

# Sizing and Designing of an Electrochemical reactor for carbon dioxide reduction

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**by**

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Last but not the least, I want to sincerely thank everyone who played a part, big or small,in making this project a meaningful one.

**Shubhendu Kumar**

# Abstract

The release of carbon dioxide ( $CO_2$ ) into the atmosphere poses a significant threat to the environment and ecosystems, presenting substantial challenges to sustainable development within modern industries. The escalating risks associated with global warming underscore the urgent necessity for the development of technologically and economically viable methods to reduce atmospheric  $CO_2$  levels. Among these methods, carbon capture and utilization technologies have emerged as pivotal strategies.

Within this framework,  $CO_2$  electrochemical reduction ( $CO_2$  ECR) stands out as one of the most promising approaches for mitigating the adverse effects of elevated  $CO_2$  concentrations in the atmosphere. The goal of this project is to examine  $CO_2$  reduction by electrochemical means and to develop polymer exchange membrane (PEM) cells specifically designed for  $CO_2$  reduction.

By exploring thee areas, this project aims to further the ongoing efforts to improve  $CO_2$  ECR technologies and fight climate change while promoting sustainable development.

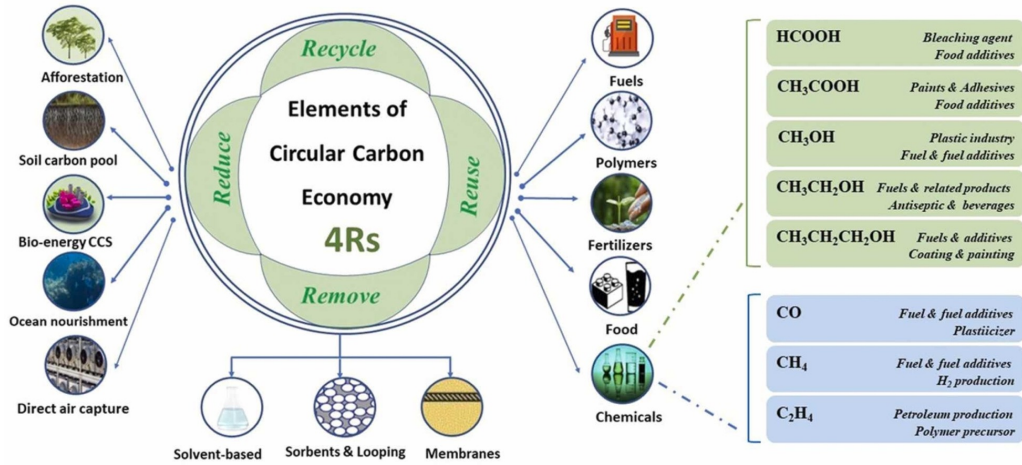


FIGURE 1: Graphical Abstract [9]

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# 1 Introduction

The concept of  $CO_2$  utilization as an alternate means of reducing carbon emissions and atmospheric  $CO_2$  as a substitute for carbon capture and sequestration (CCS) has been attracting increasing interest in recent years. The  $CO_2$  electrochemical reduction ( $CO_2$  ECR) is a propitious technology that provides various chemical productions including alcohols, hydrocarbons, and formate. These chemicals are used as long-term energy storage materials that can successfully replace the products derived from fossil fuels. Therefore, this technology can effectively close the anthropogenic carbon cycle, reduce the  $CO_2$  level in the atmosphere, and reach a carbon neutral economy.

Formic acid is an intermediary value feedstock that is used in textile industries, pharmaceutical industry and agriculture. In fact, it is an essential chemical that is used as a preservative, antibacterial agent, and in hydrogen storage  $CO_2$  conversion into manageable feed stocks for chemicals and fuels offers both a carbon neutral manufacturing process cycle and the potential for achieving an economically significant reduction in atmospheric  $CO_2$  when applied on a global scale using renewable energy resources, such as solar, wind, nuclear, and tidal technologies. The focus of this project is on the experimental work in developing a new method of electrochemically converting  $CO_2$  directly into a pure aqueous formic acid product, which can be directly used as a renewable chemical feedstock.

The reduction of  $CO_2$  to formate/formic acid has been investigated by many researchers over the past 30 years and is summarized in several excellent review papers. The research can be divided into studies involving metal electrodes and metal catalysts in the form of flat plates, high surface area electrode materials, and metal organic catalysts, and in the implementation of gas diffusion electrodes (GDEs) operating in both aqueous and non-aqueous electrolytes [11]. Presently, though, several limitations need to be overcome before the process can be profit-oriented. It has generally been found that the Faradaic efficiency of  $CO_2$  conversion to formate/formic acid is significantly lower at lower aqueous pH conditions (pH 3–5) than at higher pH conditions (pH 7–11) [11]. The reason is that the competing

cathodic hydrogen generation reaction can dominate at low pH, notably lowering the cell formic acid/formate Faradaic efficiency. Because of this limitation, none has operated an electrochemical system generating only formic acid. These systems have always produced alkali metal formate salts because of the cell electrolyte requirement. A formate salt product from these cells would have to go through a second step acidification process in order to produce formic acid.

Another formic acid/formate operating issue is that better gas diffusion electrodes need to be evolved. GDEs have the advantage in that they allow direct contact between gaseous  $CO_2$  and the electrochemical catalysts, improving mass transfer and allowing the reduction reactions to occur at significantly higher concentrations of  $CO_2$ . But the GDEs that have been reported so far have issues with liquid flooding, even after hours of operation, so they need improvement. Besides  $CO_2$  ECR technology, other technologies including photochemical, photoelectrochemical, biochemical, and thermochemical for  $CO_2$  conversion are also available. Yet,  $CO_2$  ECR has a great capability owing to its operation under ambient conditions (temperature and pressure), practical operation, and possible integration with renewable energy resources for efficient power supply.

## 1.1 Problem Statement

Carbon dioxide ( $CO_2$ ) emissions are a significant contributors to climate change and global warming. The adverse effects of  $CO_2$  emissions on the environment and human health have led to a growing urgency for developing effective methods for its reduction and utilization. Converting  $CO_2$  into value-added chemicals like formic acid offers sustainable solution to mitigate its adverse effects. One promising approach is the electrochemical reduction of  $CO_2$  to valuable chemicals such as formic acid ( $HCOOH$ ), which holds potential for various industrial applications like agriculture, chemical synthesis and energy storage. The objective of this project is to design and size an electrochemical reactor system capable of efficiently converting



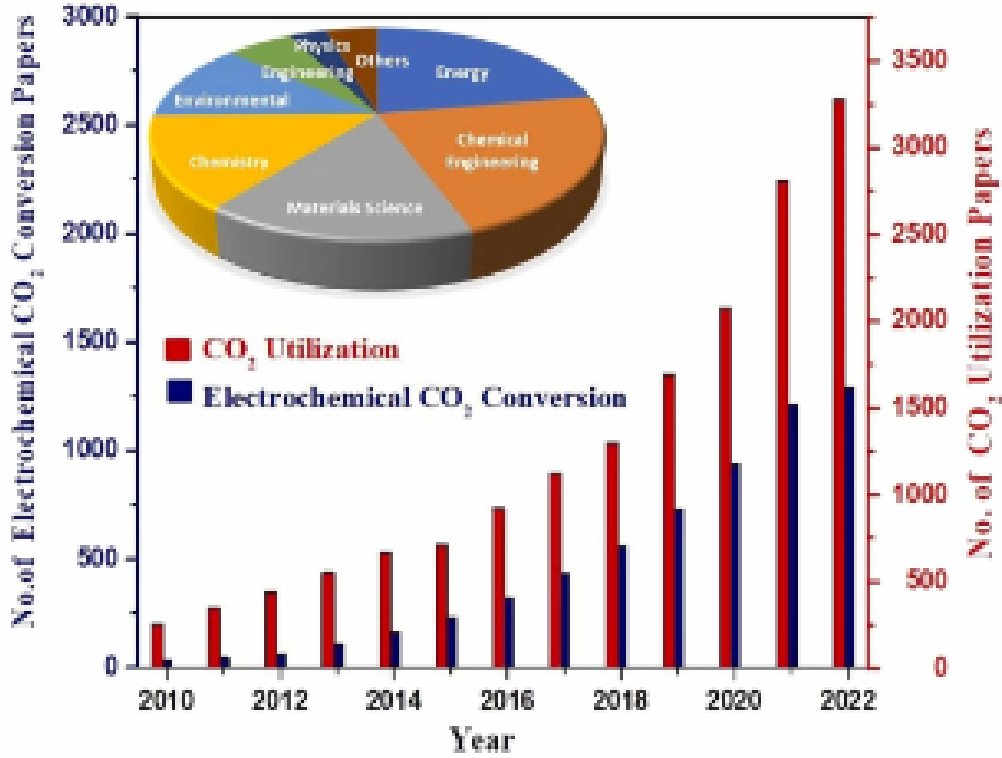


FIGURE 2: Bar diagram representing the number of publications with, “ $CO_2$  utilization” and “electrochemical  $CO_2$  conversion,” reported over the past decade, with the distribution of core content of the publications over the subject area (embedded pie chart). [9]

$CO_2$  into formic acid using a polymer exchange membrane flow cell (PEMFC). The challenge lies in optimizing the reactor design and operating conditions to achieve high conversion rates and selectivity toward formic acid production while minimize energy consumption and costs.

## 1.2 Need of the Study

The need for studying the sizing and designing of an electrochemical reactor for carbon dioxide reduction:

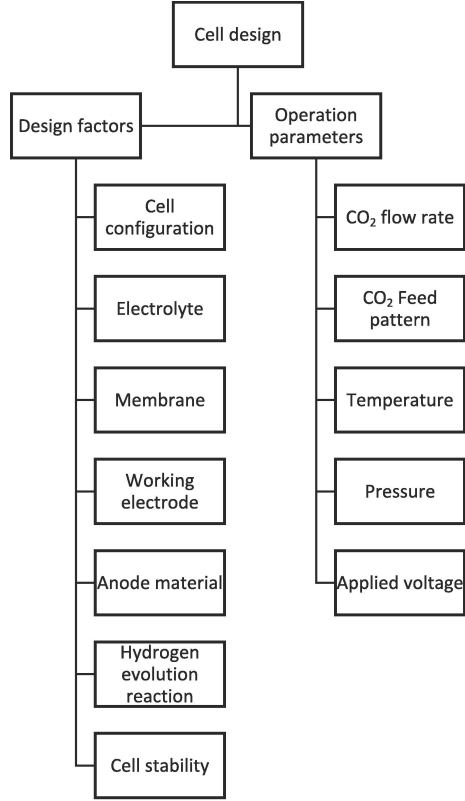


FIGURE 3: Factors affecting the cell design [4]

- **Climate Change Mitigation:** The excessive emission of carbon dioxide ( $CO_2$ ) is a significant contributor to climate change. Developing efficient methods to reduce  $CO_2$  levels is imperative for mitigating its adverse effects on the environment.
- **Renewable Energy Integration:** Electrochemical reactors offer a promising avenue for converting  $CO_2$  into valuable products using renewable energy sources such as solar or wind power. Understanding the design parameters enables the efficient integration of renewable energy into the process.
- **Resource Conservation:** Utilizing  $CO_2$  as a feedstock for valuable products not only reduces greenhouse gas emissions but also conserves natural resources by offering an alternative to traditional chemical processes that rely on fossil fuels.

- **Industrial Applications:** The products generated through  $CO_2$  reduction can have various industrial applications, including fuel production, chemical synthesis, and materials manufacturing. Optimizing the design of electrochemical reactors ensures scalability and cost-effectiveness for industrial implementation.
- **Energy Transition:** As societies worldwide strive towards a low-carbon future, technologies for  $CO_2$  reduction play a crucial role in facilitating the transition to a sustainable energy economy. Designing efficient electrochemical reactors contributes to this transition by providing a viable pathway for  $CO_2$  utilization.
- **Research and Innovation:** Studying the sizing and design of electrochemical reactors for  $CO_2$  reduction fosters innovation in materials science, electrochemistry, and process engineering. This research contributes to advancing the state-of-the-art in sustainable technologies and drives further improvements in efficiency and performance.

These points collectively underscore the significance of studying the sizing and designing of electrochemical reactors for carbon dioxide reduction, emphasizing its relevance in addressing environmental challenges, promoting sustainable development, and driving technological innovation.[\[4\]](#)

### 1.3 Literature Survey

Based on the current literature, most review articles on CO<sub>2</sub> ECR (Electrochemical reaction) to formate/formic acid are limited to the synthesis of electrocatalysts. For instance, Zhang et al. [12] reviewed the CO<sub>2</sub> ECR mechanism and the catalysts used for formate production discussing their properties and performance. While Al-Tamreh et al. [1] provided an overview of the CO<sub>2</sub> ECR into formate process, focusing on the catalysts used and providing guidelines for efficient catalysts design, however, this paper provided a general overview of the types of electrolysis cells without discussing the effect of design factors, operation parameters and cell configuration on formate production. Liang et al. [6] reviewed the CO<sub>2</sub> ECR electrolysis cells design without focusing on the cells examined specifically for formate/formic acid production and the influence of the operating parameters. Duarah et al. [3] offered a comprehensive review on the most common catalysts used for CO<sub>2</sub> ECR to formic acid. The authors outlined the effect of temperature and pressure on the conversion process and highlighted the techno-economic feasibility of formic acid production via CO<sub>2</sub> ECR. Masel et al. [7] reviewed the current advances in formate/formic acid production focusing on catalysts for industrial application. In this context, the current report summarizes the electrolysis cell designs for formate/-formic acid production, focusing on their features, advantages, and disadvantages. In addition, the review discusses the effect of operational (e.g. temperature) and design (e.g. electrode size, cell configuration) parameters for formic acid production. Endrodi et al. [5] reported the first multi-layered CO<sub>2</sub> electrolyzer stack for scaling up an electrolysis processes, effectively converting CO<sub>2</sub> into high-pressure gaseous product. Sean et al. [8] focused on reactor engineering to improve the reaction rate and scalability, and they examined reaction mechanisms using in situ and operando techniques.

## 2 Sizing and Designing of Electrochemical reactor

### 2.1 Experimental methods

Key to the work was the development of a novel 3-compartment formic acid cell design. The anode compartment operates on a DI water feed, the GDE (Gas Diffusion Electrode) cathode operates in a pH range of 7–11, and the formic acid stream in the center compartment operates at a pH of 1–5 with an input stream of DI water. The center compartment is bounded by a cation membrane on the anode compartment side and by an anion membrane on the cathode compartment side. These two membranes adjoin the cell center compartment without adding a significant voltage resistance. [11]

### 2.2 Three compartment Formic acid cell (Electrochemical reactor) configuration

The 3-compartment formic acid cell configuration detail provides a summary detail of the various anode, cathode, and center flow compartment configurations that were evaluated. The formic acid cell consisted of three compartments: a cathode compartment where the cathode operates at a pH of 7–11 using a **Sustainion**<sup>TM</sup> anionic ionomer, a center flow compartment that is held at a pH between 1 and 5 using strongly acidic ion-exchange bead electrolyte media, and an anode compartment that is even more acidic using a zero gap spacing with the anode where a Nafion membrane ionomer serves as the electrolyte.

$CO_2$  gas was introduced into the cathode compartment and flowing into the GDE cathode catalyst structure, where  $CO_2$  reacts with water coming from the center compartment through the anion membrane to the GDE catalyst/membrane interface to form formate ions. The generated formate ions ionically pass through the

anion exchange membrane into the center flow compartment. The reaction in the anode compartment is the oxidation of water into protons ( $H^+$ ) and oxygen, with the protons passing through a PFSA (perfluorinated sulfonic acid) cation exchange membrane into the center flow compartment. The protons and formate ions combine in the center flow compartment to produce formic acid. Deionized water is passed into the center flow compartment to remove the formic acid product from the cell. The formic acid cell design does not require any supporting salt electrolytes, only deionized water is used for both the anode compartment and center flow compartment. [11]

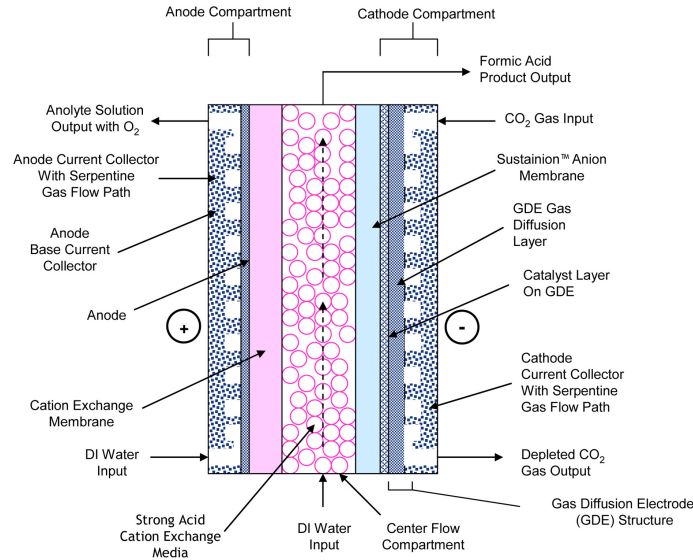


FIGURE 4: Formic acid 3-compartment cell configuration [11]

## 2.3 Formic acid cell (Electrochemical reactor) configuration summary

[11] Cell active membrane geometric area:  $5 \text{ cm}^2$

Cell operating temperature: Ambient, 20–25 °C

Cell current density:  $140 \text{ mA/cm}^2$

Cell voltage: 3.5 V

### 2.3.1 Cathode configurations

- Cathode - POCO Graphite block with serpentine flow path
- GDE Cathode - Toray paper, 50 % PTFE proofing
- GDE Catalyst - Sn Nanoparticles (99.9 %, 60–80 nm, US Research Nanomaterials, Inc.), catalyst layer air atomized onto GDE cathode with varying amounts of PTFE suspension and 5 % imidazolium-based ionomer, and 5 % carbon nanotubes.
- $CO_2$  flow rate - 20 ml/min, not humidified for ambient temperature operations.

### 2.3.2 Anode configurations

- Anode 1 - POCO Graphite block with serpentine flow path. The anode was a GDE electrode with a  $2\text{ mg/cm}^2$   $IrO_2$  catalyst (99.99 %, Alfa Aesar) onto 5 % PTFE proofing Toray paper.
- Anode 2- Titanium Grade 2 anode block with serpentine flow path. Anode screen having  $IrO_2$ -based metal oxide coating on expanded titanium (Water Star) was spot welded onto the titanium anode block.

### 2.3.3 Centre Flow Compartment

- Ion Exchange media: Amberlite IR-120 strong acid ion exchange resin fill, 620–830  $\mu\text{m}$  beads, and other selected ion exchange resins.

- Center Compartment: 1 mm thickness, 2.25 cm  $\times$  2.25 cm, 0.50 mL (empty), estimated 40 % void volume, i.e., 0.2 mL free volume with ion exchange resin.
- Center Compartment frame: Polycarbonate, machined flow path for solution flow in/out.
- DI Water feed: Selected rate of 0.03–1 mL/min into center flow compartment.

#### **2.3.4 Anolyte Recirculation Rate**

- DI water, 8–12 mL/min

#### **2.3.5 Anion Membrane**

- Dioxide Materials Sustainion™ X37 imidazolium-based anion exchange membrane: 60–80 micron thickness (wet), ion exchange capacity of 1.05 mEq/g (950 EW), membrane conductivity in water, through plane, of about 60–70 mS/cm

#### **2.3.6 Cation Membrane**

- DuPont Nafion Membranes Tested: 212, 115, 324



## 2.4 Three compartment Formic Acid cell (Electrochemical reactor) test system and isometric cell drawing

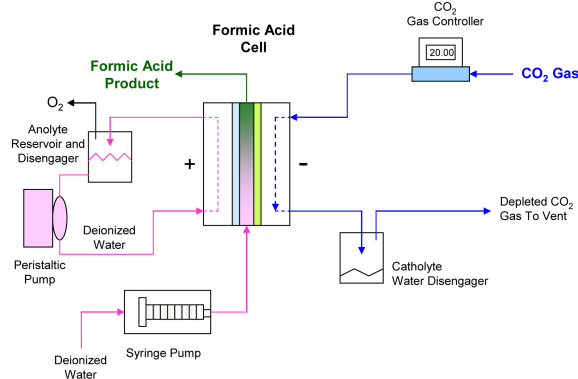


FIGURE 5: Formic acid cell experimental test system set up[11]

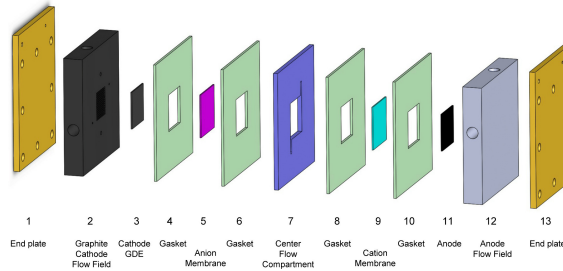


FIGURE 6: Formic acid cell exploded isometric assembly drawing [11]

## 2.5 Formic acid cell (Electrochemical reactor) compartment reactions and ion transport

The formic acid cell has a complex set of reactions that occur at the anode, the GDE cathode, and the center flow compartment. The center flow compartment is bounded by a cation exchange on the anode side and an anion exchange membrane on the cathode side. Fig. 6 shows the proposed main and secondary reactions as well as ion transport that may occur during cell operation.

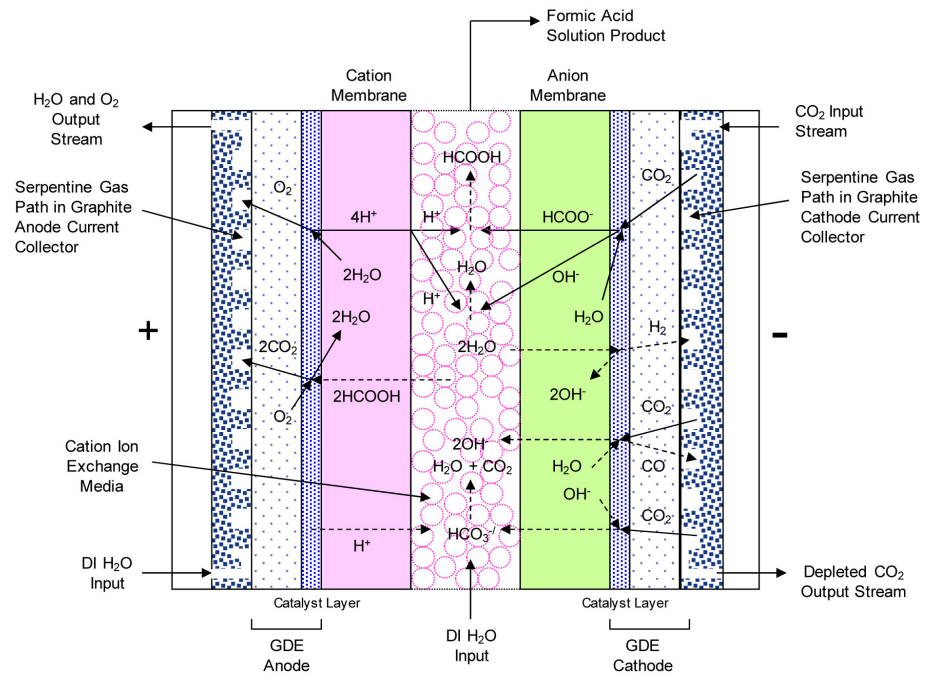


FIGURE 7: Formic acid cell configuration showing proposed electrochemical reactions and ion transport. [11]

## 3 Study methodology

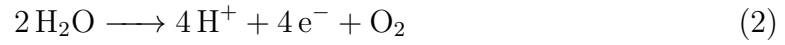
### 3.1 Reactions involved [\[11\]](#)

#### 3.1.1 Main Reactions:

The electrochemical reduction of  $CO_2$  starts when  $CO_2$  reacts with water on the cathode forming formate ( $HCOO^-$ ) and hydroxide ( $OH^-$ ) ions:



Simultaneously, the oxidation of water occurs at the anode, forming oxygen gas and protons ( $H^+$ ):

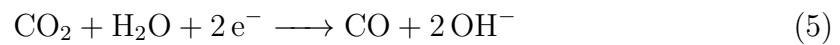


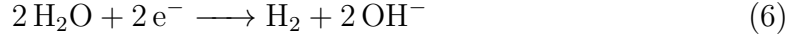
Both the formate ions and hydroxide ions migrate through the anion exchange membrane into the center flow compartment where they meet the protons produced from the anode compartment which pass through the cation membrane to yield formic acid and water:



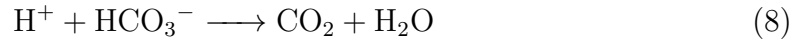
#### 3.1.2 Side Reactions:

Side reactions that can occur on the cathode:

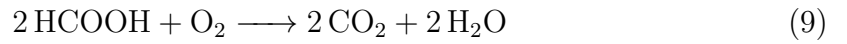




The bicarbonate ion ( $\text{HCO}_3^-$ ) can move through the anion exchange membrane where it reacts with protons produced on the anode to produce  $\text{CO}_2$ :



Formic acid losses by oxidation at the anode:



### 3.2 Material balances calculations

Given that;

$$F_{\text{CO}_2} = 20 \text{ mL/min}$$

$$F_{\text{H}_2\text{O}}(l) = 10 \text{ mL/min}$$

[11]

Considering the process for a minute,

$$V_{\text{CO}_2} = 20 \text{ mL} = 20 \times 10^{-3} \text{ L}$$

$$V_{\text{H}_2\text{O}} = 10 \text{ mL} = 10 \times 10^{-3} \text{ L}$$

Note: Reaction references will be taken from the previous section, i.e. **3.1 Reactions involved**

We know that,

$$22.4 \text{ L of } \text{CO}_2 = 1 \text{ mole of } \text{CO}_2$$

$\Rightarrow 1 \text{ L of } CO_2 = (1/22.4) \text{ moles of } CO_2$

$\Rightarrow \text{For } 20 \text{ mL } CO_2 : n_{CO_2} = 0.89285 \text{ mole}$

And,

$18 \text{ mL of } H_2O = 1 \text{ mole of } H_2O$

$\Rightarrow 1 \text{ mL of } H_2O = (1/18) \text{ mole of } H_2O$

$\Rightarrow \text{For } 10 \text{ mL of } H_2O : n_{H_2O} = 0.55555 \text{ mole}$

Therefore, it can be said that in context of (1),  $H_2O$  is the Limiting reagent.

Since the stoichiometric coefficient of both the reagents involved is 1, that implies

$n_{CO_2} \text{ reacted with } H_2O = 0.55555 \text{ moles}$

Remaining moles of  $CO_2 = 0.89285 - 0.55555 = 0.3373 \text{ moles}$

$\Rightarrow \text{Moles of } OH^- \text{ formed} = 0.55555 \text{ moles}$

Now, This  $OH^-$  ion can react with the remaining  $CO_2$  left after (1) to form the bicarbonate ion (7) which can further travel through the anion exchange membrane to the central compartment and cause the reaction (8), forming  $CO_2$  in the central compartment. Therefore, In (7),  $n_{CO_2} = 0.3373 \text{ mole}$  and  $n_{OH^-} = 0.55555 \text{ mole}$

Here, Limiting Reagent is  $CO_2$ . Since the stoichiometric coefficients of the product and the reactants are 1,  $\Rightarrow \text{Moles of bicarbonate ions formed} = 0.3373 \text{ mole}$

In (8), Assuming all of the bicarbonate ions formed in (7) participates in (8).

$\Rightarrow \text{Moles of } CO_2 \text{ formed from (8)} = 0.3373 \text{ mole}$

Also,

Moles of  $HCOOH$  formed from (4) = 0.55555 mole Assuming no formic acid losses at the anode.

Total moles of product coming out from the central compartment (carbon dioxide + formic acid) = 0.89285 mole

Selectivity for the formation of HCOOH = (Moles of HCOOH product formed) / (Moles of  $CO_2$  formed)

$$= 0.55555/0.3373$$

$$= 1.647$$

Therefore, yield % of formic acid =  $(0.55555/0.89285) \times 100 = 62.22\%$

Now, Considering the overall reaction i.e. the formation of formic acid from water and carbon dioxide .

Let A be  $H_2O$  and B be  $CO_2$  . Volume of the reactor (V) =  $5 \text{ cm}^3 = 0.005 \text{ L}$

$n_A = 0.55555 \text{ mole}$ ,  $n_B = 0.89285 \text{ mole}$

We know,

Concentration =  $\text{Mole} \div \text{Volume}$

Therefore,

$$C_{A0} = n_A \div V$$

$$\text{and } C_{B0} = n_B \div V$$

$$C_{A0} = 111.11 \text{ mole/L and } C_{B0} = 178.57 \text{ mole/L}$$

Therefore, Conversion ( $X_A$ ) =  $(0.3373 \div 0.55555) = 0.60714 \text{ or } 60.71\%$

$$C_A = C_{A0} \times (1 - X_A) = 111.11 \times (1 - 0.60714) = 43.6506 \text{ mol/L}$$

and,

$$C_B = C_{B0} \times (1 - X_A) = 178.57 \times (1 - 0.60714) = 70.1530 \text{ mol/L}$$

Now, Solving for k (reaction rate constant) using the kinetics equation of 2nd order reaction for  $t = 60 \text{ s}$ ,

Therefore, on calculation;  $k = 0.000231 \text{ mole}/(\text{Ls})$

### 3.3 Energy balances calculations

$\Delta G^0$  values for chemical species in kJ/mole: [10]

CO : -137.2

CO<sub>2</sub> : -394.4

H<sup>+</sup> : 0

H<sub>2</sub>O : -237.1

O<sub>2</sub> : 0

OH<sup>-</sup> : -157.2

HCO<sub>3</sub><sup>-</sup> : -586.6

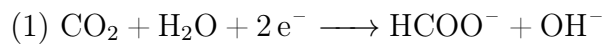
HCOO<sup>-</sup> : -355.2

For  $\Delta G^0$  values of HCOOH ,  $\Delta S^0 = 128.95 \text{ J}/(\text{moleK}) = 0.12895 \text{ kJ}/(\text{moleK})$

$\Delta H_{HCOOH} = -424.72 \text{ kJ/mole}$

$$\begin{aligned}\Delta G^0 &= \Delta H_{HCOOH} - T(\Delta S^0) \\ &= -424.72 - (298)(0.12895) = -463.1471 \text{ kJ/mole}\end{aligned}$$

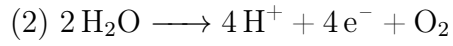
#### 3.3.1 Cathode reactions:



$$\begin{aligned}\Delta G_1^0 &= \Delta G_{products}^0 - \Delta G_{reactants}^0 \\ &= (\Delta G_{\text{HCOO}^-}^0 + \Delta G_{\text{OH}^-}^0) - (\Delta G_{\text{CO}_2}^0 + \Delta G_{\text{H}_2\text{O}}^0) \\ &= (-355.2 + (-157.2)) - (-394.4 + (-237.1)) \\ &= -512.4 - (-631.5)\end{aligned}$$

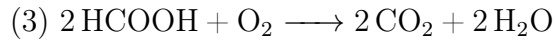
$$= 119.1 \text{ kJ/mole}$$

### 3.3.2 Anode reactions:



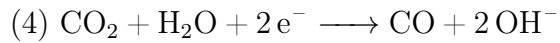
$$\Delta G_2^0 = 0 - (2 \times \Delta G_{\text{H}_2\text{O}}^0)$$

$$= 474.2 \text{ kJ/mole}$$



$$\Delta G_3^0 = ((2 \times (-394.4) + 2 \times (-237.1)) - (2 \times (-463.1471)))$$

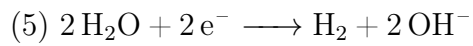
### 3.3.3 Side reactions:



$$\Delta G_4^0 = (-137.2 + (-314.4)) - (-394.4 + (-237.1))$$

$$= -451.6 - (-631.5)$$

$$= 179.9 \text{ kJ/mole}$$



$$\Delta G_5^0 = (0 + (2)(-157.2)) - ((2)(-237.1))$$

$$= -314.4 + 474.2$$

$$= 159.8 \text{ kJ/mole}$$

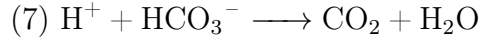


$$\Delta G_6^0 = -586.6 - (-394.4 - 157.2)$$

$$= -35 \text{ kJ/mole}$$

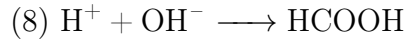


### 3.3.4 Centre Flow Compartment:



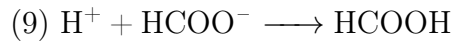
$$\Delta G_7^0 = (-631.5 - (0-586.6))$$

$$= -44.9 \text{ kJ/mole}$$



$$\Delta G_8^0 = (-237.1 - (-157.2))$$

$$= -79.9 \text{ kJ/mole}$$



$$\Delta G_9^0 = (-463.1471 - (-355.2))$$

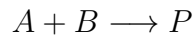
$$= -107.9471 \text{ kJ/mole}$$

Therefore, the summation of all the values of change in Gibbs' free energy among the reactions happening in the electrochemical reactor is:

$$\sum_{i=1}^n \Delta G_i^0 = 364.142 \text{ kJ/mole}$$

## 3.4 Understanding the kinetics of the reactions occurring in the reactor

For a 2nd order reaction, [\[2\]](#)



$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[P]}{dt}$$

$$\frac{d[A]}{dt} = -k[A][B]$$

Since initial concentration of both water and carbon dioxide is not the same, there-

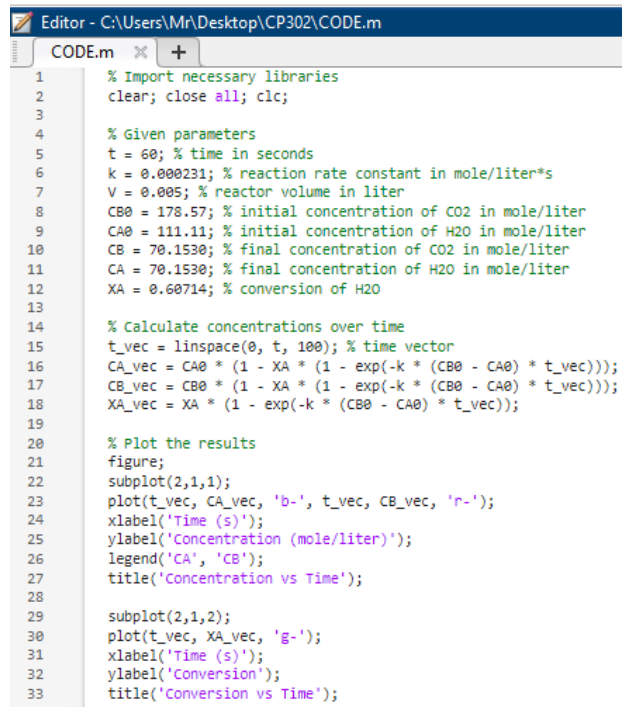
fore; on integrating we get,

$$\frac{1}{[B]_o - [A]_o} \ln \frac{[B][A]_o}{[A][B]_o} = kt$$

$$\ln \frac{[B][A]_o}{[A][B]_o} = k ([B]_o - [A]_o) t$$

### 3.5 Kinetics modelling using MATLAB

The following MATLAB simulation was used for modelling the primary reaction of the process, that is carbon dioxide reacting with water to give formic acid. In here, the concentration of A: H<sub>2</sub>O and B: CO<sub>2</sub> is taken into consideration and with time (for t = 60 s), the change in the initial concentration is seen. Same case is applied for conversion ( $X_A$ ), and its value is also simulated with respect to time.



```

1 % Import necessary libraries
2 clear; close all; clc;
3
4 % Given parameters
5 t = 60; % time in seconds
6 k = 0.000231; % reaction rate constant in mole/liter*s
7 V = 0.005; % reactor volume in liter
8 CB0 = 178.57; % initial concentration of CO2 in mole/liter
9 CA0 = 111.11; % initial concentration of H2O in mole/liter
10 CB = 70.1530; % final concentration of CO2 in mole/liter
11 CA = 70.1530; % final concentration of H2O in mole/liter
12 XA = 0.60714; % conversion of H2O
13
14 % Calculate concentrations over time
15 t_vec = linspace(0, t, 100); % time vector
16 CA_vec = CA0 * (1 - XA * (1 - exp(-k * (CB0 - CA0) * t_vec)));
17 CB_vec = CB0 * (1 - XA * (1 - exp(-k * (CB0 - CA0) * t_vec)));
18 XA_vec = XA * (1 - exp(-k * (CB0 - CA0) * t_vec));
19
20 % Plot the results
21 figure;
22 subplot(2,1,1);
23 plot(t_vec, CA_vec, 'b-', t_vec, CB_vec, 'r-');
24 xlabel('Time (s)');
25 ylabel('Concentration (mole/liter)');
26 legend('CA', 'CB');
27 title('Concentration vs Time');
28
29 subplot(2,1,2);
30 plot(t_vec, XA_vec, 'g-');
31 xlabel('Time (s)');
32 ylabel('Conversion');
33 title('Conversion vs Time');
34

```

FIGURE 8: MATLAB simulation

## 4 Results

Apart from the information of sizing of the reactor from the literature, the material balances, the energy balances and the kinetics based modelling of the reactor was done as part of designing of the system. The major results are as follows:

### 4.1 Material balances

Selectivity for the formation of  $\text{HCOOH} = 1.647$

Yield % of  $\text{HCOOH} = 62.22 \%$

Conversion of the limiting reagent (i.e.  $\text{H}_2\text{O}$ ) =  $60.71 \%$

### 4.2 Energy balances

For each of the reactions occurring in the reactor, the change in Gibbs' free energy was calculated and the summation of all of them came out to be:

$$\sum_{i=1}^n \Delta G_i^0 = 364.142 \text{ kJ/mole}$$

The positive overall Gibbs' free energy implies that the overall process is non-spontaneous i.e. it can not take place without the help of external aid (here, voltage supplied to the cell). The energy provided by the potential difference of the cell helps it to perform the process so that the necessary results can be obtained, i.e. the formation of formic acid.

### 4.3 Kinetics modelling

The following images show the final output of the code written on MATLAB pertaining to the simulation done for the primary reaction of the reactor.

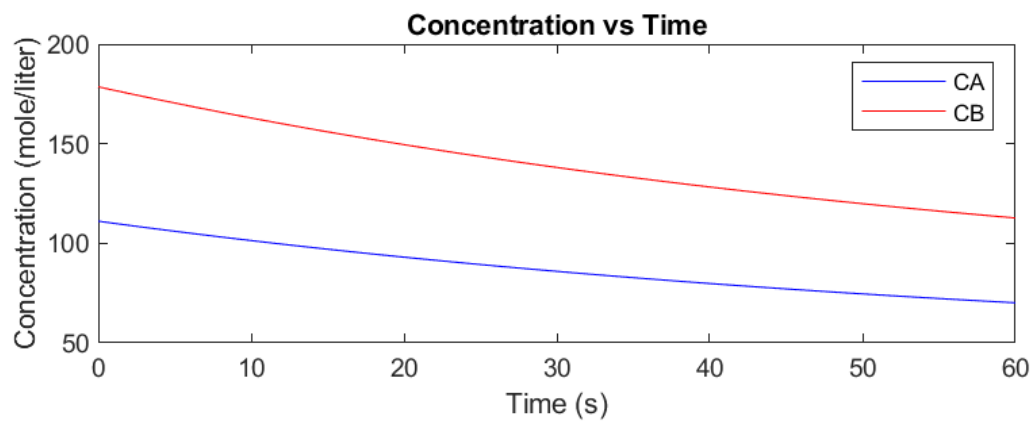


FIGURE 9: Graph of Concentration vs time

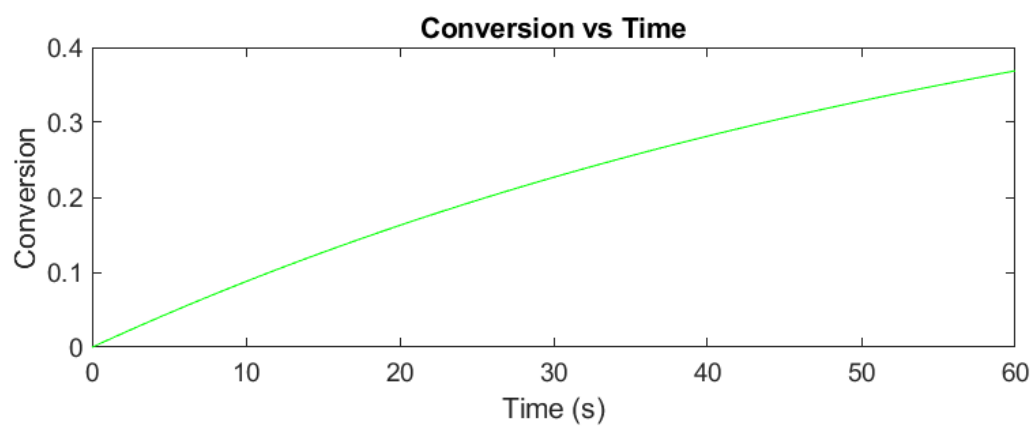


FIGURE 10: Graph of Conversion vs time

## 5 Conclusion

In conclusion, the design and analysis of the electrochemical reactor for carbon dioxide reduction to formic acid present promising prospects for sustainable chemical synthesis. Through the sizing and designing, along with comprehensive material and energy balances, the feasibility of the reactor's operation has been established. Additionally, the modeling of kinetics has provided valuable insights into the primary reaction occurring in the reactor, enhancing our understanding of the process dynamics.

Formic acid, the key product of this electrochemical process, holds significant advantages and importance in the chemical industry. Firstly, its versatility as a chemical feedstock renders it indispensable in various industrial applications, including the production of pharmaceuticals, pesticides, and synthetic fibers. Furthermore, formic acid serves as a crucial component in the manufacturing of leather, textile, and rubber products, highlighting its diverse utility.

Moreover, formic acid stands out for its environmentally friendly attributes. As a readily available and biodegradable compound, it offers a sustainable alternative to conventional chemical intermediates, contributing to the reduction of carbon footprint and environmental pollution. Its potential as a hydrogen storage medium further underscores its role in facilitating the transition towards renewable energy systems. By harnessing electrochemical methods for formic acid synthesis, this project aligns with the broader objectives of green chemistry and sustainable development. The utilization of renewable energy sources, coupled with the conversion of carbon dioxide into value-added products, embodies a paradigm shift towards a more eco-conscious chemical industry.

In essence, the successful implementation of the electrochemical reactor for formic acid production underscores its significance as a viable pathway for carbon dioxide utilization and sustainable chemical synthesis.

## 6 Possible Future Works

- **Modelling of the complete reactor system:** The current work done for the kinetics modelling was done for the primary reaction of the reactor only. Using the concepts of process design and chemical reaction engineering in an extensive way, the overall modelling can be done for the reactor.
- **Operation cycles of the reactor:** After the modelling has been done, practical experimentations can be started for checking the performance of the reactor using, Single pass operation and Recirculated center flow compartment mode operation.
- Work can be done for improving the yield and conversion of the reactor system using the concepts of Chemical Reaction Engineering.

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