Electrochemical reduction of CO₂ to Formic Acid on Pb-Sn Alloy Cathode

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Abstract. Carbon dioxide released to the atmosphere due to fossil combustion needs to be reduced to decrease the global warming effect. Electrochemical reduction of CO₂ is one of promising technology to convert CO₂ to various valuable compounds, reducing the amount of released CO₂ to the atmosphere. Metal alloys are interesting material for cathode. In this preliminary work, a CO₂ electrochemical reduction was performed on a Pb-Sn alloy cathode using catholyte of KIICO₃ and NaHCO₃ at various concentrations. An anode from Pt-Ir and H₂SO₄ 0.1 M as anolyte were used in the experiment. The CO₂ was bubbled into 400 mL catholyte at rate of 75 mL min⁻¹. It was found that Pb-Sn alloy in KIICO₃ electrolyte provides higher productivity and faradaic efficiency than in NaHCO₃. Increasing overpotential from 0.1 V to 1 V increases both formic acid productivity and efficiency. The optimum amount of formic acid produced was 9400 µmol in catholyte KIICO₃ 0.5 M with faradaic efficiency of 67.19% and conversion of 0.326%.

1. Introduction
Extensive consumption of fossil fuel increases the concentration of CO₂ in the atmosphere which contributes to the greenhouse effect. Indonesia, as the 4th populated country, fulfill almost 95% of the energy consumption by fossil fuel [1], with increasing rate of approximately 6-8% per annum. Therefore, technologies for CO₂ mitigation should be developed.

Various metal electrodes have been examined in electrochemical reduction of CO₂ to formic acids such as Pb, Pd, Pt, and Sn [2,3]. Use of metal alloy, however, is still limited. Kwon et al. have reported a selective electrochemical reduction of carbon dioxide to formic acid using indium-zinc bimetallic nanocrystals [4]. A composition of In:Zn = 0.05 shows high catalytic activity with 95% faradaic efficiency for HCOOH production. Li et al. also reported Sn-In co-deposited on Cu alloy as cathode for formic acid synthesis with faradaic efficiency of 88% [5]. Knaeco et al. used copper alloy in methanol-based electrolyte and showed methane-dominant products which proportional to copper content [6]. Choi et al. used Sn-Pb alloys powder on carbon paper as new electrocatalyst [7]. The alloys show higher electrocatalytic activity than its single metal electrode.
In this study, electrochemical reduction of CO$_2$ was conducted using Pb-Sn alloy wire. High electronic conductivity of the Pb-Sn alloy is expected to increase reaction efficiency. Effect of electrolyte types, concentration, and overpotential toward amount of formic acid produced, conversion, and current efficiency was studied. It was found that electrochemical reaction using the Pb-Sn alloy in KHCO$_3$ catholyte shows higher performance than ones in NaHCO$_3$ catholyte.

2. Methodology
Experiment was conducted using H-cell with Nafion® 212 as separator. A Pt-Ir wire anode was used as counter electrode in H$_2$SO$_4$ 0.1 M anolyte. A Pb-Sn alloy wire with surface area of 12.26 cm$^2$ was used in the catholyte of Sodium bicarbonate (NaHCO$_3$) and potassium bicarbonate (KHCO$_3$) with various concentration of 0.1 M; 0.2 M; 0.5 M. All chemicals were obtained from Merck without prior treatment before used. Electrolysis is operated under atmospheric pressure and temperature with CO$_2$ bubbling rate of 75 mL/min for 3 h. A Stability test was conducted for 5 – 7 h. The operation voltage was set at overpotential of 0.5 V, 0.75 V, and 1 V. A saturated calomel electrode (SCE) was used as reference electrode. Figure 1 shows the experimental set-up.

![Experiment set-up](image)

Figure 1. Experiment set-up

3. Result and Discussion

3.1. Working potential of reaction
Equilibrium potential of CO$_2$ reduction to formic acid is $-0.20$ V/RHE [8]. Due to activation overpotential, the potential where reaction starts observable will have onset to the equilibrium ones. Here we define the summation of equilibrium potential and activation overpotential as initial voltage. The increasing voltage will increase the electric current in the ohmic overpotential region and then reach the concentration overpotential. In this study, working overpotential was determined based on the initial voltage instead of the equilibrium ones. A current-voltage curve was prepared to calculate the initial potential, as shown in Figure 2. Table 1 shows the calculated initial voltage vs SCE at 10 mA of current.
Table 1. Initial potential data for various types and concentrations of electrolytes

| Electrolytes | Initial potential (V vs SCE) in various concentration of catholyte |
|--------------|---------------------------------------------------------------|
|              | 0.1 M   | 0.2 M   | 0.5 M   |
| NaHCO₃      | -0.766  | -1.250  | -1.298  |
| KHCO₃       | -1.351  | -1.067  | -0.802  |

The increase of electrolyte concentration will decrease cell equilibrium potential [9]. However, the initial voltage for reaction in NaHCO₃ seem requires higher voltage as the concentration increase. To confirm the trend, an experiment using potentiostat was conducted to get Tafel curve. The equilibrium potential \( E_0 \) then was determined for each curve, as shown in Figure 4. Based on the Figure 3, reaction equilibrium potential for NaHCO₃ 0.5 M, 0.2 M, and 0.1 M are 1.24 V, 1.04 V, and 0.99 V vs SCE. Those values are equivalent to 1.48 V, 1.28 V, and 1.23 V against SHE, respectively. Therefore, the trend of NaHCO₃ at various concentrations is in the correct path.
3.2. Electrochemical reduction performances

Performance of electrochemical reduction of CO$_2$ for formic acid synthesis is measured based on produced formic acid, reaction conversion, and current efficiency, shown in Table 2. Reaction in KHCO$_3$ electrolyte provides higher productivity than in NaHCO$_3$ electrolyte. Higher electrolyte conductivity of KHCO$_3$ than NaHCO$_3$ in the same concentration causes the reaction can go faster. It is also reported that KHCO$_3$ can dissolve more CO$_2$ than NaHCO$_3$, providing more reactants in the electrolyte [10].

| Catholyte type | Over potential (V) | Produced formic acid (µmol) | Reaction conversion of formic acid formation (%) | Current efficiency (%) |
|----------------|--------------------|-----------------------------|-----------------------------------------------|-----------------------|
|                | 0.5                | 0.1 M 0.2 M 0.5 M          | 0.1 M 0.2 M 0.5 M                             | 0.1 M 0.2 M 0.5 M    |
| NaHCO$_3$      |                    |                             |                                               |                       |
| 0.5            | 120                | 39 0                        | 0.004 0.001 0.000                             | 9.47 9.52 0.00       |
| 0.75           | 192 760 4480       | 0.007 0.026 0.155           | 11.93 26.43 58.94                            |                       |
| 1              | 272 5480 7680      | 0.009 0.190 0.266           | 13.09 61.63 61.84                            |                       |
| KHCO$_3$       |                    |                             |                                               |                       |
| 0.5            | 40 320 4000        | 0.001 0.011 0.139           | 10.05 23.53 61.93                            |                       |
| 0.75           | 1000 2200 6000     | 0.035 0.076 0.208           | 24.46 41.02 64.77                            |                       |
| 1              | 5040 5640 9400     | 0.175 0.196 0.326           | 61.18 62.08 67.19                            |                       |

Concentration of electrolytes has a proportional effect to performance of electrolysis. Higher concentration increases the conductivity of electrolytes [11, 12]. Moreover, CO$_2$ binding capability increase with concentration. Both conditions increase reaction efficiency and productivity. As an overpotential increases from 0.5 to 1 V, the reaction rate increases. Within the overpotential range, no side reaction and limiting current condition were observed. Faradaic efficiency however still lower than reaction on Sn-In reported by Kwon et al. (88%) or on Sn-Pb alloys reported by Choi et al. (79.8%). Low soluble CO$_2$ and contact of gas – electrode due to lack of CO$_2$ bubbling method are supposed to be the cause.

3.3. Stability of electrolysis reaction

Continuous electrolysis may cause degradation on the electrode material, as well as their performance. Therefore, a stability test was conducted on Pb-Sn electrode using KHCO$_3$ 0.5 M and 1 V overpotential for 5 hours continuous operation. Current as function of time and produced formic acid were measured as shown in Figure 4. The result show stable current and production rate, which indicates stable cathode material within 5 hours test.

Observation on the cathode before and after reaction was performed under scanning electron microscope. The cathode was used for 7 h continuous reaction prior to the examination. Figure 5 shows significant different morphology of the cathodes before and after electrochemical reaction. After reaction, a rough deposit layer was formed on the surface of cathodes. An EDX analysis revealed oxide compound of K, Pb, and Sn which increases along with electrolysis duration. The layer seems not to
affect to electrolysis performance as reaction rate keep a linear trend with time. Further research is required to examine effect of the oxide layer on cell performance.

**Figure 4.** (a) Current – time and (b) Formic acid production – time curves

**Figure 5.** The SEM results of cathode before (a and c) and after (b and d) used in electrochemical reduction of CO$_2$

4. Conclusion
We successfully synthesize formic acid from CO$_2$ via electrochemical reduction on Pb-Sn alloys. Use of KHCO$_3$ as a catholyte can produce higher amounts of formic acid, current efficiency, and conversion than NaHCO$_3$ ones. The electrolyte concentration is directly proportional to produced formic acid formed, current efficiency, and conversion. In the overpotential range of 0.5 – 1 V, the performance of electrolysis is increase without any side reactions were observed. The Pb – Sn alloys electrode is stable within electrolysis duration of 7 h.
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