 hour of reaction. On the other hand, more apparent Cu₂O patterns were observed on the LPR-Cu, but Cu(OH)₂ features almost disappeared after

the pre-treatment step at low applied potential (Figure 5c).

Soft X-ray XANES spectra was measured to further distinguish the copper states on the top layer of HPR-Cu and LPR-Cu surfaces (Figure 6). The catalyst samples were stored and transferred under the vacuum package prior to the spectroscopy measurements in order to minimize the changes of the surface (Figure S8). Figure 6a shows the Cu L-edge XANES spectra of the reference Cu(OH)2, CuO, Cu2O, and Cu-foil as well as the HPR-Cu and LPR-Cu samples. The Cu²⁺ state of Cu(OH)₂ or CuO has a single L3-edge peak distinctively at around 930 ~ 940 eV, because Cu²⁺ has 9 electrons in 3d orbitals which allows excitation of the 2p electron.⁴⁰⁻⁴¹ Meanwhile, the Cu₂O and Cu-foil have two features in the 930 ~ 940 eV region. Figure 6b shows that the Cu²⁺ states were observed on the HPR-Cu after 100 minutes of CO₂ RR, and the Cu²⁺ peak decreased after 10 hours, consistent with the XRD patterns. The LPR-Cu results in Figure 6c also show similar results to previous XRD results, where the Cu²⁺ peak decreased a lot at the initial state, and its spectrum shape was similar to that of Cu₂O, or Cu^o did not change significantly with the reaction time.

In addition, the XPS elementary analysis results indicated that the AN-Cu and HPR-Cu surfaces have relatively higher oxygen concentrations than the LPR-Cu (Table

Figure 6. Cu L-edge XANES spectra a) reference sample and An-Cu modified samples Cu L-edge, b) HPR-Cu ex-situ time dependent Cu L-edge spectra, c) LPR-Cu ex-situ time dependent Cu L-edge.

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S2). Also, according to detail analysis of XPS O 1s peak, LPR-Cu samples had more Cu₂O phase than HPR-Cu samples (Figure S9). These results also indicated that the LPR-Cu samples was more reduced than the HPR-Cu samples and that the oxidation state of the surface may affected the ethylene selectivity. Before CO₂RR, the atomic concentration ratio of O to Cu (O/Cu) on the HPR-Cu was 1.15, whereas LPR-Cu had an O/Cu ratio of o.10, an almost one order of magnitude lower oxygen amount.

These results also imply that the more abundant oxygen (Cu²⁺ and Cu⁺) state of the Cu-based catalysts resulted in their better C₂H₄ selectivity. High resolution XPS of the Cu 3p spectra also showed that the HPR-Cu had a higher intensity Cu²⁺ peak than the LPR-Cu (Figure Sio and S11). The Cu XPS spectra of the as-prepared AN-Cu had only Cu[°] and Cu²⁺ states on the surface, but after the reduction pre-treatment, Cu⁺, Cu^o, and Cu²⁺ peaks were observed on the HPR-Cu or LPR-Cu surfaces. Because the Cu(OH)₂ related signal was marginal on the LPR-Cu in the XRD measurements, the LPR-Cu might have Cu²⁺ peaks due to native oxide formation even with the vacuum package during sample transfer.⁴²⁻⁴³ Again, the Cu²⁺ peak was smaller on the LPR-Cu compared with the HPR-Cu. Meanwhile, between AN-Cu and HPR-Cu, the HPR-Cu achieved a lower overpotential to C_2H_4 production than just anodized copper.

However, all surface analysis measurement were performed in ex-situ manners which have innate limitations to estimate the copper oxidation states in a real operational condition of CO₂RR. In other words, the surface state can be distorted due to the ex-situ condition although cares have been taken during sample storage and transfer. For instance, it is possible that the HPR-Cu catalyst surface are preferentially re-oxidized to have the mixed oxide states after the CO₂RR compared to the LPR-Cu or Cu foil, then the mixed oxide states would be an indirect observation of the catalyst surface not the origin of the enhanced activity for ethylene production.

Based on the observation of the higher oxygen content and the mixed valences of Cu-O on the active catalysts, it is proposed that mixed valences are related to stable and selective C₂H₄ production, while simple Cu₂O/Cu catalysts are vulnerable to product changes from C_2H_4 to CH_4 . The mixed valences of Cu-O can be related with the active species of the ethylene production or can be the consequence of the structural changes. It is still controversial whether the CO, RR active species in the O-Cu combination catalysts are Cu⁺ or Cu^o. Recent in-situ spectroscopy studies have suggested that the oxidized states of copper reduces to metallic Cu° under the negatively biased condition during the CO₂ RR although there can still be a contribution from the oxygen species.¹⁴⁻¹⁵ The role of subsurface oxygen in ethylene formation has been proposed, but little study has been taken to keep those oxygen species stable in the copper matrix.²⁴⁻²⁶ Our study suggests that a harsh electrochemical reduction treatment applied to the anodized copper contributes to the high ethylene production activity with expanded durability, and it can affect the surface properties of the oxygen containing on the copper surface.

Conclusion

In this study, we found that a Cu(OH)₂ nanowire catalyst stably retained an average of 38.1% Faradaic efficiency for ethylene production over 40 hours from the CO₂ reduction reaction, and high selectivity of ethylene over methane was achieved. We identified that an electrochemical treatment condition on the as-prepared Cu(OH), catalyst causes the highly selective and stable ethylene generation. When the electrochemical reduction pre-treatment was applied to Cu(OH)₂ at mild biased potential, the copper species were vulnerable to reducing environment, which quickly changed products from ethylene to methane. Meanwhile, when the pre-treatment was applied under a highly biased harsh condition, the catalyst can have much extended durability for selective C-C coupling. From the ex-situ surface analysis by XRD, XPS, and XANES, it was found that C₂H₄ production was favored on the catalysts containing mixed oxidized copper species along with high oxygen content, while sharp increase of CH₄ production was observed when Cu²⁺ disappeared on the surface. These results show the relation between the durability of ethylene production and Cu-O containing surface states. This will provide new strategies to control the selectivity and durability of O-Cu combination catalysts for electrochemical CO₂ conversion to value-added chemicals.

ASSOCIATED CONTENT

Supporting Information.

This Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Additional gas product quantitative data and CO₂ RR post SEM and additional XPS data

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Time (h)

Faradaic Efficiency (%)

C₂H₄ ⊂ CH₄

SYNOPSIS TOC.