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Conversion of CO_2 to Formic Acid Using a Solid-State Electrolyte Device at Different Voltages

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Abstract

A potential environmentally beneficial method to reduce greenhouse gas emissions is the electrochemical conversion of CO_2 to useful products like formic acid (HCOOH). However, a number of challenges must be addressed in order to synthesize formic acid at high concentrations. One of them is the generation of formate mixtures in conventional liquid reactors, which requires extensive purification processes to generate pure formic acid. A three-compartment reactor that introduces a solid-state electrolyte (SSE) between the anode and cathode has been developed to solve this issue. Numerous factors, such as the flow rates at which liquid and gas are utilized, have an impact on the reactor's performance. In this investigation, pure CO_2 gas was used with flow rates of 0.05 to 0.15 lpm entering the anode and 0.035–0.095 lpm of deionized water (DI) entering the cathode compartment at different voltages (2,98 V and 4,42 V). The results of this study demonstrate that a higher CO_2 gas flow rate increased Faraday Efficiency (FE), as did the rise in DI flow rate. Furthermore, the inclination of HCOOH concentration was related to the increasing CO_2 flowrate, but it declined along with the rise of DI flow rate. This trend was similar for the two voltages used in this experiment, but the reactor's performance at 4,42 V was slightly better than its performance at 2,98 V. The highest formic acid concentration that could be produced in this experiment was 3.3% with a CO_2 gas flow rate of 0.15 lpm and a DI water flow rate of 0.035 lpm.

Keywords: *Carbondioxide; electrochemical; formic acid; three-compartment reactor*

1. Introduction

The primary contributor to air pollution and the greenhouse gas effect is the excessive global production of carbon dioxide (CO_2), especially as a result of the burning of fossil fuels for energy and power generation [1]. When CO_2 accumulates in the atmosphere, it can absorb and then release infrared radiation, which results in global warming. The rise in sea level, the intensity of extreme weather, changes in precipitation patterns, and other changes to the earth's surface are all driven by an increase in the global temperature. Warmer air will multiply pollutants, spores, and pollen, resulting in an increase in allergies and respiratory diseases [2]. Therefore, it is essential to reduce the amount of stored CO_2 and other GHG emissions.

Future carbon emissions reductions have been viewed as possible with the use of carbon capture and storage (CCS) [3]. However, despite three decades of development, technology still encounters challenges because of high design costs and unfeasible operations for applications like improved oil and gas recovery. The uncertainty also relates to the durability of CO_2 storage and whether this gas will be permanently deposited beneath [2].

Creating technology that lowers CO_2 emissions by turning them into specific, economically viable chemical and fuel end products is one strategy to lessen ambient atmospheric CO_2 levels [4]. The investigation is being carried out to develop a new technique for electrochemically converting CO_2 directly into a pure aqueous formic acid product that may be used immediately as a sustainable chemical feedstock. It is also proposed that formic acid can be utilized as a convenient means of hydrogen storage.

Over the past 30 years, a large number of researchers have studied the reduction of CO_2 to formic acid, which has been compiled in a number of outstanding review studies [5, 6, 7]. One of the studies is involving gas diffusion electrodes (GDEs) that operate in both aqueous and non-aqueous electrolytes [8,9].

However, a few challenges must be overcome before technology becomes available for commercial purposes. The faradaic efficiency (FE) of converting CO_2 to formic acid has often been shown to be much lower in less aqueous pH circumstances (pH 3-5) than at higher pH values (pH 7–11). Because the competing cathodic hydrogen production reaction can become dominant at low pH levels, the cell's formic acid FE is greatly reduced. This restriction has prevented anyone from operating an electrochemical device that produces exclusively formic acid. The necessity of the cell electrolyte in these systems has always resulted in the production of alkali metal-formate salts. To convert a formate salt product from these cells into formic acid, a second-stage acidification procedure would be necessary.

Another issue with the operation of formic acid and formate is the requirement for better gas diffusion electrodes (GDE). The benefit of GDEs is that they enable direct interaction between gaseous CO_2 and electrochemical catalysts, which enhances mass transfer and permits reduction reactions to take place at much greater CO_2 concentrations. However, even after hours of operation, the GDEs that have been recorded so far have liquid flooding difficulties, so they require improvement.

To overcome the problem, two significant advancements were made to reduce the obstacles to commercialization. First, the frequently employed GDE structure was altered by including an anion exchange membrane, enabling the operation of a GDE cathode without liquid flooding. In order to prevent hydrogen from forming, the cell design has been adjusted to hold the cathode at a pH between 7 and 11, and an acidic center compartment was used where the resulting formate stream is acidic, allowing us to make formic acid instead of formate salts. The cell design only uses DI water and does not call for the addition of salts as electrolytes.

The performance of the reactor depends on some parameters, just like current densities, center compartment single-pass flow rate, and the flow rate of CO_2 inside the reactor [10]. This study was performed to determine the effect of its parameters on the electrolysis process of CO_2 at different voltages. It will be used as a basic reference for the commercialization of this technology.

2. Experimental Section

2.1 Materials

Chemicals and Materials: Deionized water (DI water) (18.2 MΩ cm-1, from Milli-Q water system); formic acid (reagent grade >95% Sigma-Aldrich); sodium hydroxide (standardized 0.1 N, LabChem Inc. for titrations); 1% phenolphthalein solution (LabChem); Amberlite® IR120 (hydrogen form, Sigma-Aldrich); Dowex® 50WX2 (hydrogen form, Sigma-Aldrich); Dow Amberlite® IRN-77 (ion exchange resin, nuclear grade, VWR Scientific); Duolite® Resin C433 (Alfa Aesar); Dupont Nafion@ 115, 212, and 324 membranes (Ion Power Inc.). Liquid CO_2 ($NuCO_2$, Stuart, FL) was used as the gas supply and vaporized for use in the lab.

Analytical: Formic acid concentrations were determined by titration using a 0.1N standardized NaOH reagent, phenolphthalein indicator, and a Class A 50 mL burette. Formic acid sample size weights and volumes for the titration were large enough to obtain titration volumes of about 20 mL or more, so as to minimize the error in the formic acid concentrations to less than 1%.

The equipments used in the research is shown in table 1 and figure 1.

Table 1. The specification of equipments

No	Name of Equipments	Specification	Vendor/suplier
1	CO2 Electrolizer	5 cm^2 flexolyzer – FA Formic Acid Cell - Solid-state electrolyte - Sustainion anion-membrane - Nafion membrane - Anode GDE	Dioxide Materials
2	Power Supply	Switchable DC regulated 3010-III, - Output : 0-30 V / 0-10A - Input : AC 220V + 10%	Onglai Fixtool
3	Peristaltic Pump	21092020 CW-CCW pump 3x5" 24V	Awallaptop
4	Syringe pump	TOP – 5510 - AC power supply : 0,1 A - Flow rate range : 0,1 – 150 mL/h - Dosage range : 0,01 – 99,99 μg/kg/min	TOP Corporation
5	CO_2 tank	Diameter : 14cm High : 69,5cm Weigh : 16kg Capacity : 7L/5kg Type : with handle	Union
6	Gas flow regulator	0 – 1 Lpm	A Care Technology

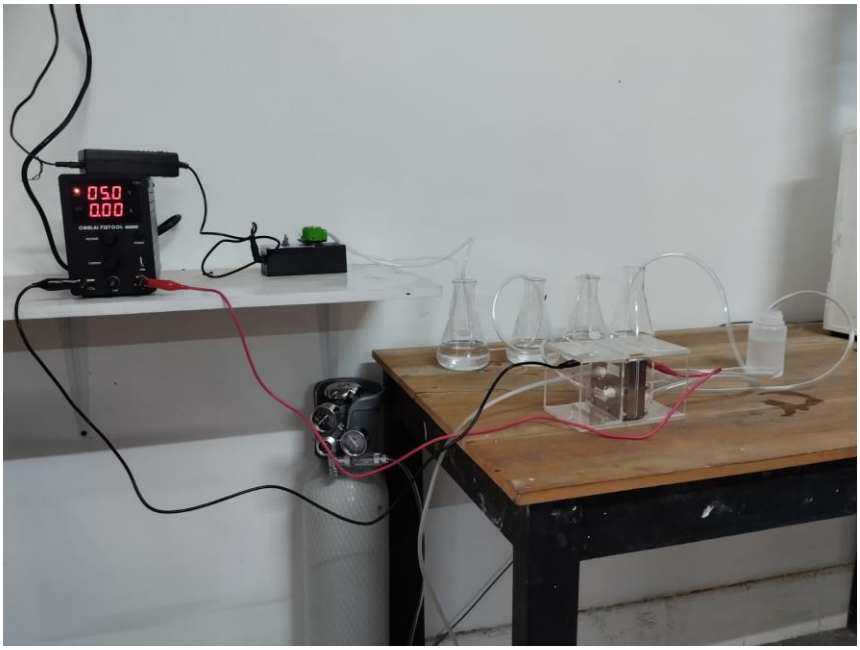


Figure 1. The Experimental Apparatus

2.2 Methods

The operation configuration of the CO_2 electrolysis equipment into formic acid is shown in Figure 2.

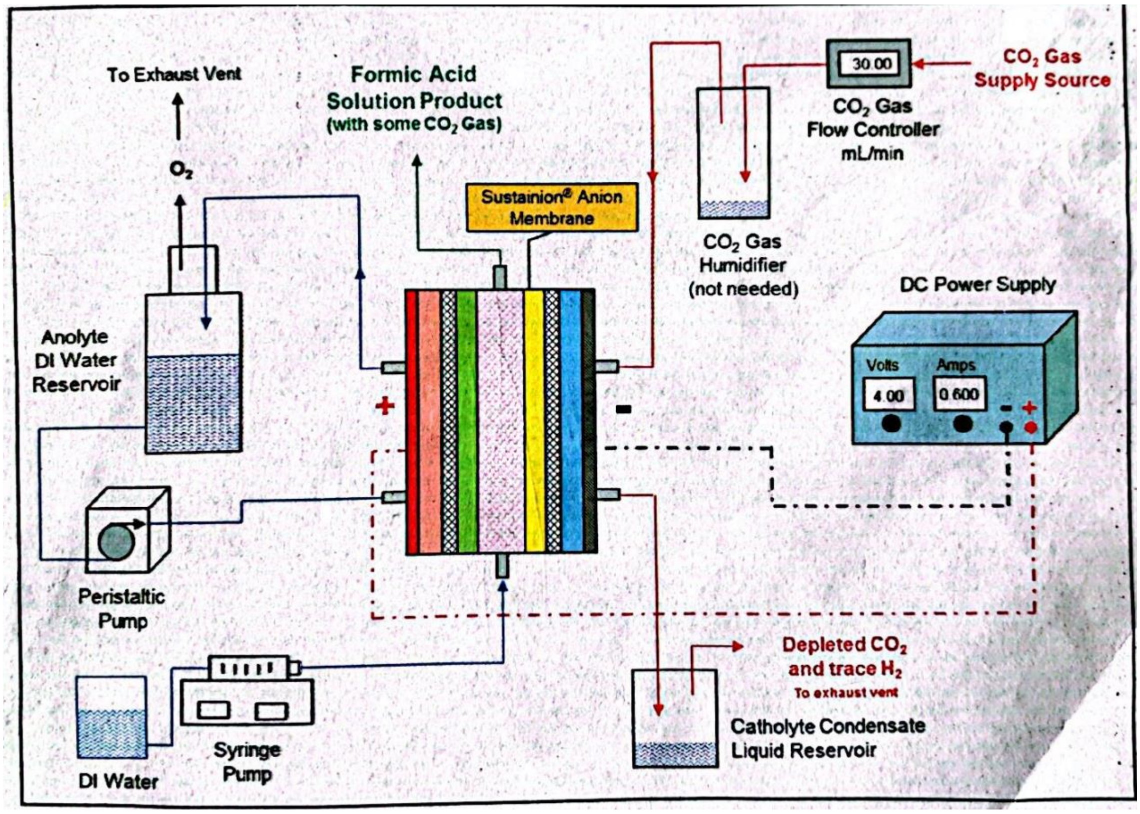


Figure 2. The configuration of equipments

This effort involved the construction of a novel designed three-compartment formic acid cell structure using solid-state electrolyte (SSE). The anode compartment functions with a specific DI water feed, the GDE cathode functions with varied CO_2 feed rates, and the formic acid stream in the center compartment flows with an input flow with a distinct DI water rate. On the sides opposing the anode compartment and the cathode compartment, cation and anion membranes, respectively, define the boundaries of the center compartment. The reactor's performance at two different voltages was evaluated using the Faraday efficiency of the process and the formic acid concentration in the center-compartment effluent.

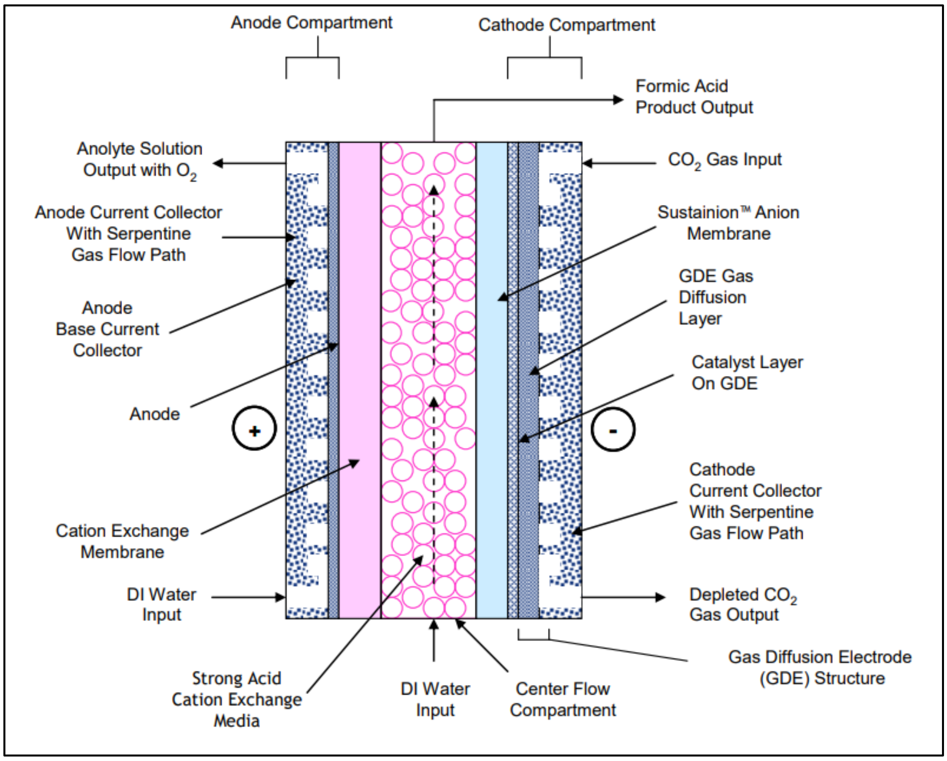


Figure 3. The three-compartment formic acid cell diagram

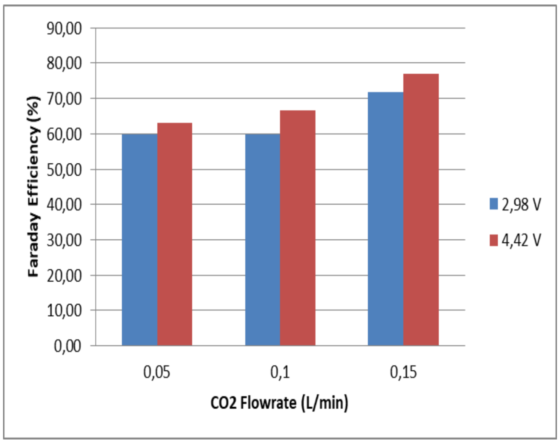
Figure 3 illustrates the three-compartment formic acid cell diagram. The formic acid cell was composed of three compartments: an anode compartment that is even more acidic using a zero-gap spacing or center part with the anode, and a Nafion membrane ionomer as the electrolyte. The cathode compartment operates using a Sustainion™ anionic ionomer. When CO_2 and DI water are combined, formate ions are created. DI water enters the cathode compartment from the center compartment, travels across the anion membrane, and then makes contact with the catalyst and membrane through the GDE cathode catalyst structure.

To get to the center flow compartment, the formate ions that are generated travel ionically over the anion exchange membrane. Water in the anode compartment oxidizes to produce oxygen gas and protons (H^+). After that, the protons pass across a cation exchange membrane made of perfluorinated sulfonic acid to enter the central flow compartment. Formic acid is created in the central flow compartment by the combination of protons and formate ions. To extract the formic acid product, deionized water is injected into the cell's center flow compartment. There is no need for any additional salt electrolytes because the formic acid cell design employs only deionized water in the anode compartment and center flow compartment.

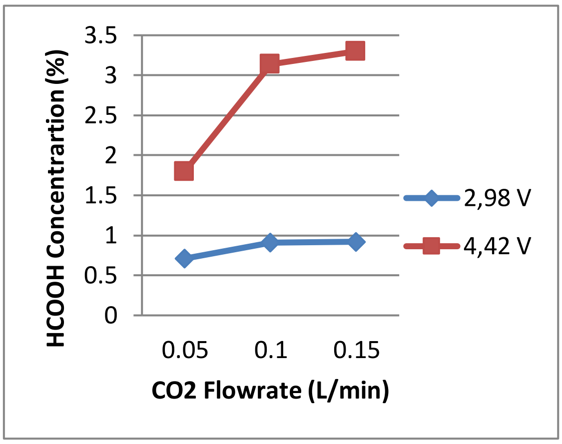
3. Results and Discussion

3.1. Influence of the gas flow rate on the electrolyzer performance

In order to investigate the effect of the CO_2 gas flow rate in the reactor, the DI water flow rate was set at 0,035 ml/min with two different voltages (2,98 V and 4,42 V). A sample from the center compartment was taken after each experiment, which lasted two hours (120 minutes), and it was analyzed in order to find out how the device produced HCOOH. The main indicators used to determine the reactor's performance in the experiment were the HCOOH concentration and the Faraday efficiency (FE). Fig. 4a and 4b shows the progress of the experiment over 2 hours.



4a



4b

The graphs provide the relationship between Faraday Efficiency (FE) and HCOOH production with CO_2 flow rates at different voltages in the electrolyzer.

It is clear to see from figure 4a that the FE of the reactor rises in a row with the rate of CO_2 that flows into the reactor, both at voltages of 2,98 V and 4,42 V. For low voltage, the FE trend is slowly upward from 59,71% at 0,05 lpm to 71,79% at 0,15 lpm gas flow rate. It is not much different with the rise of FE at high voltage, which slightly increases from 62,98% at 0.05 lpm to 76,86% at 0.15 lpm.

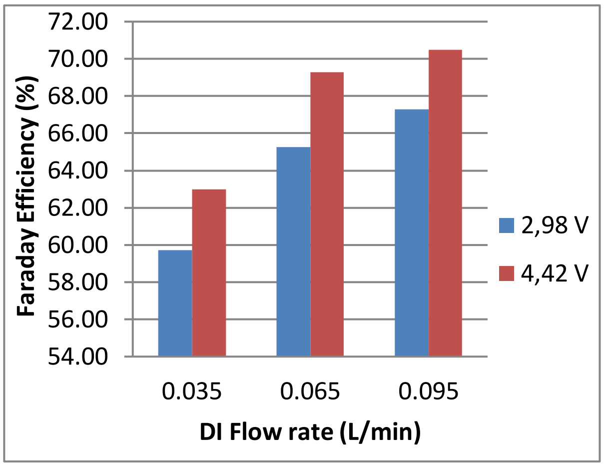
Figure 2b illustrates that the production of HCOOH in the reactor at a low voltage slightly inclines from 0,71% to 0,92% in relation to CO_2 flow rates, which climb from 0,05 lpm to 0,15% lpm. It is different with the trend of HCOOH production at high voltage, which drastically increased from 1.8% to 3.3% along with the escalating of CO_2 flow rates, from 0.05 lpm to 15 lpm.

The increase in Faraday efficiency and HCOOH concentration in the reactor output is in line with the flow rate of CO_2 to the cathode because CO_2 gas acts as a reactant, which reacts with water from the middle compartment, becomes formate ions, and interacts with protons from the anode, forming formic acid. More reactants lead to the creation of more products containing formic acid.

At a larger voltage (4.42 V), the concentration of HCOOH formed increases drastically compared to a smaller voltage (2.98 V), because the high voltage causes an electrochemical reduction reaction of CO_2 to form formate (HCOO-) and hydroxide (OH-) ions. The higher the voltage at the cathode, the easier it is. However, this drastic increase in HCOOH concentration was not accompanied by a significant increase in Faraday efficiency, so this process cannot be said to be very effective and efficient.

3.2. Influence of the liquid flow rate on the reactor performance

The effect of the liquid (DI) flow rate on the electroliser performance in terms of Faraday Efficiency (FE) and HCOOH concentration was performed by the experiment with two different voltages (2,98 V and 4,42 V) and the gas flow rate at 0,05 ml/min. The process occurred in a three-compartment reactor for 120 minutes, respectively. Fig. 5a and 5b shows the progress of the experiment over 2 hours.



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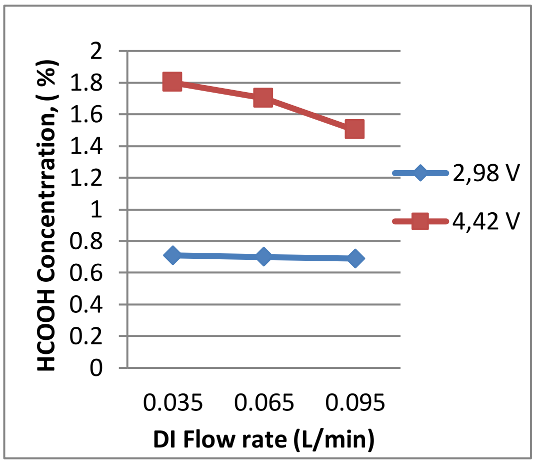

5b

Figures 5a and 5b show the trends of Faraday efficiency (FE) and HCOOH concentration in the reactor as the liquid flow rate (DI) fed to the middle compartment increases under two different voltages.

Overall, the FE value experiences a linear increase along with the increase in DI flow rate, both for voltages of 2.98 V and 4.42 V, as in Figure 5a. Meanwhile, in Figure 5b, it can be seen that the concentration of HCOOH produced in the reactor decreases as the liquid flow rate increases, both at small and large voltages.

Figure 5a shows that at voltages of 2.98 V and 4.42 V, the faraday efficiency increases with the DI flow rate. At low flow rates (0.035 lpm), the cell operating at low voltage (2.98 volts) produces a small Faraday efficiency as well (59.71%). This value increases as the DI flow rate increases, where the peak is at a DI flow rate of 0.095 lpm, which has an FE of 67.29%. This trend also applies to larger voltages, where the highest FE value of 70.48% is achieved at a DI flow rate of 0.095 lpm.

On the other hand, increasing the DI flow rate in the middle compartment actually reduces the concentration of HCOOH produced, both at low and high voltages. For a voltage of 2.98V, the decreasing trend in HCOOH concentration is not significant, from 0.71% to 0.69% when the DI flow rate is increased from 0.035 lpm to 0.095 lpm. However, the decrease in HCOOH concentration at a voltage of 4.42 V was more significant, from 1.8% to 1.5% as the DI flow rate increased from 0.035 lpm to 0.095 lpm. This decrease occurs because as the concentration of formic acid in the central compartment of the cell increases, a larger fraction of the formic acid product may cross into the anolyte compartment of the cell through the cation membrane, where the formic acid can be lost through a CO_2 reformation reaction.

4. Conclusion

In the CO_2 electrolysis process, the concentration of formic acid formed increases as the CO_2 flow rate increases and the deionized water flow rate decreases, where a voltage of 4.42 V shows slightly better results than 2.98 V. The highest concentration of formic acid obtained was 3.3% at a CO_2 flow rate of 0.15 liters/minute and a deionized water flow rate of 0.035 liters/minute at a voltage of 4.42 V.

For the CO_2 electrolysis process to become HCOOH, further research needs to be carried out with greater voltage variations. Apart from that, it is necessary to carry out continuous testing over a long period of time to comprehensively determine the performance of the three-compartment reactor equipment.

The innovative architecture of the formic acid cell suggests a possible path for the commercial application of formic acid in the future as a chemical feedstock that is sustainable for producing downstream chemicals and as a workable chemical-based energy storage medium for the production and storage of hydrogen.

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