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

Pramujo Widiatmoko, Isdiriyani Nurdin, Hary Devianto, Budi Prakarsa, and Henry Hudoyo

Department of Chemical Engineering, Institut Teknologi Bandung, Bandung 40132 Indonesia

E-mail: pramujo@che.itb.ac.id

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 KHCO₃ 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 KHCO₃ 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 KHCO₃ 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 CO₂ 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 KHCO₃ catholyte shows higher performance than ones in NaHCO₃ 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 H₂SO₄ 0.1 M anolyte. A Pb-Sn alloy wire with surface area of 12.26 cm² was used in the catholyte of Sodium bicarbonate (NaHCO₃) and potassium bicarbonate (KHCO₃) 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 CO₂ 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.

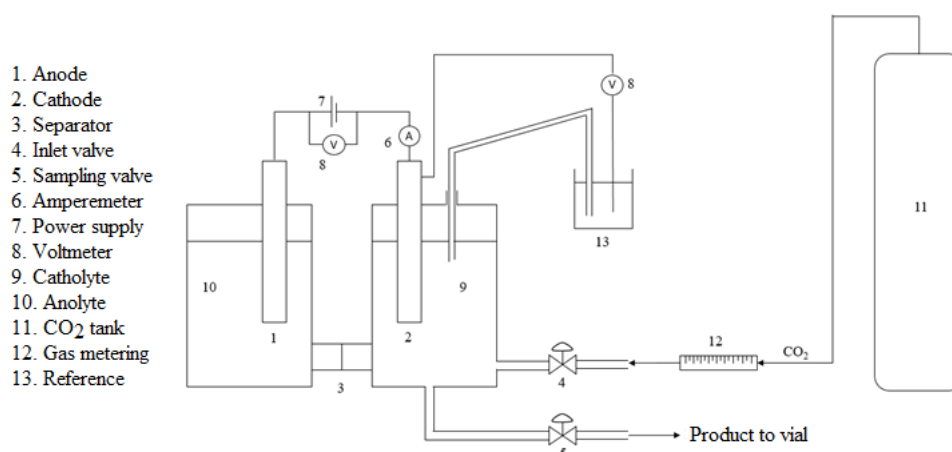


Figure 1. Experiment set-up

3. Result and Discussion

3.1. Working potential of reaction

Equilibrium potential of CO₂ 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.

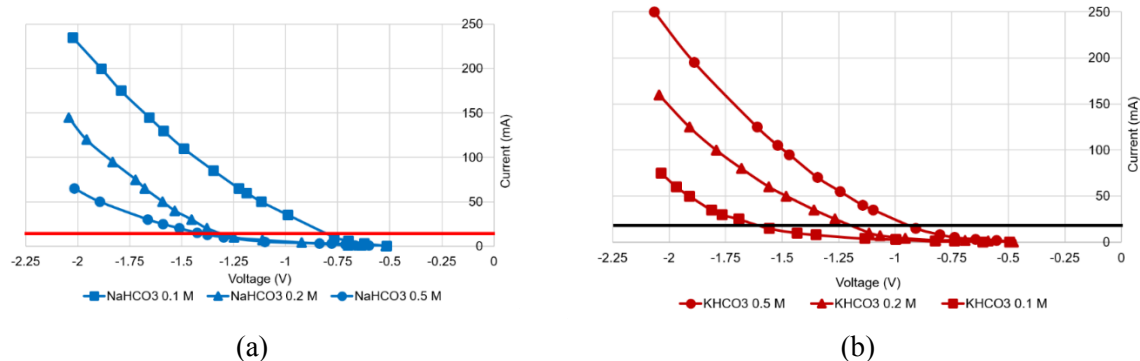
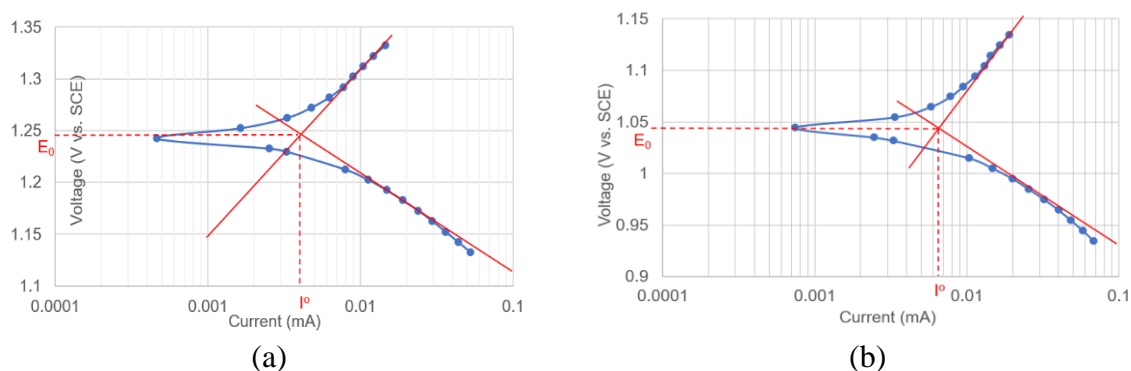


Figure 2. I-V curves for (a) NaHCO_3 and (b) KHCO_3 at various concentration

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
NaHCO_3	-0.766	-1.250	-1.298
KHCO_3	-1.351	-1.067	-0.802

The increase of electrolyte concentration will decrease cell equilibrium potential [9]. However, the initial voltage for reaction in NaHCO_3 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 NaHCO_3 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 NaHCO_3 at various concentrations is in the correct path.



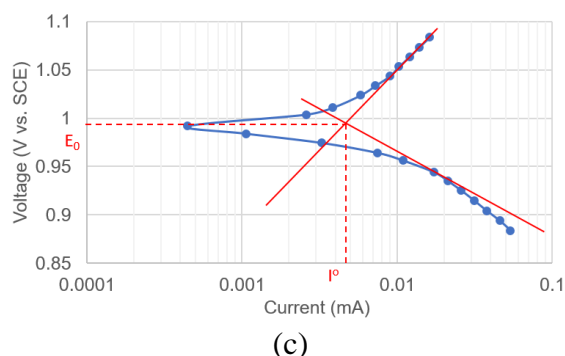


Figure 3. Tafel curve for electrolysis cells with electrolyte NaHCO₃ (a) 0.5 M; (b) 0.2 M; (c) 0.1 M

3.2. Electrochemical reduction performances

Performance of electrochemical reduction of CO₂ for formic acid synthesis is measured based on produced formic acid, reaction conversion, and current efficiency, shown in Table 2. Reaction in KHCO₃ electrolyte provides higher productivity than in NaHCO₃ electrolyte. Higher electrolyte conductivity of KHCO₃ than NaHCO₃ in the same concentration causes the reaction can go faster. It is also reported that KHCO₃ can dissolve more CO₂ than NaHCO₃, providing more reactants in the electrolyte [10].

Table 2. Electrochemical reduction parameters

Catholyte type	Over potential (V)	Produced formic acid (μmol)			Reaction conversion of formic acid formation (%)			Current efficiency (%)		
		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, CO₂ 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 CO₂ and contact of gas – electrode due to lack of CO₂ 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 KHCO₃ 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.

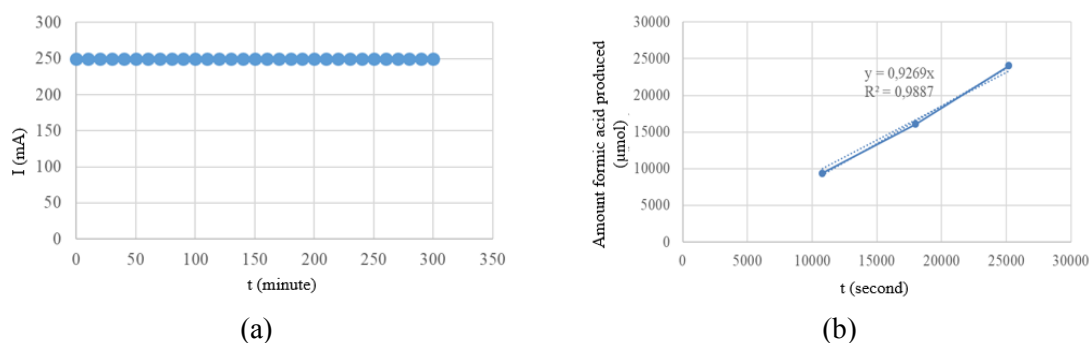


Figure 4. (a) Current – time and (b) Formic acid production – time curves

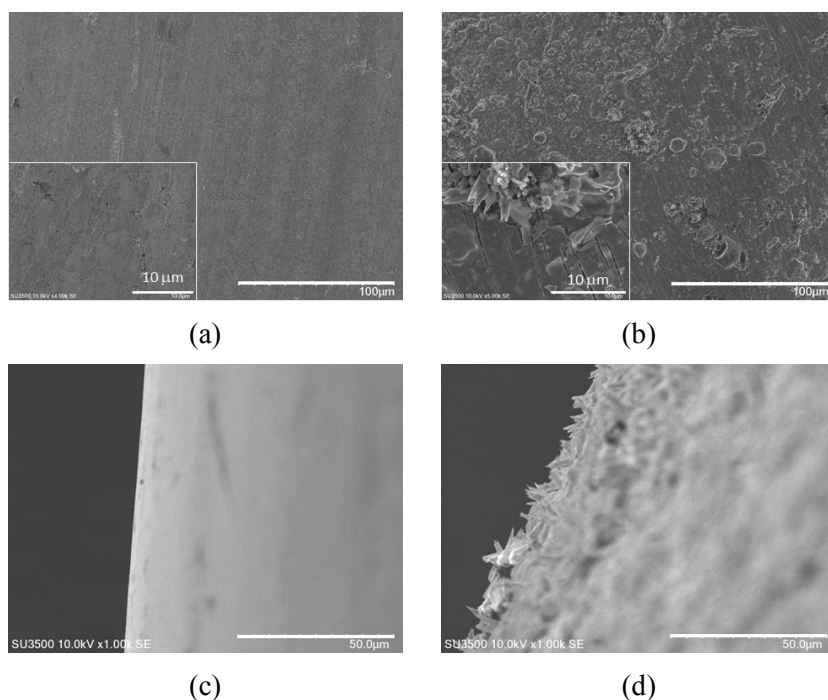


Figure 5. The SEM results of cathode before (a and c) and after (b and d) used in electrochemical reduction of CO_2

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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