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Electrochemical tubular fixed-bed reactor for conversion of pressurized CO2 to CO

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Electrochemical tubular fixed-bed reactor for conversion of pressurized CO_2 to CO

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เครื่องปฏิกรณ์เคมีไฟฟ้าแบบท่อเบดนิ่งสำหรับการเปลี่ยนคาร์บอนไดออกไซด์ความดันสูงเป็นคาร์บอนมอนอกไซด์

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Field of Study	Chemical Engineering
Thesis Advisor	Assistant Professor PALANG BUMROONGSAKULSAWAT, Ph.D.

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ภัควัฒน์ เซ่งฉิม : เครื่องปฏิกรณ์เคมีไฟฟ้าแบบท่อเบดนิ่งสำหรับการเปลี่ยนคาร์บอนไดออกไซด์ความดันสูงเป็นคาร์บอนมอนอกไซด์. (Electrochemical tubular fixed-bed reactor for conversion of pressurized CO_2 to CO) อ.ที่ปรึกษาหลัก : ผศ. ดร.พลัง บำรุงสกุลสวัสดิ์

ปฏิกิริยาการลดคาร์บอนไดออกไซด์ถูกใช้ในการกระตุ้นการเปลี่ยนคาร์บอนไดออกไซด์เป็นคาร์บอนมอนอกไซด์ โดยปกติกระบวนการนี้จะศึกษาในสารละลายอิ่มตัวด้วยคาร์บอนไดออกไซด์ที่สถานะของเหลวโดยที่ความสามารถในการละลายของคาร์บอนไดออกไซด์ในน้ำมีค่าที่ต่ำมาก (0.033 โมลาร์) ที่ความดัน 1 บาร์และที่อุณหภูมิห้อง ส่งผลต่ออัตราการเกิดปฏิกิริยาและการถ่ายโอนมวล ในงานวิจัยนี้ได้ศึกษาเครื่องปฏิกรณ์เคมีไฟฟ้าแบบท่อเบดนิ่งสำหรับปฏิกิริยาการเปลี่ยนคาร์บอนไดออกไซด์เป็นคาร์บอนมอนอกไซด์โดยมีการออกแบบจะคำนึงถึงการขยายขนาดได้ง่ายและเครื่องปฏิกรณ์ประกอบด้วยเซลล์เคมีไฟฟ้าหลายเซลล์ที่สามารถต่อกันเป็นแบบอนุกรมได้ โดยแต่ละเซลล์ประกอบไปด้วย 3 ส่วนหลัก คือ แอโนด, อิเล็กโทรไลต์แข็ง และแคโทด นอกจากนี้โลหะซิงค์ถูกนำมาใช้เป็นตัวเร่งปฏิกิริยาเคมีไฟฟ้าสำหรับการเปลี่ยนคาร์บอนไดออกไซด์เป็นคาร์บอนมอนอกไซด์ โดยที่มีน้ำไหลผ่านเซลล์เพื่อรักษาค่าการนำไฟฟ้าของอิเล็กโทรไลต์และเพื่อรักษาปฏิกิริยาไฟฟ้าเคมี การศึกษาผลกระทบของความดัน อัตราการไหลและความต่างศักย์ที่ให้แก่ระบบที่มีผลต่ออัตราการเกิดปฏิกิริยาและผลผลิต จากการทดลองที่ความดัน 10 บาร์ อัตราการไหลที่ 60 มิลลิลิตรต่อนาทีและความต่างศักย์ 7 โวลต์ ค่าความเข้มข้นของคาร์บอนมอนอกไซด์ได้ 1272 ส่วนในล้านส่วนและประสิทธิภาพของฟาราเดย์สูงที่สุดอยู่ที่ 19.61 เปอร์เซ็นต์

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Pakawat Sengchim : Electrochemical tubular fixed-bed reactor for conversion of pressurized CO_2 to CO. Advisor: Asst. Prof. PALANG BUMROONGSAKULSAWAT, Ph.D.

Electrochemical CO_2 reduction reaction (CO_2RR) can be used for activating the stable CO_2 molecule to the more active CO for downstream purposes. Usually, this process is carried out in CO_2-saturated aqueous solutions. The low solubility of CO_2 in water of 0.033 M at 1 bar of CO_2 and room temperature hinders both kinetics and mass transfer. In this study, a novel electrochemical tubular reactor for electrochemical CO_2RR is proposed. The design was made with ease of scale-up in mind. A reactor can contain multiple electrochemical cells connected in series. Each cell consists of 3 main parts: porous anode, porous solid electrolyte, and porous cathode, all of which allow bulk flow of gas streams through the tubular reactor. Zn is the active electrocatalyst at the cathode for the conversion of CO_2 to CO. Water is trickled through the cells to maintain electrolyte conductivity and also to sustain electrochemical reactions. The effects of CO_2 pressure and flow rate and applied voltage on the CO_2 conversion rate and yield are studied. About 1272 ppm of CO concentration and 19.61% of highest CO faradaic efficiency was obtained from a preliminary experiment conducted at 60 ml min^{-1}, 7 V of CO_2 at 10 bar.

Field of Study:	Chemical Engineering	Student's Signature .....
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CHAPTER 1
INTRODUCTION

1.1 Background

Nowadays, the concentration of greenhouse gases in the atmosphere is increasing. The main part is carbon dioxide (CO_2), which is strongly linked to global warming and climate change issues. As a potential solution to this challenge, CO_2 may be converted into valuable products via a carbon dioxide reduction reaction (CO_2RR) [1]. CO_2RR has been proposed as a promising method to combat rising carbon dioxide levels by converting CO_2 into renewable fuels or valuable chemicals. There are several other methods in CO_2 utilization, namely thermal catalysis, photochemical reduction, photoelectrochemical reduction, and enzymatic CO_2 conversion [1, 2]. In comparison with these methods, electrochemical CO_2RR is considered as one of the most useful techniques for the decarbonization process which utilizes clean energy sources and carry out at room temperature. Moreover, electrochemical CO_2RR can be obtained high CO selectivity [1, 3]. CO is an essential product because it is mainly used as a feedstock for the Fischer–Tropsch synthesis, methanol production, and pharmaceutical industry [4].

Generally, Electrochemical CO_2RR is challenging because the low solubility of CO_2 in aqueous electrolytes at ambient conditions hinders mass transfer of CO_2 [5]. An interesting strategy to reduce mass transfer limitation is the utilization of gas diffusion electrodes (GDE), and the process carried out at high pressure [6]. Zn catalysts are known to selectivity lead to the product of CO [7]. There are 2 main reactions, CO_2RR at the cathode and oxygen evolution reaction (OER) at the anode. The hydrogen

evolution reaction (HER) is competing with CO at the cathode. These reactions are presented in Eqs. (1)-(6).

Cathode reaction (CO_2RR)

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (1)$$

$$CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^- \quad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (3)$$

Anode reaction (OER)

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (4)$$

Overall reaction

$$CO_2 + H_2O \rightarrow CO + H_2 + O_2 \quad (5)$$

In this study, a novel scalable electrochemical tubular fixed-bed reactor is developed for gas-phase CO_2 reduction to CO. It features only a single chamber; cathode and anode products are mixed as the reaction gas mixture flows along the reactor. Even though the generated mixture of CO and O_2 presents risk of explosion, this can be avoided by operating outside the flammability limits. For example, flue gas from an incinerator, which contains ca. 5 % CO_2 diluted in mostly N_2, may be suitable for this reactor. The reactor is made from stainless steel and reactor lining is 3D printed. Saturated CO_2 gas was fed through a porous cathode that consists of Zn catalyst deposited on a carbon support. The effects of CO_2 flow rates, pressure, and applied cell voltages on CO production rates and faradaic yields are studied.

1.2 Objective

To study the behavior of the novel electrochemical tubular fixed-bed reactor for electrochemical reduction of CO_2 to CO.

1.3 Scope of Study

1.3.1. Pressure applied to the reactor (1-10 bar)

1.3.2. Catalyst is Zinc granules and Zinc deposited on graphite felt

1.3.3. Reaction Conditions were applied voltage (5-8 V), CO_2 flow rate (60, 200 ml/min), and water is continuously trickled through the bed at 1 mL/min

1.3.4. anion exchange resin beads are used as the electrolyte in the cell.

1.4 Expected Benefits

1.4.1. To overcome the main hurdle of the CO_2 electrochemical conversion in aqueous solution, its low solubility, and to achieve good faradaic efficiency in CO.

1.4.2. To explore conditions for scale-up.

1.5 Action Plan

No	Activities	Month									
		Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun
1	Literature review										
2	Planning the experiment and setting up the reactor										
3	Electrochemical of high pressurized CO_2										
4	Fabrication of Zn-deposit graphite felt as cathode										
5	Gathering the result and writing thesis										

CHAPTER 2
THEORY AND LITERATURE REVIEWS

2.1. Electrochemical CO_2 reduction reaction

Electrochemical CO_2RR is considered as one of the most useful techniques for the decarbonization process into fuel and chemical products such as CO, CH_4, HCOOH, and some other products [1, 8]. The electrochemical CO_2RR occurs at the interface of electrode/electrolyte, which involves three main steps: (i) absorption of the CO_2 on the surface of the catalysts; (ii) transfer of at least two protons and electrons to break one of the oxygen-carbon bonds forming a water molecule in the case of CO or subsequent further protonation; (iii) desorption of the final products from the electrode surface [1, 9]. However, CO_2RR occurs to need a large negative potential and the E_0 value of hydrogen evolution reaction (HER) derived from hydrolysis of water is relatively positive compared to other C1 products. Then, HER becomes the main competitive reaction of CO_2RR [9]. Due to this, the CO_2RR for converting CO_2 into CO, the reaction $CO_2(g)$ --> $CO(g) + ½ O_2(g)$ has an E^0 value of -1.334 V vs SHE, indicating that it is a non-spontaneous reaction. As a result, this cell requires a voltage greater than the equilibrium electrode potential same as the electrolytic cell. When a cell receives an electrical current from an applied voltage, the electron can transfer from the anode to the cathode, provided that the electron transfers in the system according to the Faraday's law because the electric current that flows through an electrochemical cell is related to the moles of electrons and subsequently occur the CO_2RR.

The cell of electrochemical CO_2RR consists of cathode and anode in which CO_2 was continuously fed and applied voltage. At the cathode, there was a CO_2RR and HER

and at the anode, there was an oxygen evolution reaction (OER) from water is oxidized to molecular oxygen [9, 10]. According to the thermodynamic theory, the minimum potential required for a CO_2RR is the half-cell standard potential described by $E^0 = -\Delta G^0/nF$, where $-\Delta G^0$ is the Gibbs free energy at 1 atm and 298 K, n is the number of moles of electrons transferred in the half-cell reaction, and F is faraday constant (96485 C/mol) [11]. For conversion of CO_2 to CO, the half-cell reaction $CO_2(g) + 2H^+(aq) + 2e^-$ --> $CO(g) + H_2O(l)$ with ΔG^0 = 20.09 kJ/mol has E^0= -0.104 V vs SHE. Other half-cell standard potentials are shown in Table. 1.

Table 1 Half-cell reaction pathways at cathode and anode in electrochemical CO_2 reduction [9-12]

Electrode	Half-Electrochemical Reactions	E_0 (V vs SHE)
Cathode reaction (CO_2RR)	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.104
	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.250
	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	+0.016
	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	+0.169
	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	+0.064
(HER)	$2H^+ + 2e^- \rightarrow H_2$	0.000
Anode reaction (OER)	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	+1.230

However, the applied voltage affects to consumes CO_2 concentration at the electrode surface, the overall reaction rate can be limited by the rates of CO_2 transfer.

Moreover, according to the Nernst equation, the change in concentration affects the equilibrium electrode potential and this effect can be approximated by the concentration overpotential as the equation (6). Thus, the electrochemical cell improves the minimum energy requirements for CO_2RR [11, 13] which the Nernst equation gives the relationship between the equilibrium electrode potential and the concentration or partial pressure. The Nernst equation for conversion CO_2 to CO as shown in equation (6) [14].

$$E^0 = \frac{\Delta G_f}{nF} - \frac{RT}{nF}\ln\frac{p_{CO_2}}{p_{CO}\sqrt{p_{O_2}}} \quad (6)$$

Where ΔG_f is the Gibbs free energy of formation, R is the gas constant, T is the absolute temperature, n is the moles of electrons transferred in the reaction, F is Faraday's constant, p_{CO2} is the partial pressure of CO_2, p_{CO} is the partial pressure of CO, and p_{O2} is the partial pressure of O_2.

Furthermore, the difference between the electrode potential and the equilibrium electrode potential is referred to the reaction rate or the electron transfer rate. The kinetics of the electrochemical cell depends on the electrode potential and the equilibrium electrode potential. According to the Butler-Volmer equation as equation (7), increasing the electrode potential affects the electrical current with the exponential relationship [15]. Suppose the electrical current is increased following the cell voltage. It means the electron transfer rate in the electrochemical cell same increased.

$$j = j_0\{exp[-\alpha F\eta/RT] - exp[(1-\alpha) F\eta/RT]\} \quad (7)$$

Where j is the electrode current density, j_0 is the exchange current density, α is the charge transfer coefficient dimensionless, F is Faraday's constant, η is the activation overpotential defined as the difference between the electrode potential

and the equilibrium electrode potential, R is the gas constant, and T is the absolute temperature.

A CO_2 reduction electrocatalyst that can selectivity produce desired chemicals while suppressing undesired side reactions is essential to achieve a highly efficient system [6, 16]. Many researchers have investigated the selectivity of products with various metals at the cathode side such as Pd, Ag, Zn, Cu, Sn, Ru, Pt, Ni. Based on the primary CO_2 reduction product, CO selective metals (e.g., Au, Ag, and Zn), formic acid selective metals (e.g., Sn, In, and Pb), and hydrogen-selective metals (e.g., Fe, Ni, and Pt). [16, 17] as shown in Fig. 1.

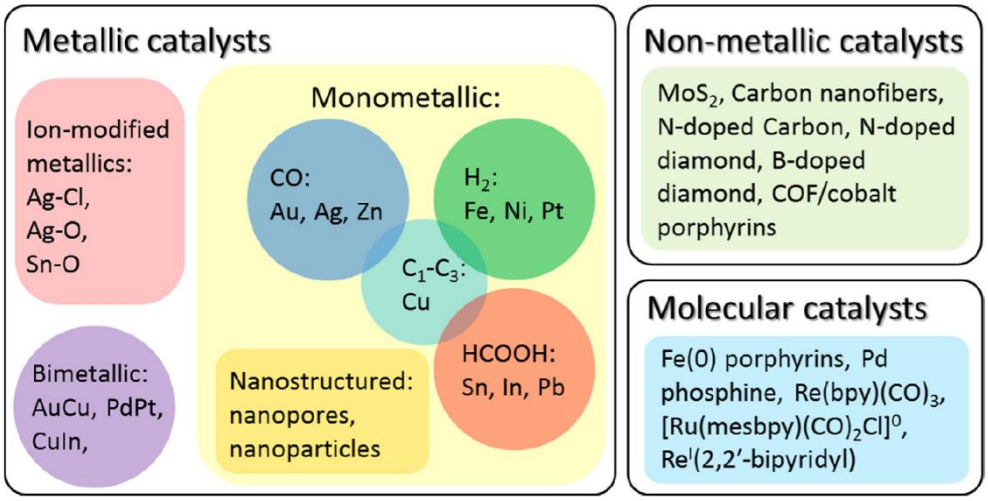


Fig. 1 An outline of electrocatalysts for CO_2 reduction [9].

A key challenge of electrochemical CO_2RR is the preparation of catalysts with high activity, selectivity, and stability [5, 16]. Au and Ag are known as the best metal catalysts for conversion CO_2 to CO with high activity and selectivity. However, it is

difficult to use on a large scale in industrialization, due to the high price and scarce reserve of precious metals [5]. Zn, as an earth-abundant metal, is one of the choices to use as a catalyst to produce CO but with relatively lower activity and CO selectivity than Au and Au. To improve the activity and selectivity of Zn catalysts, many alternatives have been used in the preparation of catalysts such as electrodeposition, anodization, oxide reduction [5, 16, 17].

The mechanism of electrochemical CO_2RR for produce CO_2 to CO. At the beginning, CO_2 and HCO_3^- are absorbed on the surface of the electrode. Subsequently, (1) CO_2 is reduced to CO_2^{*-} by one electron from electrochemical process; (2) the CO_2^{*-} is electrochemically reduced to the reaction intermediate of $COOH^*$; (3) the $COOH^*$ is reduced with an electron and a proton to CO^* that desorbs from Zn to produce the CO gas [18].

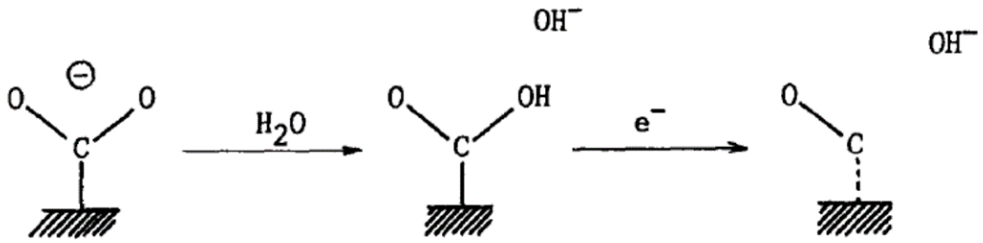


Fig. 2 Mechanism of electrochemical CO_2RR for produce CO_2 to CO [19]

2.2. Faradaic Efficiency

Faradaic efficiency (FE) is the parameter of the desired product. It is defined as the electric charge used for the formation of the desired product over the total charge passed between the electrodes. The faradaic efficiency represents the selectivity toward a specific product, thus an improvement on the FE can directly increase the

amount of CO_2 converted to the desired product, reduce product separation cost, and lower the energy penalty of the electrocatalysis.

2.3 CO_2 in aqueous solution

Carbon dioxide dissolves in water leading to the formation of CO_2 species such as carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). The equilibrium concentration of these species is a function of the partial pressure of CO_2 and the pH. Under ambient pressure, the solubility of CO_2 in water is about 0.034 mol/L and pH = 3.9. The equation (8) shows that introducing CO_2 in an aqueous solution leads to a complex series of reversible reactions between CO_2 species. In the solution with a pH up to about 6, CO_2 is in the form of a weak carboxylic acid; at pH between 6 and 10.3, HCO_3^- anions are formed; and at pH above 10.3, HCO_3^- deprotonates further to CO_3^{2-} [11]. Other approaches to increasing the solubility of CO_2 involved the use of high-pressure CO_2 or the use of non-aqueous solvent [20].

$$CO_2 \leftrightarrow CO_{2\,(aq)} \leftrightarrow H_2CO_{3(aq)} \leftrightarrow HCO^-_{3(aq)} + H_3O^+ \leftrightarrow CO^{2-}_{3(aq)} + H_3O^+ \qquad (8)$$

2.4. Electrochemical of high pressurized CO_2

In aqueous solvents, the hydrogen evolution reaction (HER) is a competitive reaction with CO_2 reduction reaction (CO_2RR) because the solubility of CO_2 in water at ambient pressure is low which indicate mass transfer limitations [21]. One strategy to overcome this limitation, the partial pressure of CO_2 in the gas fed into the electrolyzer impacts the rate of CO_2 mass transfer to the electrode surface due CO_2 solvent solubility relationship [11]. However, the high-pressure CO_2RR requires balancing the

pressure in the anode and cathode chambers to prevent damage to the separator [6, 21].

Hara et al. (1995) [22] studies the electrochemical reduction of CO_2 at high pressure (30 atm) in an aqueous $KHCO_3$ solution. The electrolysis cell was carried out in a glass cell in a stainless-steel autoclave. The catholyte and anolyte compartments were separated by a Nafion 417 sheet. The electrolyte was deaerated by bubbling CO_2 for 30 min, a known pressure of CO_2 was introduced into the electrolysis cell. In the Zn electrode under a CO_2 pressure of 30 atm at a current density of 163 mA/cm^2, CO with faradaic efficiencies of 49%.

In Table. 2, summarizes a typical example report of CO_2 pressure (1, 30 atm) on product selectivity over different metal electrodes by Hara et al. For group C, catalysts like Ag, Zn, and Sn, did not report a major shift in the type of CO_2RR products at higher pressure but the faradaic efficiency towards CO and HCOOH did increase which was affected to increased CO_2 solubility at high pressure [11, 19].

Table 2 Effect of pressure on the product distribution of different metal electrodes in an electrochemical CO_2RR process [22]

Group	Cathode catalyst	Effect of pressure	
		Major products at 1 atm	Major products at 30 atm
A	Ti, Nb, Ta, Mo, Mn, Al	H_2	H_2
B	Zr, Cr, W, Fe, Rh, Ni, Pd, Pt, Si	H_2	CO and HCOOH

C	Ag, Au, Zn, In, Sn, Pb, Bi	CO and HCOOH	CO and HCOOH
D	Cu	CH_4 and C_2H_6	CO and HCOOH

In the undivided cell. Proietto et al. (2021) [6] studies the electrochemical reduction of pressurized CO_2 to overcome the low solubility of CO_2 in an aqueous solution and achieve good faradaic efficiency. The electrolysis was performed in CO_2 saturated water solution of 0.2 K_2SO_4 at a silver plate cathode. In this report when the pressure was increased, could lead to a strong enhancement of the CO production. In the same way, the best faradaic efficiency of CO was 67% (30 bar) at 12 mA/cm^2 as shown in Fig. 2. They explain the enhancement of the CO_2 concentration in the bulk is effective to assist the electrocatalytic properties of CO generation.

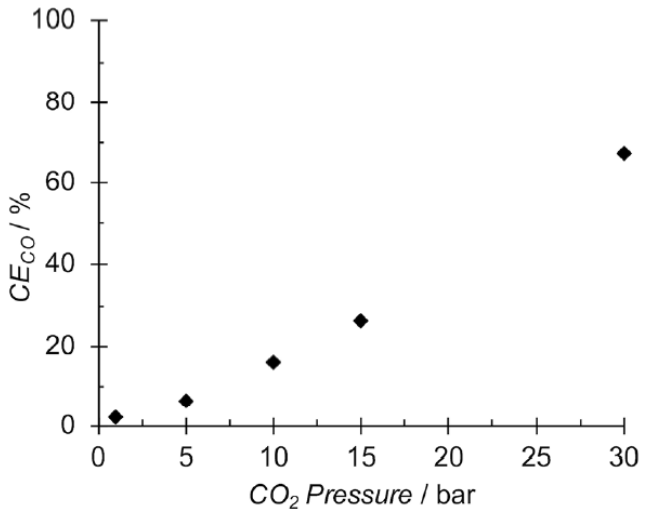


Fig. 3 Effect of the pressure of CO_2 on the current efficiency of CO at 12 mA/cm^2 [6].

Gabardo et al. (2018) [23] studies to boost the performance of the electrochemical reduction of CO_2 with high alkalinity electrolytes to reduce the

overpotentials needed to generate CO from CO_2 on a silver catalyst. However, these conditions have detrimental effects on product selectivity, increasing the production of formic acid. Therefore, the electrolyzers will need to operate at higher pressure together with high alkalinity electrolytes to achieve the problem. As they hypothesized that an increased concentration of CO_2 on the surface catalyst due to the increase in pressure could lead to increase CO faradaic efficiency and the reaction switching from formic acid to CO and reduce the factors of forming formic acid. From the results in 10 M KOH, the faradaic efficiency of CO increased from 42% (1 atm) to 85% (7 atm) at the current density of 300 mA/cm^2. However, the faradaic efficiency of formic acid decreased from 38.2% (1 atm) to 12% (7 atm) as shown in Fig. 3.

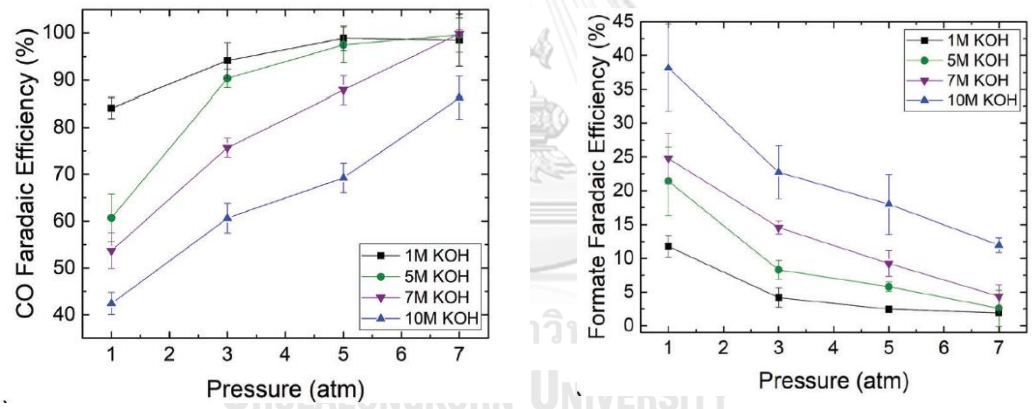


Fig. 4 Effect of pressure on CO_2RR at 300 mA/cm^2 at various pressures and KOH concentrations [23].

In the membrane electrode assembly (MEA). Messias et al. (2019) [24] The main objective of this study was to investigate the effect of pressure and the scalability of the process. They have used an inexpensive commercial foil of the common metal zinc as an electrocatalyst. The reactor was operated at 45°C which faradaic efficiency

of CO from 62% at 10 bar to 82% at 30 bar as shown in Fig. 4. The cell potentials of electrolysis carried out in semi-continuous mode were in the range of -3.5 V to -3.9 V vs Ag/Ag^{+} QRE. A flow rate of electrolyte at 1 ml/min containing 90 wt% H_2O and EMIMOTf. The effect of pressure at 30 bar shows a significant influence on CO selectivity and CO productivities. From in Fig. 5 at 10 bar, observe that CO production is higher and presents a maximum at a flow rate of 2.5 ml min^{-1}. However, increasing the CO flow rate causes a decrease in the residence time of CO_2 at the electrode surface, influencing the H_2/CO ratio.

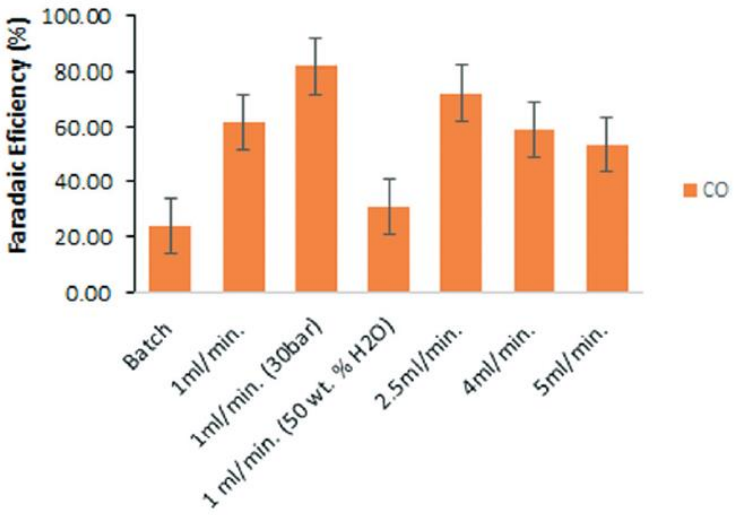


Fig. 5 Faradaic efficiencies of CO obtained at 45 °C [24]

Meanwhile, Dufek and co-workers (2012) [18]. use Ag-based gas diffusion electrode (Ag GDE) and pressurized CO_2 to address CO_2 reduction is hindered by poor kinetics and limited CO_2 solubility in aqueous solution. The advantage of performing the reduction at high pressure is increasing the pressure increases the solubility of CO_2 according to Henry's law. From the result, they have shown an increase in the faradaic

efficiency for CO generation occurred as the pressure was increased from ambient. At pressures above 15 atm, the faradaic efficiency of CO generation was above 80% at 225 mA/cm^2 and 60 °C.as shown in Fig. 5. In the pressurized cell, the determination of the faradaic efficiency (FE) is complicated by residence time of gases in the system due to the lag time. Thus, elevating flow rate of CO_2 were operated to more effectively sweep product gases from the pressurized electrolysis system and to more readily follow the real-time cell performance.

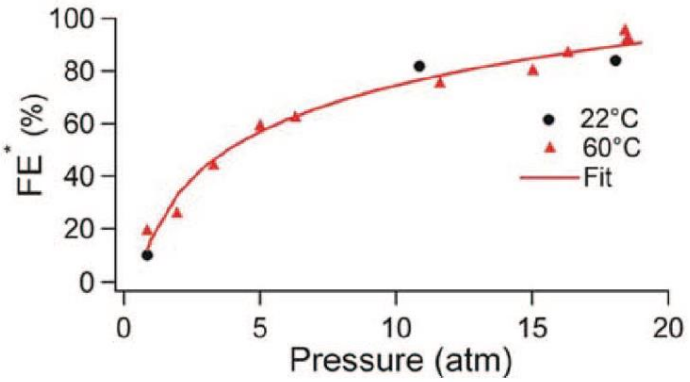


Fig. 6 Impact of pressure on faradaic efficiency of CO [18]

2.5. Electrodeposition of Zn catalysts

The non-noble metal Zn is one of the promising materials because of its abundant reserves and particularly selective production of CO, but the Zn metal reduces CO_2 to CO with low activity and CO selectivity than the noble metal Au and Ag catalyst [17]. To overcome this limitation, efforts have been made to increase the active surface area of a Zn electrocatalyst and allow a much higher CO selectivity [16].

In this report, develop the Zn electrode with the electrodeposition to study the behavior of the tubular reactor. The electrodeposition process is metallic coating onto the porous support (base material), which occurs through the electrochemical reduction of metal ions from an electrolyte. The electrodeposition process consists of the object to be coated or called cathode, electrolyte, anode, and the power supply to make the current flow [25].

Table 3 Summary of CO_2RR to CO of Zn catalyst

Researcher	Catalyst	Experimental Condition	CO Faradaic Efficiency
Wen Luo, et al. (2019) [17]	Zn foil	H-cell 0.1 M $KHCO_3$ -0.95 V vs RHE	50%
	Porous Zn (P-Zn)	H-cell 0.1 M $KHCO_3$ -0.95 V vs RHE	95%
Lu, Y. et al. (2018) [26]	ED Zn	H-cell 0.5 M $KHCO_3$ -1.1 V vs RHE	80%
Jonathan Rosen, et al. (2015) [27]	Electrodeposited Zn dendrites	H-cell 0.5 M $NaHCO_3$ -1.1 V vs RHE	79%
Da Hye Won, et al. (2016) [28]	Hexagonal Zn	H-cell 0.5 M $KHCO_3$ -0.95 V vs RHE	85.4%
Bin hao Qin, et al. (2018) [7]	Electrodeposited Zn catalyst on Cu foam	H-cell 0.1 M $KHCO_3$ -0.9 V vs RHE	85%

In an H-cell reactor. Luo et al. (2019) [17] Zn electrocatalyst is synthesized using an electrochemical method to boost the performance of CO_2RR with electrodeposition method to prepare porous Zn catalyst (P-Zn); that is, the sample deposition of Zn onto the Cu mesh. Interesting this report is the enhanced CO_2 reduction performance of the P-Zn in selectivity compare with Zn foil. From the results, porous Zn catalyst can convert CO_2 to CO at high faradaic efficiency (FE_{CO}, ~95%), compared with that of Zn foil (FE_{CO}, =50%) as shown in Fig. 7a. Because the Cu mesh used as support played the role in increasing the surface area of P-Zn, and the difference mainly corresponds to lower FEs for H_2 on P–Zn as shown in Fig 7b.

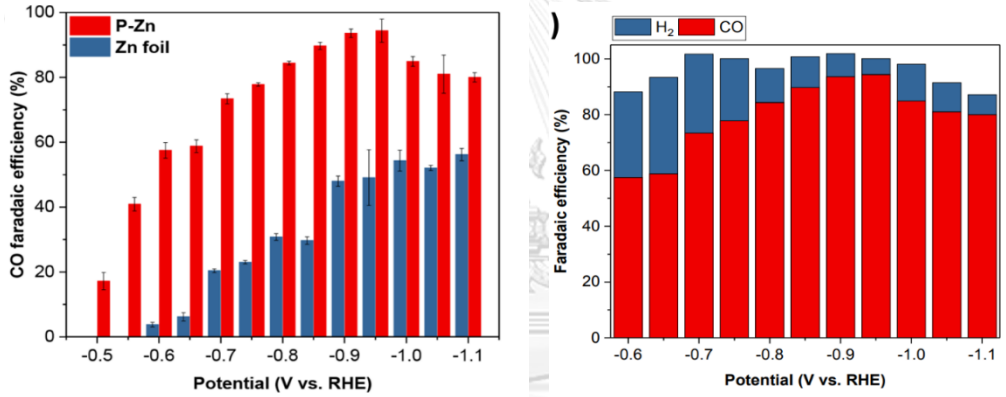


Fig. 7 (a) CO faradaic efficiency for P-Zn and Zn foil and (b) Products distribution of P-Zn in an H-cell reactor [17].

Luo et al. (2018) [29] studies the ZnO catalysts were synthesized on Zn foil substrates using various preparation methods, containing hydrothermal, spray-coating, and electrodeposition methods. The result found that ZnO catalysts with different morphologies, are nanowires, nanoparticles, and nanoflowers form respectively. Then, the synthesized ZnO catalysts were electrochemically reduced at −1.6 V versus reversible hydrogen electrode (RHE) cause a porous morphology composed of thin hexagonal flakes, which exhibited a higher surface area. The CO_2RR performances of this catalysts were evaluated in H-cell with CO_2-saturated 0.1 $KHCO_3$ as the electrolyte.

It shows that all three catalysts are highly selective towards CO with exceeding 90% FE at moderate overpotentials.

Won et al. (2016) [28] have reported that a hexagonal Zn catalyst that was electrodeposited on a Zn foil had good selectivity of CO. They prepare the hexagonal Zn catalyst by electrodeposition of $ZnCl_2$ on Zn foil. The CO_2RR performances were carried out at potential range from -0.6 to -1.1 V (vs RHE) in a CO_2-saturated 0.5M $KHCO_3$ electrolyte. The highest FE for CO was 85.4% at -0.95 V on the hexagonal Zn, which compared with Zn foil was 25.1% of FE for CO as shown in Fig. 8. In summary, they found that development of the hexagonal Zn catalyst was high selectivity towards CO. In particular, DFT calculations demonstrated that (101) facet is appropriate to CO production due to its lower reduction potential for CO2 reduction to CO and higher energy barrier for HER.

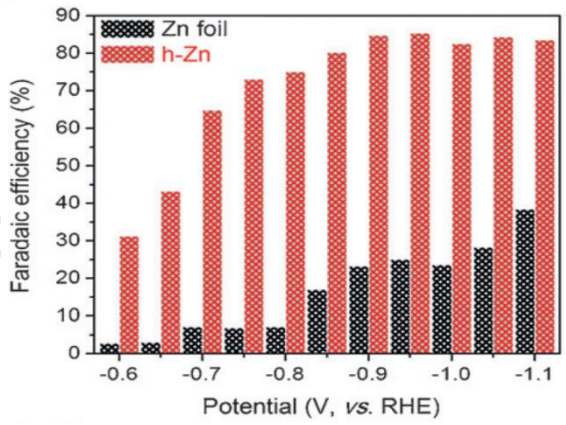


Fig. 8 Faradaic of CO at various constant potentials ranging from -0.6 to -1.1 V [28].

Qin et al. (2018) [7] studies Zn catalysts have been prepared on electrochemically polished Cu foam by the electrochemical deposition method. For electrocatalytic test for CO_2RR performances was conducted in an airtight H-cell. the Faradaic efficiency (FE) of CO_2RR to syngas is greater than 85% at -0.9V vs RHE in aqueous solution.

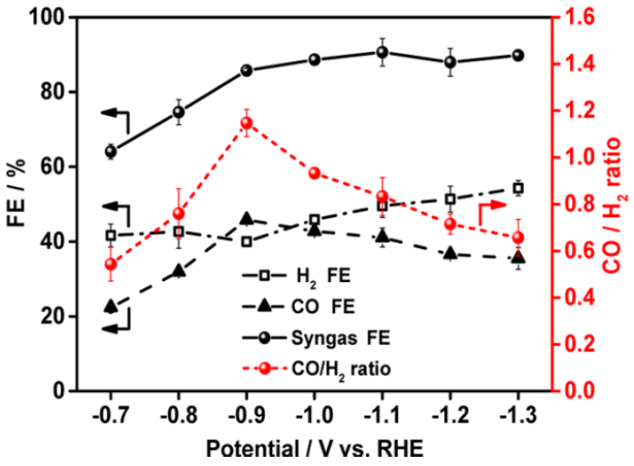


Fig. 9 FEs of CO, H_2, and syngas and CO/H_2 ratios for CO_2RR on Zn catalysts in CO_2-saturated 0.1 M $KHCO_3$ at 40 °C with different potentials [7].

CHAPTER 3
METHODOLOGY

3.1 Reactor Design

The reactor was made from stainless steel. A reactor lining made by 3D printing was inserted inside the reactor to prevent a short circuit. In Fig. 10 displays the configuration details and the 14 mm cell diameter. There are three main parts in the cell. First, the porous cathode is zinc granules (Sigma-Aldrich) or zinc deposited on graphite felt as a cathode for converting CO_2 to CO that formed at a thickness of 3 mm. Second, the porous solid electrolyte is formed from a 2 mm thick bed of anion-

exchange resin beads (Amberlite IRA402 Chloride form) for ionic conductivity and separation of the electrodes and the anode is platinized titanium mesh (Fuel Cell Store). Finally, graphite felt is used to provide compression for firm electrical contacts between cell components.

Fig. 10 Electrochemical CO_2RR cell configuration

3.2 Experimental

This work consists of 2 parts: electrochemical conversion of pressurized CO_2 with Zn granule cathodes and Zn graphite felt as cathodes.

3.2.1. Fabrication of Zn-deposit graphite felt as cathode

The cathode was prepared by the electrodeposition method at room temperature and atmospheric pressure. Graphite felt (diameter 14 mm) is used to support which high porosity, high conductivity, and high surface area for disperse gas. A titanium plate was used as the working electrode and the counter electrode in the electrodeposition process, respectively. This process uses 0.1M of $ZnSO_4 \cdot 7H_2O$ (Sigma-

Aldrich) 100 ml as an electrolyte and deposition at a constant 10 mA for 30 mins, as presented in Fig 11.

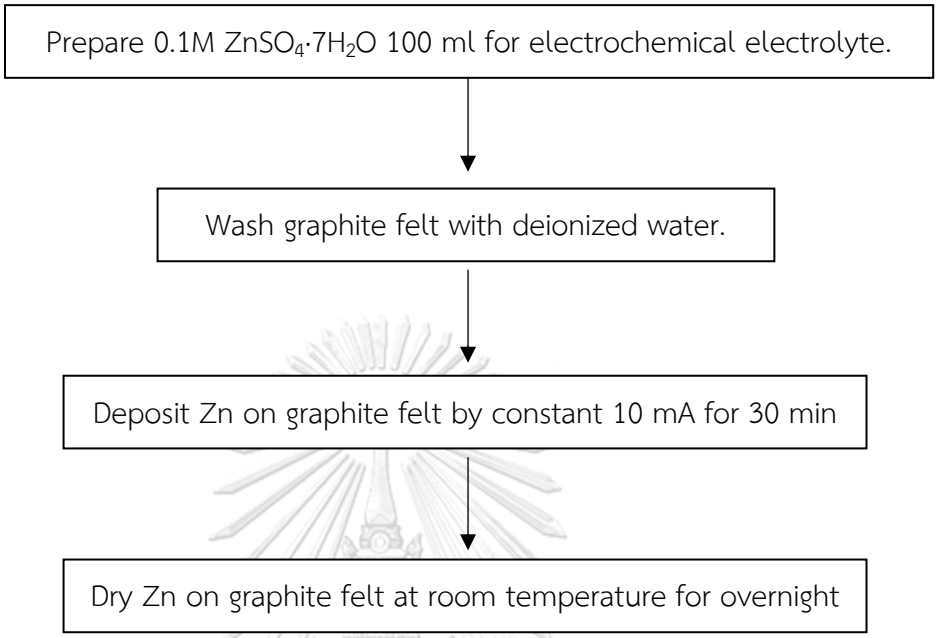


Fig. 11 Schematic of Fabrication of Zn-deposited on graphite felt as cathode

3.2.2. Electrochemical CO_2 reduction

Gas mixtures containing CO_2 are fed continuously to the tubular reactor. The flow rate is controlled by a mass flow controller. Potentiostat galvanostat Autolab PGSTAT101 is used to apply cell voltages for electrochemical CO_2RR. Water is continuously trickled through the bed at 1 mL/min to sustain the ionic conductivity of the anion-exchange resin bed. Before the test, water was saturated with CO_2 by flowing CO_2 at desired pressure in the water drum overnight, and flowing CO_2 was maintained during the reaction. CO concentration was analyzed by Infrared Gas Analyzer (Model IR200, YOKOGAWA) in real-time as presented in Fig. 12. The effects of Pressure (1.5, 3, 8, and 10 bar), CO_2 flow rates (60 and 200 ml min^{-1}), and applied cell voltages (5, 6, 7, and 8 V) will be studied.

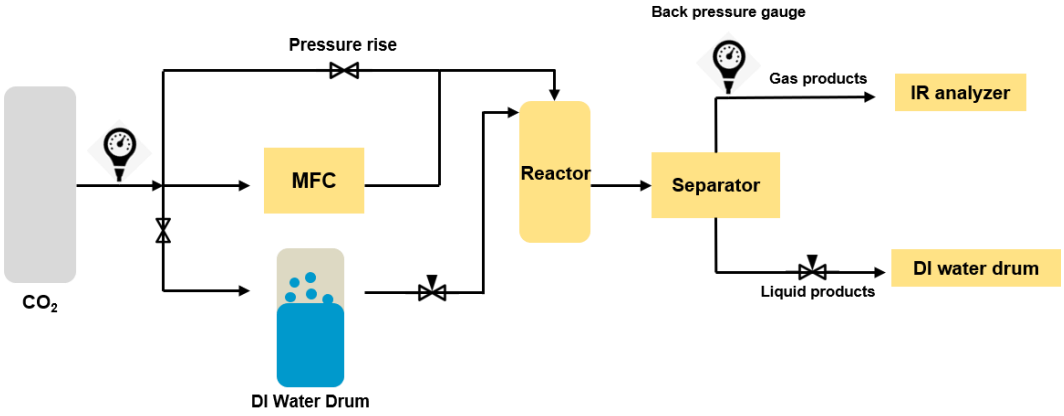


Fig. 12 Schematic of Electrochemical of high pressurized CO_2

3.3 Characterization and Product Analysis

3.3.1. Characterization

3.3.1.1 Scanning electron microscopy with Energy-dispersive X-Ray (SEM-EDX) is a technique that scans the surface with the electron beam. The electrons beam interacts with the sample and a number of signals are produced for detecting a surface of graphite felt. Furthermore, EDX could characterize and measure the elemental composition to confirm that Zn-metal can deposit on graphite felt with the electrodeposition method.

3.3.2. Product analysis

3.3.2.1 The Current from CO_2RR in an electrochemical tubular reactor could calculate Faradaic efficiency of CO product by Eqs. (9).

$$FE\% = \frac{\text{Number of moles of electrons required for reducing } CO_2 \text{ to CO}}{\text{Total number of moles of electrons passed}}$$

$$= \frac{y \int_0^t C_{CO} dt \times \text{flowrate} \times F}{\int_0^t I dt} \quad (9)$$

When

y = Stoichiometric coefficient of electron in Eqs (1), which is 2.

C_{CO} = Concentration of CO produced at various times

F = Faraday constant

I = Electric current

t = Time

CHARTER 4
RESULTS AND DISCUSSION

The purpose of this work was to study the behavior of the novel electrochemical tubular fixed-bed reactor for electrochemical reduction of CO_2 to CO. The high pressure, applied voltage, and CO_2 flow rate are interesting parameters for preliminary electrochemical CO_2 reduction. In the experimental, the catalyst is Zn granule, and Zn-deposit on graphite felt. Fig. 13 shows the SEM image of Carbon felt, and Zn particles appeared on graphite felt.

The SEM morphology of graphite felt, a smooth carbon fiber with a diameter of 10 um, is shown in Fig. 13a. After the electrodeposition, Zn was disorderly formed

on the carbon fiber with a diameter of about ~10 um in Fig. 13b; however, Zn was only deposited on the surface and not inside the graphite felt, as can be seen from pure carbon fiber inside. Zn morphology on graphite felt is shown in Fig. 3c as hexagonal flakes. In Fig. 13d shows the SEM morphology of Zn granules with spherical, nonspherical shapes and rough surfaces with a diameter of ~0.5-1 mm.

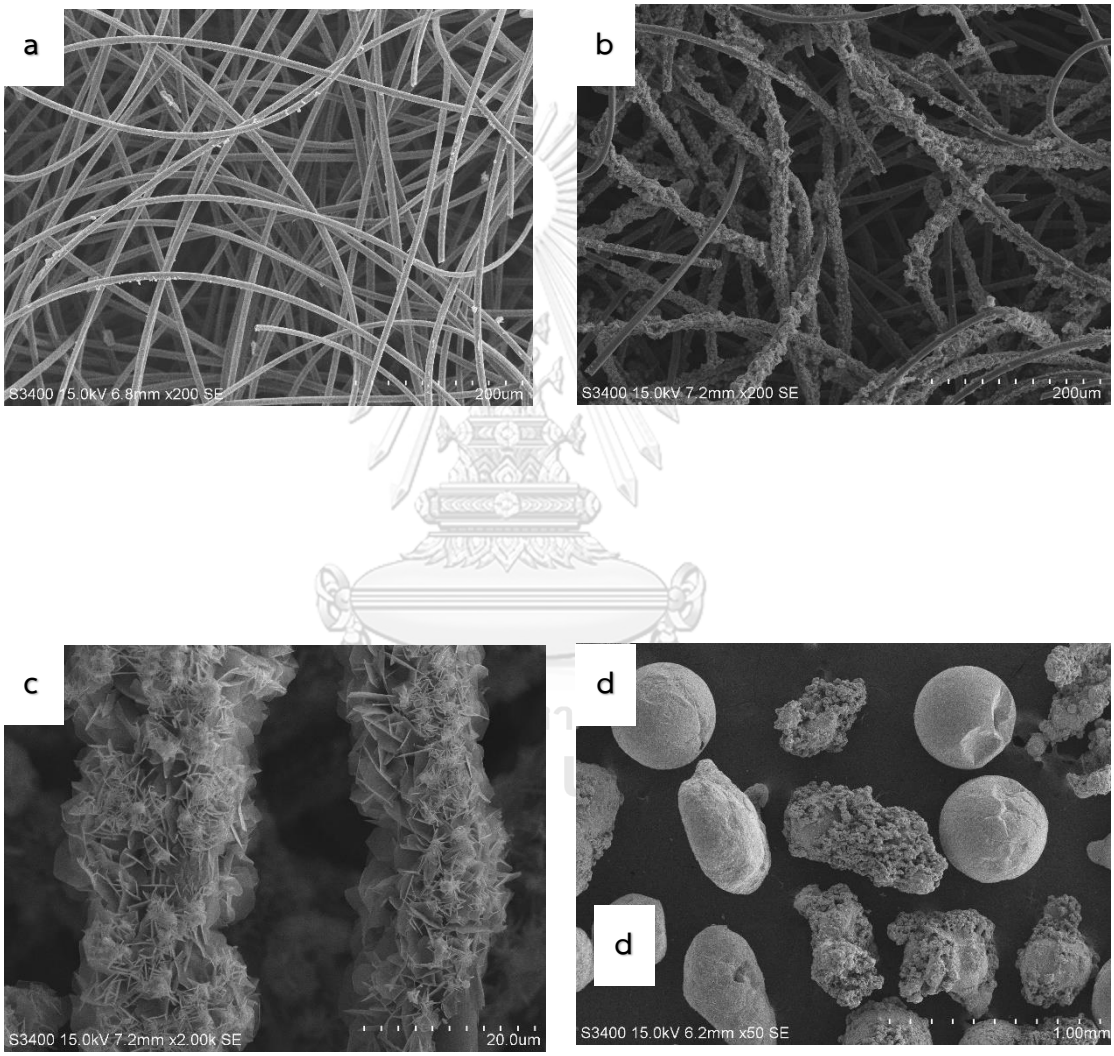


Fig. 13 SEM analysis of (a) Graphite felt , (b, c) Zn deposited on graphite felt, and (d) Zn granules.

4.1 CO_2 reduction reaction

The summary of electrochemical CO_2RR experiment both of Zn Granules and Zn deposited on graphite felt as shown in Table 4, 5 respectively.

Table 4 Summary of electrochemical CO_2RR in tubular fixed-bed reactor of Zn granules

CO_2 pressure (bar)	Voltage (V)	CO_2 flow rate (ml min^{-1})	$\%FE_{CO}$	Current (mA)	CO concentration (ppm)
1.5	8	60	4.72	40.09	245
3	8	60	6.44	91.25	755
8	8	60	10.99	82.07	1225
10	7	60	19.61	50.53	1272
10	8	60	11.42	82.41	1402
3	5	60	15.32	19.83	390
3	6	60	12.28	42.20	665
3	7	60	9.00	67.69	782
3	8	60	6.44	91.25	755
3	5	200	2.95	14.43	54
3	6	200	3.20	13.36	55
3	7	200	4.06	15.41	80
3	8	200	4.55	18.35	107

Table 5 Summary of electrochemical CO_2RR in tubular fixed-bed reactor of Zn deposited on graphite felt

CO_2 pressure (bar)	Voltage (V)	CO_2 flow rate (ml min^{-1})	$\%FE_{CO}$	Current (mA)	CO concentration (ppm)
3	8	60	3.90	9.73	84
10	8	60	10.24	11.26	148
3	5	200	1.91	6.12	14

3	6	200	1.99	8.78	22
3	7	200	1.84	12.17	29
3	8	200	1.53	12.64	25

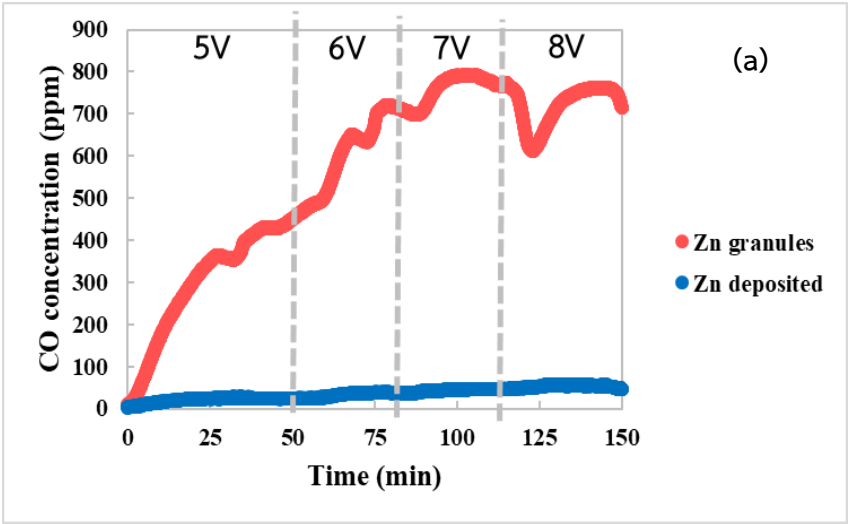
4.1.1 Voltage effect

The voltage condition used in the electrochemical tubular reactor is 5-8 V, CO_2 flow rate and pressure were controlled at 60 ml min^{-1} and 3 bar, respectively. As a result, the highest faradaic efficiency, CO concentration, is 15.324% at 5 V and 782 ppm at 7 V.

When the applied voltage was elevated in the electrochemical CO_2 reduction reaction, the concentration of CO increased as well, which is consistent with the current that occurred. However, the higher voltage effect CO_2 on the surface of the electrode is quickly consumed, inhibiting the mass transfer limited. [26, 30]. As a result, the CO concentration at 8 V is lower than at 7 V, which occurs from producing more hydrogen evolution reaction (HER) instead of a CO_2 reduction reaction at a high applied voltage, as shown in Fig. 14, and affects decreasing the CO faradaic efficiency as shown in Fig. 15. Additionally, Zn deposited is not inhibiting the mass transfer limited due to the low-rate CO produced.

Fig. 14 and Fig. 15 can explain the Zn electrode both Zn granules and Zn deposited in electrochemical CO_2RR. From the results, CO concentration and CO faradaic efficiency of Zn granules are higher than Zn deposited which indicates the rate of CO produced in Zn deposited is low. Possibility, (1) Zn deposited to have a low quantity of Zn on graphite felt. The SEM image in fig. 13b, it shows Zn covered the graphite felt surface only, and lower current during the reaction which indicates the low active sites for CO_2 reduction [27, 28] (2) The quantity of Zn on graphite felt is not detectable after the CO_2RR experiment with Zn deposited for two hours, which influences the rate of CO production and Zn deposited is poor durability. As a

consequence, it can be said that Zn granules perform better than Zn placed at the same thickness of porous cathode.



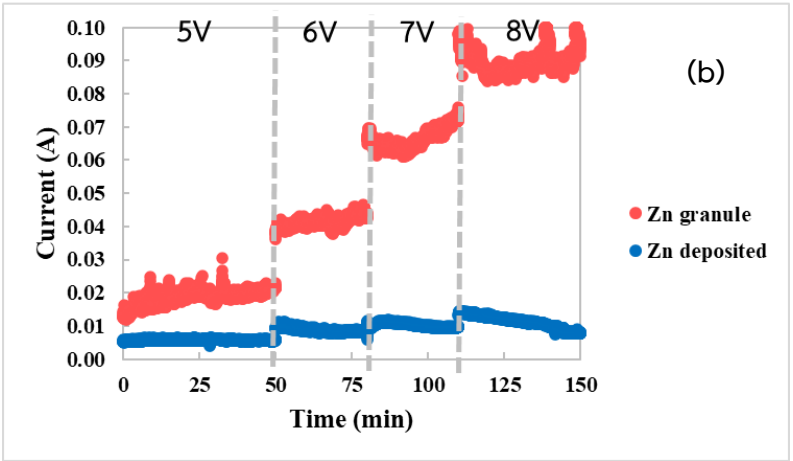


Fig. 14 (a) CO concentration (ppm), (b) current and Time (min) at 3 bar and CO_2 flow rate 60 ml min^{-1} of Zn granules and Zn deposited.

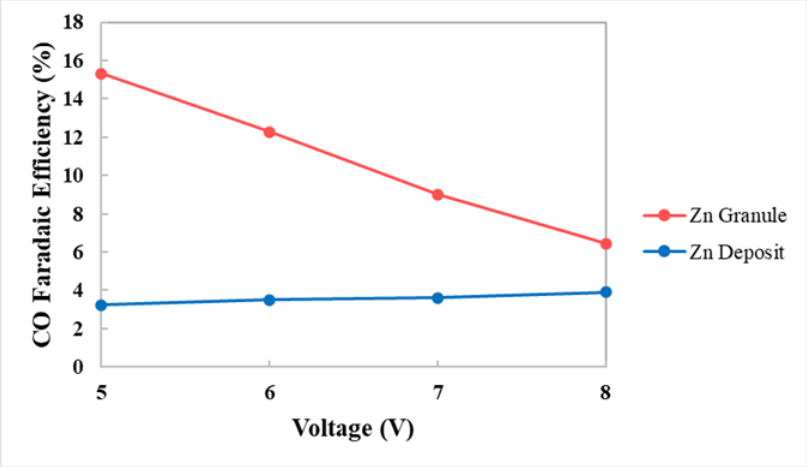


Fig. 15 CO faradaic efficiency (%) and voltage (5-8 V) at 3 bar and CO_2 flow rate 60 ml min^{-1} of (a) Zn granules, (b) Zn deposited on graphite felt.

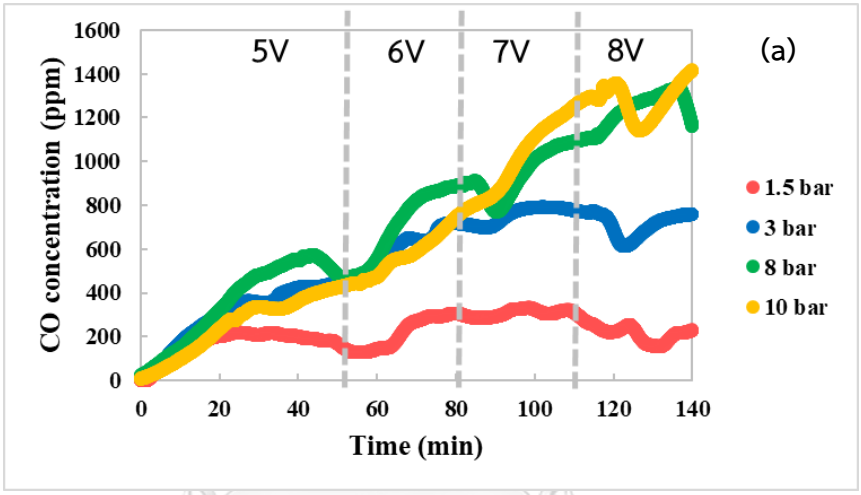
4.1.2 Pressure effect

The pressure condition in the electrochemical tubular reactor is 1.5, 3, 8, and 10 bar. During the experiment, the voltage and CO_2 flow rate were controlled at 5-8 V and 60 ml min^{-1}, respectively. As shown in Fig. 16, CO concentration increased from 245 ppm at 1.5 bar to 1402 ppm at 10 bar of Zn granules. From the results, when the pressure was increased, the CO concentration was enhanced in Zn granules.

Moreover, the CO faradaic efficiency calculated from experimental data, as shown in Fig. 17, increased the same as the CO concentration in both Zn granules and Zn deposited, which the CO faradaic efficiency of Zn granules increased from 6.44% (3 bar) to 11.42% (10 bar) and Zn deposited is increased from 3.9% (3 bar) to 10.24% (10 bar). For this reason, increasing the CO_2 partial pressure impacts the increased concentration of CO_2 in the electrolyte, which affects the increase in CO_2 surface coverage and reduces the number of protons adsorbed on the catalyst surface to suppress H_2 production, leading to an increase in the CO faradaic efficiency and

decreasing the current density [11, 31] that observes from the current at 10 bar lower than 3 bar in Fig. 16b.

The result can hypothesize that high pressure is enhancing help toward CO faradaic efficiency for the electrochemical tubular fixed-bed reactor. Nevertheless, this result is a preliminary study of the behavior of the system and the major competing side reaction; HER needs to be minimized for an optimal CO_2 reduction reaction.



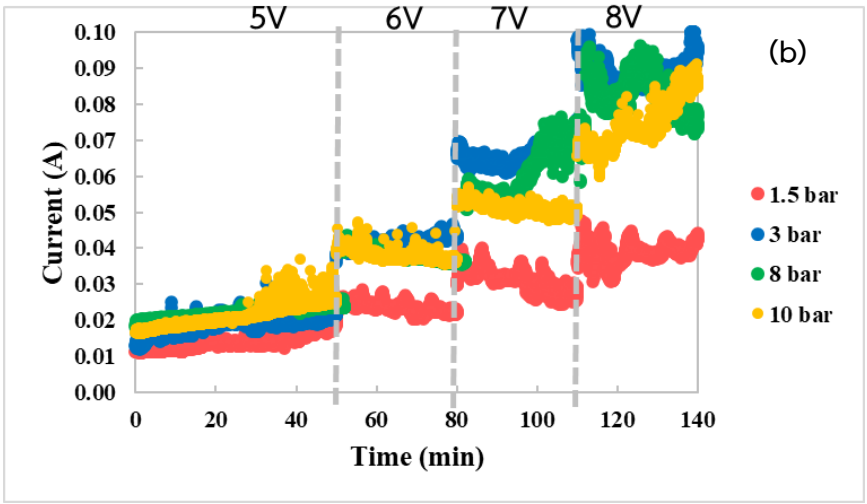


Fig. 16 (a) CO concentration (ppm), (b) Current (A) and various pressure (bar) at 8V and CO_2 flow rate 60 ml min^{-1} of Zn granules.

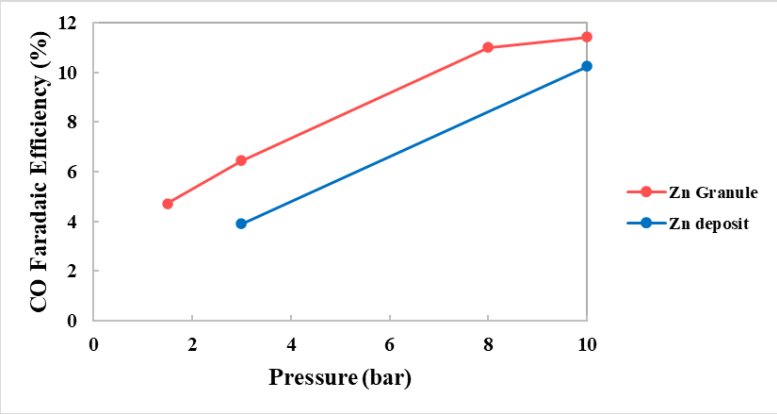


Fig. 17 CO faradaic efficiency (%) and various pressure (bar) at 8V and CO2 flow rate 60 ml min^{-1} of Zn granules and Zn deposited.

Fig. 18 displays the CO faradaic efficiency and current with applied various voltages from the experiment at each pressure. At 1.5 and 3 bar, the CO faradaic efficiency decreased when the voltage increased due to the over-applied voltage effect, and the highest CO faradaic efficiency was both 5 V. However, at the higher pressure (8 and 10 bar), the highest CO faradaic efficiency shifted from 5 V to 6 V (8 bar) and 7 V (10 bar) as shown in fig. 18a which operates under high-pressure conditions affects the increase of CO_2 on the surface coverage from the pressure effect causes a decrease in mass transfer limited effect of CO_2, is enough for the CO_2 reduction reaction to produce CO and it can increase the voltage for enhancing the CO faradaic efficiency. The highest CO faradaic efficiency has 19.61% at 10 bar (7 V). Furthermore, the increase of CO_2 on the surface coverage affects the decreasing H_2 formation which causes the total current is decreased. In fig. 18b, the total current for CO_2 reduction at 3 and 8 bar have higher than 10 bar.

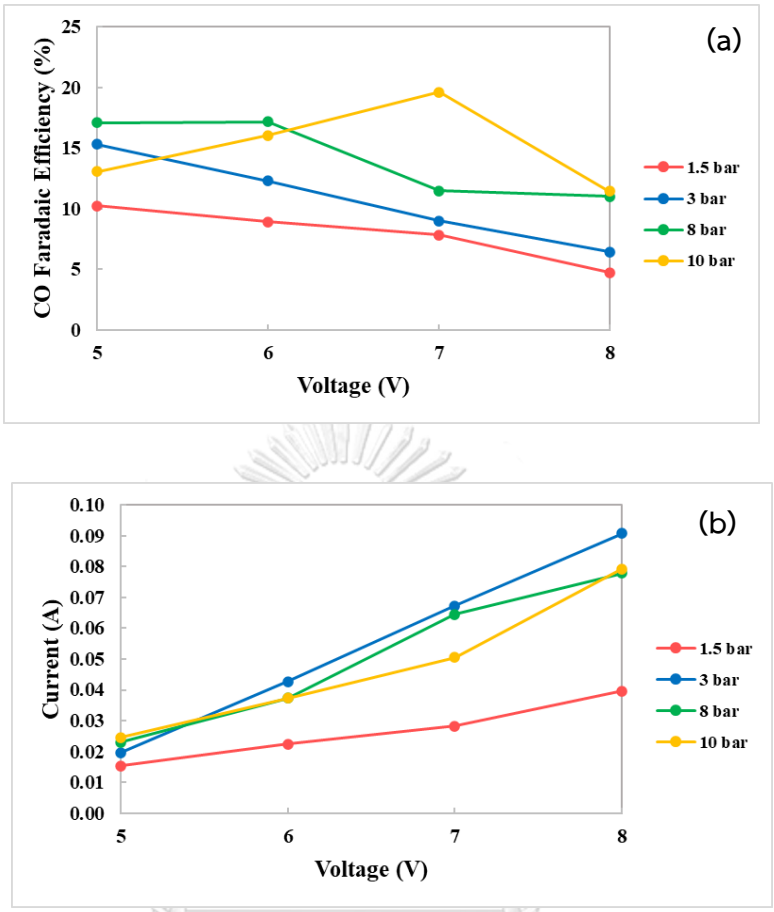


Fig. 18 (a) CO faradaic efficiency (%), (b) Current and voltage (5-8 V) at 1.5, 3, 8, 10 bar and CO_2 flow rate 60 ml min^{-1} of Zn granules.

4.1.3 CO_2 flow rate effect

The CO_2 flow rate condition used in the electrochemical tubular reactor is 60, 200 ml min^{-1}. Voltage and pressure were controlled at 5-8 V and 3 bar, respectively. The determination of the CO faradaic efficiency is made difficult by the residence time of product gases that result in a lag in the system. So, increasing the CO_2 flow rate can solve this problem; increasing the CO_2 flow rate can reduce residence time, and the

product gases are quickly flowed into the IR analyzer and can follow the real-time result [18]. However, the higher CO_2 flow rate cause decreasing CO concentration as shown in fig.19, the CO concentration decreased from ~800 ppm (60 ml min^{-1}) to ~100 ppm (200 ml min^{-1}) because a higher CO_2 flow rate effected to decreases the contact time between catalyst and reactant, leading to a decrease in CO production and CO faradaic efficiency in the system.

As illustrated in fig. 20 of Zn granules at 60 ml min^{-1}, the CO_2 reduction process has mass transfers limited at a higher voltage. The higher CO_2 flow rate has no effect on mass transfers at 200 ml min^{-1} because the increasing CO_2 flow rate reduces CO production and the amount of CO_2 on the surface is sufficient for the CO_2 reduction.

The CO_2 flow rate effect of Zn deposited on graphite felt at 60-200 ml min^{-1}, both CO concentration and current have slightly difference which concludes the flow rate is not effective for the CO concentration and CO faradaic efficiency. So, Using Zn deposited in electrochemical CO_2RR in a tubular reactor suggests a higher flow rate for reducing lag in the system, which can follow the real-time product gases.

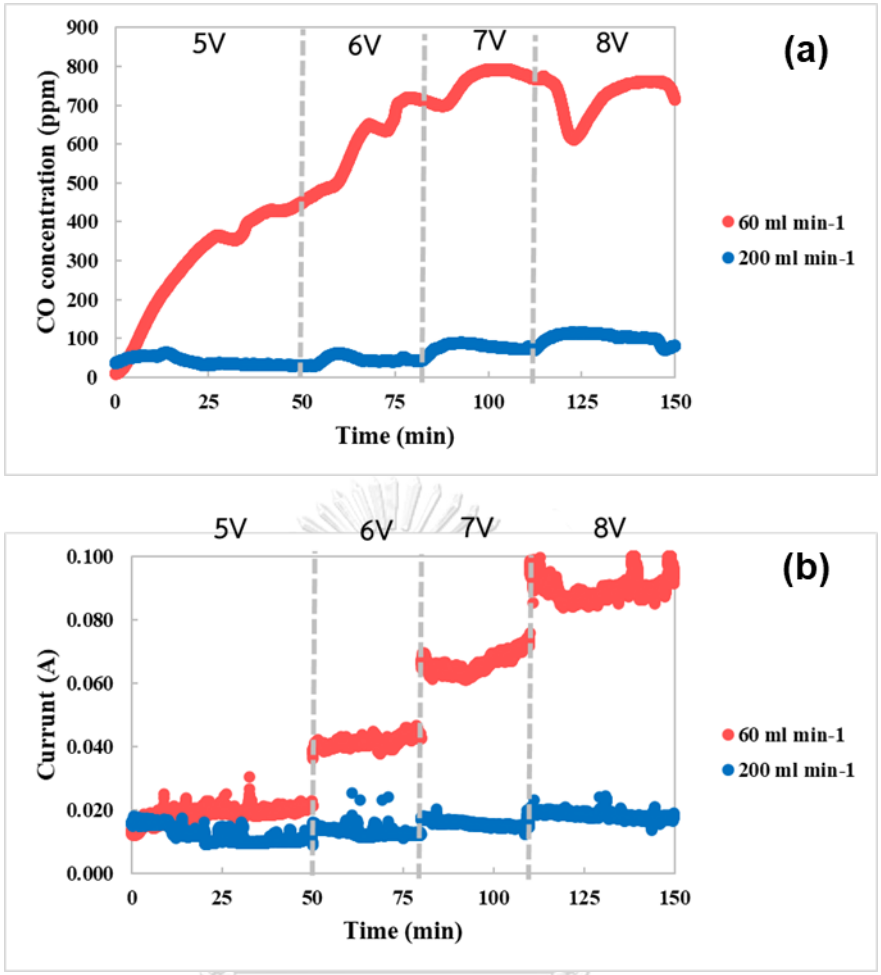


Fig. 19 (a) CO concentration, (b) Current of various CO_2 flow rate (60, 200 ml min^{-1}) and Voltage (5-8 V) at 3 bar of Zn granules

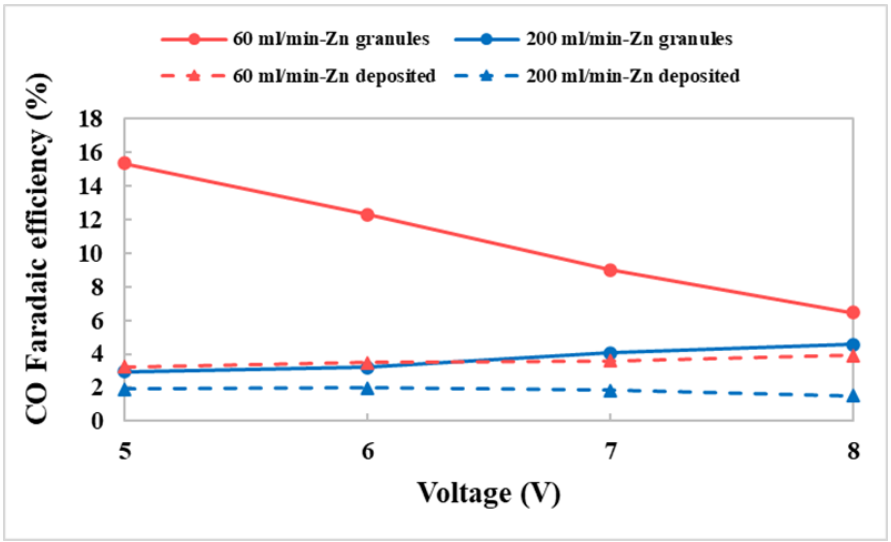
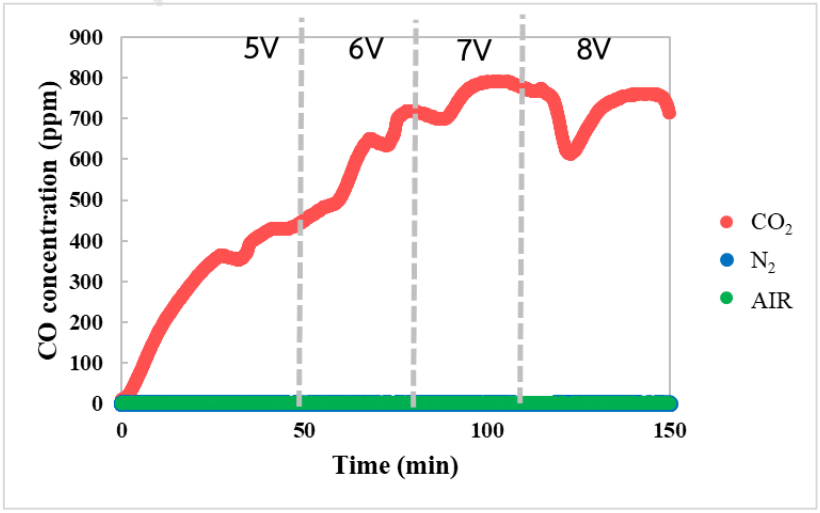


Fig. 20 CO faradaic efficiency of various CO_2 flow rate (60, 200 ml min^{-1}) and Time (min) at 3 bar of Zn granules

4.2 Blank Test

From the results, the behavior of electrochemical CO_2RR for CO_2 to CO production for confirming CO products is produced with CO_2RR by feed N_2 replacing the saturated CO_2 gas. The result is shown in Fig. 21a; the amount of CO detected with Infrared Gas Analyzer (IR) was negligible compared with CO_2RR at 3 bar, 5-8 V, 60 ml min^{-1}, resulting indicates the CO production was produced via saturated CO_2. The current of feed N_2 is lower than the CO_2RR, which is OER current from only water splitting.

For scale-up in the electrochemical tubular fixed-bed can be a series. Therefore, the possibility of reducing O_2 gas in the next cell decreases the CO faradaic efficiency and CO concentration in the system by feeding Air into the system instead of the saturated CO_2 gas. In Fig. 21b, the current of Air is 1/3 or 1/4 times of CO_2 reduction, indicating the O_2 gas is reduced. Thus, the scale-up the electrochemical tubular fixed-bed must be considering the O_2 gas again.



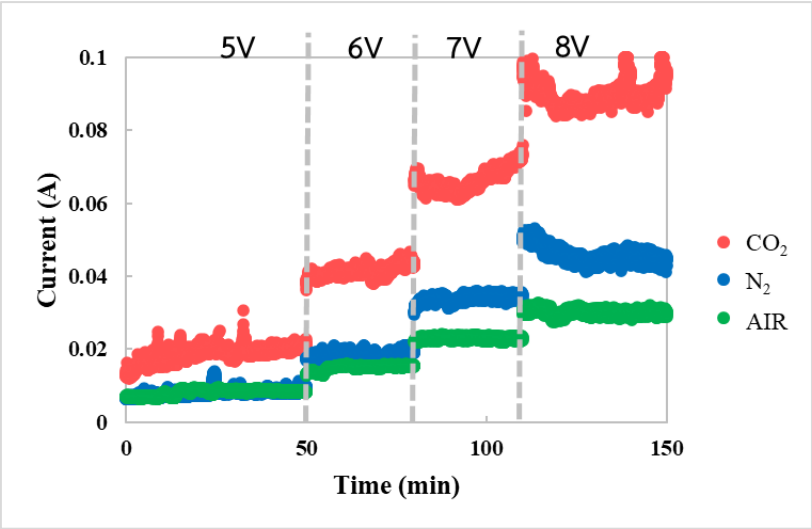


Fig. 21 (a) CO concentration (ppm), (b) Current (A) of blank test comparing at 3 bar, 5-8 V, 60 ml min^{-1} and Time (min)

CHAPTER 5

CONCLUSION AND SUGGESTIONS

5.1 Conclusions

Electrochemical CO_2RR is usually studied in the liquid phase by electrolyte solution with saturated CO_2 in conventional H-type cells. However, the solubility of CO_2 is low at room temperature and atmospheric pressure leads to mass transfer limitations. So, the development of type cells from H-cell become to tubular is a good

choice for solving this problem because the tubular reactor can carry out at high pressure.

The Electrochemical tubular reactor was studied at high pressure, voltage, and CO_2 flow rate. As soon as increase the pressure, the CO concentration and faradaic efficiency rise. At 10 bar, the highest CO faradaic efficiency of 19.61%. Moreover, at the high-pressure exhibits increase CO faradaic efficiency, CO concentration at higher voltage. The applied voltage suggested for the electrochemical tubular reactor is around 5 V. The effect of the CO_2 flow rate is an essential parameter for reducing the lag time that happens in the system. Nevertheless, the CO_2 flow rate leads to low CO faradaic efficiency same.

The behavior of CO production was observed by N_2 gas, indicate the CO gas occurred with Electrochemical CO_2 reduction reaction on cathode by saturated CO_2 and the behavior O_2 gas for the future CO_2 reduction reaction cell, cannot reduced on the cathode.

5.2 Suggestions

- The thickness of the ion-exchange resin bead can be improved to reduce the resistance for the scale-up part of the electrochemical tubular fixed-bed reactor.
- The other product gas and liquid product are produced in the electrochemical CO_2RR should be detect to analyze and study the behavior of cell.

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