Electrochemical reduction of carbon dioxide on copper-based cathodes in electrochemical tubular fixed bed reactor



A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Engineering in Chemical Engineering Department of Chemical Engineering FACULTY OF ENGINEERING Chulalongkorn University Academic Year 2021 Copyright of Chulalongkorn University

ปฏิกิริยารีดักชั้นเชิงเคมีไฟฟ้าของก๊าซคาร์บอนไดออกไซด์บนขั้วแคโทดทองแดงในเครื่องปฏิกรณ์ เคมีไฟฟ้าเบดนิ่งแบบท่อ



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กันย์จิรา จรรยา : ปฏิกิริยารีดักชันเชิงเคมีไฟฟ้าของก๊าซคาร์บอนไดออกไซด์บนขั้ว แคโทดทองแดงในเครื่องปฏิกรณ์เคมีไฟฟ้าเบดนิ่งแบบท่อ. (Electrochemical reduction of carbon dioxide on copper-based cathodes in electrochemical tubular fixed bed reactor) อ.ที่ปรึกษาหลัก : ผศ. ดร.พลัง บำรุงสกุลสวัสดิ์

. ปฏิกิริยารีดักชั้นเชิงเคมีไฟฟ้าของก๊าซคาร์บอนไดออกไซด์ถูกใช้ในการลดปริมาณก๊าซ คาร์บอนไดออกไซด์ในชั้นบรรยากาศโดยการแลกเปลี่ยนโปรตอนและอิเล็กตรอน โดยการกระจาย ตัวของผลิตภัณฑ์ที่เกิดขึ้นจะขึ้นกับขั้วแคโทดซึ่งคอปเปอร์คือโลหะที่มีคุณสมบัติและความสามารถ ้ในการเร่งการเปลี่ยนก๊าซคาร์บอนไดออกไซด์เป็นสารประเภทไฮโดรคาร์บอน เช่น ก๊าซเอทิลีน ด้วย ปฏิกิริยารีดักชั้น แต่ปัญหาหลักคือค่าการละลายของก๊าซคาร์บอนไดออกไซด์ในสารละลายอิเล็ก โทรไลต์มีค่าน้อยที่อุณหภูมิต่ำและความดันบรรยากาศส่งผลต่อการถ่ายโอนมวลและอัตราการ เกิดปฏิกิริยา ในงานวิจัยนี้ประสิทธิภาพของปฏิกิริยารีดักชั้นจะถูกพัฒนาด้วยการเพิ่มความดัน โดย ้ใช้คอปเปอร์โฟมที่มีสารละลายไอโอโนเมอร์เป็นขั้วแคโทดในเครื่องปฏิกรณ์แบบเบดนิ่งสำหรับ ปฏิกิริยาแบบต่อเนื่องในการเปลี่ยนก๊าซคาร์บอนไดออกไซด์เป็นก๊าซเอทิลีน โดยสังเกตุการเลือก เกิดของก๊าซเอทิลีนเมื่อเพิ่มความดันของก๊าซคาร์บอนไดออกไซด์ พบว่าประสิทธิภาพของฟาราเดย์ ของก๊าซเอทิลีนที่ 10 บาร์จะสูงที่สุดและสูงกว่า 3 และ 4 เท่าที่ 5 และ 3 บาร์ตามลำดับ และ ประสิทธิภาพขงฟาราเดย์ของก๊าซคาร์บอนมอนอกไซด์จะลดลงเนื่องจากถูกใช้เป็นสารมัธยันตร์ใน การเกิดก๊าซเอทิลีน นอกจากนี้ผลกระทบของความต่างศักย์ได้ทำการศึกษา พบว่าเมื่อความต่าง ้ศักย์ของเซลล์และกระแสถูกปรับให้สูงขึ้นจะส่งผลให้ประสิทธิภาพของฟาราเดย์ของเอทิลีนและ คาร์บอนมอนอกไซด์ลดลงเนื่องมาจากโปรตรอนที่เกิดจากน้ำจะเข้ามาดูดซับที่ผิวได้ดีกว่าสารมัธ ยันต์และไปยับยั้งการเกิดปฏิกิริยารีดักชั้นเชิงเคมีไฟฟ้าของก๊าซคาร์บอนไดออกไซด์

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CO2 electrochemical reduction reaction (CO2ERR) has been investigated with an aim to eventually become a means to decrease the concentration of CO₂ in the atmosphere to hydrocarbons by proton and electron transfer. The product distribution strongly depends on cathode materials. Copper is a unique metal in its ability to catalyze the electrochemical reduction of CO₂ to various hydrocarbons including ethylene, but the main problems are the poor solubility CO₂ in aqueous solutions. In this study, the performance of CO₂ERR is improved by increasing pressure. The ionomer copper foam is used as a cathode in the electrochemical tubular fixed bed reactor for continuous conversion of CO₂ to ethylene to observe the selectivity of CO₂ pressure. The result show faradic efficiency (FE) of ethylene on 10 bar is 2 and 6 times higher than 5 and 3 bar, respectively and FE of CO is decreased for C-C coupling to ethylene production. Moreover, The effect of cell voltages are studied by potentialstat controlling. the results show FE of ethylene and CO are decreased because protons reduce intermediated CO on the cathode surface and lead to suppress CO₂ reduction while cell voltage and current are increased.

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Student's Signature Advisor's Signature

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CHAPTER 1

INTRODUCTION

1.1 Background

Concentration of CO₂ in the atmosphere has increased by 30% since the industrial revolution and fossil fuel utilization. Excessive CO₂ in the atmosphere causes natural disasters such as rising global temperatures and rising sea levels. The main cause of this problem is the one-way injection of carbon from fossil fuels/resources into the atmosphere. However, banning their usage would also cut the supply of carbon sources for human civilization, unless processes for converting CO₂ to valuable products are in place. Many technologies for CO₂ utilization exist: reforming, hydrogenation, Biological conversion and carbon dioxide electrochemical reduction reaction (CO2ERR). CO2ERR is to convert CO2 into carbon-containing products such as carbon monoxide (CO), methane (CH₄), formic acid (HCOOH), methanol (CH₃OH), ethylene (C_2H_4) and ethanol (C_2H_5OH) by proton and electron transfer [1, 2].CO₂ERR offers several means of control: electrode material, current density, applied voltage, electrolyte composition and concentrations. The reaction can also be carried out at ambient temperature and pressure, unlike other thermochemical methods in which elevated temperature and pressure are virtually always required. There are 2 main reactions. First, water is oxidized to oxygen at an anode call "oxygen evolution reaction (OER)". Second, CO2ERR occurs at cathode and product production depend on cathode catalyst or material. Moreover, Hydrogen evolution reaction concomitant occurs at cathode.

Traditional electrochemical CO_2ERR is performed in divided electrochemical cells. An ion-exchange membrane is used to form 2 chambers in an electrochemical cell so that carbon products from the cathode are not mixed with oxygen from the anode. Nevertheless, pressurization in this type of cell is

difficult in practice. An excessive pressure difference between the anode and cathode chambers can lead to membrane rupture. Furthermore, CO_2 transport from the cathode chamber to the anode chamber in the form of bicarbonate through an anion-exchange membrane, which is commonly used, is somewhat unavoidable, leading to decreased single-pass conversion.

In this work, we design and study a single-chamber tubular fixed-bed electrochemical reactor for CO_2ERR that is not affected by the two problems described earlier. Nonetheless, the single-chamber design allows carbon products and oxygen to come into contact and presents risk of explosion. However, it may be useful for conversion of heavily diluted CO_2 sources such as flue gases; the existence of inert N_2 put the gas composition outside the flammability limits. In this application, purification of CO_2 is not needed and hence its cost may be eliminated.

Ethylene is a raw material used in manufacture of polymers such as polyethylene terephthalate (PET), polyethylene, polyvinylchloride (PVC) and polystyrene (PS). For high ethylene production, copper is probably the only metal which can produce C_{2+} compounds by multielectron reaction [1-4]. In addition, copper-based catalysts have unique properties among metal catalysts for electrochemical reduction of CO_2 to fuel or hydrocarbons. However, the practical application of Cu-based catalyst in the CO_2 ERR still faces problems such as low current density, poor stability and poor selectivity. Therefore, developing efficient process conditions to achieve high current densities, selectivity and stability would very likely affect the feasibility of CO_2 ERR technology.

In this study, Copper foam (Cu foam) and ionomer copper foam (I-Cu foam) will be employed in our single-chamber reactor. The Cu foam and I-Cu foam are then used as a cathode in the electrochemical tubular fixed bed reactor for continuous conversion of CO_2 to ethylene to observe the catalyst's selectivity and activity. the performance of CO_2 ERR is improved by increasing pressure and cell voltage.

1.2 Research objective

1.2.1 To study electrochemical CO_2ERR with Copper cathode in electrochemical tubular fixed-bed reactor.

1.2.2 To study the effects of Copper cathode preparation methods on CO_2ERR in electrochemical tubular fixed-bed reactor.

1.2.3 To study effects of pressures and applied cell voltage on electrochemical CO_2ERR in electrochemical tubular fixed-bed reactor.

1.3 Scope of study

1.3.1 Electrochemical CO_2ERR performed in an electrochemical tubular fixed bed reactor.

1.3.2 Effects of cell potential and pressure.

1.4 Expected benefit

1.4.1 A prototype of single-chamber electrochemical tubular fixed bed reactor for electrochemical conversion of diluted CO_2 into ethylene.

CHAPTER 2

THEORY and LITERATURE REVIEWS

2.1 Theory

2.1.1 Electrochemical CO₂ reduction reaction (CO₂ERR)

 $CO_2 ERR$ has been investigated to decrease concentration of CO_2 in atmosphere to value-added chemicals by proton and electron transfer. The product from $CO_2 ERR$ is depending on active metal catalyst. Moreover, Morphology, pH, Electrolyte and structure have effect to produce products. The products from $CO_2 ERR$ is considered by (1) Chemical adsorption of CO_2 on the surface of a catalyst (cathode). (2) Electron transfer and/or proton migration to break C–O bonds and/or form C–H bonds. (3) Rearrangement of product species followed by desorption from electrode surface and diffusion into electrolyte [5].

In general, the cell of electrochemical CO_2ERR consists of cathodic compartment, where the reduction process is governed by a multi-step-based coordination chemistry comprising two, six, eight, and twelve electrons for the formation of the common products CO, CH_3OH , CH_4 , and C_2H_4 , respectively as shown in table 1., and anodic compartment, where oxygen evolution occurs and produces acidic condition on electrode. Accordingly, an electrode of anode should resist and be stable in acidic condition such as Titanium (Ti) and Platinum (Pt). The two compartments are separated by membrane, which has a role of protecting "short circuit" and provides the ionic conduction for allowing the current flow through the system.

Table **1** The chemical equation and the corresponding standard electrode potential (V vs. SHE)[1, 6-8].

Half electrochemical thermodynamic reaction	V vs. SHE	Eq.
$CO_2(g) + 2H^+ + 2e^- \rightleftharpoons CO(g) + H_2O(l)$	- 0.106	1
$CO_2(g) + 2H_2O(l) + 2e^- \rightleftharpoons CO(g) + 2OH^-$	- 0.934	2
$CO_2(g) + H^+ + 6e^- \rightleftharpoons CH_3OH(l) + H_2O(l)$	0.016	3
$CO_2(g) + 5H_2O(l) + 6e^- \rightleftharpoons CH_3OH(l) + 6OH^-$	- 0.812	4
$CO_2(g) + 8H^+ + 8e^- \Longrightarrow CH_4(g) + 2H_2O(l)$	0.169	5
$CO_2(g) + 6H_2O(l) + 8e^- \rightleftharpoons CH_4(g) + 8OH^-$	- 0.659	6
$2CO_2(g) + 12H^+ + 12e^- \rightleftharpoons CH_2CH_2(g) + 4H_2O(l)$	0.064	7
$2CO_2(g) + 8H_2O(l) + 12e^- \rightleftharpoons CH_2CH_2(g) + 12OH^-$	- 0.764	8

CO₂ERR is alternative method for CO₂ transforming to hydrocarbon and alcohol, that has advantages 1. The parameters during electrochemical synthesis can be easily and precisely controlled, including the reaction electrode, current density, applied voltage, electrolyte composition and concentrations 2. The preparation process is under mild conditions (at ambient temperature and pressure) 3. Electricity can be provided through renewable energy sources (solar, wind, tidal, etc.) without generating any new sources of carbon dioxide[1, 9].

AGA

2.1.2 Ethylene

Ethylene (Fig. 1) is a widely raw material used in the manufacture of polymers (e.g. packaging, automotive and electrical applications). Furthermore, as compared to C_{1+} , the C_{2+} product has a greater market price. For high ethylene production, Copper is the only special metal that can produce C_{2+} compounds by multielectron reaction [1-4]. In addition, Cu-based catalyst has unique properties among metal catalyst has

been considered as a material for electrochemical reduction of CO_2 to fuel or hydrocarbon.

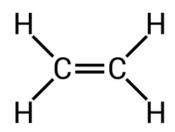


Figure 1 Molecule of ethylene

2.1.3 Active metal

Various catalysts have been studied for the CO₂ERR such as pure material, metal alloys and inorganic compounds (metal oxide, sulfides, etc.) in electrolytes (primarily 0.1M KHCO₃). They can be divided into four groups based on the principal reduction product: (*i*) Cu, the only metal that is reducing CO₂ to hydrocarbon, alcohol and other carbon containing chemicals at a significant rate; (*ii*) Au, Ag, Zn, Pd and Ga, from which CO is the major product; (*iii*) Pb, In, Sn and Bi, primary producing formate; (*iv*) Ni, Fe, Pt, and Ti, where only hydrogen evolution, but no CO₂ reduction, is observed at steady state. The CO₂ reduction capability of the metals in groups *i* and *ii* is attributed to the stabilization of *CO₂⁻⁻ and/or *COOH (* denotes a surface adsorption site) on their surfaces, whereas the formation of formate on group *iii* metals is believed to occur via hydration of nonadsorbing CO₂⁻⁻. Group *iv* metals are believed to bind to the intermediate *CO too strongly, which inhibits the continual reduction of CO₂, leaving only the evolution of hydrogen from the interstitial sites among adsorbed CO. [1-4, 9, 10].

2.1.4 Electrophoretic deposition

Electrophoretic deposition (EPD) is a colloidal technique used in ceramic manufacture that offers the following advantages: fast formation time, simple

apparatus, no substrate shape constraint, and no need for binder burnout because the green coating includes few or no organics. The EPD method, in comparison to other advanced shaping processes, is particularly adaptable since it can be quickly adjusted for a given purpose. With just modest changes in electrode design and positioning, deposition may be done on a flat, cylindrical, or any other shaped substrate. Despite the fact that it is a wet process, EPD allows for simple control of the thickness and shape of deposited films by adjusting the deposition duration and applied potential. When a DC electric field is applied to charged powder particles distributed or suspended in a liquid media, they are attracted and deposited onto a conductive substrate of opposite charge. The term "electrodeposition" is often used interchangeably to refer to either electroplating or electrophoretic deposition, however it is more commonly used to refer to the former. The contrast between the two processes is seen in Table 2. Depending on which electrode the deposition happens on, EPD can be one of two forms of electrophoretic deposition. Deposition occurs on the cathode when the particles are positively charged, and the process is known as cathodic electrophoretic deposition. Anodic electrophoretic deposition is the deposition of negatively charged particles on a positive electrode (anode). Any of the two modes of deposition can be achieved by modifying the surface charge on the particles. The two electrophoretic deposition processes are shown schematically in Fig. 2. [11].

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	•	
Property	Electroplating	Electrophoretic
		deposition
Moving species	lons	Solid particles
Charge transfer on deposition	lon reduction	None
Required conductance of liquid medium	High	Low
Preferred liquid	Water	Organic

Table 2 Characteristics of electrodeposition techniques.[11]

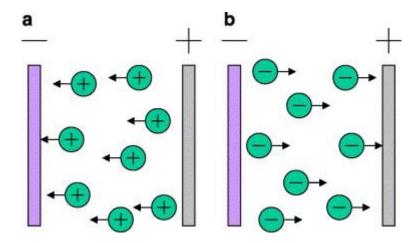


Figure 2 Schematic illustration of electrophoretic deposition process. (a) Cathodic EPD and (b) anodic EPD.

2.2 Literature reviews

This part focus on ethylene production in gas phase. First, The Cu-based catalyst cathode were synthesized by synthesis route. Second, The performance of Cu-based catalyst cathode in reactor for ethylene production. Moreover, facet, potential, and pressure are considered.

Copper based catalyst has been studied about selectivity and activity for CO₂ reduction by conduct relationship between structure and performance such as crystal plane, size, morphology and defect.

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2.2.1 Facets effect

Different copper facets exhibit different performance and intermediate reactions. For example, Hori et al. [12, 13] purposed that Cu(100) surfaces mostly produce C_2H_4 with a small amount of CH₄, whereas Cu(110) and Cu(111) surfaces primarily form CH₄ with very small C_2H_4 . the electrochemical reduction of CO₂ to CH₄ and C_2H_4 from aqueous solutions at copper foil electrodes with high current efficiencies

Gian Luca De Gregorio et al. [3] study investigated physical on Cu single crystals in an H-cell. The catalytic performances were tested in a gas-fed flow cell

with 1M KOH as supporting electrolyte. Faradic efficiency of each product vs potential for morphology report in Fig. 3, when compared to the Cu_{sphere} catalysts of the potential, the Cu_{cubic} catalysts had a greater selectivity for ethylene. The conversion of CO_2 to ethylene in the (100) facets ranged from 55 percent at 100 mA/cm² and -0.65 vs RHE to around 60 percent at 200 mA/cm² and -0.7V vs RHE. Methane was the major product of $Cu_{octahedral}$ catalysts. At 100 mA/cm² and -0.91V versus RHE, the greatest FE was 53%. With the least amount of H₂ output. Ethylene is also available as a product, although only with a conversion efficiency of 10%.

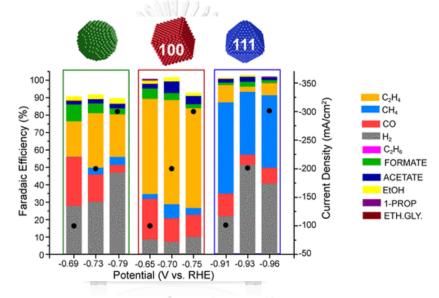


Figure 3 Faradaic efficiencies vs potential for Cu_{sph} (200 μ g/cm²), Cu_{cub} (250 μ g/cm²), and Cu_{oh} (50 μ g/cm²) deposited on a GDL and measured in the gas-fed flow cell in 1 M KOH.

Yugang Gao et al. [3] study effect of morphology of Cu_2O such as cubic (c) with {100}, Octahedral (o) with {111}, and truncated-octahedral (t) with both {100} and {111} to CO_2 reduction in H-type cell. Morphology Cu_2O catalysts were synthesized by we chemical method. Polyvinylpyrrolidone (PVP) (0g for c, 4g for o, and 6g for t), $CuCl_2.2H_2O$, and NaOH were mixed for 30 min. after stirred, ascorbic acid was added in solution and continuous stirred for 3 h. The mixture solution was aged in water bath at 55 °C. then, all product ware precipitated by centrifuge for

removing liquid solution. The morphology as prepared were characterized by scanning electron microscopy (SEM) that shown in Fig 4. The result show activity and selectivity of morphology's effects on CO₂ reduction were in Fig. 5. C_2H_4 production increased in order, c-Cu₂O < o-Cu₂O < t-Cu₂O (with FE38%, 45% and 59%, respectively).

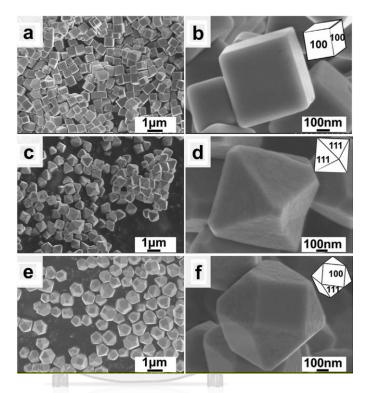


Figure 4 SEM images of a,b) c-Cu₂O, c,d) o-Cu₂O, and e,f) t-Cu₂O.

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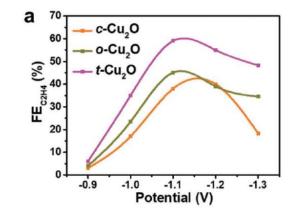


Figure 5 Faradic of ethylene value for c-Cu₂O, o-Cu₂O, and t-Cu₂O as a function of the potential.

2.2.2 Defect effect

The defects, are caused by vacancies, dislocations, surface strain, and grain boundary, can improved CO_2 reduction performance. First, the defects can affect the surface properties and optimize the binding energy or adsorption energy of reaction intermediates, and reaction pathway. Secondly, defects can change the reaction environment and increase the number of active sites to promote the reduction reaction [7].

Bingxing, Jianline et al. [14] investigated ethylene production from CO_2 on nanodefective Cu nanosheets. The nano defect Cu nanosheet (n-CuNS) were prepared by reduction method for CuO nanosheet. Figure 6 shows the pits are ~2-14 nm. For comparison performance between with/without defect copper nanosheet (CuNS) in CO_2 ERR, the current density at -1.18 V vs RHE on n-CuNS is 6 times higher than CuNS. The ethylene faradic efficiency over n-CuNS maintains values of >60% in a wide potential range of -0.88 to -1.48 V vs RHE. A maximum ethylene FE of 83.2% can be achieve at -1.18 V vs RHE as shown in figure 7.

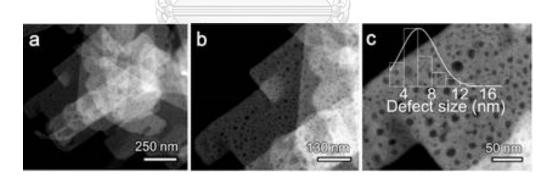
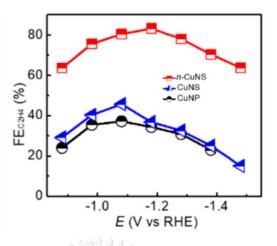


Figure 6 Structural characterization of defect CuO nanosheet (a-c).





2.2.3 Pressure

The other challenge is conversion rate that limited by the poor solubility of CO_2 in aqueous electrolyte (The concentration of CO_2 in aqueous solutions at 1 atm is 0.033 mol dm⁻³). From the Henry's Law, it is understood that increasing the concentration of dissolved CO_2 in the electrolyte can be achieved by decreasing temperature or increasing pressure.

Kohjiro Hara et al. [15] investigate hydrocarbon production in electrochemical reduction on Cu electrode by increasing CO₂ pressure. The results demonstrate that CO₂ reduction efficiencies are low at low CO₂ pressures, and the principal product is H_2 produced by water reduction. The efficiency of H_2 production decreases as CO₂ pressure rises, and hydrocarbons become the main product. When the CO₂ pressure is increased further, the production efficiency for HCOOH and/or CO is increased as seen in Fig. 8. Recep Kas et al. [2] study the process conditions in CO₂ electroreduction for hydrocarbon selectivity. CO₂ pressure, local CO concentration, and CO surface coverage are all higher. The increase in the amount of adsorbed CO from the surface as pressure rises reflects this as well.

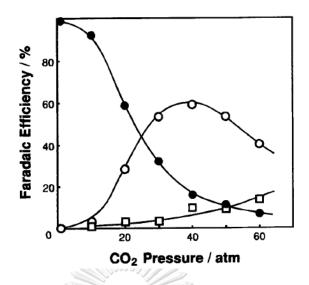


Figure 8 Effect of CO₂ pressure on the electrochemical reduction of CO₂ on a Cu electrode without stirring electrolyte of 0.1 mol dm⁻³ KHCO₃ at 25°C. Current density: 163 mA cm⁻². ($^{\circ}$) Hydrocarbons, ($^{\bullet}$) H₂, and (\square) HCOOH.

2.2.4 Electrolyte

Electrolyte can impact on the CO₂ERR performance. There are one more factor that have complex relations with local environment on surface such as pH, buffer electrolyte and interaction of proton donor. The pH of electrolyte is concern to the activity because CO_2 can react with the electrolyte or by-product leading to increase local pH by HCO_3^- and CO_3^{2-} produced. Hori et al investigate selectivity of CH_4 and C_2H_4 at cathode in pH dependent. The result show FE of ethylene is greater, when pH is increased by type of electrolyte, as show in table 3 [16]. The CO reduction has a mechanism pathway for CH_4 and C_2H_4 formation. Xinyi Chen et al. investigate conversion of CO_2 to ethylene The FE for ethylene production reaches from 72% to 87% at a cathode potential of -0.47 V in 1 to 10 M KOH.

Electrolyte	рН	FE / %						
		CH ₄	C_2H_4	EtOH	n-PrOH	НСНО	H ₂	Total
Phosphate	6.0	16.80	1.70	0.00	0.00	0.02	75.40	93.90
KHCO3	9.6	16.20	5.50	2.70	0.30	0.03	65.40	90.10
КОН	12.9	1.00	14.10	5.80	1.10	0.05	70.70	92.80

Table 3 Faradaic Efficiencies of Various Products from the Electroreduction of CO at a Cu Electrode in Aqueous Solutions. [16]



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CHAPTER 3

EXPERIMENTIAL

This research study effect of CO_2 pressure and the potential for CO_2 reduction in an electrochemical tubular fixed-bed reactor. The products were detected and analyzed by Gas chromatography and an Infrared gas analyzer. However, the main product is ethylene gas.

3.1 Chemicals and Materials

3.1.1 Copper foam
3.1.2 Graphite felt
3.1.3 sustainion XA-9 in 5% ethanol
3.1.4 Au wire (99.99%)
3.1.5 Nafion solution
3.1.6 Platinize Ti mesh
3.1.8 Carbon Black
3.1.9 2-isopropanol

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3.2 Methodology

3.2.1 Preparation of copper electrodes

3.2.1.1 Preparation of copper foam electrodes with/without ionomer.

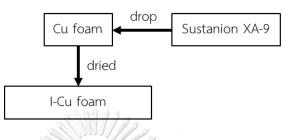


Figure 9 block flow diagram for copper foam electrode preparation.

From fig.10, 200 μ L of sustainion are dropped on copper foam (diameter 1.4 cm), then dry with air. The electrode is called "I-Cu foam".

3.2.2 Preparation of an electrochemical CO₂ERR cell

A cell for electrochemical CO₂ERR consists of 3 main parts. Cu foam and I-Cu foam is used as the cathode. Pieces of platinized Ti mesh are used as current collectors and the anode. Additional pieces of graphite felt are used to provide compression for firm electrical contacts between cell components. A bed of ion-exchange resin (Amberlite IRA-402) is placed between the cathode and anode as an electrolyte. Fig.12. shows the configuration of these cell components.

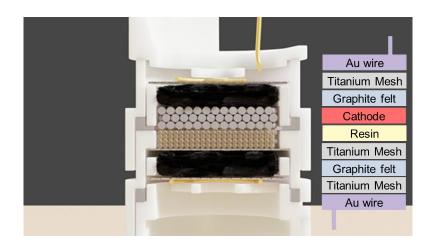


Figure 10 CO₂ERR Cell configuration

3.2.3 Electrochemical measurements

High-purity CO_2 gas is fed continuously to the electrochemical tubular fixed bed reactor. A mass flow controller is installed to control the flow rate. Deionized water is saturated with CO_2 in the water drum and driven to the reactor by the pressurized CO_2 . A needle value is installed to control the flow rate of the water; only a low flow rate is needed just to moisten the ion-exchange resin so that its electrical conductivity is sustained. The reaction contains a CO_2 flow rate of 60 ml min⁻¹ and a CO_2 -saturated water flow rate of H₂O 1 ml min⁻¹. The products are detected and analyzed by Gas Chromatography (GC-2014) and Infrared Gas Analyzer (Model IR200, YOKOKAWA) in real time. Fig.13. illustrates the reactor system used in this work.

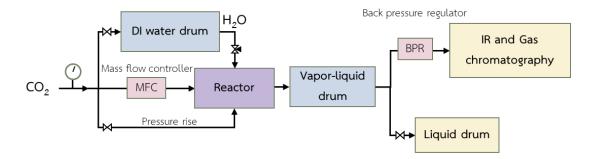


Figure 11 Block flow diagram of novel electrochemical tubular fixed bed reactor for CO_2 reduction to ethylene production

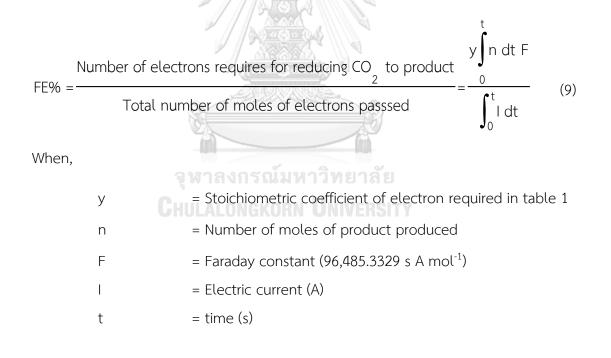
3.2.5 Characterization and Product analysis

SEM-EDX (Scanning electron microscopy with Energy Dispersive X-Ray) is a technology that uses an electron beam to scan the surface. The electron beam interacts with the material, resulting in a multitude of signals that may be used to identify a catalyst surface. EDX might also be used to describe and measure elemental composition.

X-Ray Diffraction (XRD) is a method that uses X-rays to diffract into a specified angle to characterize crystal structure and crystallite size.

A product from CO₂ERR in electrochemical packed bed reactor are analyzed by Gas chromatography and IR for identification and measuring products concentration.

The Current from CO_2ERR in electrochemical packed bed reactor could calculate Faradaic efficiency of CH_4 product by Eq. (9).



CHAPTER 4

RESULTS and DISCUSSIONS

An electrochemical tubular fixed-bed reactor was developed by scaling up for CO_2 reduction in the gas phase for ethylene production. The effect of cathode preparation, CO_2 pressure (3, 5, and 10 bar), and potential (5, 6, and 7 V) were investigated. There were two forms of cathode: commercial copper foam (Cu foam) and ionomer copper foam (I-Cu foam). The behavior of CO and C_2H_4 was observed using Gas Chromatography (GC-2014) and an Infrared Gas Analyzer (Model IR200, YOKOKAWA).

4.1 Characterization of Cu foam electrodes

The diffractogram of copper electrode (fig.14) shows characteristic diffraction peaks (111), (200), and (220) of Cu at 2theta values of 43.3°, 50.4°, and 74.1°, respectively, according to JCPDS-ICDD ref. 004-0836. The crystallite size of CU foam, I-Cu foam, and post run I-Cu foam calculated by Scherrer's equation from this XRD pattern is 24.20, 26.08, and 28.02 nm, respectively.

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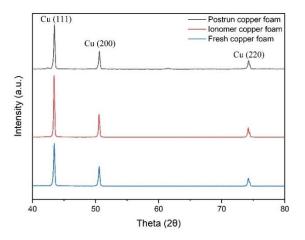


Figure 12 XRD patterns of fresh copper foam, ionomer copper foam and post run copper foam

The surface of Cu foam and I-Cu foam before and after CO_2 reduction were examined by SEM. From fig.15, the surface of Cu foam and I-Cu foam after CO_2 reduction are rough when compared with before the CO_2ERR . There is also unexpected formation of possibly cubic particles, which may also be Cu. Nevertheless, this matter has not been pursued further. In addition, Stefan Popović et al reported densely packed 6 nm spherical Cu nanoparticles undergo a structural transformation into electrocatalytically active cubic particles and doesn't affect to performance of C_2 and C_3 production from CO_2 reduction for 10 h [17].

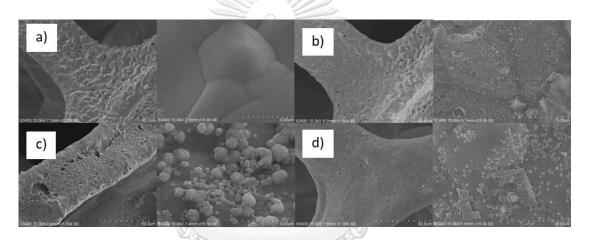


Figure 13 SEM of Cu foam a) before and b) after CO_2 reduction and I-Cu foam c) before and d) after CO_2 reduction at 3 bar.

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4.2 Effects of ionomer (Sustainion XA-9) coating on Cu foam

The results from the electrochemical reduction of CO_2 at 3 bar with a CO_2 flow rate of 60 ml min⁻¹ and a trickling rate of CO_2 -saturated water of 1 ml min⁻¹ are shown in fig 16-18. The cell voltages applied during the 120 min experiment were as follows: 5 V for 60 min, 6 V for 30 min, and 7 V for 30 min. Fig 16 shows the concentrations of CO and ethylene from the reactor. At this pressure, ethylene concentrations were < 20 ppm but that from I-Cu foam was clearly higher. Ethylene voltage and then decrease gradually at higher cell voltages. The concentrations of CO were clearly higher with a peak CO concentration from the I-Cu foam. The overall trends were similar to those of ethylene concentrations.

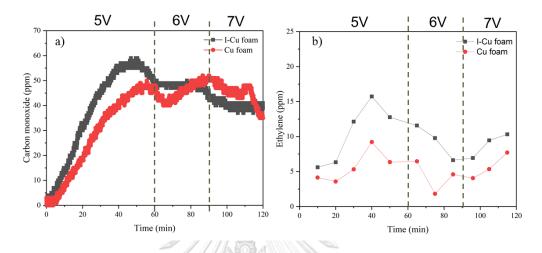


Figure 14 The concentration of a) CO and b) ethylene from Cu foam and I-Cu foam at 3 bar. During the 120 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min and 7 V for 30 min.

Fig 17 shows the currents from the applied cell voltages during the 120 min experiment. The currents form the two types of electrodes were close to one another and had similar trends. At 7 V, the currents appeared to increase somewhat abruptly and then fall steadily. In addition, an increase in the current as the cell voltage increased did not appear to be exponential. This suggests that the main resistance of the cell was from the electrolyte, i.e. the 2 mm thick resin bed, which is not designed by the manufacturer to be used as an electrolyte.

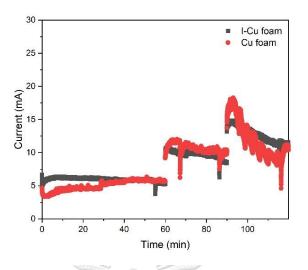


Figure 15 The current density for Cu foam and I-Cu foam at condition 3 bar. During the 120 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min, and 7 V for 30 min.

Fig 18 compares the faradaic efficiencies of ethylene and CO from Cu foam and I-Cu foam electrodes at different applied cell voltages. At 5 V, the faradaic efficiencies of ethylene were higher than those of CO despite the lower ethylene concentrations shown in Fig 16 because they reduction to ethylene and CO requires 12 and 2 mol of electrons, respectively, per 1 mol of product. The faradaic efficiencies of both products were comparable to their counterparts at cell voltages of 5 V but dropped significantly at 6 and 7 V. This was consistent with the lower CO and ethylene concentrations at higher cell voltages previously shown in fig 16 and the higher total currents in fig 17. Lower faradaic efficiencies of the two products are believed to be mainly caused by an increase in the H₂ evolution rate concomitant to any aqueous systems.

The faradaic efficiencies of both products from I-Cu foam were higher than those from Cu foam. This indicates that Sustainion XA-9 increased faradaic efficiencies for the formation of the two products. The ionomer might selectively suppress to the formation of ethylene because of the distribution and content of ionomer can directly influence the protonic and electronic conductivity of the catalyst layer [18]. The mechanism plausibly involved modification of electrode surface pH. Without the ionomer, the surface pH at the Cu foam was supposedly low (3-4) as it was covered with a layer of CO_2^- saturated water without any added salts. With the anion-exchange ionomer, the electrode coating converted CO_2 with the absorbed OH^- into HCO_3^- and CO_3^{2-} [19] and possibly raised the surface pH to 7-8.

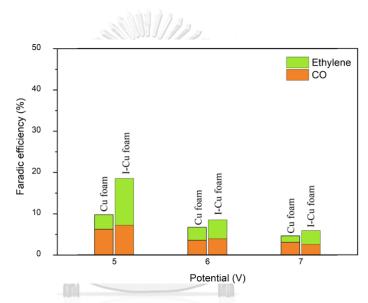


Figure 16 Effect of ionomer (sustainion XA9) on the electrochemical reduction of CO_2 on Cu foam and I-Cu foam at 3 bar.

4.3 Effect of pressure

The results from the electrochemical reduction of CO_2 at 3, 5 and 10 bar with a CO_2 flow rate of 60 ml min⁻¹ and a trickling rate of CO_2 -saturated water of 1 ml min⁻¹ are shown in fig 19-21. The cell voltages applied during the 120 min experiment were as follows: 5 V for 60 min, 6 V for 30 min, and 7 V for 30 min. Fig.19 shows the concentration of CO and ethylene from reactor. CO concentration were>40 ppm 3 bar. Ethylene concentration were highest at 10 bar. Concentration of ethylene and CO were otherwise trended because CO intermediate was used for CO_2 transformation to ethylene when pressure was increased.

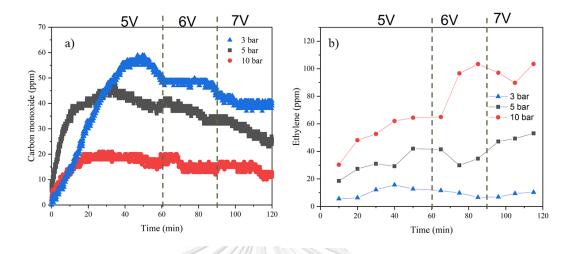


Figure 17 The concentration of a) CO and b) ethylene from I-Cu foam at different pressure. During the 150 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min and 7 V for 30 min.

Fig 20 shows the currents from the applied cell voltages during the 150 min experiment. The currents form the different pressure were increased meanwhile ethylene concentration were increased and CO concentration were decreased. So, the number of electrons introduced is utilized to adsorb CO intermediate on the surface and transform to ethylene. At 10 bar, the current was lower than at 5 bar but ethylene concentration was higher than 3 and 5 bar. In addition, CO molecules adsorbed on the electrode surface suppress H₂ production, resulting in a decrease in the current density [20-22].

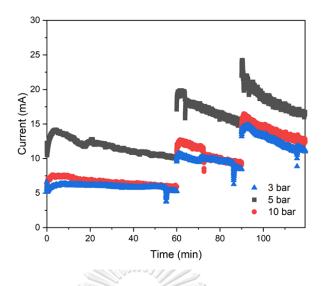


Figure 18 The current for I-Cu foam at different pressure. During the 150 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min, and 7 V for 30 min.

Fig.21 compares the faradic efficiency of CO and ethylene at 3, 5 and 10 bar and different applied voltage. At 5 V with 3, 5, and 10 bar, faradic efficiency of C_2H_4 was 11.34, 14.07, and 45.13 %, respectively. And faradic efficiency of CO was 7.16, 3.89, and 2.30 %, respectively. When increasing CO₂ pressure, faradic efficiency of both products was kept to pointing the same thing. Faradic efficiency of ethylene gas was increasing and CO was decreasing. In addition, faradic efficiency of ethylene on 10 bar is greater than 4 and 3 times at 3 and 5 bar, respectively. Meanwhile, the mass transfer of CO intermediate on the I-Cu foam can be accelerated to C-C coupling at higher pressure [2, 15, 23]. At 3 bar, faradic efficiency of CO and ethylene are lowest because CO intermediate are replaced by H intermediate on surface. So, Hydrogen evolution reaction are dominant than CO₂ reduction at the cathode [1, 15]. The highest faradic efficiency of ethylene values of 33% at 5V and 10 bar.

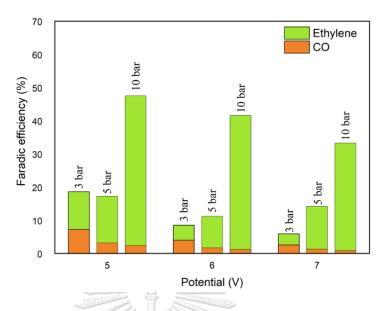


Figure 19 Effect of pressure on the electrochemical reduction of CO₂ on I-Cu foam.

4.4 Effect of cell voltage

Fig.22 compares the faradic efficiency of CO and ethylene at 5, 6, and 7 V and 3, 5, and 10 bar, the result show at 5 V in each pressure were suggested that optimize applied voltage for electrochemical tubular reactor. In addition, low potential is selectively to formation of CO and ethylene. For increasing potential, total faradic efficiencies of both products were decreased that faradic efficiencies of CO were decrease and faradic efficiencies of ethylene were increased because CO intermediates are coupling to ethylene. Moreover, the current increased with cell voltage increased, total gas FE decreased with increasing voltage, corresponding to a shift toward liquid products at higher voltages[24].

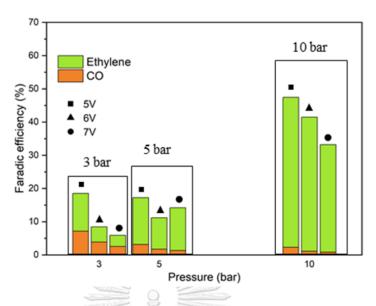


Figure 20 Effect of potential on the electrochemical reduction of CO₂ on I-Cu foam.

4.5 Effect of type of gas

For observing the behavior of products from CO2ERR by using CO2, N2, and air feed for reactant gas and using I-Cu foam as a cathode at condition 3 bar with a CO₂ flow rate of 60 ml min⁻¹ and a trickling rate of CO₂-saturated water of 1 ml min⁻¹ are shown in fig 25, The concentration of carbon monoxide and ethylene aren't produced when $N_{\rm 2}$ and air feed to CO_{2}ERR in the electrochemical tubular fixed-bed reactor. In addition, N₂ feed as reatant gas was observed the behavior of CO and ethylene concentration wasn't occurred by using the inert gas. Meanwhile, CO concentration at condition CO₂ feed as reatant only occured at the cathode. Moreover, single-chamber tubular fixed-bed electrochemical reactor for CO₂ERR are design and study the effect of pressure but there are main problem that products from cathode and anode (e.g. CO₂, CO, C₂H₄, and O₂) are mixed in the single-chamber but we also confirmed the O₂ concentration weren't reduced at cathode by air feed condition as shown in fig.25. Moreover, air feed can prove the hypothesize for electrochemical can be in series in the future. Furthermore, this system uses water as a reactant in an electrochemical tubular reactor. To provide comparison, a

conventional electrochemical reduction reactor that utilized salt solution (e.g. $NaHCO_3$ and $KHCO_3$) as the reactant. Salt can act as a corrosion agent in the reactor.

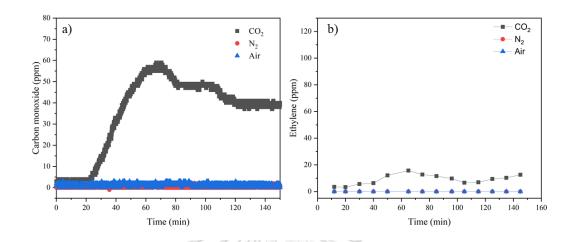


Figure 21 The concentration of a) CO and b) ethylene from I-Cu foam at different 60 ml min⁻¹ reactant gas. During the 150 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min, 7 V for 30 min and 8 V for 30 min.



CHAPTER 5

CONCLUSIONS and SUGGESTIONS

5.1 Conclusions

The performance of CO_2ERR is observed by the behavior of carbon monoxide and ethylene production with a CO_2 flow rate of 60 ml min⁻¹ and a trickling rate of CO_2 -saturated water of 1 ml min⁻¹. During the 10 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min, and 7 V for 30 min.The ionomer effect on copper foam represents the faradic efficiencies of CO and ethylene from I-Cu foam is greater than Cu foam at condition 3 bar in each cell voltage, so ionomer can improve the performance of CO_2ERR on surface of copper foam and change pathway for CO_2 reduction.

Considering the effect of CO_2 pressure and potential, During the 150 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min, and 7 V for 30 min. that ethylene concentration are increased and CO concentration are decreased when pressure increased. the ethylene and CO concentration are otherwise trended because CO intermediate more adsorb on I-Cu foam's surface and suppress H intermediate adsorption. So, CO_2 reduction can produce more carbon products, be accelerated to C-C coupling and inhibit H₂ evolution reaction.

The performance of CO_2ERR is confirmed by N_2 feed for reactant. The CO and ethylene concentration using I-Cu foam as cathode doesn't occur in this system. In addition, the concentration of CO and ethylene only occurs at the cathode. Moreover, the electrochemical tubular fixed bed reactor is easy to operate and clean system. Also, it doesn't produce corrosive salt.

5.2 Suggestions

By-products including H_2 and O_2 from CO_2 reduction in the electrochemical should detect and analyze to study the behavior.

The thickness of resin should be optimized for decreased resistance between $\rm CO_2 ERR$ cell.





APPENDIX A

FARADIC EFFICIENCY CALCULATION

A.1 Faradic efficiency

Faradic efficiency of electrochemical CO_2ERR is calculated by number of moles of electrons for producing product (e_{output}) divided by total number of mole of electrons transferred in cell (e_{input}) as follow

 $FE(\%) = \frac{e_{output}}{e_{input}} \times 100$

e_{output} = y∫n dt

Number of moles of electrons for producing product (e_{output}) :

Where,

y is a number of electrons required to produced product from half-cell reaction of C_2H_4 .

n is an amount of product (mol)

Total number of moles of electrons transferred in cell (e_{input})

$$e_{input} = \frac{Q}{F}; Q = \int I dt$$

Where,

I is a recorded current (A)

t is required time (sec)

F is Faraday constant (96485 C mol_e^{-1})

			n dt (ppm min)
Cathode	Pressure (bar)			
		5	6	7
Cu foam	3	83.1	141.937	74.187
I-Cu foam	3	281.719	188.909	179.606
I-Cu foam	5	657.18	679.857	993.005
I-Cu foam	10	1205.889	1808.06	1903.817

Table 4 Data of ethylene concentration from GC. (CO₂ 60 ml min⁻¹ and H₂O 1 ml min⁻¹)

Table 5 Data of CO concentration from IR. (CO $_2$ 60 ml min⁻¹ and H $_2$ O 1 ml min⁻¹)

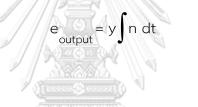
		∫ _{n dt} (ppm min) Potential (V)		
Cathode	Pressure (bar)			
		5	7	
Cu foam	3	892.783	968.75	883.475
I-Cu foam	3	1067.4	966.091	798.65
I-Cu foam	5	885.458	737.483	601.3
I-Cu foam	จุ10าลงก	369.85	ຊັຍ306.017	294.592

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			$\int_{I dt}$ (mA min)	
Cathode	Pressure (bar)	Potential (V)		
		5	6	7
Cu foam	3	112.543	213.768	225.874
I-Cu foam	3	117.541	195.746	252.233
I-Cu foam	5	220.997	338.781	364.992
I-Cu foam	10	126.461	212.033	278.594

Table 6 Data of current from potentialstat . (CO $_{\rm 2}$ 60 ml min $^{-1}$ and H $_{\rm 2}\rm O$ 1 ml min $^{-1})$

Example for faradic efficiency of C_2H_4 calculation for Cu foam at 5V and 3 bar.



When,

$$y = 12 \text{ from eq.8}$$

$$\int n \, dt = \int ppm_{\substack{C,H\\2^{-4}}} dt \times \frac{60ml}{min} \times \frac{K \text{ mol}}{8.314 \text{ m}^{3}\text{Pa}} \times \frac{101325\text{Pa}}{atm} \times \frac{1}{298.15\text{K}} \times \frac{1}{10^{6}} \frac{\text{m}^{3}}{10^{6}\text{ml}}$$

$$\int n \, dt = 2.038 \times 10^{-7} \text{mol}_{\substack{C_{2}H\\2^{-4}}}$$

So,

$$e_{output} = \frac{12mol_{e^{-}}}{1mol_{C_{2}H_{4}}} \times 2.038 \times 10^{-7}mol_{C_{2}H_{4}}$$
$$e_{output} = 2.446 \times 10^{-6}mol_{e^{-}}$$

$$e_{input} = \frac{Q}{F}; Q = \int I dt$$

When,

$$e_{input} = \frac{\int I \, dt}{F}$$

$$e_{input} = 112.543 \text{ mA minx} \frac{\text{mol}_{e^{-}}}{96485 \text{ A s}} \times \frac{A}{1000 \text{ mA}} \times \frac{60 \text{ s}}{\text{min}}$$

$$e_{input} = 6.999 \times 10^{-5} \text{ mol}_{e^{-}}$$

$$FE(\%) = \frac{e_{output}}{e_{input}} \times 100$$

$$FE(\%) = \frac{2.446 \times 10^{-6} \text{ mol}}{6.99 \times 10^{-5} \text{ mol}} \times 100$$

$$FE(\%) = 3.50$$

$$FE(\%) = 3.50$$

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APPENDIX B

CHARACTERIZATION of CATHODES

B.1 XRD

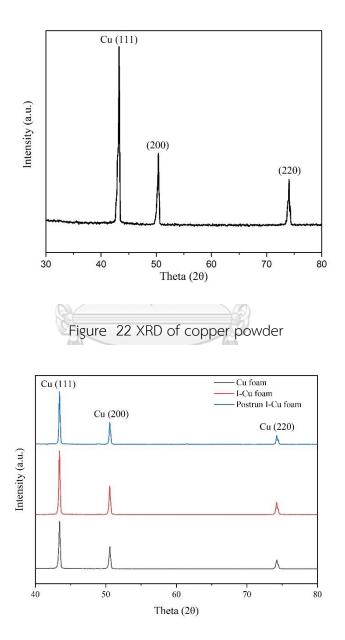


Figure 23 XRD of fresh Cu foam, I-Cu foam and post run I-Cu foam.

B.2 SEM

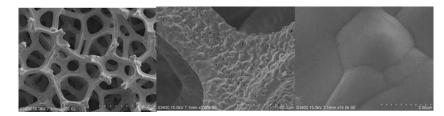


Figure 24 SEM of fresh Cu foam.



Figure 25 SEM of fresh I-Cu foam.

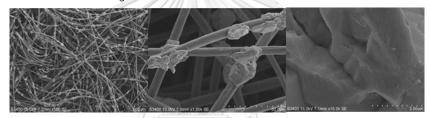


Figure 26 SEM of fresh Cu-elec.

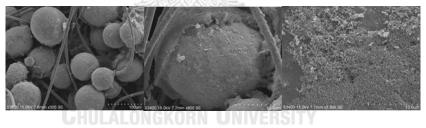


Figure 27 SEM of fresh Cu-ink.

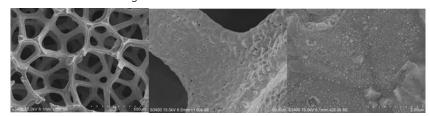


Figure 28 SEM of post run Cu foam at 3 bar.

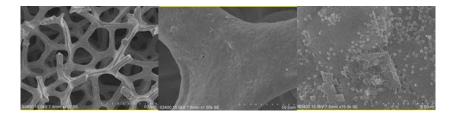


Figure 29 SEM of post run I-Cu foam at condition 3 bar.

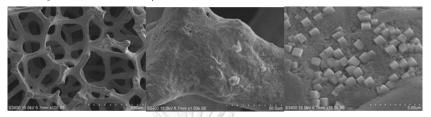


Figure 30 SEM of post run I-Cu foam at condition 5 bar.

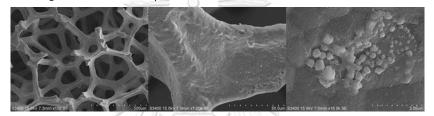


Figure 31 SEM of post run I-Cu foam at condition 10 bar.



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B.3 EDX

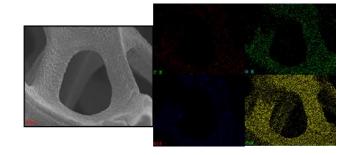
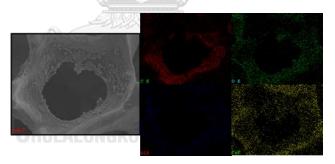


Figure 32 element dispersion of fresh Cu foam.

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Table	7 element dispersion of fresh Cu foam.	

		CO.
Element	Wt%	At%
СК	00.91	04.39
OK	02.05 🥖	07.38
AlK	00.19	00.41
CuK	96.84 🎽	87.82
Matrix	100	100
I		1 Stranger



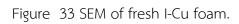


Table 8 element dispersion of I-Cu foam.

Element	Wt%	At%
CK	22.80	55.60
OK	06.35	11.63
AlK	00.17	00.19
CuK	70.67	32.58
Matrix	100	100

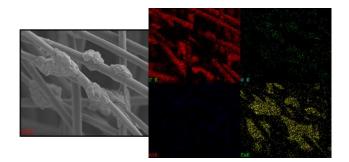


Figure 34 SEM of fresh Cu-elec.

Table 9 element dispersion of Cu-elec.

Element	Wt%	At%
CK	52.20	84.40
OK	01.03	01.25
AlK	00.15	00.11
CuK	46.62	14.25
Matrix	100	100

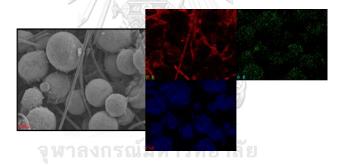




Table 10 element dispersion of Cu-ink.

Element	Wt%	At%
СК	35.98	73.29
OK	01.80	02.76
CuK	62.22	23.96
Matrix	100	100

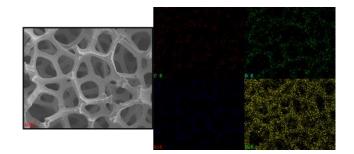


Figure 36 SEM of post run Cu foam at condition 3 bar.

Table 11 element dispersion of post run Cu foam at condition 3 bar.

Element	Wt%	At%
СК	01.51	07.11
ОК	02.04	07.19
AlK	00.14	00.29
CuK	96.30	85.41
Matrix	100	100

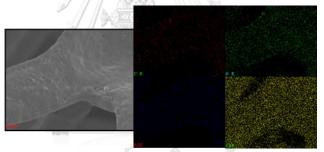


Figure 37 SEM of post run I-Cu foam at condition 3 bar. Table 12 element dispersion of post run I-Cu foam at condition 3 bar.

Element	Wt%	At%
СК	00.93	04.47
ОК	02.03	07.30
AlK	00.20	00.43
CuK	96.84	87.80
Matrix	100	100

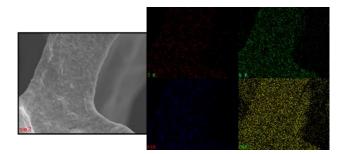


Figure 38 SEM of post run I-Cu foam at condition 5 bar.

Table 13 element dispersion of post run I-Cu foam at condition 5 bar.

Element	Wt%	At%
СК	02.61	10.81
OK	04.27	13.29
AlK	02.74	05.05
CuK	90.39	70.85
Matrix	100	100

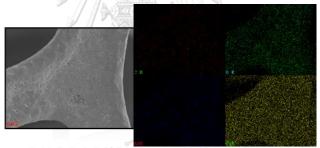


Figure 39 SEM of post run I-Cu foam at condition 10 bar. Table 14 Element dispersion of post run I-Cu foam at condition 10 bar.

Element	Wt%	At%
СК	01.19	05.40
OK	03.95	13.41
AlK	00.13	00.26
CuK	94.72	80.93
Matrix	100	100

APPENDIX C

ELECTROCHEMICAL REDUCTION PERFORMANCE

C.1 Faradic efficiency of products in each condition.

Table 15 Faradic efficiency of CO and ethylene for 20 min. (H_2O 1 ml min⁻¹ and CO_2 60 ml min⁻¹)

	Pressure (bar)	Faradic efficiency (%)						
Cathode		Potential (V)						
		5	5 6			7		
		CO	C ₂ H ₄	CO	C ₂ H ₄	CO	C ₂ H ₄	
Cu foam	3	6.25	3.50	3.57	3.14	3.08	1.55	
I-Cu foam	3	7.16	11.34	3.89	4.56	2.49	3.37	
I-Cu foam	5	3.16	14.07	1.71	9.49	1.29	12.87	
I-Cu foam	10	2.30	45.13	1.13	40.35	0.83	32.34	

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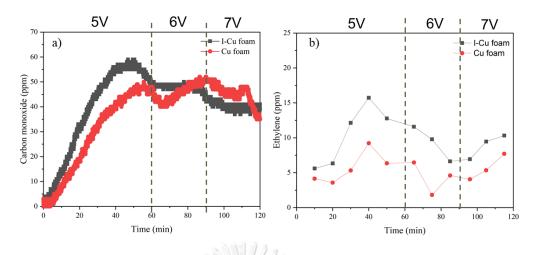


Figure 40 The concentration of a) CO and b) ethylene from Cu foam and I-Cu foam at 3 bar. During the 120 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min and 7 V for 30 min.

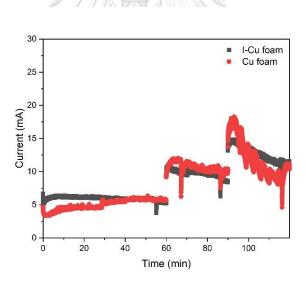


Figure 41 The current density for Cu foam and I-Cu foam at condition 3 bar. During the 120 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min, and 7 V for 30 min.

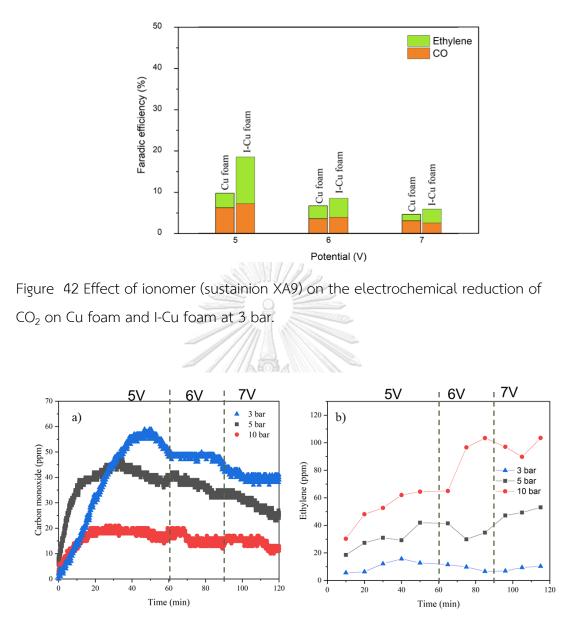


Figure 43 The concentration of a) CO and b) ethylene from I-Cu foam at different pressure. During the 150 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min and 7 V for 30 min.

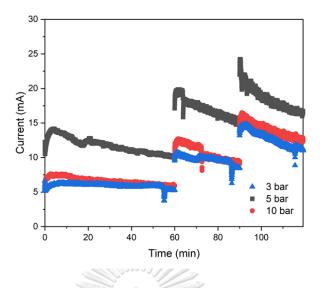


Figure 44 The current for I-Cu foam at different pressure. During the 150 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min, and 7 V for 30 min.

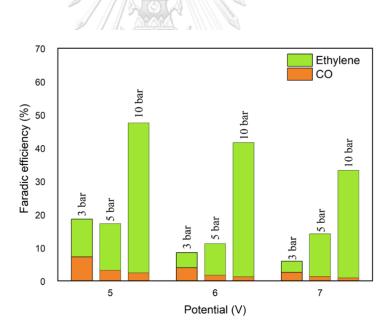


Figure 45 Effect of pressure on the electrochemical reduction of CO_2 on I-Cu foam.

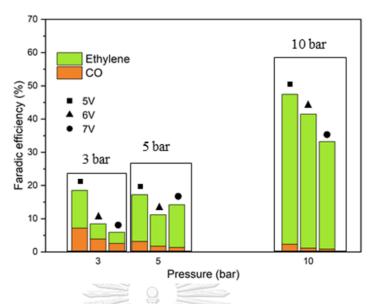


Figure 46 Effect of potential on the electrochemical reduction of CO₂ on I-Cu foam.

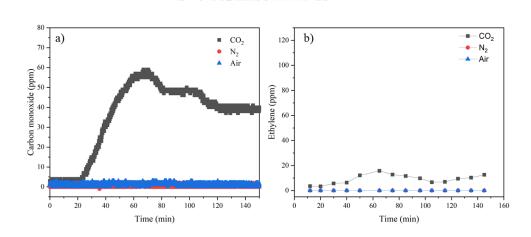


Figure 47 The concentration of a) CO and b) ethylene from I-Cu foam at different 60 ml min⁻¹ reactant gas. During the 150 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min, 7 V for 30 min and 8 V for 30 min.

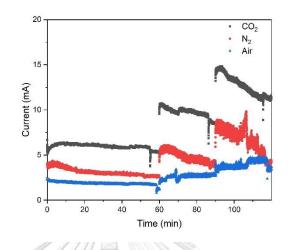


Figure 48 The current for I-Cu foam at differentreactant gas. During the 150 min experiments, the following cell voltages were applied: 5 V for 60 min, 6 V for 30 min, and 7 V for 30 min.



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