

Copper Palladium Alloy Thin Film Catalysts for Selective Electrocatalytic Reduction of Aqueous CO₂ to Hydrocarbon Products

by

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Abstract

With increasing amount of carbon dioxide in atmosphere, the electrochemical reduction of CO₂ is considered as a promising technique of utilizing and storing electrical energy from renewable sources in the form of hydrocarbon fuels. There are numerous studies on various metal electrodes, and copper, of all, is the only metallic electrocatalyst that has shown a unique ability to produce appreciable amounts of hydrocarbon products. However, the mechanism of CO₂ electroreduction on copper has not yet been elucidated, and the factors and intermediates that affect its selectivity towards C₁-C₃ chemicals is still controversial.

Among the intermediates, CO adsorption energy is known to be one of the key intermediates for producing hydrocarbons, as determined by density functional theory (DFT) calculations, and, by alloying copper with other metals, the binding energies of the CO can be stabilized. However, most copper alloys exhibit high activity for CO, but do not form hydrocarbon-based fuel products.

We hypothesize that decreased surface coverage of Cu atoms prevent the alloy from forming appreciable amounts of hydrocarbons. To understand the origin of this effect, we proposed to study CO₂ reduction on copper-palladium alloy thin film catalysts with controllable compositions. By systemically correlating surface composition to activity, we will understand to how to rationally design copper-based alloys that show high performance and selectivity for fuel formation.

Advisor: Dr. Shoji A. Hall

Reader: Dr. Chao Wang

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1. Introduction

Global warming has been a major problem around the world. It is known that the increasing demand of fossil fuels and the following excessive emission of carbon dioxide gases are the main causes of the rapid climate change. According to the U.S Department of Energy's recent report, while multiple gases contribute to the greenhouse effect, the emission of carbon dioxide accounted for over 80 % of total U.S. anthropogenic greenhouse gases emissions [1]. Therefore, global society is concentrating on developing sources of energy that are carbon-neutral to alleviate the environmental damage that are caused by the combustion of fossil fuels. Solar energy and wind energy have been considered as the promising techniques that can provide clean energy, but they are limited due to their large-scale installations and intermittent availabilities [2].

Unlike other renewable electricity that is generated from natural sources such as solar, wind, and water, renewable carbon-based fuels had only been produced from biomass until recently [3]. The electroreduction of carbon dioxide to hydrocarbon fuels is a promising process, since the amount of carbon dioxide on earth can be balanced by recycling waste CO₂ into usable hydrocarbon products. The electroreduction of CO₂ is not a thermodynamically demanding reaction; however, it is a kinetically demanding process. The critical technological challenges are to design a process that can reduce CO₂ at low potentials with high selectivity to generate desirable product at high current densities without producing unwanted byproducts. There are many factors that affect the efficiency and selectivity of the electroreduction process, such as electrode materials, surface structures, local pH, and CO₂ concentration on the electrode. Yet, the electrode material is known to be the most important factor that determine the

overpotential, efficiency, and selectivity [4-6].

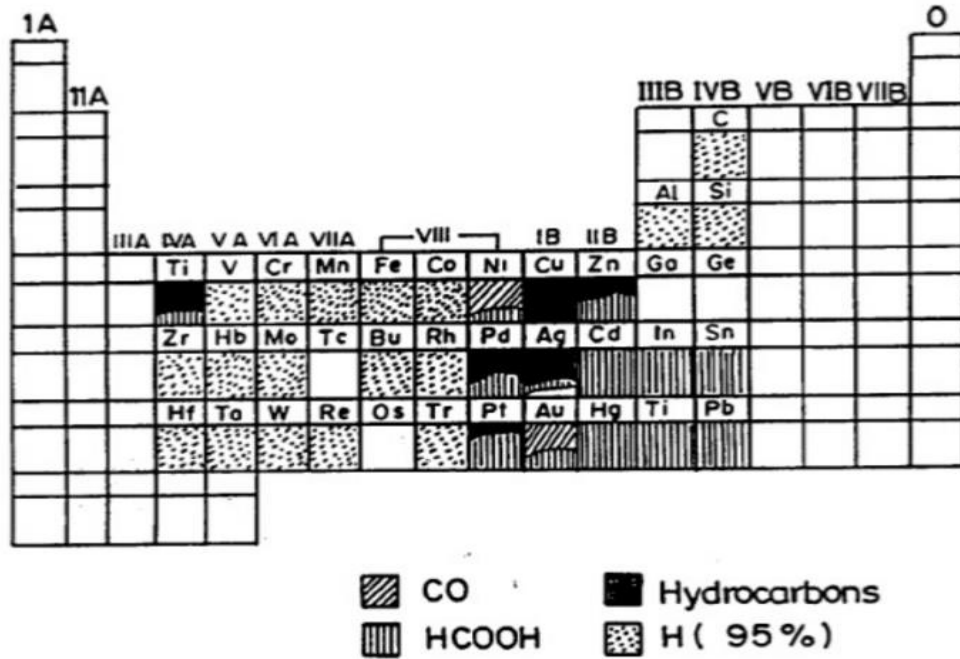
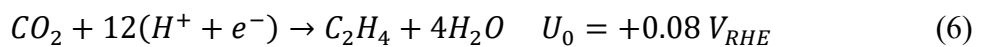
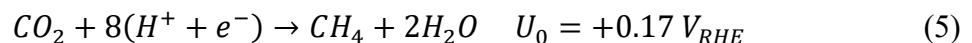
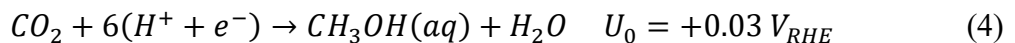
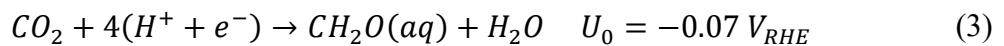
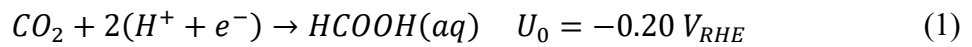


Figure 1. Periodic table for CO₂ reduction products at -2.2 V vs. saturated calomel electrode (SCE) in low temperature 0.05M KHCO₃ solution. Figure adapted from ref. 7

As shown in Figure 1, a number of researches studied the electroreduction of CO₂ on metal catalysts and found *d* metals (e.g., Pd, Pt, Cu, Ag, and Ag) can produce a myriad of carbonaceous products such as methane, ethylene, carbon monoxide, etc [4-9]. The following equations 1-6 are the most common reactions and their equilibrium potentials versus RHE (reversible hydrogen electrode):



Over decades, little progress has been made in designing electrocatalysts that can

efficiently produce hydrocarbons at reasonable ($\sim 5 \text{ mA/cm}^2$) current densities at overpotential less than 1.0 V [4][5]. Considering the equation above, CO_2 reduces to CH_4 at a potential of +0.17 V versus RHE. However, hydrogen evolution thermodynamically occurs at 0 V versus RHE at any pH, which suggests CO_2 reduction will be in competition with hydrogen evolution reaction (HER) [10]. The key challenge is to develop catalysts that can competitively drive CO_2 reduction over HER.

Among the aforementioned *d* metal catalysts, many excellent reviews conclude that copper metal is capable of catalyzing the formation of significant amounts of hydrocarbons [8][9]. Yet, the mechanism is not clearly understood, carbon monoxide appears to be an important intermediate, since both methane and ethylene can be produced by electroreduction of CO. It is unknown whether CO or a more reduced C_1 carbon source is coupled to make C_2 and longer carbon chain products. Peterson et al. have proposed DFT calculations of the key adsorbates in CO_2 reduction on various transition metals and clarified why copper exhibits the best catalytic activity. The analysis revealed the “volcano” type of CO adsorption energy and catalytic activity [11].

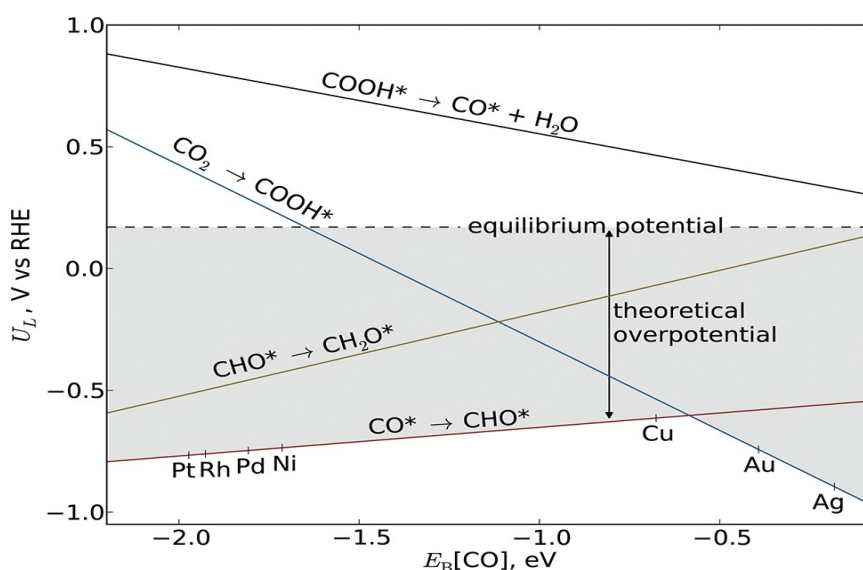


Figure 2. Volcano plot depicting scaling of CO adsorption energy and catalytic activity.

Figure adapted from ref. 11

Transition metals with high CO binding energy, such as Pt, Ni, and Fe, produce H₂ gas because reduced carbon monoxide stays on metal surfaces tightly as a poison, and the reaction becomes irreversible. On the other hand, metals with weak CO binding energy, such as Au, Ag, and Zn, tend to produce mostly CO [4]. Copper, instead, has a slightly higher than optimal CO adsorption energy. (Figure 2) Trace amounts of CH₄ can be produced via CO reduction at a nickel metal electrode, but the potential brought is slightly more negative than that of copper. Therefore, it can be deduced that the copper metal exhibits a better ability to perform CO* protonation compared to other transition metals, but it still requires an extreme overpotential to generate hydrocarbons as the dominant products. Otherwise, HER would be expected to dominate over CO₂ reduction [11].

Alloying copper with other elements has been suggested as a solution to improve the catalytic activity of this metal by reducing the CO adsorption energy [11][12]. Watanabe et al. studied many copper alloys, such as Cu-Ni, Cu-Sn, Cu-Pb, Cu-Zn, Cu-Cd, and Cu-Ag, for the CO₂ reduction in 0.05 M KHCO₃ aqueous solution. However, those alloys were found to enhance the activity of CO₂ reduction to CO and HCOOH products, while not enhancing the activity towards high-value fuel products [12]. It has been investigated that the alloy composition highly influences the selectivity and product formation potential. For example, CO₂ reduction of copper-gold alloy shows that the generation of CH₄ diminishes markedly with the Au content, while the CO was observed to be the principle product [13].

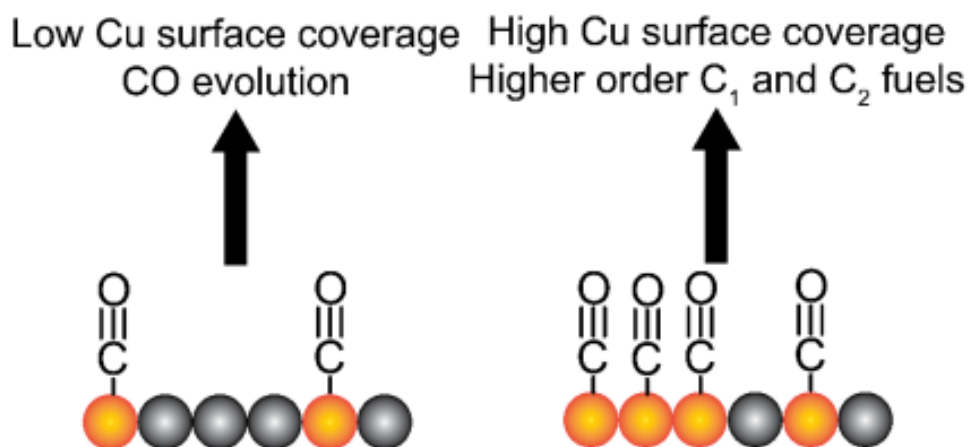


Figure 3. Schematic illustrating that high surface coverage of Cu is necessary to reduce CO₂ to high order fuels

According to the experimental results reported in the literature, the ability to generate energy dense hydrocarbon products has been rather reduced with copper alloys. For copper alloys measured for CO₂ reduction in the following researches, copper is diluted with other metals by ~25 % or more, [11-13] and it is known that copper exhibits a larger surface energy than many of the metals used to alloy with. Therefore, the amount of copper exposed on the surface may have been decreased below the levels required to form hydrocarbon or alcohol products. We suppose that the reduced catalytic performance is due to the hampered interaction among surface copper atoms caused by a low copper surface concentration (Figure 3).

Palladium is a noble metal known to have slightly lower surface energy than copper does [14][15]. Moreover, its characteristic of a high hydrogen affinity metal can lead to the formation of CH₄ by alloying with copper. Theoretical results revealed that CO as an intermediate is adsorbed on the surface of copper atoms and subsequently react with the hydrogen atoms partially adsorbed on Pd atoms [11]. Therefore, we expect that alloys of copper with palladium will have a higher surface concentration of copper and improve the faradaic efficiency for methane gas compared to alloys

prepared with other known noble metals.

Conversion of CO₂ to CO or C_x species is a relatively complex process. The catalytic activity can be influenced by many subtle factors. Ideally, high surface coverages of copper are required to form higher order fuel products, and careful control of the surface composition of copper alloys is a key to improve the selectivity of valuable hydrocarbon fuels from CO₂ reduction. Many literatures of bimetallic have not measured the surface concentration of copper on the electrode; yet, only the bulk concentration of the alloys have been described. Herein, we report the design and characterization of thin film Cu-Pd alloys to interrogate the relationship between the surface composition of copper alloys and CO₂-to-fuel formation. The preparation of smooth alloy thin films will allow us to determine the surface composition of thin films and correlate all major perturbation that affect the catalytic activity.

2. Experimental Section

2.1 Chemical and Materials

Copper (II) chloride hydrate (CuCl₂·2H₂O, Alfa Aesar, 99.99 %), sodium tetrachloropalladate (II) (Na₂PdCl₄, Acros Organics, ca. 36.4 % Pd), sodium chloride (NaCl, Acros Organics, 99.5 %), potassium hydroxide (KOH, Fisher Scientific, 99.99 %), and Chelex® 100 resin (Bio-rad) were used as received. Reagent grade water from a Milli-Q water system of Millipore (Fisher Scientific, 18.2 MΩ-cm resistivity) and hydrochloric acid (HCl, Fischer Scientific, ACS Reagent Grade) were used to prepare aqueous solutions.

2.2 Preparation of Cu-Pd thin film electrocatalyst by electrodeposition method

2.2.1 Electrodes and Instrumentation

Glassy carbon plate of 1 cm² geometric surface area (Alfa Aesar), glassy carbon rod (diameter of 5.0 mm, Alfa Aesar), silver foil of 1 cm² geometric surface area (Alfa Aesar, 99.998 %), and silver rod (diameter of 5.0 mm, Alfa Aesar, 99.95 %) were used as working electrodes for the synthesis of Pd-Cu thin film electrocatalysts. Copper rod (diameter of 5.0 mm, Alfa Aesar, 99.999 %) was also used to measure the catalytic activity of pure copper. The working electrodes used for the synthesis of thin films were successively polished with 1, 0.3, and 0.05 μm alumina slurries (CH Instruments) on microcloth polishing cloths (CH Instruments) for 5 minutes each, cleaned under bath sonication for 5 minutes in acetone and distilled water, and finally rinsed thoroughly with running distilled water. A platinum mesh (Alfa Aesar, 99.997 %) and a saturated mercury/mercury sulfate electrode (Hg/HgSO₄, CHI151, CH Instruments) were respectively used as counter and reference electrodes.

Electrochemical experiments were carried with an Autolab PGSTAT 204 (Eco-Chemie) potentiostat/galvanostat and controlled by Nova version 2.1.2 software made available by manufacturer. The rods used as working electrodes were trimmed to 4 mm by using proper cutting tools for a rotating disk electrode configuration.

2.2.2 Synthesis of Cu-Pd thin film

The electrolyte solutions of Cu-Pd were prepared by dissolving the metal sources, CuCl₂·2H₂O and Na₂PdCl₄, with 50 ml of reagent grade water. The total precursor concentration used for the synthesis of the catalyst was 10 mM. To analyze the catalytic effects of alloying of Cu metal with Pd metal, the molar ratio of Cu to Pd

were gradually controlled. ($\text{Cu}^{2+}/\text{Pd}^{2+} = 10:0, 9:1, 8:2, 6:4, 0:10$) $\text{Cu}_x\text{Pd}_{10-x}$ (x varies from 9 to 0) were used as abbreviations for the samples prepared from different precursor solutions. Initially, cyclic voltammetry (CV) was performed in potential range of 0.2 V to -1.1 V vs. Hg/HgSO₄ to determine the reduction potential of each 10 mM of Cu and Pd pure metal with the scan rates of 50 mV/s for five cycles. The thin films were electrodeposited on a glassy carbon plate, a glassy carbon RDE, a silver foil, or a silver RDE, by applying a constant potential at -0.641 V vs. Hg/HgSO₄ for 600 seconds.

2.2.3 Synthesis of Pd thin film by pulsed electrodeposition

Pure Pd was electrodeposited on a glassy carbon RDE. The electrolyte solution was prepared by using a concentration of 5 mM Na₂PdCl₄ and 0.1 M NaCl salts. The deposition was a pulsed electrodeposition carried out at -2.441 V vs. Hg/HgSO₄ for 50 ms followed by 950 ms at open circuit potential. The total deposition consisted of 500 pulse cycles.

2.3 Characterization techniques

Scanning electron microscopy (SEM, JEOL JSM-6700F) combined with energy dispersive X-ray spectroscopy (EDS) were used to characterize the morphology and determine the bulk compositions of film samples, respectively. X-ray photoelectron spectroscopy (XPS, Perkin-Elmer 5100, Mg K α radiation) was used to determine the initial surface composition of the samples and the changes in compositions after sputtering of each 10-minute cycle.

2.4 Electrochemical Measurements

The electrocatalytic reduction of CO₂ was measured on an Autolab PGSTAT 204 electrochemical setup in an aqueous 0.1 M KHCO₃ electrolyte solution with pH of

6.8, where the electrolyte solution used was prepared with Millipore water and purified of trace metal ion impurities by stirring with regenerated Chelex resin for at least 24 hours. Following regeneration method was modified by Wuttig et al. after the manufacturer's protocol [16]. Chelex was regenerated by stirring the resin for 12 hours in 1 M of HCl and rinsing with 5 L of reagent grade water. Subsequently, Chelex was dissolved in 1 M KOH for 24 hours at 60 °C with constant stirring. Chelex was then rinsed with 8 L of reagent grade water until the pH of the filtrate was below 10.8. Finally, the electrolyte solution was saturated by sparging with CO₂ gas for 20 minutes prior measurement. All experiments were performed at ambient temperature (21 ± 1 °C). For each electrolysis experiment, the cell was assembled with a Cu-Pd sample as the working electrode, a high surface area Pt-mesh counter electrode, and a Hg/HgSO₄ reference electrode. Electrode potentials were converted to the RHE scale:

$$E_{RHE} = E_{Hg/HgSO_4} + 0.638 V + 0.059 (pH) \quad (7)$$

During all experiments, the catholyte was sparged continuously with research grade CO₂ at 20 sccm, while the anolyte was sparged continuously with argon gas or CO₂ gas. The flow rate of 20 sccm was considered to provide sufficient CO₂ gas on the sample, while the high flow rate also can prevent from evolving gas bubbles on the surface. The product of H₂, CO, and other carbon products were sampled and measured with a gas chromatography mass spectrometry (GCMS-QP2010 SE, Shimadzu) in fitted with a Plot-Q Column (Resetek).

3. Results and Discussion

3.1 Synthetization of Cu-Pd thin films on various substrates

3.1.1 Determination of deposition potential of metals

The standard electrode potentials against the standard hydrogen electrode suggest that the potential required to deposit noble metals, such as Pd^{2+} , with copper has to be overpotential around 1 V (eq. 8-9). It can be deduced that the rate of noble metal deposition is much faster than the rate of copper deposition.

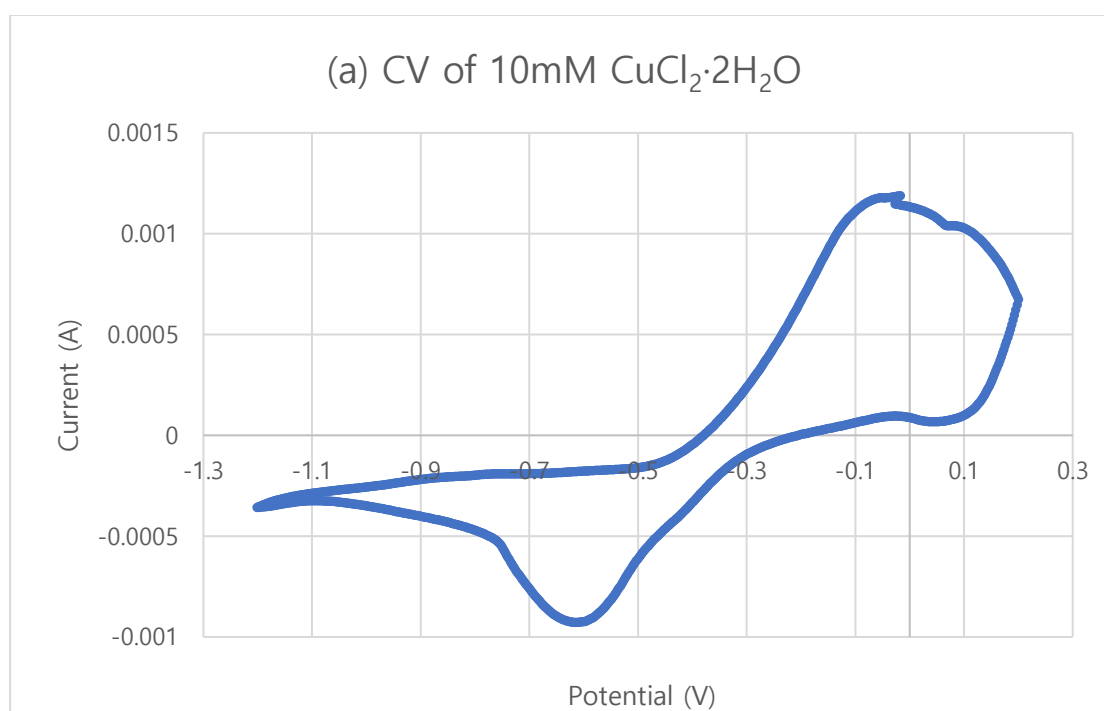
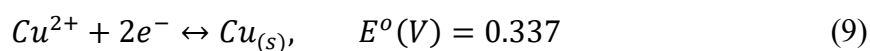
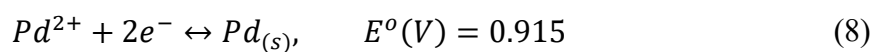


Figure 4. (a) Representative CV of a glassy carbon electrode in 10mM $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ from -1.2 V to 0.2 V vs. Hg/HgSO_4 . Scan rate = 50 mV/s

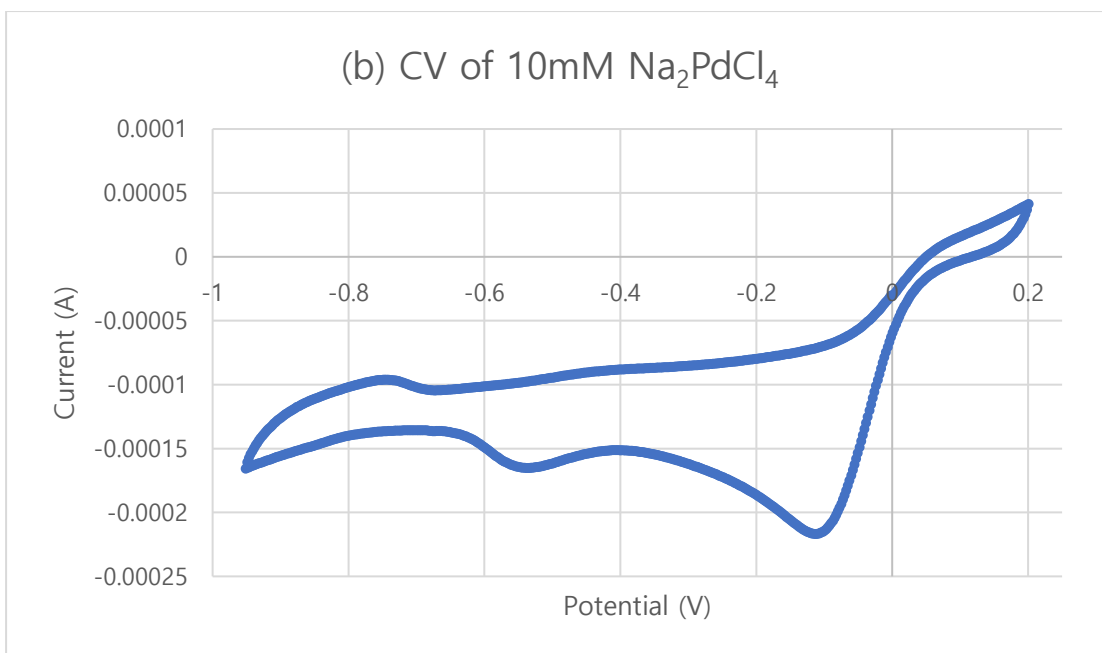


Figure 4. (b) Representative CV of a glassy carbon electrode in 10mM Na₂PdCl₄ from -1.2 V to 0.2 V vs. Hg/HgSO₄. Scan rate = 50 mV/s

The reduction potentials of Cu and Pd can be determined from the cyclic voltammetry data of each electrolyte solution used for deposition. As clearly seen in Figure 4 (a) and (b), Cu²⁺ ions were reduced to Cu metal at -0.6 V vs. Hg/HgSO₄, while Pd were reduced at potential around -0.1 V vs. Hg/HgSO₄. Therefore, more negative potential than the Cu²⁺/Cu equilibrium potential, -0.641 V vs. Hg/HgSO₄, was chosen to deposit the Pd metal salt under diffusion-limited conditions. The deposition rate of Pd could be independent of the applied potential if it is depositing under diffusion limited conditions, while the deposition of Cu²⁺ increased exponentially with the applied potential.

Cu_xPd_{10-x} films were electrochemically deposited on various substrates, a glassy carbon, a glassy carbon RDE, a silver foil, and a silver RDE, by applying a constant reducing potential of -0.641 V vs. Hg/HgSO₄ in electrolyte solution consisting 10 mM metal precursor (Figure 5).

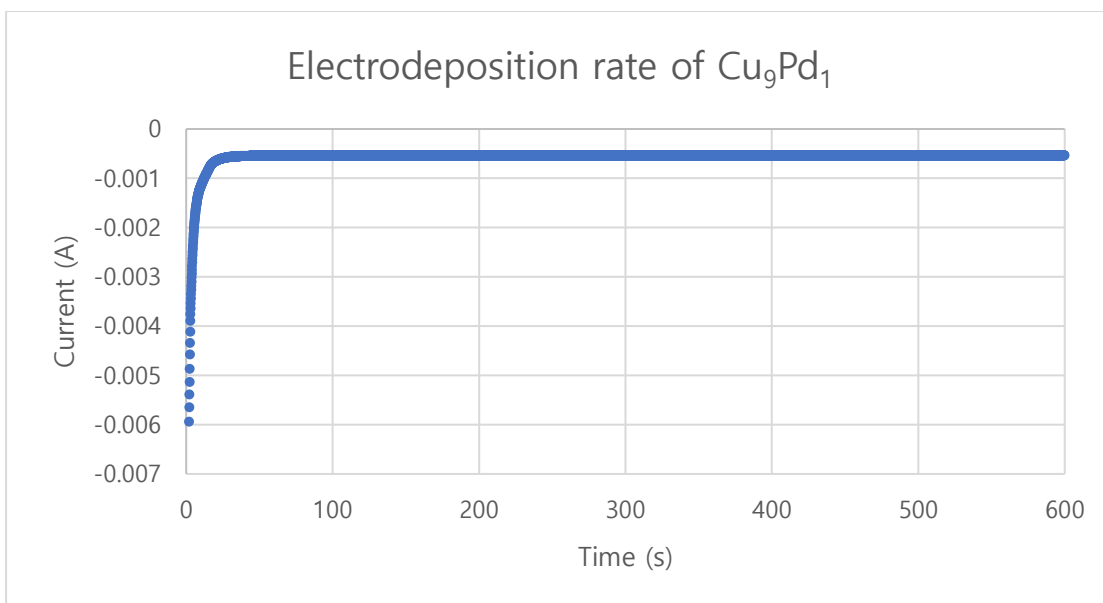


Figure 5. Chronoamperogram of electrodeposition of Cu_9Pd_1 on a glassy carbon plate at a constant potential of $-0.641 \text{ V vs. Hg/HgSO}_4$ for 600 seconds

3.1.2 Selection of an appropriate substrate for CO_2 electroreduction catalytic activity

Figure 6. (b) shows the Cu_9Pd_1 alloy prepared by electrodeposition with the method described above. A uniform thin film with low surface roughness was produced as indicated by the shiny metallic luster of the film.

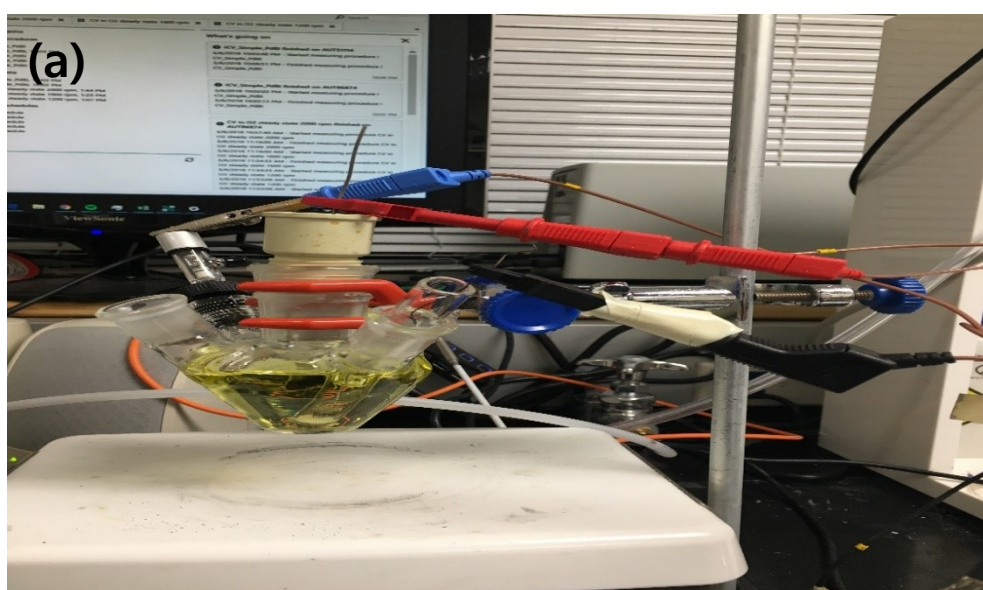




Figure 6. (a) Electrochemical cell setup for electrodeposition of Cu-Pd alloy (b) Cu-Pd alloy prepared by electrodeposition on a glassy carbon plate at -0.641 V vs. Hg/HgSO₄ for 600 s (c) Corrosion of Cu-Pd thin films after an electrochemical reduction reaction with high voltage applied

It is well known that the electrochemical reduction of CO₂ is highly dependent on the physical and chemical characteristics of electrode material. Carbon has been studied as an electrode material, and hence glassy carbon is extensively used due to its nature structure and high selectivity during electrochemical CO₂ reduction [17-23]. However, as indicated in Figure 6. (c), Cu thin-films electrodeposited on glassy carbon substrates did not adhere well to the surfaces and started to delaminate as voltages below 0 V vs. RHE were applied. Copper is not known form strong chemical bonds to Carbon, therefore we expect it to poorly adhere to carbon substrate. Thus, the intrinsic adhesion of copper films on glassy carbon is very low [19]. Low reproducibility of the samples with glassy carbon substrates supported the following hypothesis.



Figure 7. Pd thin film prepared by pulsed electrodeposition on a glassy carbon RDE

Since there are many literatures about palladium deposited on glassy carbon substrates for electrochemical experiments [21-23], it was assumed that the adhesion problem could be resolved by pulse electroplating Pd on a glassy carbon surface to increase the bonding energy between the substrate and Cu-Pd alloy (Figure 7). Nevertheless, the alloy films delaminated during CO₂ electroreduction. For the following reasons, glassy carbon is determined to not be an appropriate electrode for the project.

Meanwhile, silver substrate is considered as a reasonable substitute for glassy carbon. In the thermodynamical aspect, a negative free energy should be observed when two subjects are mixed to form an atomic bond across the interface; otherwise, those two are immiscible. Copper and silver are immiscible, hence contamination from the silver substrate should not occur. Additionally, a strong bond should be able to form the interface between the two materials [23].

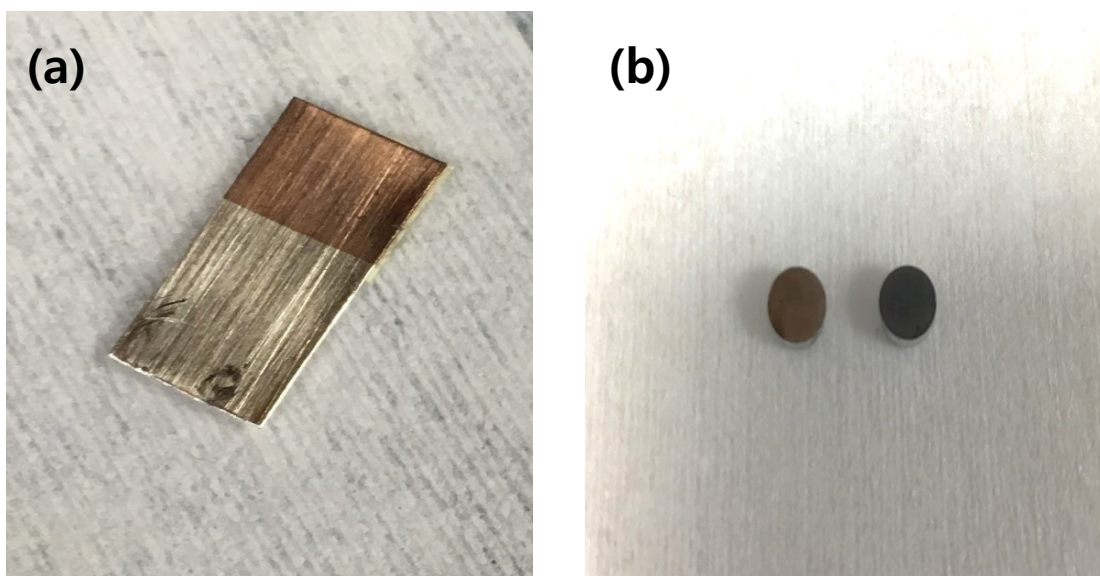


Figure 8. (a) Cu-Pd alloy prepared by electrodeposition on a silver foil at -0.641 V vs. Hg/HgSO₄ for 600 s (b) Cu₉Pd₁ (left) and Cu₆Pd₄ (right) thin films prepared by electrodeposition on silver RDE

Cu-Pd alloy films were successfully synthesized with silver-based substrates (Figure 8). Films were adhered well to the surface of both substrates even after the electroreduction reaction of CO₂. However, since high voltage was applied to yield CH₄ products, a large amount of gas bubbles was trapped on the surface of the electrodes, Figure 9 (a) and (b). The phenomenon was identified due to the reduction of proton into hydrogen gas [24]. Once the voltage was increased above the onset level of the reduction wave, gas bubbles were formed on the electrode. According to the hydrodynamic model established by Elsner group, the mass transfer rate is affected by the conditions of bubble formation, and the rate of the electrochemical process decreases along with the gas bubble evolution [25].

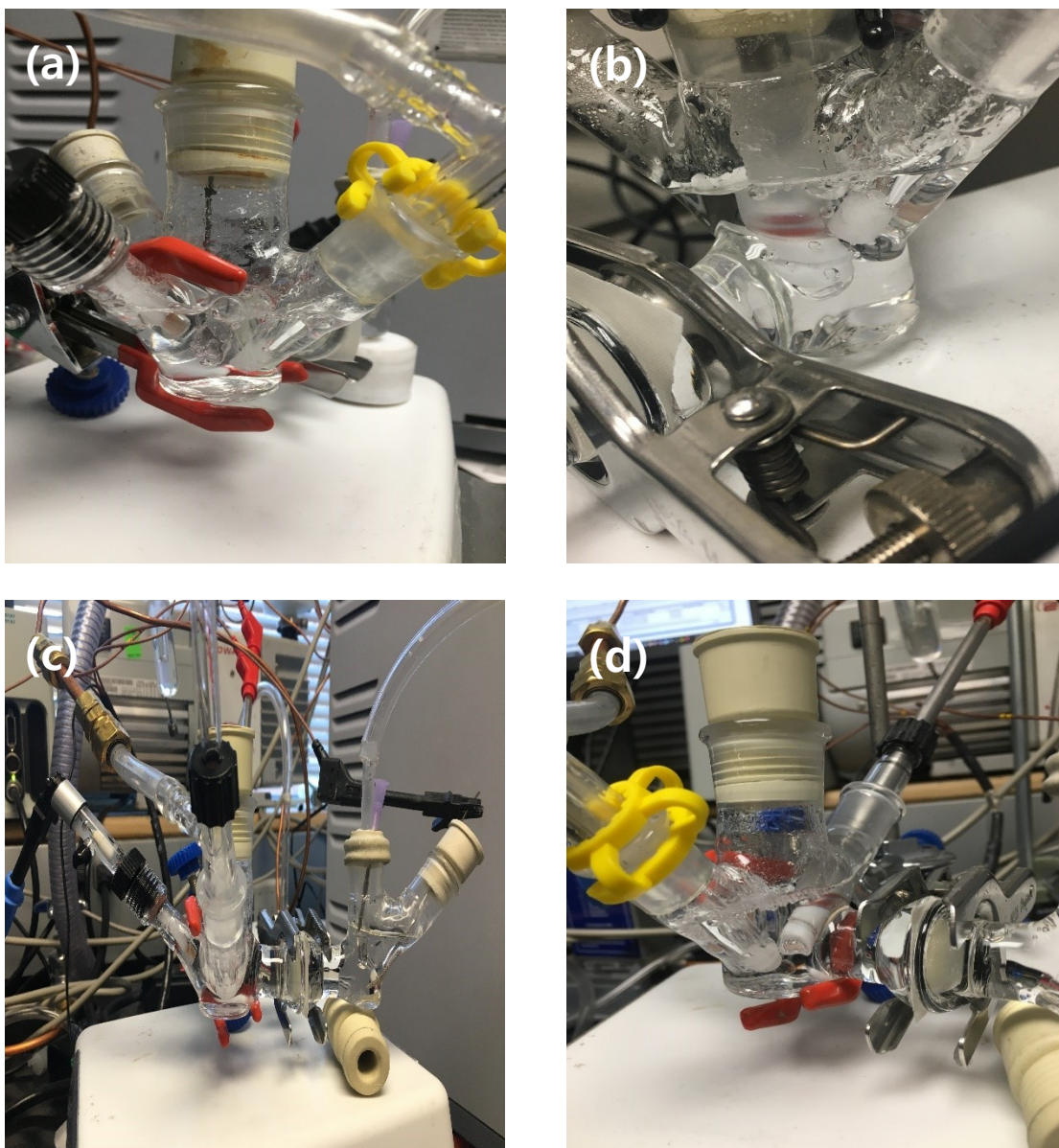


Figure 9. Evolution of gas bubbles during the electrochemical reduction of CO_2 on (a) silver foil (b) silver RDE (c) Final electrochemical cell setup of catalytic activity of CO_2 (d) Evolution of gas bubbles observed on the final cell setup using a silver RDE

To reduce the gas bubble formation on the surface, the cell was set up as shown in Figure 9 (d). The sample was inserted in a diagonal direction rather than a straight vertical direction, and bubbles that nucleated on the surface were able to dislodge from the electrode surface. Consequently, silver RDE was considered as the best substrate for the electroreduction reaction, as it can be assembled tightly with a RDE holder.

3.2 Characterization and surface analysis of Cu-Pd thin films

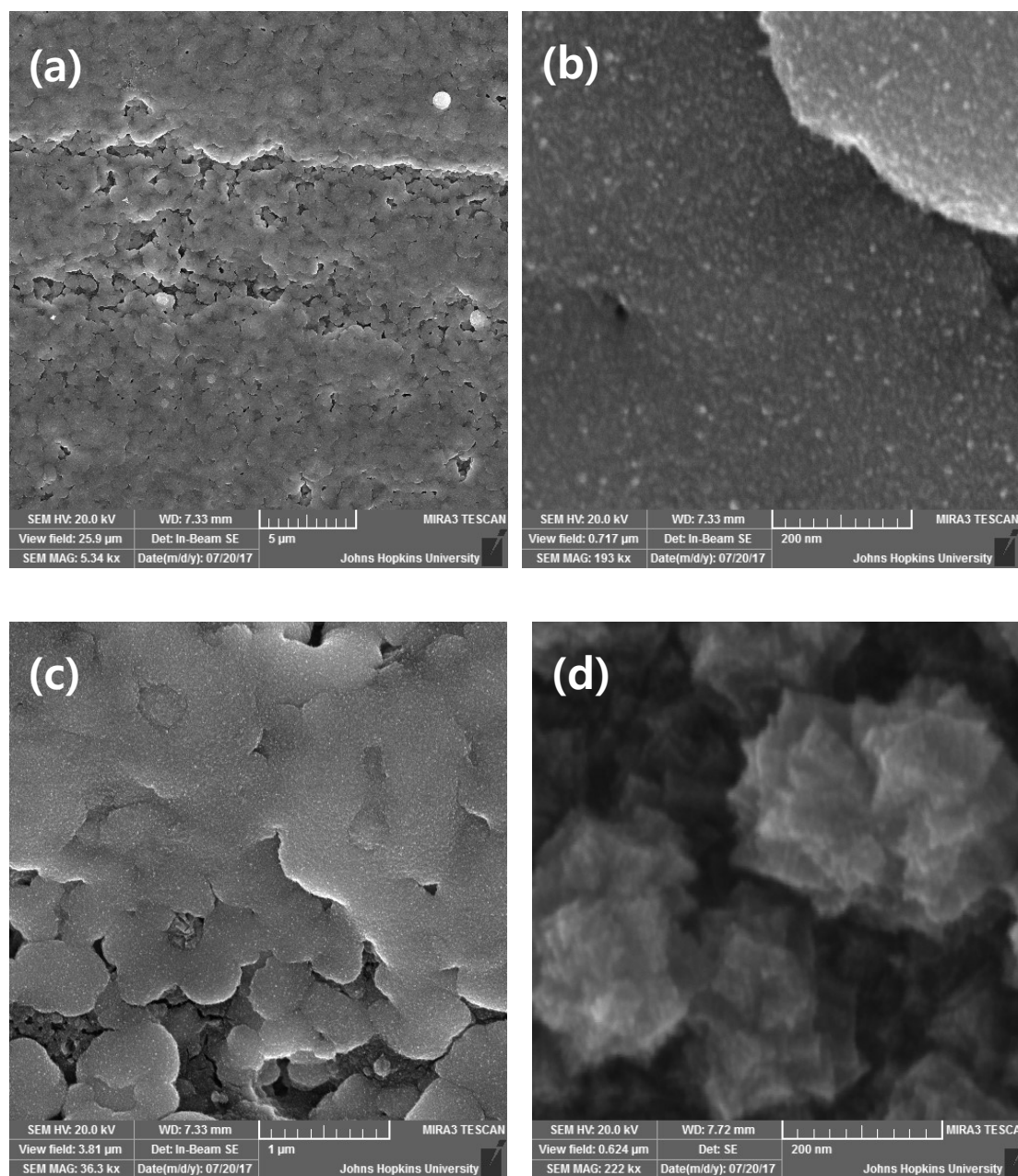


Figure 10. Top-surface SEM images of $\text{Cu}_x\text{Pd}_{1-x}$ film with different compositional ratios (a, b) Cu_9Pd_1 (c, d) Cu_6Pd_4

Morphologies of the various compositional ratio of film samples were studied by means of SEM, as shown in Figure 10. The high copper alloy shows large grains, and their size were distributed randomly, due to island-type growth of the copper film. With increasing Pd ratio, the surface structures gradually changed from flat-lined to

cauliflower-like surfaces.

The content of both palladium and copper were controlled by changing the compositional ratio of corresponding metallic precursors in the electrolyte solutions used for electrodeposition. The bulk compositional ratios of the alloys were characterized by EDS. As clearly seen in Figure 11, the content of palladium and copper in the Cu_9Pd_1 catalyst sample accorded well with the stoichiometric ratio of the starting electrolyte solution made of 1 mM of Na_2PdCl_4 and 9 mM of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

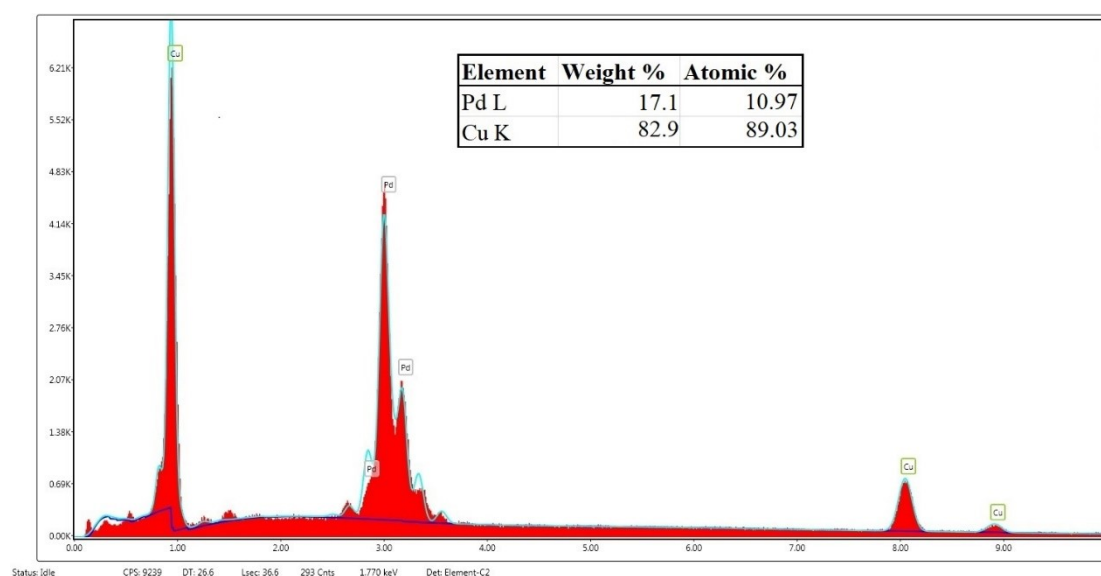


Figure 11. EDS mapping of the Cu_9Pd_1 electrocatalyst

EDS effectively provides the bulk concentration of the elements in the sample. However, due to its high depth sampling profile, several hundred nanometers to micrometers is probed, the technique is not appropriate for thin film surface analysis. Therefore, XPS analysis was performed to measure the surface composition of resulting thin film samples.

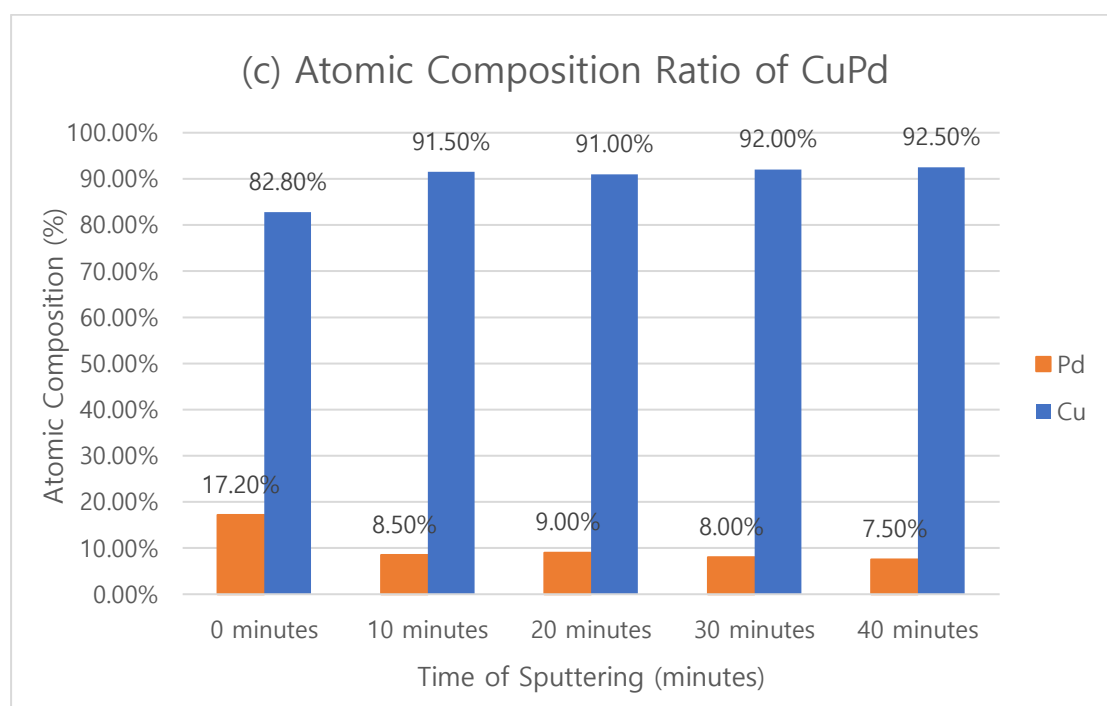
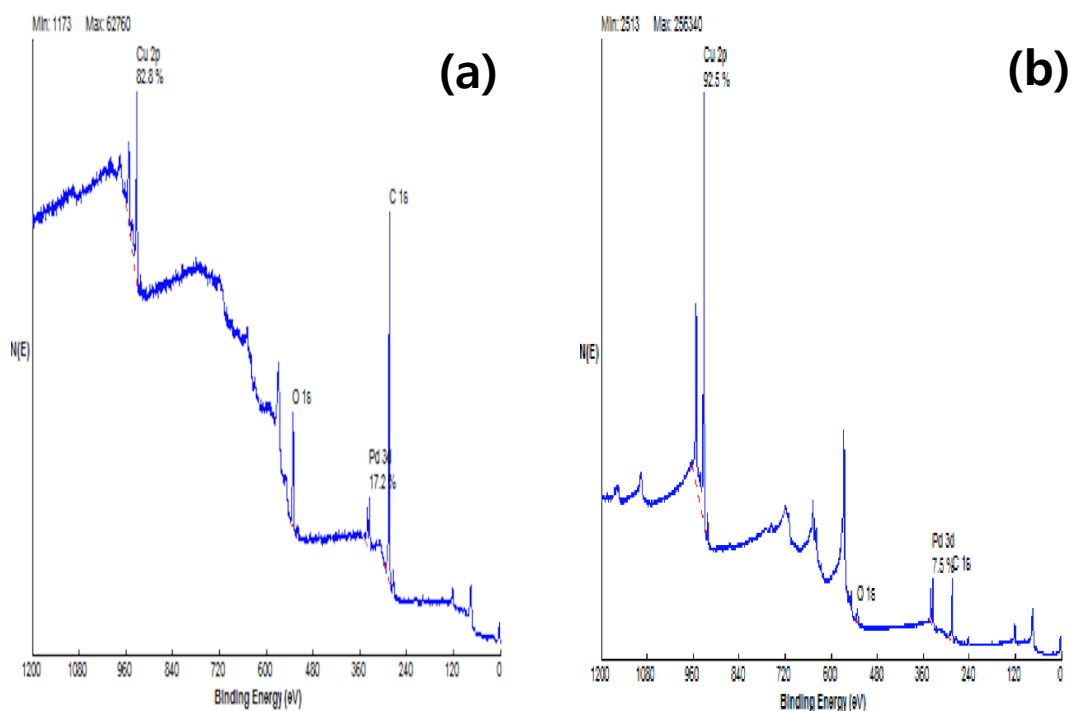


Figure 12. XPS surface analysis of the Cu₉Pd₁ electrocatalyst (a) 0 minutes sputtering (b) 40 minutes sputtering (c) Bar graph of atomic composition ratio

Interestingly, the surface composition of the sample measured was Cu_{8.2}Pd_{1.8}, which is relatively different from the bulk composition measured by EDS. After sputtering with the rate of ~5 nm for 10 minutes, the higher composition of copper

could be detected. These results experimentally demonstrate that as-synthesized alloys exhibit surface depletion of Cu relative to the bulk composition. Since most alloys studied in the literature utilize materials with < 75 % copper in the bulk, the surface composition of Cu may be substantially lower than our samples.

3.3 Electrochemical reduction of CuPd thin films to convert CO₂ into hydrocarbon fuels

3.3.1 Measured current vs. potential

The electrocatalytic activities of CuPd alloy film samples were performed in CO₂ saturated 0.1 M aqueous KHCO₃ by using a custom designed H-cell. Figure 13 (a) shows the overall current densities of CuPd catalysts and the pure copper RDE in the potential range from -0.8 V to -1.3 V vs. RHE. The copper RDE exhibited the largest total current density among the samples, and the current is more likely to be decreased by alloying Pd with Cu gradually. As the amount of voltage applied increased, bubbles were formed on the electrode surface which affect the data measurement by causing fluctuations in the current (Figure 13 b).

The faradaic efficiency (FE) of the gaseous products was calculated based on the equation below:

$$FE = \frac{n \cdot N \cdot F}{Q} \times 100\% \quad (10)$$

where N is the amount of the generated products during the process in mol, F is the faradaic constant, 96,485 C/mol, n is the number of electrons transferred in the faradaic process, and Q is the measured charge passed throughout the reaction. The number of electrons required to form H₂, CO, CH₄, and C₂H₄ are 2, 2, 8, and 12 respectively.

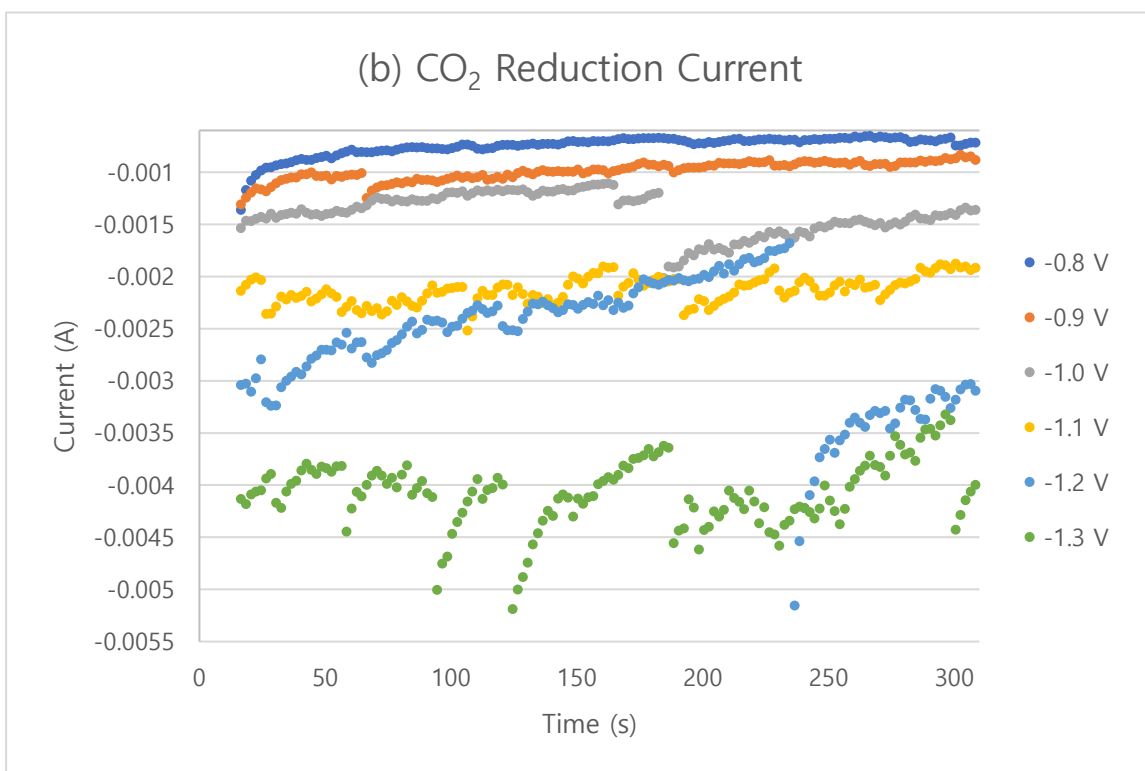
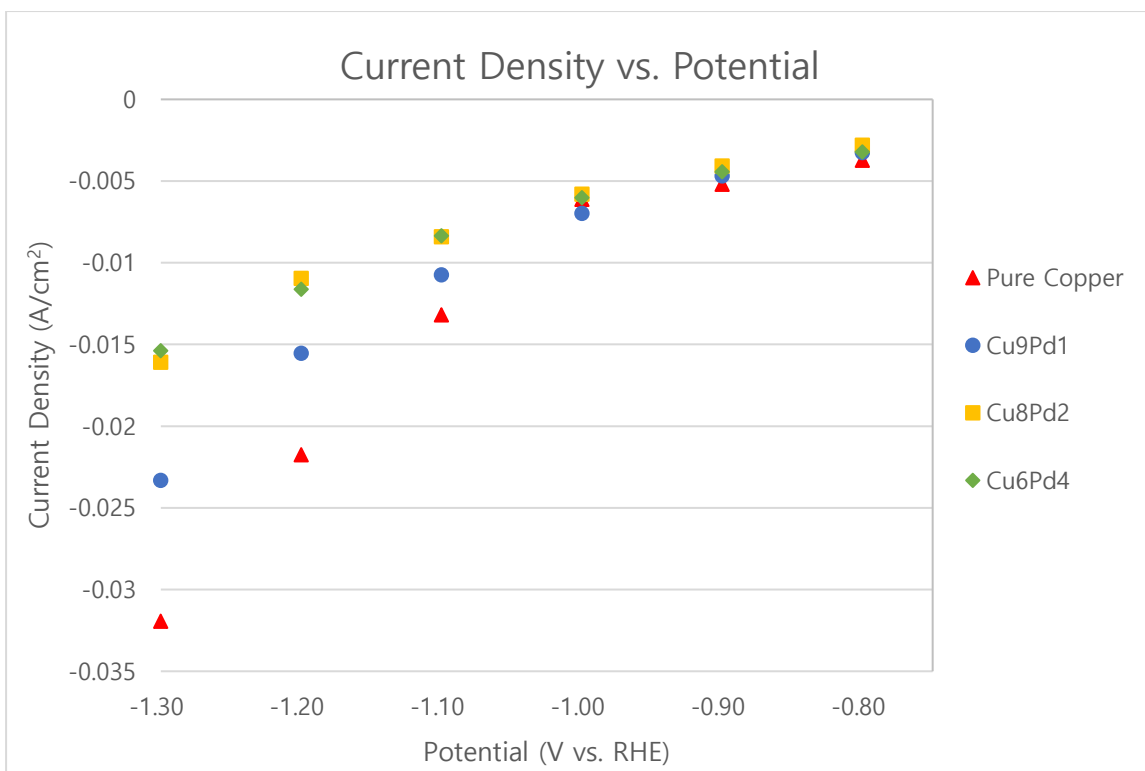
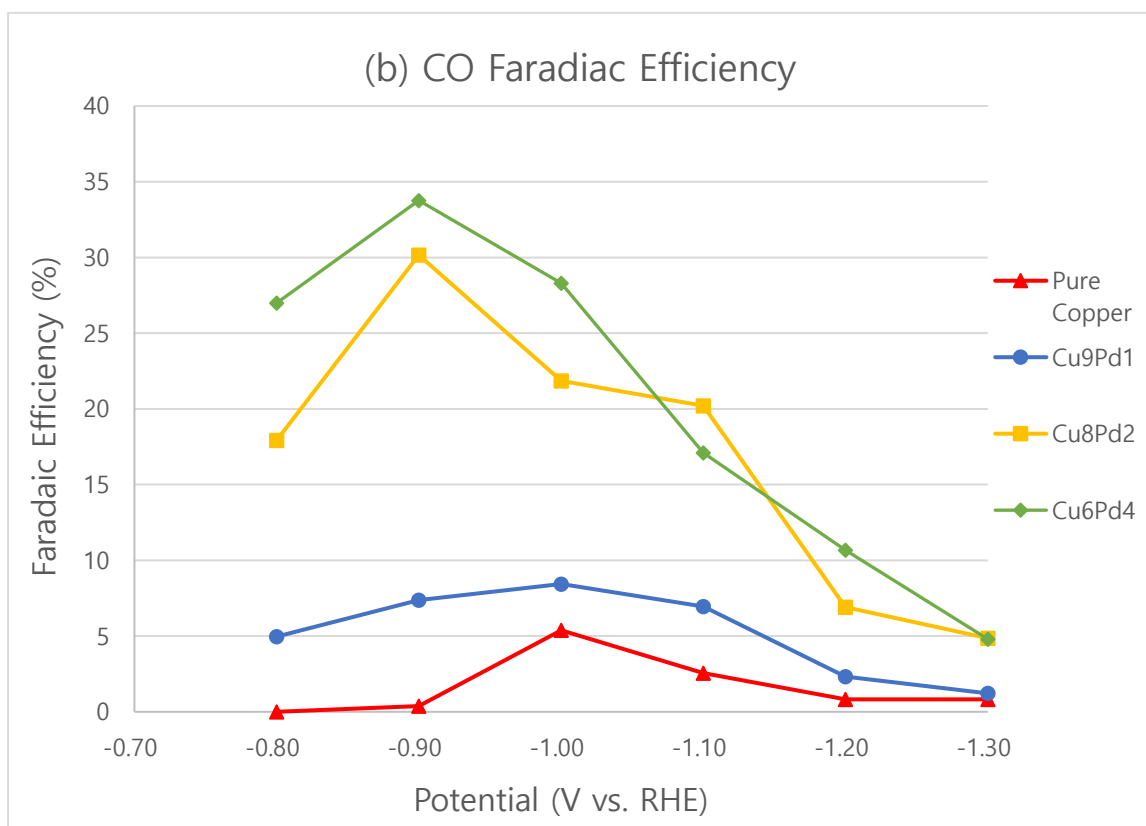
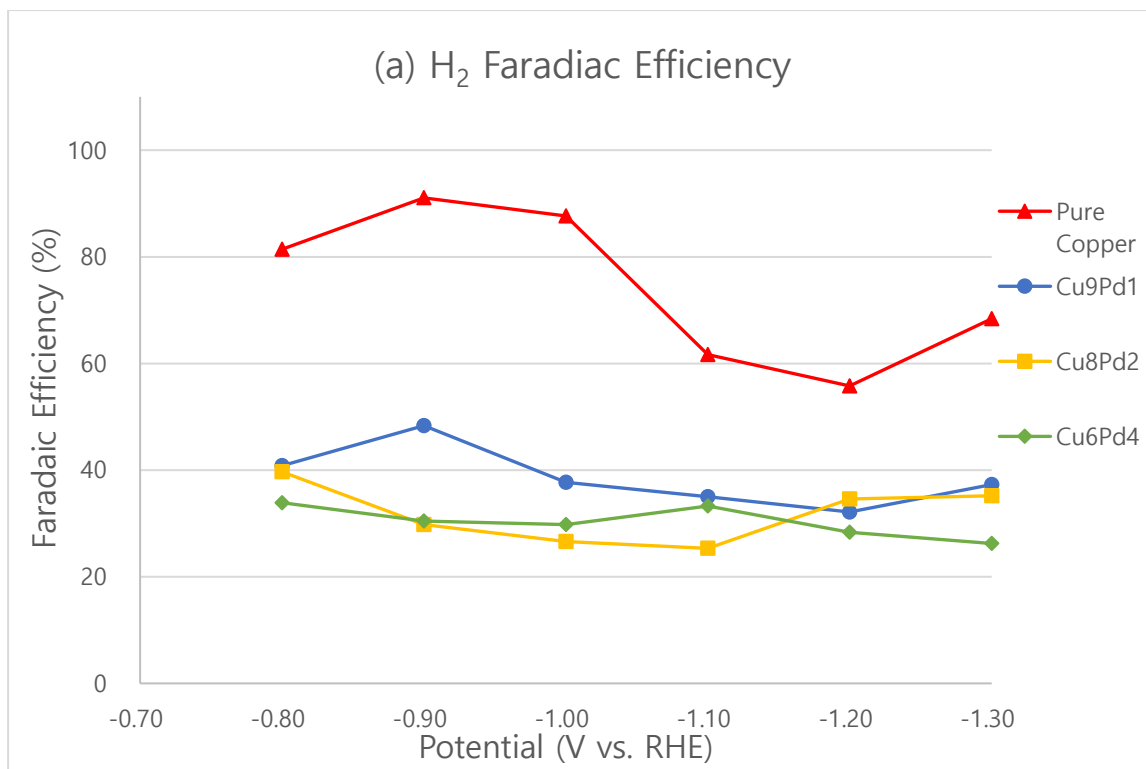


Figure 13. (a) Overall current density plots of copper metal and CuPd electrocatalysts (b) Chronoamperogram of CO₂ reduction

3.3.2 Products vs. Potential



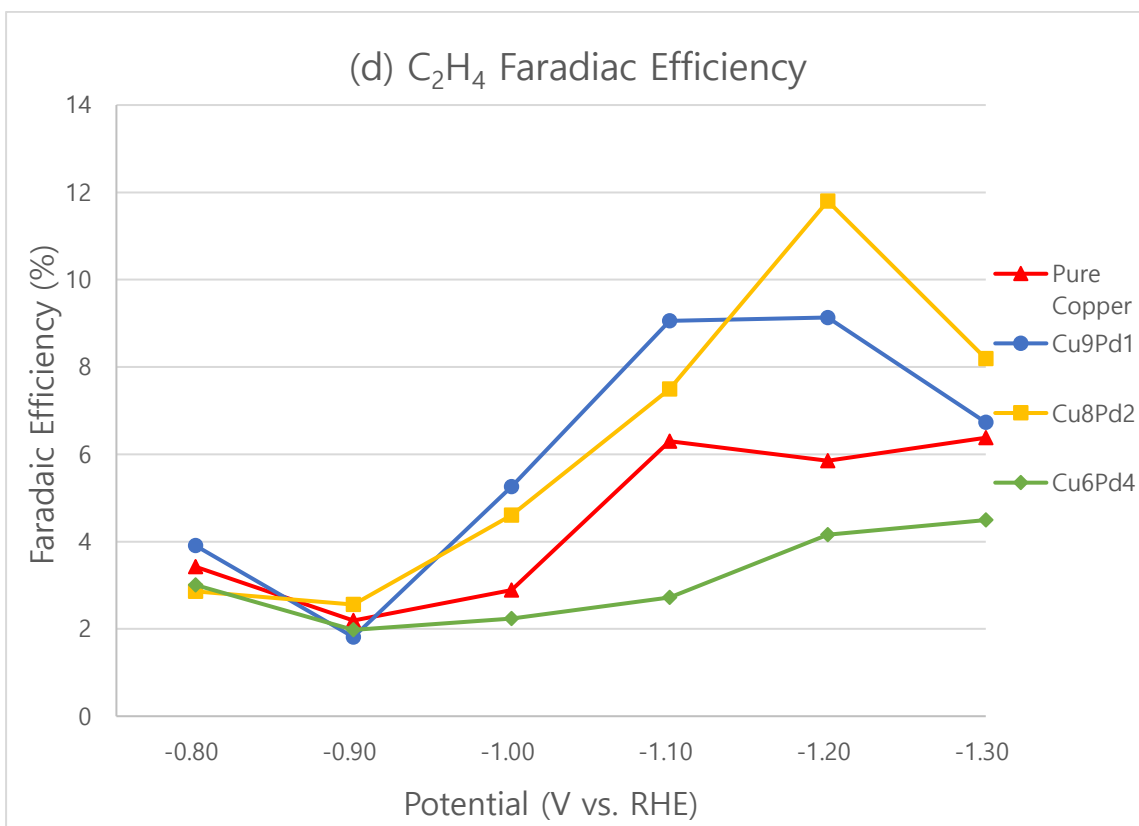
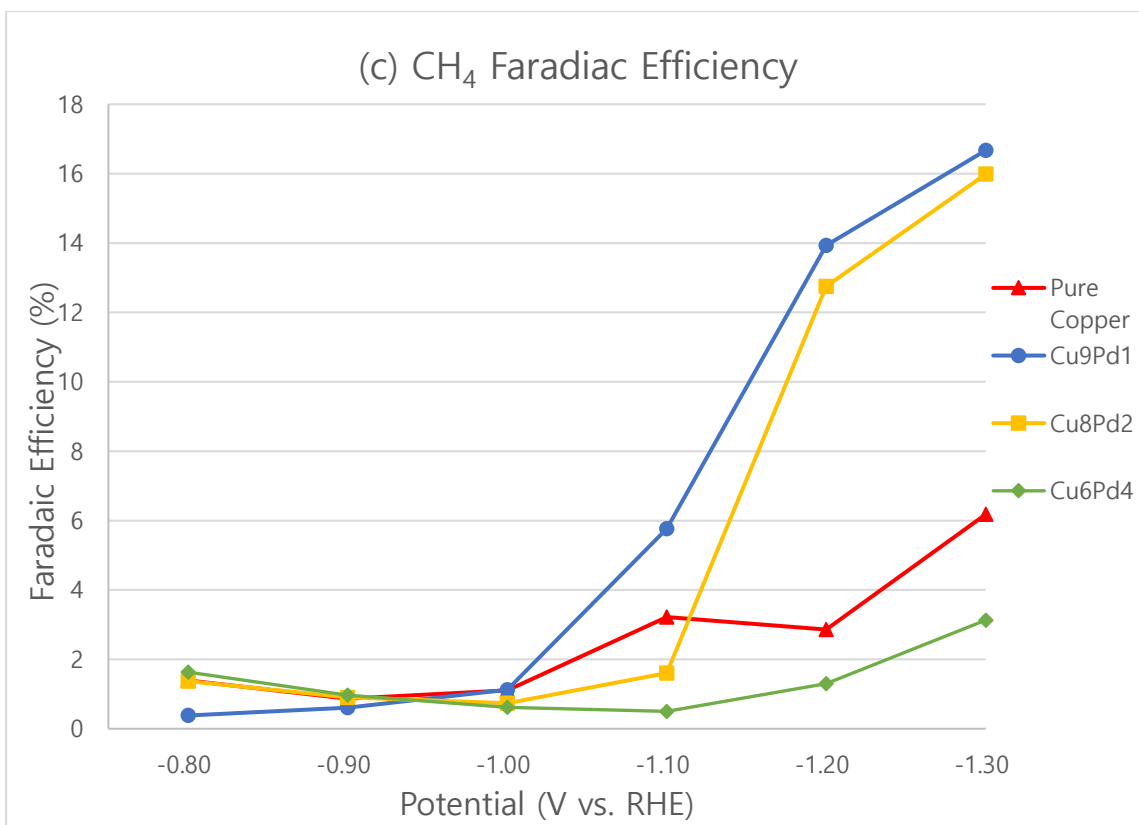


Figure 14. Faradaic efficiency plots of CuPd electrocatalysts for each product; (a) H₂ (b) CO (c) CH₄ (d) C₂H₄

Figure 14 (a)-(d) shows H₂ is the dominant product of the reaction of pure copper. Considering the correlation between the potential applied and the selectivity toward targeting products, the selectivity toward CO starts to decrease with increasing overpotential. The potential of -0.8 V vs. RHE is determined for the onset of CH₄ and C₂H₄ production from CO₂, and at the potentials lower than -1.0 V vs. RHE, C₂H₄ formation is more favored than CH₄. However, as observed by Kuhl group, at very high overpotential below -1.1 V vs. RHE, selectivity towards all C₁-C₃ products are in decline besides CH₄, whose FE tends to increase with that of H₂ [26][27]. The highest FE measured was 17% for CH₄ and 13% for C₂H₄ respectively from Cu₉Pd₁ and Cu₈Pd₂ alloy catalysts. It is clear that CuPd alloys with high copper ratios, Cu₉Pd₁ and Cu₈Pd₂, exhibit better catalytic performance in producing hydrocarbon fuels than pure copper. Yet, if too much Pd is alloyed, the amount of hydrocarbon products that can be detected dramatically decreases. By alloying Pd with Cu gradually, the FE of H₂ decreases drastically, the FEs for C₁-C₂ products increases, and the rate of CO generation also increases. It is found that CO becomes dominant product when the bimetallic alloy contains more than 20% Pd [26].

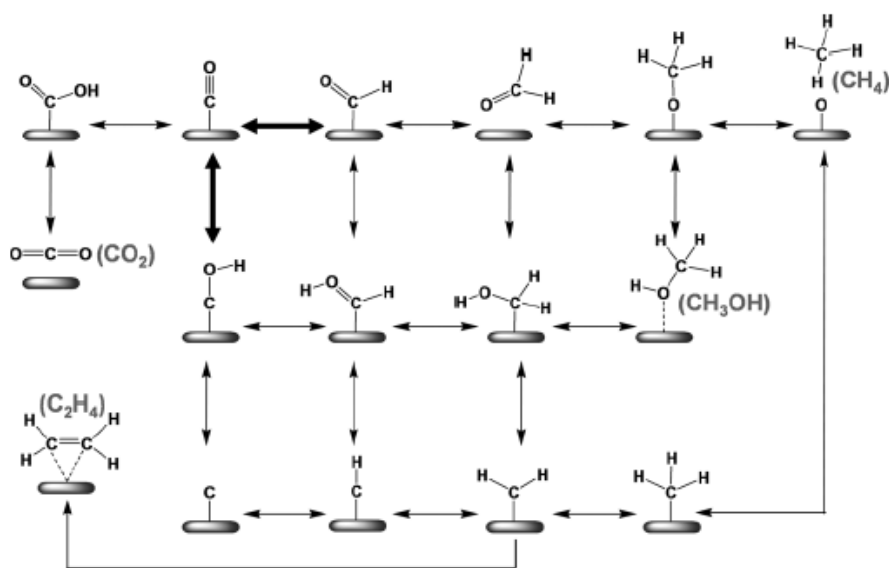


Figure 15. CO₂ reaction path on Cu(111) proposed by Nie et al. Figure adapted from ref. 28

In mechanistic point of view to form hydrocarbon by electroreduction of CO₂, C-O bond must be broken from the CO intermediate for CH₄, while C-C coupling is needed for further formation of C₂-C₃ species. The data shows that electrochemical potential can influence the rate of C-C coupling. The following decrease in C-C coupling along with the significant high overpotential can be explained by the proton and electron transfers becoming more favorable at negative potentials. Throughout the electroreduction process, C₁ species tend to be reduced all the way to CH₄ and desorb at negative potentials, instead of remaining on the electrode surface as C₁ intermediate for further coupling [27-28]. Nevertheless, in the C₂ pathway, CO intermediates are dimerized to yield a *C₂O₂⁻ intermediate by electron transfer at lower potential, while proton is transferred only after the formation of the CO dimer [29].

4. Conclusion

In this report, we have successfully synthesized copper-palladium alloy thin film catalyst with high copper ratio and investigated the selectivity for CO₂ electroreduction reaction. In many literature, glassy carbon electrode has been extensively used for electrodeposition, but herein we found that glassy carbon is not suitable for the deposition of copper due to the low intrinsic adhesion between carbon and copper. Silver substrate is rather recommended for the reaction. We also found the surface concentration of Cu alloy catalyst is much lower than the bulk concentration as the Cu surface coverage is diluted with Pd which has lower surface energy. It can be deduced that the low catalytic performances of alloy metals from other studies are due to lower surface coverage of Cu. Therefore, we determined to fabricate high Cu ratio electrodes to increase the number of Cu sites neighboring each other.

The CuPd catalysts we synthesized exhibit the FE of CH₄ 17% and of C₂H₄ 13%. The data clearly confirmed that by alloying Cu with Pd the catalytic performance of producing hydrocarbon products can be enhanced. However, if the composition ratio of Pd increases, CO becomes the dominant product while only neglectable amount of hydrocarbon products are produced. The second observation is that methane is formed at high overpotentials, while ethylene formation takes place at moderate overpotentials. This project provides insight for the design of better Cu alloy catalysts. Since there are studies indicating that crystal structures of copper electrodes and copper alloy mixing patterns affect the selectivity to C₁ to C₂ species, computational calculations and analysis of precise surface structure would be desired in the future works. Fabrication of mesoporous structure can also be a possible application.

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Curriculum Vitae

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EDUCATION

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| Sep. 2016 – Present | JOHNS HOPKINS UNIVERSITY Whiting School of Engineering <i>Masters of Science, Chemical & Biomolecular Engineering</i> | Baltimore, MD |
| Sep. 2010 – May. 2014 | NEW YORK UNIVERSITY Tandon School of Engineering <i>Bachelor of Science, Chemical & Biomolecular Engineering</i> | Brooklyn, NY <i>Cum Laude (GPA: 3.50/4.00)</i> |

RESEARCH EXPERIENCE

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| Sep. 2016 – Present | Materials Electrochemistry Laboratory Johns Hopkins University <i>Hall Research Group, Department of Materials Science and Engineering</i> <ul style="list-style-type: none">Deposited and characterized mesoporous Palladium-Copper thin film on silver substrates to catalyze the electroreduction on carbon dioxide into hydrocarbon fuels | Baltimore, MD |
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WORK EXPERIENCE

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| Aug. 2017 – Present | Johns Hopkins University <i>Electrical and Computer Engineering / Biophotonics Lab Assistant</i> <ul style="list-style-type: none">Assisted in lab experiments and maintained a safe, accident-free laboratory environment by following safety rules and good laboratory and manufacturing practicesPerformed routine tests of specified laboratory instrumentation and equipment assigned by the supervisor | Baltimore, MD |
| Dec. 2014 – Sep. 2016 | Seoul Metropolitan Police Agency Embassy Security Force <i>Auxiliary Police (Sergeant Class)</i> <ul style="list-style-type: none">Riot control and security services in the Seoul metropolitan areaConducted translation work of International Police Association's strategy documents regarding terrorism prevention and investigation | Seoul, Korea |
| May. 2014 – Dec. 2014 | PKI Inc. <i>R&D Engineer</i> <ul style="list-style-type: none">Participated in a technology development project that used pulsed plasma reactor as well as an analysis of the deposition of various thin filmsResearched on improvements in the efficiency of dye-sensitized solar cells (DSSCs) by depositing Ga-doped Zinc oxide nanoparticles | Seoul, Korea |
| Jun. 2013 – Aug. 2013 | SK Hynix Inc. <i>Summer Intern</i> <ul style="list-style-type: none">Assisted in inlay manufacturing process for RFID and IC reader antenna and performance analysis on mobile computational optimizationAnalyzed mobile payment services and categorized domestic consumers' shopping patterns in public transportation, convenience stores, and food industries | Seoul, Korea |
| Jun. 2012 – Aug. 2012 | Infosec Co., Ltd. <i>Summer Intern</i> <ul style="list-style-type: none">Identified and examined successful cases of mobile security services in Korea for U.S. market entryCompensated the coding defects in a Mobile Security Solution, 'M-Shield' by restricting users using home button to remove the application | Seoul, Korea |

EXTRA-CURRICULAR ACTIVITIES

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| Jan. 2011 – May. 2012 | KOREAN STUDENT ASSOCIATION <i>Treasurer & Public Relations Manager</i> <ul style="list-style-type: none">Managed and raised the fund of the club by volunteer activity and entertainment eventsConsulted Korean students on registration process and increased membership by leading Korean cultural campaigns | Brooklyn, NY |
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SKILLS & OTHER INFORMATION

Honors: Academic Dean's List, Promise Fund Scholarship, ChemBE 2nd Year Scholarship

Lab Techniques: XRD, SEM, EDS, XPS

Computer Language: C++, JAVA, Python, Matlab, Maple

Computer Skills: Skillful at operating computer, proficient at using MS Office Suite

Language Skills: Fluent in English, and native in Korean, intermediate in Japanese