

CP302

CAPSTONE PROJECT

SIZING AND DESIGNING OF ELECTROCHEMICAL REACTOR FOR CO₂ REDUCTION

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Problem Statement

- CO₂ emissions are major contributors to climate change.
- Converting CO₂ into formic acid offers a sustainable solution.
- Electrochemical reduction of CO₂ to formic acid is promising.
- It has applications in agriculture, chemical synthesis, and as a preservative and antibacterial agent.

Problem Statement

- **Objective:** Design and size an electrochemical reactor system.
- **Challenge:**
 - i) Optimize design and conditions for high conversion rates and selectivity, minimizing energy consumption and costs.
 - ii) Major challenge came with the lack of data in the main paper on which the project takes reference from, the paper being on experimental results but I had to do the theoretical calculations and simulations.

Literature review

- Many different research papers were studied regarding the electrochemical reduction of carbon dioxide into formic acid which focussed on using various types of cells like H-type cell, microfluidic flow cell but I chose PEM (Polymer Exchange Membrane) flow cell for my project.
- The PEM flow cell has many advantages over other electrochemical reactors, like it being a practical reactor for converting CO_2 into HCOOH , and can be used on an industrial scale.
- The use of GDE in PEM flow cells suppresses the mass transport limitation allowing a higher concentration of CO_2 in the cathodic compartment, which increases the reaction rate, and the cell efficiency. (Khaled et. al)

Literature review

- GDEs (Gas Diffusion Electrodes) 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 .
- GDEs have been reported to have issues like liquid flooding which can be avoided by using an anion exchange membrane (in our project, SustainionTM). (Masel et. al)
- The cell design is modified so that the cathode is held at a pH of 7–11 so that hydrogen formation is suppressed, and employed an acidic center compartment where the resultant product formate stream is acidic, so we can directly produce formic acid rather than a formate salt product. Only deionized water is used in the cell design, and not requiring any salt additions as electrolytes.

Sizing and Designing of electrochemical reactor

1. Three compartment Formic acid cell configuration (PEM flow cell with Sustainion™ membrane)

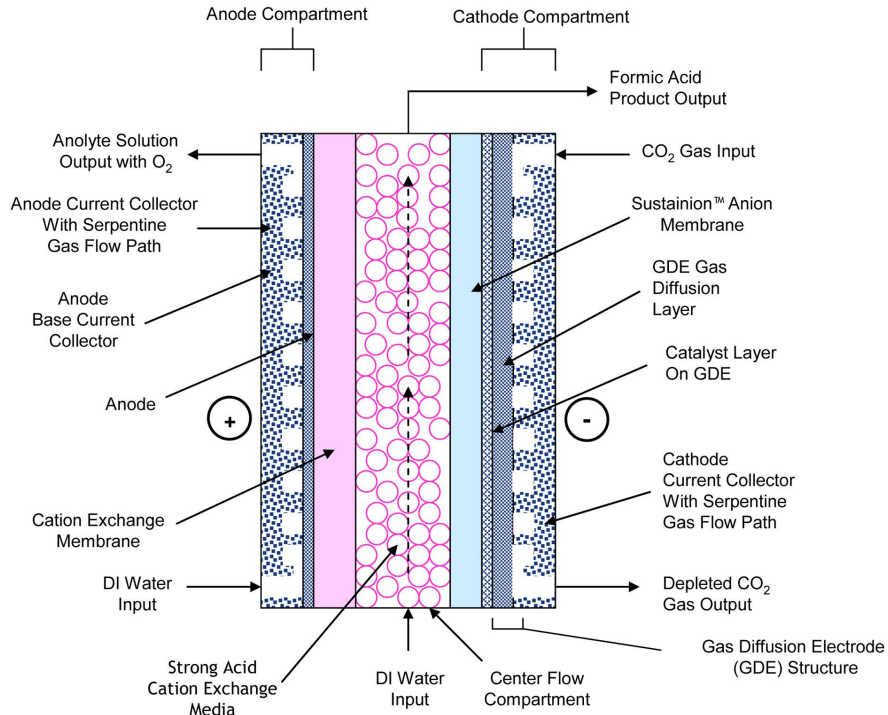


Fig. 1 Three compartment configuration

Reference -.

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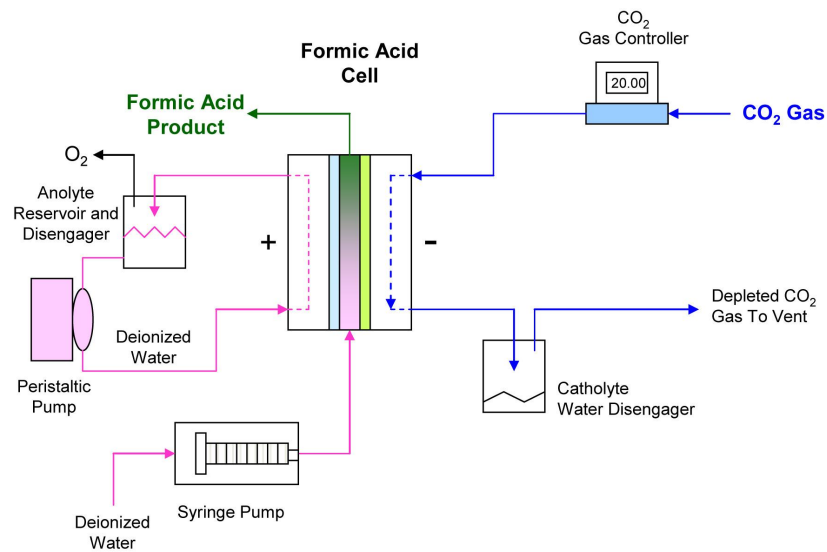


Fig. 2 Flow system setup

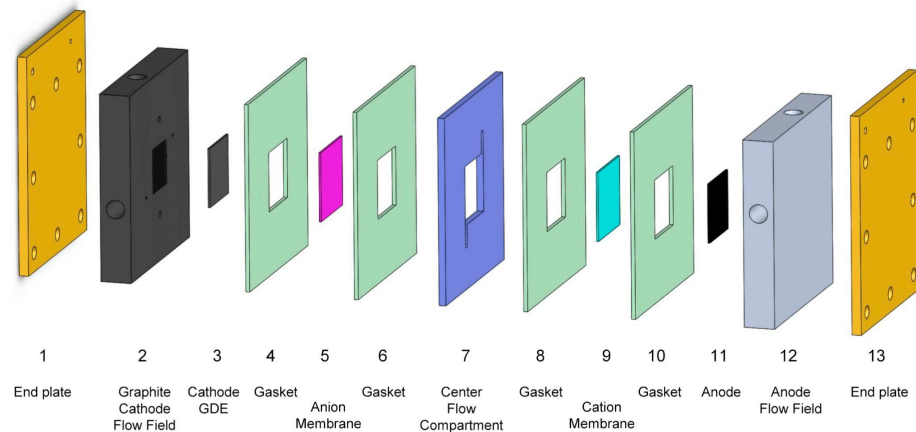
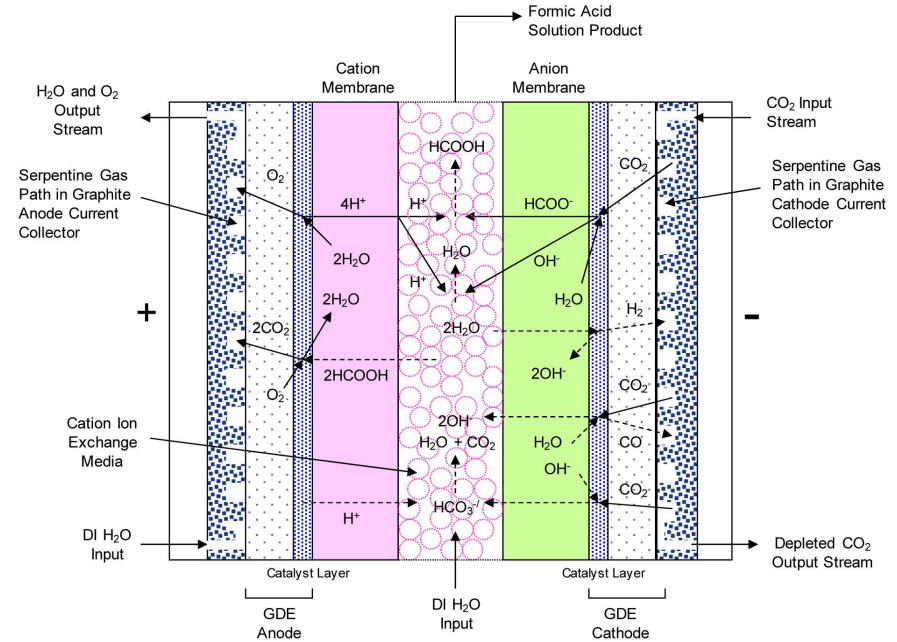


Fig. 3 Isometric assembly drawing

Reference -

https://www.sciencedirect.com/science/article/pii/S2212982017300665?ref=pdf_download&fr=RR-2&rr=85e8c1c56c6a59e4

- Cell active membrane geometric area: 5 cm²
- Cell operating temperature: Ambient, 20–25 °C
- Cell current density: 140 mA/cm²
- Cell voltage: 3.5 V [1]



Reference -

https://www.sciencedirect.com/science/article/pii/S2212982017300665?ref=pdf_download&fr=RR-2&rr=85e8c1c56c6a59e4

Fig. 4 Proposed chemical reactions and ions transport

2. Chemical reactions involved -

MAIN REACTIONS: [1]

The electrochemical reduction of CO₂ starts when CO₂ 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:



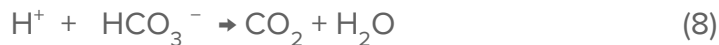
2. *Chemical reactions involved -*

SIDE REACTIONS:

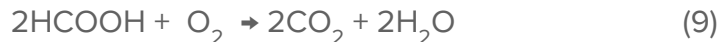
Side reactions that can occur on the cathode:



The bicarbonate ion (HCO_3^-) can move through the anion exchange membrane where it reacts with protons produced on the anode to produce CO_2 :



Formic acid losses by oxidation at the anode:



3. *Material balances*

Given that;

$$F_{\text{CO}_2} = 20 \text{ mL/min [1]}$$

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

Considering the process for a minute,

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

$$V_{\text{H}_2\text{O}} (\text{l}) = 10 \cdot 10^{-3} \text{ L}$$

We know that, 22.4 L of CO_2 (g) = 1 mole of CO_2

$$\Rightarrow (n)_{\text{CO}_2} = 0.89285 \text{ moles}$$

And,

$$18 \text{ mL of H}_2\text{O} (\text{l}) = 1 \text{ mole of H}_2\text{O} \Rightarrow (n)_{\text{H}_2\text{O}} = 0.55555 \text{ moles .}$$

3. *Material balances*

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} reacted with $\text{H}_2\text{O} = 0.55555$ moles

=> Remaining moles of $\text{CO}_2 = n'_{\text{CO}_2} = 0.89285 - 0.55555 = 0.3373$ moles

=> Moles of OH^- formed = 0.55555 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.**

3. *Material balances*

Therefore,

In (7) $n_{\text{CO}_2} = 0.3373$ moles and $n_{\text{OH}^-} = 0.55555$. Here, Limiting Reagent is CO_2 .

Since the stoichiometric coefficients of the product and the reactants are 1,

=> Moles of bicarbonate ions formed = 0.3373 moles

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

=> Moles of CO_2 formed from (8) = 0.3373 moles

Also, Moles of HCOOH formed from (4) = 0.55555 moles

Assuming no formic acid losses at the anode. Total moles of product coming out from the central compartment (carbon dioxide + formic acid) = 0.89285 moles

Selectivity for the formation of HCOOH = (Moles of HCOOH product formed) / (Moles of CO_2 formed) = $0.55555/0.3373 = 1.647$ [\[10\]](#)

Therefore, yield % of formic acid = $(0.55555/0.89285)*100 = 62.22\%$ [\[10\]](#)

3. *Material balances*

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 = Mole \div Volume . Therefore, $C_{A0} = n_A \div V$ and $C_{B0} = n_B \div V$

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

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

$C_A = C_{A0} \times (1 - X_A) = 111.11 \times (1 - 0.60714) = 43.6506 \text{ mol/L}$ and, $C_B = C_{B0} \times (1 - X_A) = 178.57 \times (1 - 0.60714) = 70.1530 \text{ mol/L}$

3. *Energy balances*

ΔG^0 values for chemical species in kJ/mol: [\[13\]](#)

CO : -137.2 , CO₂ : -394.4 , H⁺ : 0 , H₂O : -237.1 , O₂ : 0 , OH⁻ : -157.2 , HCO₃⁻ : -586.6 , HCOO⁻ : -355.2

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

$$\Delta H^0_{\text{HCOOH}} = -424.72 \text{ kJ/mol} \Rightarrow \Delta G^0 = \Delta H^0_{\text{HCOOH}} - T(\Delta S^0) = -424.72 - (298)(0.12895) = -463.1471 \text{ kJ/mol}$$

For a reaction,

$$\Delta G^0 = \Delta G^0_{\text{products}} - \Delta G^0_{\text{reactants}}$$

For each of the reactions involved, the change in Gibbs' free energy was calculated.

Then, summation of all values were done, which came out to be $\sum(\Delta G^0) = 364.142 \text{ kJ/mole}$

The positive overall Gibbs' free energy implies that the overall process is nonspontaneous 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.

Simulation of the kinetics of the reaction using MATLAB

```
Editor - C:\Users\Mr\Desktop\CP302\CODE.m
CODE.m
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');
```

Fig.5 MATLAB code

Results of the simulation

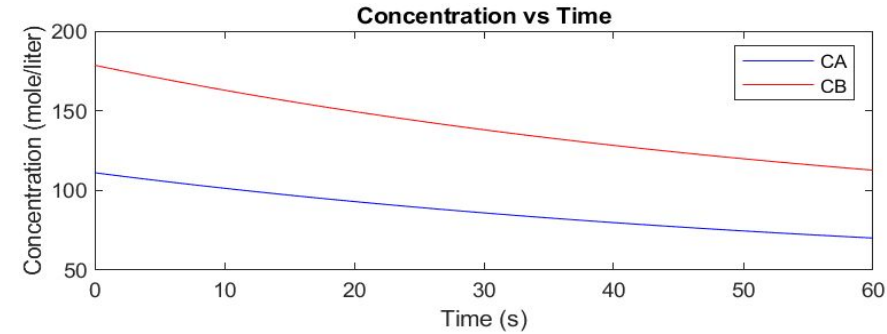


Fig. 6 Concentration (C_A and C_B) Vs Time

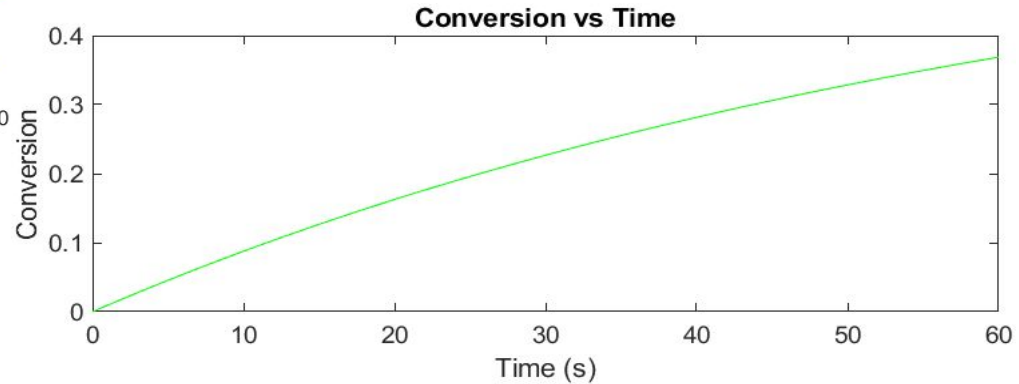


Fig. 7 Conversion Vs Time

Future work

- **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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THANK YOU!