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Research Paper

The Electrochemical Conversion of CO_2 into Methanol with $KHCO_3$ Electrolyte Using Membrane Electrode Assembly (MEA)

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Abstract
The electrochemical conversion process of CO_2 into methanol using Membrane Electrode Assembly (MEA) has been done. The MEA consists of a Pt/C catalyst in the cathode and a Cu_2O-ZnO/C catalyst in the anode. The electrodes were made using the spraying method and then characterized using Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) methods to determine the ECSA (Electrochemical Surface Area) and electrical conductivity values. Besides that, also X-Ray Diffraction (XRD) and Scanning Electrode Microscopy – Energy Dispersive X-Ray (SEM-EDX) analysis was to determine the crystal and morphological structure. The voltammogram from CV analysis indicated that the ECSA value on the Pt/C electrode was 7.2 m^2/g and the Cu_2O-ZnO/C electrodes as 0.69 m^2/g. The electrode's electrical conductivity value with Pt/C catalyst was 1.15 x 10^{-3} S/cm, and the electrode with Cu_2O-ZnO/C catalyst was 0.80 x 10^{-3} S/cm. The results of the XRD analysis confirmed the presence of Cu_2O and ZnO on the Cu_2O-ZnO/C electrode and Pt on the Pt/C electrode. Meanwhile, the results of the SEM-EDX analysis showed that the Pt/C catalyst was spread more evenly with a larger percentage than Cu_2O and ZnO. The result of the conversion of CO_2 to methanol was measured using a methanol analyzer with variations in $KHCO_3$ electrolyte concentration, variation of temperature operation, and variation of time operation. The best methanol concentrations after distillation process were 79.06 w/v %, with 1 M $KHCO_3$, at room temperature and 2 hours operation.

Keywords
MEA, $KHCO_3$, Electrochemical Conversion, CO_2, Methanol

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1. INTRODUCTION

The increasing reliance on fossil fuels has led to a surge in CO_2 emissions into the atmosphere, which is a critical contributor to global climate change and a range of other environmental problems. Currently, the concentration of CO_2 in the atmosphere surpasses 400 parts per million (ppm), making it essential to take immediate action to reduce its levels (Gao et al., 2016). Among several approaches investigated to address this issue, CO_2 hydrogenation has garnered considerable attention, demonstrating promising outcomes. Nonetheless, this method requires high temperature and pressure conditions and involves considerable hydrogen consumption, thereby reducing its efficiency. Alternatively, CO_2 reduction to hydrocarbon compounds (e.g., CH_3OH, HCOOH, CO, and CH_4) at room temperature and atmospheric pressure, employing either solar or electrical energy as the driving force, has been developed as an alternative technique (Tuyen and Le, 2011).

The electrochemical reduction process of CO_2 has emerged as a promising solution to tackle energy and environmental challenges. This process operates at room temperature, providing an excellent way to store electrical energy while minimizing CO_2 emissions. Moreover, it can utilize water as a proton source (Aeshala et al., 2013). Compared to other CO_2 reduction methods, electrochemical reduction offers several advantages, including the selectivity of the cathodic product, and the tools and materials used are simple and economical.

Among various electrodes used in CO_2 reduction, Cu elec-

trodes have attracted considerable attention due to their economic feasibility and high selectivity for the formation of CH_3OH (Huang Fu et al., 2019). However, Cu electrodes are prone to deactivation over time due to impurities from the reactant source that close the catalyst pores, leading to the formation of unwanted by-products. To address this issue, Cu electrodes can be modified with Zn to stabilize Cu atoms and remove impurities (Albo and Irabien, 2016).

One method of the electrochemical reduction of CO_2 to produce CH_3OH is using the Membrane Electrode Assembly (MEA). The MEA is commonly used in fuel cells, serving as the central component of the electrochemical reaction. It comprises two electrodes, the cathode (reduction electrode) and the anode (oxidation electrode), which are positioned on opposite sides of the electrolytic membrane (Rohendi et al., 2013). The electrochemical reaction in cathode and anode can be described in Equations (1) to (3) (Hazarika and Manna, 2019):

Cathode Reaction :

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2OE^0 = 0,38V \quad (1)$$

Anode Reaction:

$$3H_2O \rightarrow 6H^+ + 6e^- 3/2O_2E^0 = 1,23V \quad (2)$$

Overall Reaction: :

$$CO_2 + 2H_2O \rightarrow CH_3OH + 3/2O_2E^0 = 1,61V \quad (3)$$

In addition, bicarbonate salts such as $KHCO_3$ and $NaHCO_3$ can be employed as supporting electrolytes for CO_2 reduction. Studies have shown that $KHCO_3$ concentration significantly affects the electrochemical reduction of CO_2, with the highest CO_2 reduction faradic efficiency being obtained at a low $KHCO_3$ concentration of 0.1 mol L^{-1}. These findings have been supported by measurements using both galvanostatic Hori et al. (1987) and potentiostatics (Zhong et al., 2017). The aim of this study was to convert CO_2 to methanol using an electrolyzer which contain MEA, with a Pt/C catalyst in the cathode and a Cu_2O-ZnO/C catalyst in the anode of MEA.

2. EXPERIMENTAL SECTION

2.1 Materials

Cu_2O Catalyst Powders (Sigma Aldrich), ZnO Catalyst Powders (Sigma Aldrich), Carbon Vulcan XC-72R (Fuel Cell Store), Ammonium Bicarbonate (Sigma Aldrich), 2-Propanol, PTFE Emulsion 60%wt (Fuel Cell Store), Carbon Paper Avcarb P75T (Fuel Cell Store), Pt/C Catalyst Powder (Fuel Cell Store), Nafion 117 Membrane (Fuel Cell Store), NaOH, $KHCO_3$, CO_2.

2.2 Methods

2.2.1 Catalyst and Electrode Preparations

Cu_2O and ZnO catalyst powders (Sigma Aldrich) with ratio 1:1 was mixed with carbon vulcan XC-72R (Fuel Cell Store). The percentage catalyst in carbon vulcan is 40 wt%, with catalyst loading of 1 mg/cm^2. The mixture was then milled for 3 hours in an HEM Machine to produce the Cu_2O-ZnO/C catalyst composite (Albo and Irabien, 2016).

To prepare the electrodes, Carbon Vulcan XC-72R was mixed with 2-Propanol and Ammonium Bicarbonate (Sigma-Aldrich), stirred in an ultrasonic homogenizer for 30 minutes, and 0.08 g PTFE emulsion 60 wt% (Fuel Cell Store) was added and stirred for an additional 10 minutes to create ink. This ink was sprayed onto Avcarb P75T Carbon Paper (Fuel Cell Store) and sintered at 350°C for 3 hours to create a Gas Diffusion Layer (GDL). The anode used a Pt/C catalyst with a loading of 1 mg/cm^2, while the cathode used a Cu_2O-ZnO/C catalyst with the same loading and a mass ratio of Cu_2O to ZnO of 1:1. To create the catalyst mixture, the catalyst powder was mixed with 2-propanol, nafion 20 wt% solution, and was agitated for 30 minutes in an ultrasonic homogenizer. PTFE was then added and stirred for 10 minutes to create ink, which was sprayed onto the GDL until the electrodes were coated with Pt/C (cathode) and Cu_2O-ZnO/C catalyst (anode). Finally, the electrodes were sintered at 350°C for 3 hours (Carmo et al., 2019).

2.2.2 Electrode Characterization

The electrode (consisting of cathode and anode) underwent X-ray diffraction (XRD) analysis (Rigaku MiniFlex 600) to characterize its structure, Scanning Electron Microscopy–Energy Dispersive X-Ray (SEM-EDX) analysis to morphology and quantitative compositional information, while the ECSA was determined by measuring its catalytic activity using the CV method. The PGSTAT204 Potentiostat (Autolab Metrohm) was used to conduct the test, with an Ag/AgCl electrode serving as a reference for comparison to the working electrode. Platinum rods were utilized as counter electrodes, while Cu_2O-ZnO/C and Pt/C electrodes were utilized as working electrode. The electrolyte utilized was 1 M NaOH.

The electrical conductivity of the electrode was determined using the EIS method. The measurement data was then used to create a Nyquist plot using NOVA software, with the real impedance on the x-axis and imaginary impedance on the y-axis. The Nyquist plot was fitted to the equivalent circuit required for analysis. To obtain the total real resistance of the electrode, EIS measurements were used to determine both the solution resistance (Rs) and charge transfer resistance (Rp). The Potentiostat/Galvanostat PGSTAT204 Metrohm tool was used to collect the data, which measures the electrode's response to electric charge in the electrolyte solution and records the conducted electric current.

2.2.3 MEA and Stack Preparation

The MEA used in the experiment had a size of 10 x 10 cm^2 and consisted of two electrodes (anode and cathode) and an electrolyte membrane. To assemble the MEA, the two electrodes were combined on an activated Nafion-117 membrane (Fuel Cell Store) and subjected to heat at 135°C and 2000 psi for 3 minutes. The assembled MEA was then installed in a stack with the following arrangement: endplate, gasket, reactant chamber, gasket, current collector, MEA, current collector, gasket, reactant chamber, gasket, and endplate. During the conversion process, a voltage of 1.8 V was used.

2.2.4 The Electrochemical Conversion of CO_2 to CH_3OH

In this study, $KHCO_3$ utilized as an electrolyte on the cathode side. During the experiment, $KHCO_3$ concentrations of 0.1, 0.3, 0.7, 1.0, and 1.3 M were used in the cathode compartment, while H_2O was used in the anode compartment. A mass flow controller was used to regulate the CO_2 flow rate at 60 mL/min, and a power supply with a voltage of 1.8 V with current density of 0,2 mA/cm^2 was used as the source of electrical energy. The electrolyte was pumped into the cell with a peristaltic pump, while CO_2 was continuously flowed into the cathode compartment. The experiment was run for 120 minutes, and liquid samples were collected from the electrolyte tank at the outlet of the electrochemical cell. These samples were analyzed using an Analox AM5 methanol analyzer to determine the optimal concentration of $KHCO_3$ electrolyte.

Once the optimum concentration of $KHCO_3$ solution was determined, the study proceeded to investigate the effects of varying operating temperature and time on the reduction of CO_2 to CH_3OH. The operating temperature was varied at room temperature (25°C), 40, 50, and 60°C using the optimal concentration of $KHCO_3$. Furthermore, the operating time was varied at 2, 4, 6, and 8 hours at the optimal concentration and temperature.

3. RESULTS AND DISCUSSION

3.1 Electrode Fabrication and Characterization

Electrochemical conversion of CO_2 to methanol can be achieved using MEA with a Cu_2O-ZnO/C catalyst composite on the cathode and Pt/C on the anode, along with a Nafion-117 membrane as an electrolyte, which can facilitate the conversion process with greater efficiency (Ganesh, 2014). In this conversion process, Cu_2O acts as the primary catalyst to facilitate CO_2 reduction, while ZnO serves as a stabilizing catalyst. Meanwhile, the Pt/C catalyst on the anode is the best catalyst for the HER process and is commonly used in fuel cell applications. The Nafion-117 membrane is typically used as an electrolyte membrane in Direct Methanol Fuel Cells, with the advantage of reducing methanol crossover. The product of fabrication of electrode and MEA are presented in Figure 1.

3.2 X-Ray Diffraction (XRD) Characterization

X-Ray Diffraction was utilized to determine both of the crystal structure and size of the particle of the catalysts, as evidenced

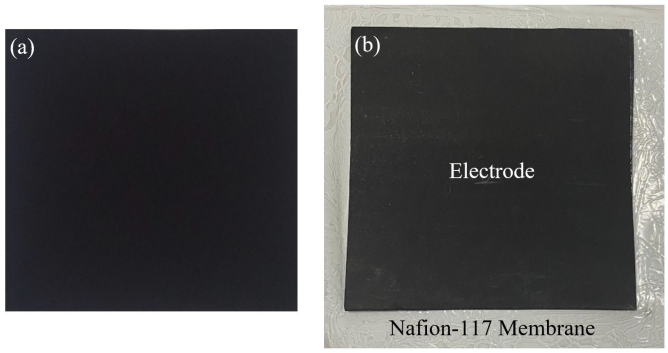

Figure 1. The Electrode with Cu_2O-ZnO/C Catalyst; (b) Membrane Electrode Assembly (MEA) with Cu_2O-ZnO/C Catalyst at Cathode and Pt/C Catalyst in Anode

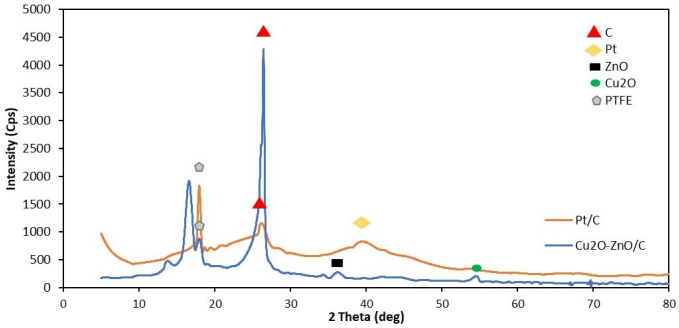

Figure 2. XRD Diffractogram of Electrode with Catalyst Cu_2O-ZnO/C and Pt/C

by the 2θ position. The results of the XRD measurement on the electrode using Cu_2O-ZnO/C and Pt/C catalysts can be found in Figure 2.

Based on the results shown in Figure 2, Cu_2O-ZnO/C and Pt/C catalysts exhibit distinctive diffraction peaks that have been identified through comparison with the JCPDS database. In Figure 2(a), the diffractogram of the electrode with Cu_2O-ZnO/C catalyst reveals a diffraction peak, which corresponds to the presence of Cu_2O as confirmed by JCPDS number 34-1354 (Babamoradi et al., 2018). Similarly, Figure 2(b) displays the diffractogram of the Pt/C catalyst, which exhibits a diffraction peak at 2θ = 50.37, indicating the presence of Pt as validated by JCPDS number 87-0646 (Li et al., 2021). Additionally, the diffraction peaks observed at 2θ = 20-30 and 2θ = 28 in Figure 2 are attributed to the presence of PTFE (JCPDS number 47-2217 12) (Hussain et al., 2012) and carbon (JCPDS number 50-0926) (Taha et al., 2021), respectively.

The XRD analysis data can also be used to calculate the crystal size using the Debye-Scherrer equation (French et al., 2005; Sivagami and Asharani, 2022). Based on the calculations, the smallest crystal size is possessed by Pt metal from the Pt/C electrode, which is 1.296 nm, while the crystal size of Cu_2O from the Cu_2O-ZnO/C electrode is 18.100 nm and ZnO is

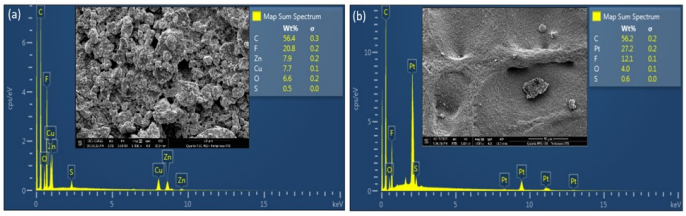

Figure 3. The Analysis Results of SEM-EDX from the Electrode (a) Cu_2O-ZnO/C, and (b) Pt/C

7.542 nm. The crystal size has an impact on the particle size, where generally, smaller crystal sizes correspond to smaller particle sizes. In addition to affecting the particle size, the crystal size also influences the surface area, whereby smaller crystal sizes result in larger surface areas (Rohendi et al., 2022).

3.3 SEM-EDX Characterization

The characterization using SEM aims to observe the morphology of the Cu_2O-ZnO/C and Pt/C electrodes, while the EDX analysis results show the percentage of each component at the analyzed spot. The SEM-EDX characterization results of both electrodes are shown in Figure 3.

Based on Figure 3, it can be observed that the electrode with Pt/C catalyst is more evenly dispersed, while the electrode with Cu_2O-ZnO/C catalyst tends to agglomerate. The agglomeration occurring in the electrode with Cu_2O-ZnO/C catalyst is due to the composite nature of the Cu_2O and ZnO catalysts, as well as their larger particle size compared to Pt/C. This is consistent with the XRD analysis results. The catalyst agglomeration in the Cu_2O-ZnO/C electrode leads to a smaller surface area and easier cracking (Rohendi et al., 2022).

According to the findings of the EDX analysis (Figure 3), the Cu_2O and ZnO percentages observed in the Cu_2O-ZnO/C electrode are significantly lower compared to the percentage of Pt in the Pt/C electrode. This discrepancy can be attributed to particle size variations. The larger particle size of Cu_2O and ZnO results in a smaller percentage, as indicated by the EDX analysis results. Apart from the catalyst element, it can be seen that there are other elements such as F and S which come from Nafion solution and PTFE, and O element which comes from the catalyst oxide.

3.4 Measurement of Catalytic Activity Using the CV Method

The CV method is used to determine the catalytic activity of the electrode by forming a voltammogram. Based on the available voltammogram, the ECSA value of the electrode can be determined. The experiments were conducted using a scan rate of 0.05 V/s for Cu_2O-ZnO/C and 0.1 V/s for Pt/C. The resulting voltammograms of the Cu_2O-ZnO/C and Pt/C electrodes are presented in Figures 4 and 5, respectively.

The CV test generates a voltammogram curve that illustrates a reversible reaction with the formation of two current peaks, an anodic peak (top curve) and a cathodic peak (bottom curve). These peaks demonstrate the occurrence of oxidation

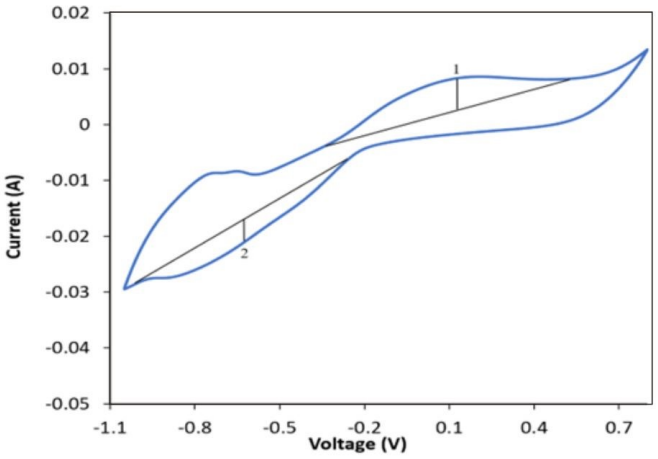

Figure 4. Voltammogram Curve of Electrode with Pt/C Catalyst

and reduction reactions at the Cu_2O-ZnO/C and Pt/C electrodes, and they provide a means to determine the voltage and current values that correspond to the catalytic activity of the electrode (Amin et al., 2018). The size of the peak is dependent on the number and speed of electrons that are released or captured. The voltammogram curve reveals the presence of a redox faradic reaction at the electrode, where oxide is formed from the reaction between the electrolyte and the electrode surface. The anodic peak indicates the formation of oxide, while the cathodic peak represents the release of oxide that occurs back and forth. However, the oxide produced can also block the electrode, leading to a decrease in the ECSA value (Xu et al., 2012).

The ECSA value of the Cu_2O-ZnO/C electrode was found to be 0.69 m^2/g, while that of the Pt/C electrode was 7.2 m^2/g. The calculation of the ECSA value refers to the equation proposed in the previous paper (Cooper, 2009; Eris et al., 2018). This result indicates that the ECSA value of the Pt/C electrode is greater than that of the Cu_2O-ZnO/C electrode. One factor that can increase the ECSA value is the distribution of the catalyst on the electrode, which depends on particle size (Huy et al., 2016). Smaller catalyst particles can enhance the catalyst distribution. In this case, the particle size of Pt/C was found to be smaller than that of Cu_2O-ZnO/C. The size of particle of the Cu_2O catalyst was measured to be approximately 31 nm and 32 nm based on TEM measurement (Topnani et al., 2010). A higher ECSA value signifies that a large number of active sites are present on the electrode surface, resulting in optimal electrochemical reaction.

3.5 Measurement of Electrical Conductivity Value Using the EIS Method

In order to ascertain the conductivity values of the Cu_2O-ZnO/C and Pt/C electrodes, EIS analysis was conducted (Shyamal et al., 2019). The Nyquist curve, which was obtained from the EIS measurement, was utilized to calculate the conductivity

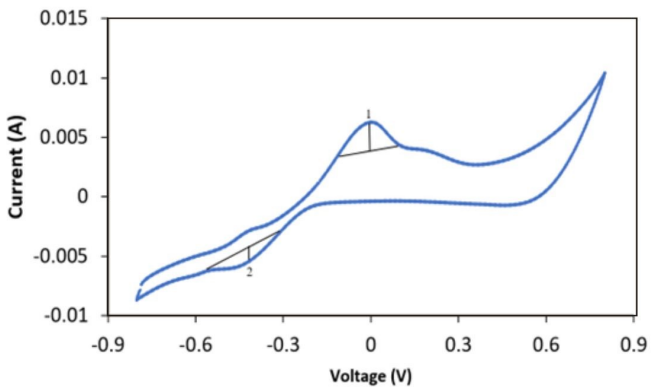

Figure 5. Voltammogram Curve of Electrode with Cu_2O-ZnO/C Catalyst

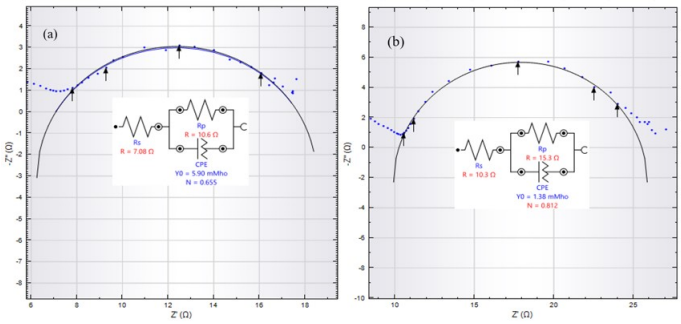

Figure 6. Nyquist Curve of Electrode with (a) Pt/C and (b) Cu_2O-ZnO/C Catalyst

value of each electrode, as illustrated in Figure 6.

The results of the EIS analysis showed that the Cu_2O-ZnO/C electrode had an electrical conductivity value of 0.799 x 10^{-3} S/cm with an impedance value of 25.536 Ω, while the Pt/C electrode had an electrical conductivity value of 1.154 x 10^{-3} S/cm with an impedance value of 17.678 Ω. The electrical conductivity of the electrode is determined by using an equation from previous literature (Zhang et al., 2022) in conjunction with an electronic circuit simulation that results from fitting the Nyquist curve. These results indicate that the electrical conductivity value of the Pt/C electrode is higher than that of the Cu_2O-ZnO/C electrode.

The disparity in electrical conductivity values can be explained by the variance in impedance values. Lower impedance values indicate less resistance to the flow of electrons, resulting in higher conductivity values. Furthermore, a higher EIS value indicates a more uniform distribution of catalyst particles, which can enhance the conductivity value even further (Sakellis et al., 2014). However, the occurrence of agglomeration in the catalyst ink can cause a decrease in conductivity value. Overall, the EIS analysis provided important information on the conductivity of the electrodes, which is crucial for understanding their performance in electrochemical reactions.

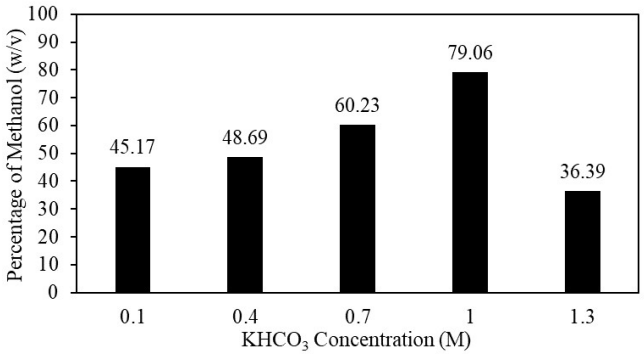

Figure 7. The Effect of $KHCO_3$ Concentration on Methanol Percentage

3.6 Result of CO_2 Conversion to Methanol

The objective of this study was to transform carbon dioxide (CO_2) into methanol by utilizing an electrolyzer with MEA as the reaction center. During the process of electrolysis, water (H_2O) was oxidized on the anode side to produce O_2 and generating protons (H^+) that moved through the electrolyte membrane to the cathode side. On the cathode side, these protons reacted with CO_2, resulting methanol as products (Al Kalbani et al., 2016).

3.6.1 Variations of $KHCO_3$ Concentration

Various concentrations of $KHCO_3$ solution as an electrolyte are used to observe the effect of $KHCO_3$ concentration on the productivity of methanol resulting from the conversion. $KHCO_3$ facilitates the dissolution of CO_2 in the liquid phase in the cathode chamber (Zhong et al., 2017). The use of $KHCO_3$ as an electrolyte has been used by several researchers (Albo and Irabien, 2016; Liang et al., 2020; Merino Garcia et al., 2016).

The data obtained from the conversion of CO_2 to methanol using different concentrations of $KHCO_3$ electrolyte (Figure 7) showed that the highest average percentage of methanol was achieved at a concentration of 1 M, resulting in a methanol content of 79.06 w/v%. In contrast, lower concentrations of 0.7 M, 0.4 M, and 0.1 M resulted in smaller yields of 60.23, 48.69, and 45.17 w/v%, respectively. This can be attributed to the fact that, at low concentrations, the electrolyte fails to provide enough anions to maintain the pH, resulting in a less efficient CO_2 reduction. Moreover, at lower concentrations, the hydrogen evolution reaction (HER) takes place instead of methanol formation. However, the use of an electrolyte with a concentration of 1.3 M resulted in a very low percentage of methanol, namely 36.39 w/v%. This is because at high concentrations, the buffer capacity increases due to an increase in the number of HCO_3^- ions, which leads to a decrease in CO_2 solubility (König et al., 2019). Therefore, the electrolyte with a concentration of 1 M was chosen to investigate the effect of temperature on the conversion of CO_2 to methanol.

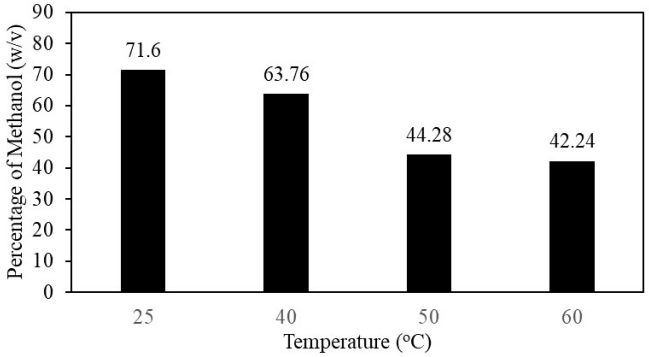

Figure 8. The Effect of $KHCO_3$ Temperature on Methanol Percentage

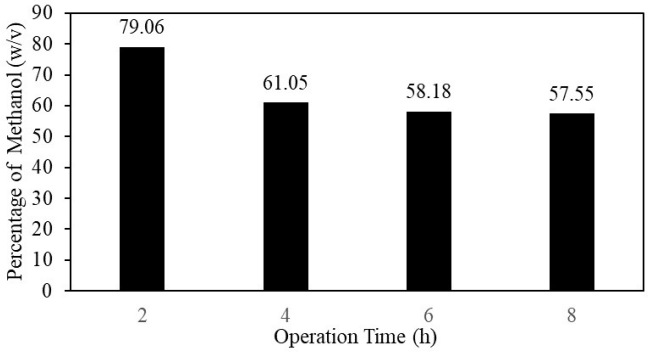

Figure 9. The Effect of Operation Time on Methanol Percentage

3.6.2 Variations of $KHCO_3$ Temperature

Methanol concentration was measured using a methanol analyzer after distillation, and the results showed that the highest average percentage of methanol (79.06 w/v%) was obtained at room temperature (25°C). This is because the reaction at room temperature is able to reduce the overpotential in the reaction related to the formation of CO_2^- intermediate groups (Ganesh, 2014b). While operating temperatures of 40, 50, and 60°C yielded lower percentages (63.76, 44.28, and 42.24 w/v%, respectively) (Figure 8). The decrease in methanol production at higher temperatures can be attributed to the decreasing solubility of CO_2 (Altway et al., 2016) . Additionally, the acidity (pH) of the $KHCO_3$ electrolyte was found to affect the conversion of CO_2 into methanol. $KHCO_3$ not only helps transfer CO_2 in the reaction, but it also provides an anion supply that can prevent pH changes during the electrochemical reduction reaction.

3.6.3 Variations of Operation Time

The other aim of this study was to investigate the conversion of CO_2 into methanol with variations in operating time using $KHCO_3$ electrolyte with a concentration of 1M and room temperature as the operating temperature. The results showed that the percentage of methanol produced decreased with increasing operating time. The highest average percentage of methanol was obtained at room temperature and 2 hours of operation time, which was 79.06 w/v%. On the other hand, the lowest average percentages of methanol were obtained at operation times of 4, 6, and 8 hours, which were 61.05 w/v%, 58.18 w/v%, and 57.55 w/v%, respectively (Figure 9).

The decrease in the percentage of methanol with increasing operating time can be attributed to the decrease in the solubility of CO_2 due to the increasing of pH of solutions. As the conversion process continues, the pH of the solution increases due to the formation of KOH, and the electrolyte solution becomes increasingly alkaline in nature. This results in a reduction in the solubility of CO_2, which hampers the conversion process (König et al., 2019).

Overall, the study highlights the importance of optimizing the operating time for the conversion of CO_2 into methanol using $KHCO_3$ electrolyte, and suggests that shorter operation times may lead to higher yields of methanol.

The electrochemical conversion of CO_2 into methanol, utilizing $KHCO_3$, offers significant advantages in term of high methanol productivity. However, this process has encountered challenges as the resulting methanol product becomes mixed with the $KHCO_3$ solution. The distillation process is one of the best alternatives in separating methanol from $KHCO_3$ as well as efforts to increase the percentage or purify methanol.

4. CONCLUSION

The research indicates that the Cu_2O-ZnO/C electrode has lower electrochemical and electrical conductivity properties compared to the Pt/C electrode, based on measurements of ECSA and conductivity using the CV and EIS methods, respectively. The electrochemical conversion of CO_2 to methanol using $KHCO_3$ solution as an electrolyte, conducted at room temperature with low operating time, offers the advantage of reducing production costs. However, it poses challenges in effectively separating the methanol product from the $KHCO_3$ solution. Nevertheless, this research provides valuable insights into the impact of electrolyte concentration, operating time, and temperature on methanol productivity.

5. ACKNOWLEDGMENT

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