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Electrochemical reduction
of liquid CO₂ in high pressure cell

고압반응용기를 이용한 액화 이산화탄소의 전기화학적 환원 반응

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ABSTRACT

Electrochemical reduction

of liquid CO$_2$ in high pressure cell

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Carbon dioxide(CO$_2$) which is the representative greenhouse gas accelerates global warming. The amount of CO$_2$ emission increased dramatically in the use of fossil fuels since the industrial revolution. In order to solve the carbon imbalance brought by mankind, research to make value-added compounds from CO$_2$ through electrochemical reduction has been drawing attention. To electrochemically react CO$_2$, the problem of low faradaic efficiency and low selectivity must be solved. In this study, we noticed that low solubility of CO$_2$ in water can lead to a decrease in faradic efficiency. Electrochemical reduction reaction using liquefied carbon dioxide was studied to increase the low solubility of carbon dioxide.

To proceed electrochemical reaction using liquefied carbon dioxide, a new high pressure cell was designed and electrochemically reacted with liquid CO$_2$ using the high pressure cell was conducted. Experiments were conducted under various
conditions such as the amount of co-solvent, the amount of water, the counter electrode and the working electrode to obtain optimum electrochemical conditions using liquid CO\textsubscript{2} with the high pressure cell. In addition, bulk electrolysis was carried out under various conditions such as pressure, potential, water amount, etc. with Ni and Cu electrode and C\textsubscript{4} hydrocarbons were produced. Products were analyzed using GC and GC-MS and faradaic efficiency was calculated. We have also discovered the possibility of reaction of acetonitrile(ACN) used as co-solvent, using N,N-dimethylformamide(DMF) as a new solvent.

This study has significance in that the reaction proceeds by using liquid CO\textsubscript{2} in the electrochemical reaction of CO\textsubscript{2} which has focused on improving the catalyst. Based on this research we expect to be able to develop new technology to make value-added hydrocarbon through electrochemical reaction using liquid CO\textsubscript{2}.

**Key words: Liquid CO\textsubscript{2}, CO\textsubscript{2} reduction, High pressure cell, Electrochemical reaction**

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Electrolysis was conducted with -2.5V, charge passed 200C.
Chapter 1. Introduction

1.1 Carbon dioxide emission

Carbon dioxide (CO$_2$) which is the representative greenhouse gas accelerates global warming. The amount of CO$_2$ emission increased dramatically in the use of fossil fuels since the industrial revolution. Since 1750, CO$_2$ has increased by 36% and these levels are much higher than the increased level during the past 800 thousand years.$^{[1],[2]}$ Looking at Figure 1.1$^{[3]}$, we can see that the increase in CO$_2$ concentration is directly related to the temperature of the earth, while comparing the concentration of CO$_2$ and the global temperature

Figure 1.2 is a schematic representation of the carbon cycle on the earth. Carbon on the earth can exist as a gas phase, a solid state or an aqueous solution, which are circulated through various pathways and are balanced. On the basis of the use of fossil fuels the production of gas greatly increased, resulting in an imbalance in the carbon cycle. Most of the gas generated for the use of fossil fuels is carbon dioxide, which is pointed out as the main cause of global warming. Actually, looking at atmospheric CO$_2$ in Figure 1.3, we can observe the dramatic rise of atmospheric CO$_2$. It can be confirmed that the CO$_2$ concentration which was 316.91ppm in 1960 increased to 410.67ppm in 2019.
Therefore, in order to solve the carbon imbalance brought by mankind, Paris Agreement was adopted at 2015 United nations Climate Change Conference. The content of Paris Agreement is an international commitment to maintain the increase in the average temperature of the earth below 2°C compared to before the industrial revolution and to further limit the temperature rise to 1.5°C of less. Each country has to decide on reduction targets for greenhouse gas by themselves and practice the target. The Republic of Korea also agrees with the goal of a 37% reduction compared with the predicted value by 2030.[4]
Figure 1.1 The graph of Global Temperature and Carbon dioxide from 1880 to 2010.
Figure 1.2 The scheme of carbon cycle
Figure 1.3 Monthly mean atmospheric carbon dioxide at Mauna Loa Observatory, Hawaii. The red curve represents the carbon dioxide data measured as the mole fraction in dry air, on Mauna Loa constitute. The black curve represents the seasonally corrected data.
1.2 Carbon value-adding

1.2.1 Electrochemical reduction of CO₂

From these viewpoints, researches to reduce and utilize atmospheric CO₂ have been drawing attention. Figure 1.4 shows chemical scheme of carbon. Looking at Figure 1.2, CO₂ is completely oxidized gaseous carbon. By reducing CO₂, it is possible to synthesize more valuable compounds such as formic acid, methanol, methane. Because CO₂ has a chemically stable structure, it is not easy for the reaction to proceed, because a strong reducing agent is required to proceed the reduction reaction. Therefore, the reaction can proceed with the condition of high temperature or high pressure.

However, when using electrochemistry, the reaction proceeds by using electrons instead of oxidizing agent and reducing agent, and in the case of CO₂, by adding proton source and voltage, it is relatively easy to convert CO₂ to various valuable carbon compound.

1.2.2 Problem of CO₂ electrochemical reaction

When CO₂ is reduced electrochemically, carbon monoxide(CO), formate(HCOOH), methane(CH₄) and other hydrocarbons are generated. Figure 1.5 summarizes these reactions. In order to electrochemically react carbon dioxide, we face various challenges. First a high overpotential is require, it shows low selectivity and faradaic efficiency(FE), and low current density by
low solubility of CO₂.[8] There is also a problem in that it is a competitive reaction with aqueous evolution reaction form aqueous solution.[9] Many researchers are making efforts to solve this problem.

In previous studies, the tendency was investigated focusing on the catalytic properties of the metal electrode. According to Table 1.1[10], it can be classified into 4 groups according to the products obtainable by reducing the catalytic activity and selectivity CO₂ of polycrystalline metal electrodes.- CO group (Au, Ag, Zn, Pd, Ga), HCOOH group (Pb, Hg, Tl, In, Sn, Cd, Bi), H₂ group (Ni, Fe, Pt, Ti) and Cu. Most of the metal produced C₁ chemicals (CO, HCOOH), and the Cu electrode reduced CO₂ to various hydrocarbons such as methane(CH₄), ethylene(C₂H₄), ethane(C₂H₆) and propanol(C₃H₇OH), but Cu shows low selectivity.

Since then, in the case of catalysts based on copper, the studies have concentrated on using alloy electrodes[11] and using the structure of electrodes[12] to increase the selectivity of valuable compounds and enhance the faradaic efficiency. Efforts have been made to selectively produce valuable hydrocarbons but research have not yet shown high figures in selectivity faradic efficiency.
Figure 1.4 Chemical scheme of carbon.
Figure 1.5 Thermodynamic potentials of various cathodic reactions possible in the system of CO₂ reduction reaction

\[
\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{CO} + \text{H}_2\text{O} \quad -0.51 \text{ vs NHE} \ (1) \\
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{HCOOH} \quad -0.58 \text{ vs NHE} \ (2) \\
\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow \text{HCHO} + \text{H}_2\text{O} \quad -0.55 \text{ vs NHE} \ (3) \\
\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad -0.39 \text{ vs NHE} \ (4) \\
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad -0.24 \text{ vs NHE} \ (5) \\
2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- & \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O} \quad -0.31 \text{ vs NHE} \ (6) \\
2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- & \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \quad -0.33 \text{ vs NHE} \ (7)
\end{align*}
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**Table 1.1** Various metal electrodes and their CO\(_2\) reduction products. Faradaic efficiencies of each product are indicated.
1.3. High pressure and liquid CO\textsubscript{2}

1.3.1 solubility of CO\textsubscript{2}

We tried concentrating on the solubility of CO\textsubscript{2} as a cause of low faradaic efficiency and selectivity. Looking at Figure 1.6, which is the graph of solubility of carbon dioxide in water, it can be confirmed that a small amount of about 0.2g is dissolved in 100ml of water at room temperature\textsuperscript{[13]} In order to solve this problem, some studies dissolve carbon dioxide in an organic solvent such as acetonitrile (ACN), tetrahydrofuran (THF), N,N-dimethylformamide (DMF). These methods also have solubility of about 10 to 20 times higher than solubility in water, but it still have low solubility.\textsuperscript{(Figure 1.7)} These low solubility can cause faradaic efficiency degradation by allowing water and organic solvent to react instead of CO\textsubscript{2} from the electrode.\textsuperscript{[9]}

1.3.2 High pressure CO\textsubscript{2}

There is a way to use high pressure CO\textsubscript{2} to solve the problem of low FE and low selectivity\textsuperscript{[14]} Using high pressure CO\textsubscript{2}, more CO\textsubscript{2} becomes soluble in solvent, Larger concentrations of CO\textsubscript{2} at the electrode result in higher current density and yields. There are studies using high pressure CO\textsubscript{2}. High CO\textsubscript{2} pressure reduces the hydrogen evolution reaction and increases the selectivity of formic acid\textsuperscript{[15]}, methanol\textsuperscript{[16]} and other hydrocarbons.\textsuperscript{[17]} There are not many previous studies, but when using liquid CO\textsubscript{2}, it was expected to solve the problem of low solubility of CO\textsubscript{2} and increase selectivity.
Figure 1.6 Solubility of carbon dioxide in water
Figure 1.7 Solubility of carbon dioxide in organic solvents such as CH₃COOH, Pyridine, CH₃OH, C₂H₅OH
1.4 Liquid CO₂

1.4.1 Liquid CO₂

Liquid CO₂ has the characteristic of being non-toxic, inexpensive, non-flammable and relatively inert. Also, looking at the phase diagram of CO₂ (Figure 1.8), it is an attractive solvent in that it can be made easily with low pressure. Utilizing this properties, Abbott & Harper[18] investigated the electrochemical properties of liquid CO₂. Experiment was carried out by solving hydrophobic electrolytes (tetrakis(decyl)ammonium tetraphenylborate) in liquid. They measured the conductivity and double-layer capacitance of liquid CO₂, revealing that a high concentration of supporting electrolyte increases solvent conductivity. There is a problem of very low electric conductivity due to the characteristics of CO₂ having a low dielectric constant (ε<2). Due to this problem, there was a difficulty of proceeding the electrochemical reaction.
Figure 1.8 Phase diagram of CO$_2$
1.4.2 Co-solvent

The low dielectric constant of dioxide and the low solubility of salt show low electric conductivity. In order to increase the electric conductivity, co-solvent has come to appear. Co-solvent means using both liquid CO$_2$ and other solvents that can dissolve the salt. Goldfarb et al.$^{[19]}$ studied dielectric and voltammetric properties according to the proportion of methanol as co-solvent. They observed that the dielectric constant increases as the mole fraction of methanol increases.

The most extensive study of the use of co-solvents on the phase behavior and conductivity of liquid CO$_2$ was studied by Bartlett et al.$^{[20]}$ They use acetonitrile(ACN) and methanol as co-solvent for liquid CO$_2$. Using tetrabutylammonium tetrafluoroborate(TBABF$_4$) as a supporting electrolyte, ACN have the solubility of salt 5 times higher than methanol. The high solubility of supporting electrolyte means better electrical conductivity, and for later experiments ACN is used as the co-solvent.

1.4.3 Direct reduction of Liquid CO$_2$

Experiments using liquid CO$_2$ have largely progressed in two directions. It has been used to directly react CO$_2$ used as a so liquid CO$_2$ as a solvent for other reactions, such as replacing an alcohol with an aldehyde or converting a halogen element$^{[21]}$ into a carboxyl group.$^{[22]}$

We decided concentrate on the fundamental reaction of direct
reduction of CO$_2$ rather than application by solvent. In a previous study to direct react liquid CO$_2$, C$_2$ hydrocarbons were generated using Pt electrode$^{[23]}$, and Cu has been used to obtain interesting results such as showing faradaic efficiency different from atmospheric pressure conditions.$^{[24]}$ However, there are only three prior studies that are lack of reliability and research under various conditions.

Among many electrodes, The optimum condition is found in the liquid CO$_2$ reaction by using Cu electrode which is the most commonly used for CO$_2$ reduction reaction and H$_2$ group(Ni, Pt, Ti, Fe). If the faradaic efficiency changes and the H$_2$ group yields a product other than H$_2$, it may be interesting. In addition, if the experiment is carried out under various conditions such as potential, water content, co-solvent, etc., it will become the basic of the liquid CO$_2$ reaction to be carried out later.
Chapter 2. Manufacture of High pressure cell and Experiment

2.1 Manufacture of High pressure cell

2.1.1 Previous study of high pressure cell

The first task we need to perform to carry out liquid CO$_2$ experiments was to study the researches about high pressure cell. Most of high pressure cell is sufficient to apply pressure to withstand, but in our experiment we need to proceed with the electrochemical reaction. So we need to create a new design of high pressure cell.

Figure 2.1 shows the high pressure cell that the Abbott group used for liquid CO$_2$ reaction experiments.[23] The Abbott group used 15ml cell, the interval between the working electrode and counter electrode was 2mm and it was very narrow. There was a gas container for the gas analysis. Figure 2.2 show the high pressure cell that the Zhao and Guying et al.[25] 30ml cell was used and the distance between the electrodes was 3mm. In addition, they attached a gas bag for gas analysis.

As a result of observing these high pressure cell, the size of the container was small and there was a gas collecting container for gas analysis. In particular, to solve the low electric conductivity of liquid CO$_2$ the distance between the electrodes is very small.
Figure 2.1 Structure of high pressure cell of the Abbott group
Figure 2.2 Structure of high pressure cell of Zhao and Guying group (1) gas inlet; (2) gas outlet; (3) quasi-reference electrode (Pt wire); (4) cathode (Cu plank); (5) anode (Pt plank); (6) Teflon packing; (7) Teflon; (8) stirrer.
2.1.2 Previous cell in our lab

The design of the high pressure reactor which existed in our laboratory is the same as Figure 2.3. It was made of stainless steel to be able to withstand high pressure, was installed the electrodes for electrochemical reaction.

As a result of the reaction with existing cell, there were various problems existed in the high pressure cell. The biggest issue among them is that the distance between the working electrode and counter electrode is 2.5cm, which is much wider than the previous studies. Looking at system resistance in Figure 2.4(a), when using an electrolyte concentration of 0.5M, it showed the lowest resistance and its resistance was about 200ohm. 200ohm is so big that it is not suitable for electrochemical reaction. In addition, when we looked at the current density measured in Figure 2.4(b), it was observed that even with a high potential of -3.0V applied, it shows very low current density of 0.174mAcm\(^{-2}\).

Besides, it took a long time to react because of large volume of the cell(135ml). In order to observe the internal phase change, we make a window on the top of the cell, but it was difficult to observe the inside because it was difficult to enter the light into the cell. Also, there was a difficulty in gas analysis because there was no gas container for gas analysis.
Figure 2.3 The draft of High pressure cell. It has gas outlet and inlet, pressure gauge, and electrode connector. The distance between the working electrode and counter electrode was 2.5 cm and volume of the cell was 135 ml.
Figure 2.4 Electrochemical properties of the high pressure cell. ACN 30ml+TBABF$_4$ 0.2M, 0.5M and 1M concentration was used as co-solvent. Working electrode is Cu electrode. Counter electrode and Reference electrode is Pt electrode (a) System resistance(ohm) by concentration of electrolyte(mol/L) (b) Current density(mA cm$^{-2}$) by potential(V vs. Pt)
2.1.3 New high pressure cell

To solve these problem we design and manufacture a new high pressure cell for liquid CO\textsubscript{2} electrochemical reaction. Figure 2.5 is a picture of a newly designed high pressure cell. The distance between the electrodes was 5mm and it was made very closely to solve the electric conductivity of CO\textsubscript{2}. The capacity of the cell was 60ml, reduced to half of the previous cell and made with quartz. We made windows on both sides of the cell so that we can observe changes inside the container. We also added a heating system so that the temperature can be changed and later make supercritical CO\textsubscript{2} experiment possible. Finally we prepared a gas collecting container for analysis of gas.

Figure 2.6 shows the actual high pressure cell. The barometer is attached to the cell and gas container. The atmospheric pressure can be measured. By reducing the distance between the electrodes to 5mm, the size of the resistance is reduced to 10 to 20 ohms enabling electrochemical experiments. Also we were able to observe liquid CO\textsubscript{2} inside the high pressure cell through the window.
Figure 2.5 Blueprint of new high pressure cell. The distance between working electrode and counter electrode is 5mm. The capacity of the cell was 60ml.

There are windows on both sides of the cell.
Figure 2.6 Actual appearance of high pressure cell. (a) Overall appearance of high pressure cell. (b) The lid of high pressure cell.
2.2 Experimental

2.2.1 Materials

Acetonitrile (ACN, 99.9%) were purchased from Daeung Chemicals. Tetrabutylammonium tetrafluoroborate (TBABF$_4$, 98%) were purchased from Tokyo Chemical Industry. N,N-Dimethylformamide (DMF, 99.8%) were purchased from Sigma-Aldrich. Copper foil (Cu, 0.1mm thick), Platinum foil (Pt, 0.025mm thick), Magnesium foil (Mg, 0.25mm thick) and Nickel foil (Ni, 0.1mm thick) were purchased from Alfa Aesa. High purity deionized water (18.2 MWcm$^{-1}$) was used in the procedures.

2.2.2 Electrochemical analysis

Prior to use, the metal foils were polished with sandpaper, cleaned with diluted HCl (aq.) and rinsed with distilled water. Reference electrode used Pt electrode as quasi-reference electrode. ACN used molecular sieves to remove water. Co-solvent was prepared by dissolving 0.5M TBABF$_4$ in ACN. Co-solvent and water (protone source) were put in Quartz cell and the quartz cell was put in high pressure cell. Using a cooler, CO$_2$ line was set to 0℃ and CO$_2$ was injected using gas pump. Using the pump, the pressure was increased until the interior of the cell reaches 90bar. After electrolysis, liquid CO$_2$ was vaporized by gas container and gas is collected using gas bag. 1 mL of headspace gas was transferred by syringe for gas chromatography (GC)
The liquid product remaining after vaporization was analyzed by gas chromatography-mass spectrometry (GC-MS) analysis.

### 2.2.3. Analytic methods

A potentiostat (VSP-300, Bio-logic) was used for voltammetric measurements and bulk electrolysis. The quantitative measurement of the gas phase from the headspace of the electrochemical cell was performed by gas chromatography (GC, PerkinElmer, NARL8502 Model 4003). Liquid-and solid-phase products dissolved in the organic solvents were detected by gas chromatography-mass spectrometry (GC-MS, Agilent 5977) using an automatic liquid sampler.
Chapter 3. Results and Discussions

3.1 Optimization

3.1.1 Acetonitrile

In order to find optimal conditions for reaction experiment of liquid CO₂, we conducted experiments under various conditions. The amount of ACN as co-solvent was adjusted at the very beginning. We prepared tetrabutylammonium tetrafluoroborate(TBABF₄, 0.5M) electrolyte in ACN dissolved in co-solvent. Experiments were carried out using the Cu electrode as the working electrode most frequently used in the CO₂ electrochemical reaction and using Pt electrode as the counter electrode and reference electrode. To investigate 10%, 20% and 30% of the total volume, we added 6, 12 and 18ml co-solvent, then liquefied CO₂ to 90bar pressure and experimented. Cyclic voltammetry was done from 0V to -2.5V. Cyclic voltammetry scans was recorded at a 100mVs⁻¹.

As the amount of ACN increased, we could observe that the current density increased and the resistance decreased(Figure 3.1). Also, when we measured the resistance, it showed 37.6ohm at 6ml, 15.2ohm at 12ml and 12.8ohm at 18ml(Figure 3.2). The characteristic of 18ml does not improve greatly and shows the same value as 12ml, so we are proceeding with experiments after considering it as the optimum condition of 12ml.
Figure 3.1 Cyclic voltammetry data of liquid CO$_2$ with various concentrations of co-solvent (ACN+TBABF$_4$ 0.5M) at 100mVs$^{-1}$. Working electrode was Cu, Counter and reference electrode were Pt electrode.
Figure 3.2 Resistance of liquid CO$_2$ system with various concentration of co-solvent (ACN+TBABF$_4$).
3.1.2 Proton source

In order to react carbon dioxide to obtain hydrocarbons, proton source is necessary.\cite{26} When CO\(_2\) reduction experiments proceed in aqueous solution, water will be used for proton source and participate in the reaction. However, to use ACN for co-solvent with liquid CO\(_2\), additional proton source must be included. Melchaeva et al. Conducted experiments on various proton sources of liquid CO\(_2\)\cite{24}

To increase the current density and promote CO\(_2\) electroreduction toward organic products, the amount of proton source also needs to be optimized. We used water which is the most basic proton source. Using Cu electrode as the working electrode to add 0, 0.2, 0.5 and 1ml of water, the experiment result is shown in Figure 3.3, and the Ni electrode was used as the working electrode to set the amount of water to 0, 0.5 and 1ml. The results of the experiment are shown in Figure 3.4. As a result of the experiment, we can observe that the current density increases when the amount of water is increased. In Figure 3.5, resistance was measured for Cu and Ni electrodes. As a result, we could observe that the resistance decreases as the amount of water increases. However, after 0.5 ml showed similar characteristics without a clear increase. We guessed that the optimum conditions for the other catalytic properties of copper and nickel may be different, but it shows the same tendency. As the amount of water increases, it is expected that the hydrogen evolution reaction will increase. Therefore, the amount of water was fixed to 0.5 ml(0.83%).
Figure 3.3 Cyclic voltammetry of liquid CO$_2$ with different amounts of water using Cu electrode as working electrode at 100mVs$^{-1}$. Co-solvent was used 20% ACN and TBABF$_4$(0.5M) electrolyte
Figure 3.4 Cyclic voltammetry of liquid CO$_2$ with different amounts of water using Ni electrode as working electrode at 100mVs$^{-1}$. Co-solvent was used 20% ACN and TBABF$_4$(0.5M) electrolyte
Figure 3.5 Resistance of liquid CO$_2$ with different amounts of water using Ni and Cu electrode as working electrode.
3.1.3 Counter electrode

We promoted the optimization of the counter electrode. The counter electrode mainly used platinum electrode and magnesium electrode which is a sacrificial electrode.\[^{[27]}\] In the platinum electrode, water may react to generate oxygen generation reaction, which causes hydrogen ions to be generated. This results in a loss of Faraday efficiency and the generated hydrogen ions can proceed with other reactions.\[^{[28]}\] On the other hand, magnesium electrode reacts with magnesium ions to form magnesium ions, so that other reactants do not react, minimizing energy loss. If carboxylation reaction occurs, carboxylic acid can be obtained via acid treatment.\[^{[29]}\] Therefore, experiments were conducted on Pt electrode and Mg electrode.

We experimented using Cu electrode as working electrode and Pt electrode and Mg electrode respectively as counter electrode. Also, cyclic voltammetry graph was drawn by adding 0 ml and 0.5 ml of water to each counter electrode and comparing them. (Figure 3.6) As a result of performing cyclic voltammetry, we could not find a big difference between the two electrodes.

After that, bulk electrolysis was carried out along the counter electrode, and then faradaic efficiency was compared. Faradaic efficiency is a value that defines the reduction efficiency of a specific product from the viewpoint of electron transfer. Faradaic efficiency can be calculated by dividing the amount of electrons generated by the experiment by the amount of electrons that are theoretically generated. This can be calculated by dividing it into the number
of moles of the product and the amount of charge accumulated by the number of electrons faraday constant(F) required for production.[30]

\[
\text{Faradaic efficiency(\%) } = \frac{\text{Experimental evolution}}{\text{Theoretical evolution}} \times 100
\]

\[
= \frac{Q_{\text{exp}}}{Q_{\text{theo}}} \times 100
\]

\[
= \frac{\sum (\text{mol} \times n_i) \times F}{I \times t} \times 100
\]

Since the number of electrons necessary for generation and the faraday constant(F) value are fixed and it is possible to know the amount of electric charge flowed using the potentiostat device. Therefore, it is most important to calculate the number of moles of the product precisely.

Analysis of gaseous products used GC(Figure 3.7). As a result of GC analysis, hydrogen(H₂) was observed as the main product, the amount of methane(CH₄) and carbon monoxide(CO) was very small amount, and it was considered as an error. In order to quantify the amount of gaseous product, the following method was used. First, after connecting with the liquid carbon dioxide gas storage container and vaporizing it, measure the pressure and obtain the volume of the gas storage container and multiply ①. After discharging the gas inside the gas container, vaporize the remaining liquefied CO₂ again, measure the pressure, obtain the total volume of the high pressure container and the gas container and multiply ②. Add ① and ② to determine the total gas volume. Extract 1ml of gas using syringe and proceed with GC analysis. Faradaic efficiency was
calculated by quantifying the amount of gas produced using the volume per ml of GC.

GC-MS was then used to analyze the liquid product. As a result of GC-MS analysis, butanal, 2-butanone, methyl vinyl ketone (MVK), formic acid, butanoic acid were observed as main products. (Figure 3.8, Figure 3.9) In order to quantify the amount of analyzed liquid product, we used the following method. Taking formic acid as an example, GC-MS analysis was carried out according to the concentration of formic acid to obtain area value and a trend line between concentration and area was obtained. Using this, we were able to calculate the faradaic efficiency by calculating the concentration using the area of formic acid of analyzed GC-MS and quantifying the amount produced. Faradaic efficiency could be similarly calculated for butanal, 2-butanone, methyl vinyl ketone.

Bulk electrolysis was performed at -2.5 V until the amount of electric charge was 200 C. When Mg electrode was used for the counter electrode, carboxylate was formed in the carboxylation reaction. Therefore, in the case of Mg electrode as counter electrode, after acid treatment, faradaic efficiency was calculated. The calculated faradaic efficiency is summarized in Figure 3.10 and Table 3.1. As a result of analysis, there was no difference between Mg electrode and Pt electrode in the product, but when using Pt electrode, it showed high faradaic efficiency. It turned out that loss of faradaic efficiency occurs in acid treatment process.

There was no significant difference between the Pt electrode and the Mg electrode from the CV results, and there was no big difference in the
comparison of the products after the Bulk electrolysis. However, when the Pt electrode was used, the sum total of faradaic efficiency appeared, which means that faradaic efficiency measurement was made more accurate using Pt electrode. Therefore, we used a platinum electrode as the counter electrode.
Figure 3.6 Cyclic voltammetry of liquid CO$_2$ with different amounts of water and different working electrode at 100mVs$^{-1}$. Co-solvent was used 20% ACN and TBABF$_4$(0.5M) electrolyte.
Figure 3.7 GC results from bulk electrolysis at -2.5V with charge passed 200C, using Ni electrode.
Figure 3.8 Gas chromatography-mass spectrometry (GC-MS) results from bulk electrolysis at -2.5V with charge passed 200C. Retention time was 2.5 to 4.8 min.
(a) Ni electrode (b) Cu electrode
Figure 3.9 Gas chromatography-mass spectrometry (GC-MS) results from bulk electrolysis at -2.5V with charge passed 200C. Retention time was 7.7 to 8.6min
(a) Ni electrode (b) Cu electrode
Figure 3.10 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO₂ with different counter electrode. Electrolysis was conducted with -2.5V, charge passed 200C.

<table>
<thead>
<tr>
<th></th>
<th>H₂</th>
<th>butanal</th>
<th>MV</th>
<th>K</th>
<th>2-butanon e</th>
<th>Formic acid</th>
<th>Butanoic acid</th>
<th>total</th>
</tr>
</thead>
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<tr>
<td>Cu_Pt</td>
<td>41.46</td>
<td>14.94</td>
<td>12.26</td>
<td>1.49</td>
<td>11.62</td>
<td>11.63</td>
<td>93.4</td>
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<td>12.94</td>
<td>0.43</td>
<td>13.35</td>
<td>21.76</td>
<td>91.51</td>
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<td>7.65</td>
<td>13.44</td>
<td>75.69</td>
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</tr>
</tbody>
</table>

Table 3.1 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO₂ with different counter electrode. Electrolysis was conducted with -2.5V, charge passed 200C
3.1.4 Working Electrode

Finally, we conducted experiments on working electrodes. Depending on the product that can be obtained by reducing CO₂, the metals were classified into four groups - CO group (Au, Ag, Zn, Pd, Ga), HCOOH group (Pb, Hg, Tl, In, Sn, Cd, Bi), H₂ group (Ni, Fe, Pt, Ti) and Cu. Among these, Cu which produces the product of C₂ and more, and H₂ group (Ni, Fe, Pt, Ti) were experimented in order to reduce the occurrence of H₂ and obtain a more valuable product.

Bulk electrolysis was performed at -2.5 V until it reached an electric charge amount of 200 C. The results of faradaic efficiency analysis are shown in Figure 3.11 and Table 3.2. When using Cu electrode, showed the highest faradaic efficiency, and in H₂ group Ni electrode showed the highest faradaic efficiency. Therefore, more detailed experiments were conducted on Cu and Ni electrode.

Ultimately we used a high pressure reactor to react liquid CO₂, we used ACN 20% dissolved TBABF₄ at 0.5 M co-solvent in solution and 0.5 ml water(0.83%) for proton source. We used copper and nickel as the working electrode, and platinum electrode as the counter electrode.
Figure 3.11 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO$_2$ with different working electrode. Electrolysis was conducted with -2.5V, charge passed 200C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\text{H}_2$</th>
<th>Butanal</th>
<th>MVK</th>
<th>2-butanone</th>
<th>Formic acid</th>
<th>Butanoic acid</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu_Pt</td>
<td>41.46</td>
<td>14.94</td>
<td>12.26</td>
<td>1.49</td>
<td>11.62</td>
<td>11.63</td>
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<tr>
<td>Ni_Pt</td>
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<td>12.25</td>
<td>12.94</td>
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<td>66.44</td>
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</table>

Table 3.2 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO$_2$ with different working electrode. Electrolysis was conducted with -2.5V, charge passed 200C
3.2 Electrochemical characterization

3.2.1 Effect of pressure

To investigate the tendency of pressure increase, we conducted experiments at 1 bar, 30 bar, and 90 bar under the conditions of atmospheric pressure, high pressure, and liquid CO\textsubscript{2} respectively and proceeded with bulk electrolysis at -2.5 V. The results of the faradaic efficiency analysis of Cu electrode and Ni electrode are shown in Figure 3.12, Figure 3.13 and Table 3.3. The change in faradaic efficiency and selectivity was found to be caused by the change in the pressure, and in the case of Cu electrode, as the pressure increased, H\textsubscript{2} and C\textsubscript{4} hydrocarbons. But it was difficult to find a clear trend in the case of Ni electrode.
Figure 3.12 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO$_2$ with different pressure using Cu electrode. Electrolysis was conducted with -2.5V, charge passed 200C.
Figure 3.13 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO₂ with different pressure using Ni electrode. Electrolysis was conducted with -2.5V, charge passed 200C.
<table>
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<th></th>
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<td>20.51</td>
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**Table 3.3** Faradaic efficiency(%) of products from electrochemical reduction of liquid CO\textsubscript{2} with different pressure. Electrolysis was conducted with -2.5V, charge passed 200C.
3.2.2 Effect of potential

We can observe that current density increases drastically from -1.5V in CV graph in Figure 3.2 and Figure 3.3. This makes it possible to know that CO2 reduction reaction occurs after -1.5 V. In order to investigate the effect by voltage, bulk electrolysis experiments were conducted for -2.5V, -2.25V and -2.0V. As the voltage increased, the overall Faraday efficiency showed a tendency to increase, and the smaller the potential, the less hydrogen and formic acid production could be observed. (Figure 3.14)

When calculating the faradaic efficiency in previous studies, it showed about 20 to 30% comprehension and explained the remaining as loss. The faradaic efficiency of H2 was measured to be larger than that of previous papers, which means that less loss occurred in calculation of faradaic efficiency. It can be seen that our result was measured more accurately. Also, it detects the C4 product not reported in the existing paper, and its amount is 34.95% ~ 47.38%. This discovered that the lost part could be C4 product.
Figure 3.14 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO₂ with different potential. Electrolysis was conducted with -2.5V, charge passed 200C.

<table>
<thead>
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<th>Catalyst_Potential</th>
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<th>Ni_Pt</th>
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</tr>
<tr>
<td>2-butanolone</td>
<td>1.49</td>
<td>0.43</td>
</tr>
<tr>
<td>Formic acid</td>
<td>11.62</td>
<td>13.35</td>
</tr>
<tr>
<td>Butanoic acid</td>
<td>11.63</td>
<td>21.76</td>
</tr>
<tr>
<td>total</td>
<td>93.4</td>
<td>91.51</td>
</tr>
</tbody>
</table>

Table 3.4 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO₂ with different potential. Electrolysis was conducted with -2.5V, charge passed 200C.
3.2.3 Effect of water

An experiment was also conducted to investigate the effect according to the amount of water. Bulk electrolysis was carried out at -2.5 V by placing 0.5 ml and 2.5 ml of water of Cu electrode and Ni electrode, respectively. Looking at Figure 3.15, we can observe that the amount of hydrogen generation increases as the amount of water increases, which means that the hydrogen evolution reaction has increased. This has the same meaning as the reason for not further increasing the amount of water from the optimization experiment. It is possible to reduce the hydrogen generation reaction competing with the carbon dioxide reduction reaction and to increase the efficiency of the reaction of carbon dioxide.

In the case of Cu electrode, C₄ hydrocarbons tended to decrease as the amount of water increased, which indicates that water inhibited the CO₂ reaction. Conversely, in the case of Ni electrode, C₄ hydrocarbons tended to increase as the amount of water increased. In the case of Ni electrode, CO is adsorbed and interferes with the reaction of CO₂, but it can be considered that H₂O is adsorbed in that space, and the CO₂ reduction reaction has progressed well. Butanoic acid could not be observed as the amount of water increased. It means that water interferes with the production of butanoic acid.
**Figure 3.15** Faradaic efficiency(%) of products from electrochemical reduction of liquid CO$_2$ with different amounts of water. Electrolysis was conducted with -2.5V, charge passed 200C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H$_2$ (%)</th>
<th>butanal (%)</th>
<th>MVK (%)</th>
<th>2-butanone (%)</th>
<th>Formic acid (%)</th>
<th>Butanoic acid (%)</th>
<th>total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu_0.5ml</td>
<td>41.46</td>
<td>14.94</td>
<td>12.26</td>
<td>1.49</td>
<td>11.62</td>
<td>11.63</td>
<td>93.4</td>
</tr>
<tr>
<td>Cu_2.5ml</td>
<td>67.11</td>
<td>0</td>
<td>6.32</td>
<td>0.37</td>
<td>8.74</td>
<td>0</td>
<td>82.54</td>
</tr>
<tr>
<td>Ni_0.5ml</td>
<td>30.78</td>
<td>12.25</td>
<td>12.94</td>
<td>0.43</td>
<td>13.35</td>
<td>21.76</td>
<td>91.51</td>
</tr>
<tr>
<td>Ni_2.5ml</td>
<td>42.86</td>
<td>11.03</td>
<td>25.12</td>
<td>1.03</td>
<td>18.87</td>
<td>0</td>
<td>98.91</td>
</tr>
</tbody>
</table>

**Table 3.5** Faradaic efficiency(%) of products from electrochemical reduction of liquid CO$_2$ with different amounts of water. Electrolysis was conducted with -2.5V, charge passed 200C.
3.2.4 Effect of co-solvent

While observing the progress of the experiment, when we saw that the formation of C₄ hydrocarbons was the main generation rather than the production of C₂ and C₃ product, we had to consider the reaction of ACN used for co-solvent. Therefore, in addition to ACN, we tried the experiment using N,N-dimethylformamide (DMF). As in the previous experiment, we used DMF as co-solvent, 20% in the cell, and advanced bulk electrolysis at -2.5 V. Looking at **Figure 3.16**, in the experiment using DMF, no C₄ product was observed, which tells us that ACN could react and produce C₄ product.

Next, CV graph was drawn for ACN and DMF, respectively. (**Figure 3.17**) DMF shows a lower current density than ACN, but it is a current density that electrochemical reaction is possible. Considering the possibility of ACN reaction, DMF not reacting with CO₂ It shows that a good co-solvent can be made.

Finally, when DMF was used, we conducted experiments according to the amount of water. Looking at **Figure 3.18**, the C₄ product could not be observed regardless of the amount of water. Also, when the amount of water increases, the hydrogen production reaction increases, the production of hydrogen increases, and the amount of formic acid decreases. Thus, the hydrogen production reaction and the carbon dioxide reduction reaction are competitive.
Figure 3.16 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO$_2$ with different co-solvent. Electrolysis was conducted with -2.5V, charge passed 200C

<table>
<thead>
<tr>
<th></th>
<th>H$_2$</th>
<th>butanal</th>
<th>MVK</th>
<th>2-butanone</th>
<th>Formic acid</th>
<th>Butanoic acid</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACN_Cu</td>
<td>41.46</td>
<td>14.94</td>
<td>12.26</td>
<td>1.49</td>
<td>11.62</td>
<td>11.63</td>
<td>93.4</td>
</tr>
<tr>
<td>ACN_Ni</td>
<td>30.78</td>
<td>12.25</td>
<td>12.94</td>
<td>0.43</td>
<td>13.35</td>
<td>21.76</td>
<td>91.51</td>
</tr>
<tr>
<td>DMF_Cu</td>
<td>44.01</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14.28</td>
<td>0</td>
<td>58.29</td>
</tr>
<tr>
<td>DMF_Ni</td>
<td>88.22</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.71</td>
<td>0</td>
<td>92.93</td>
</tr>
</tbody>
</table>

Table 3.6 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO$_2$ with different co-solvent. Electrolysis was conducted with -2.5V, charge passed 200C
Figure 3.17 Cyclic voltammetry of liquid CO$_2$ with different co-solvent and different working electrode at 100mVs$^{-1}$. Co-solvent was used 20% ACN and TBABF$_4$(0.5M) electrolyte (a) Cu electrode (b) Ni electrode
Figure 3.18 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO₂ with different amounts of water using DMF co-solvent. Electrolysis was conducted with -2.5V, charge passed 200C

<table>
<thead>
<tr>
<th></th>
<th>H₂</th>
<th>butanal</th>
<th>MVK</th>
<th>2-butanone</th>
<th>Formic acid</th>
<th>Butanoic acid</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF_Cu_0.5ml</td>
<td>44.01</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14.28</td>
<td>0</td>
<td>58.29</td>
</tr>
<tr>
<td>DMF_Cu_2.5ml</td>
<td>58.56</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>11.38</td>
<td>0</td>
<td>69.94</td>
</tr>
</tbody>
</table>

Table 3.7 Faradaic efficiency(%) of products from electrochemical reduction of liquid CO₂ with different amounts of water using DMF co-solvent. Electrolysis was conducted with -2.5V, charge passed 200C
Chapter 4. Conclusion

We produced a high pressure reaction vessel suitable for the experiment of liquid CO₂. While decreasing the distance between the electrodes to 5 mm, the current density increased more than 10 times compared to the previous cell and the resistance decreased from 200 ohms to 15 ohms. Liquid CO₂ observation is possible via window, and it is possible to analyze gas product using gas container.

The optimum conditions for the liquid CO₂ experiment were obtained using the manufactured high pressure cell. It was optimized under various conditions such as amount of co-solvent, amount of water, counter electrode and working electrode. As a result, it was optimum when 20% of co-solvent and 0.83% of water were put, and Pt electrode was used for the counter electrode and Cu electrode and Ni electrode were used for the working electrode.

We conducted experiments under various conditions such as pressure, voltage, amount of water, co-solvent etc. In each case we could observe the C₄ product, and we could observe that faradaic efficiency and selectivity change according to the conditions. In particular, C₄ product which could not be found in the existing paper and higher H₂ faradaic efficiency mean that accurate product measurement was done more than existing paper. Also, we discovered the possibility of ACN reaction by using DMF as a new co-solvent, and the
electric conductivity of DMF tends to be lower than that of ACN, but in the reaction of liquid CO\textsubscript{2} in which the solvent does not react showed that DMF could be used with suitable co-solvent.

In this research, it is significant in terms of the research to react electrochemically by using high pressure and liquid CO\textsubscript{2} in the electrochemical reaction of CO\textsubscript{2}, which has focused on improving the catalyst. Based on this research we expect to be able to develop new technology to make value-added hydrocarbon through electrochemical reaction using liquid CO\textsubscript{2}.
References


[8] Rakowski Dubois, Mary, and Daniel L. Dubois. "Development of


국 문 초 록

이산화탄소는 대표적인 온실가스로 지구온난화를 가속화시키고 있다. 산업시대 이후 화석연료의 사용으로 이산화탄소의 생성량이 크게 증가했다. 인류가 초래한 탄소 불균형을 해소하기 위해 전기화학적 환원을 통해 이산화탄소로부터 고부가가치 화합물을 만드는 연구가 주목받아왔다. 이산화탄소를 전기화학적으로 반응시키기 위해서는 낮은 선택성과 낮은 페러데이 효율의 문제가 해결되어야 한다. 본 연구는 이산화탄소의 물에 대한 낮은 용해도는 페러데이 효율의 저하를 가져올 수 있다는 점에 주목하였다. 이러한 문제를 해결하기 위해 이산화탄소의 낮은 용해도를 증가시키기 위해 액화 이산화탄소를 이용한 전기화학적 환원 반응을 연구하였다.

액화 이산화탄소를 이용한 전기화학 반응을 진행하기 위해 새로운 고압반응용기를 설계하였으며, 고압반응용기를 이용하여 액화 이산화탄소를 전기화학적으로 반응시키는 연구를 진행하였다. 액화 이산화탄소를 활용하여 최적의 전기화학 조건을 얻기 위해 co-solvent의 양, 물의 양, 상대 전극, 작동 전극 등 다양한 조건에서 실험을 진행하였고, 제작된 고압반응용기에서 최적의 반응 조건을 찾았다. 또한 니켈과 구리전극에 대하여 압력, 전압, 물의 양 등 다양한 조건에서 별도전해하여 C4 탄화수소를 생산해냈다. GC와 GC-MS
을 이용해 생성물을 분석하고, 패러데이 효율을 계산하였다. 또한 디메틸포름아마이드를 새로운 용매로 사용하여 기존의 co-solvent로 사용되던 아세토나이트릴의 반응 가능성을 발견하였다.

본 학위 연구는 촉매개선에 집중되어있던 이산화탄소 전기화학 반응에서 고압, 더 나아가 액화 이산화탄소를 이용해 반응을 진행시키는 연구라는 점에서 의의를 갖는다. 본 연구를 기반으로 액화 이산화탄소를 이용한 전기화학 반응을 통해 고부가가치의 탄화수소를 만드는 새로운 기술 개발할 수 있을 것으로 기대한다.

주요어: 액화 이산화탄소, 이산화탄소 환원, 고압반응용기, 전기화학 반응

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