Effect of Bubble Size on Electrochemical Reduction of Carbon dioxide to Formic Acid

Pramujo Widiatmoko*, Wibawa Hendra Saputera, Hary Devianto, Isdiriayani Nurdin, Esperanza Rivana and Albert Angkasa

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

*pramujo@che.itb.ac.id

Abstract. A variety of technologies to diminish greenhouse gases CO₂ emission have been extensively explored in recent years. One promising technology called electrochemical reduction of CO₂ have been developed to convert CO₂ into value-added chemicals, such as methanol, ethanol, ethylene, and formic acid. One of important parameter that need to be considered is the size of CO₂ bubbles. In general, decreasing bubbles size can increase retention time of carbon dioxide in an electrolyte. In this research, effect of the microbubble size on the effectiveness of electrochemical reduction of carbon dioxide to formic acid was studied. Bubbles with average diameter 0.321 and 0.952 mm were generated through perforated glass apparatus. The FTIR analysis showed peak at 1634 cm⁻¹ which attributed to C=O bonding of formic acid. Smaller bubble size showed relatively more stable and higher electric current during electrolysis, indicating better retention time of carbon dioxide in the electrolyte. Keywords: Microbubbles; Electrochemical reduction of CO₂; Formic Acid; Retention time; Size effect; Electrolyte composition

1. Introduction

Concerning on the global warming issue, recycling of CO₂ into valuable chemicals through electrolysis recently become attractive [1]. The electroreduction of CO₂ at various metal electrodes yields many kinds of organic substances, e.g. CO, CH₄, C₂H₆, and Ethanol [2]. Transition metals such as Au, Ag and Zn produce CO while p-block metals e.g. Sn, Pb and In mainly produce formate. In formic acid production, the Pb electrode shows high selectivity while the Sn electrode shows high current efficiency [3].

The electrolyte used for the electrocatalytic reduction of CO₂, both aqueous and non-aqueous, also have been summarized [4]. Common catholyte used in the process is KHCO₃ as aqueous solution [5]. Low solubility of CO₂ in water under standard conditions (about 34 mM), however, is a key challenge to improve efficiency of the electrocatalytic reduction of CO₂ [6]. Usage of organic electrolytes such as acetonitrile, dimethyl formamide, and methanol increase solubility of CO₂ up to eight times [7]. Despite the solubility is higher when using organic solvent, toxicity of the organic solvent and safety hazards are need to be considered. It is also important to ensure that the products come from the CO₂ reactant instead of the electrolytes.

Another interesting method to overcome the solubility problem is using smaller bubble size of CO₂. Smaller bubble size decreases rising velocity, retain the CO₂ in the electrolyte longer. In example, the 0.4 mm bubble diameter has theoretical rising velocity of 0.05 m/s meanwhile 0.1 mm bubble has almost
one tenth at about 0.003 m/s [8]. Moreover, the microbubble, with 10-50 µm in diameter, tend to gradually decrease the size by time and dissolve the gas into surrounding water [9, 10]. While CO\textsubscript{2} concentration on the cathode surface decrease due to formation of formic acid, high concentration of CO\textsubscript{2} in catholyte is maintained by dissolution of CO\textsubscript{2} gas from the bubble. This condition ensures high mass transfer during the reaction.

In this work, effect of bubble size to performance of CO\textsubscript{2} electrochemical reduction to formic acid was studied. Alloy of Pb-Sn electrode was used to optimize both selectivity and current efficiency. The result show that smaller bubble size increases performance of the electrolysis. It is also shown that diameter ratio of electrode ring to reactor affects the performance.

2. Methodology
This work was carried out by bubbling CO\textsubscript{2} gas using sparger into reactor during electrolysis, with equipment’s arrangement shown in Figure 1. Two spargers types were used i.e. the CO\textsubscript{2} atomizer and bubble stone. Arise bubble was photographed using microscope and analyzed using ImageJ software to measure cross-sectional diameter. The Sn-Pb alloy wire with 90 cm length was used as cathode in a spiral shaped with various diameter, while Pt-Ir wire was used as anode. Solution of KHCO\textsubscript{3} 0.5 M was used as a catholyte solution and H\textsubscript{2}SO\textsubscript{4} 0.1 M as anolyte. Prior to electrolysis, the catholyte was saturated by CO\textsubscript{2} bubbling for 1 hour. The electrolysis was carried out at overpotential of 1 V for 3 hours. Electric current was recorded every 10 minutes. Theoretical formic acid formed was calculated based on data of electric current vs. time using the Faraday’s law of electrolysis. Reaction products was analyzed using Fourier-Transform Infrared Spectroscopy (FTIR).

![Figure 1. Schematic diagram of experiment.](image)

3. Result and Discussion

3.1. Bubble generation
The spargers produce different size of bubble, as shown in Figure 2. The CO\textsubscript{2} atomizer and the bubble stone sparger produce bubble diameter of 0.35 mm and 1.96 mm in average at diameter ratio of electrode spiral to reactor (D\textsubscript{e}/D\textsubscript{t}) of 0.25. With increasing the D\textsubscript{e}/D\textsubscript{t} ratio, secondary peak of bigger bubble size rises at 0.48 mm and 2.65 mm, respectively. In this case, the diameter of reactor (D\textsubscript{t}), was kept constant.
Terminal rising velocity ($U_t$) of the bubble at low Reynold number can be predicted using Stokes equation as shown in Equation (1), where $\Delta \rho$, $r$, $g$, and $\mu$ are density difference between the bubble and water, radius of bubble, gravitational acceleration, and water dynamic viscosity, respectively [11].

$$U_{t(ST)} = \frac{2r^2\Delta \rho g}{9\mu}$$

(1)

Average terminal rising velocity for the bubbles produced using the CO$_2$ atomizer and the bubble stone sparger are shown in Table 1. The terminal rising velocity in this work was calculated based on properties under 30°C and 1 atm condition. The value of $\Delta \rho$, $g$, and $\mu$ are 993.886 kg/m$^3$, 9.806 m/s$^2$, and 0.0007972 kg/(m.s), respectively.

![Figure 2](image.png)

**Figure 2.** Distribution of bubbles generated in reactor with $D_e/D_t$ ratio of (a) 0.25 and (b) 0.5.

| Type of sparger | Bubble size (mm) | Terminal rising velocity (m/s) |
|----------------|-----------------|--------------------------------|
| Atomizer       | 0.35            | 0.083                          |
|                | 0.48            | 0.156                          |
| Bubble stone   | 1.96            | 2.609                          |
|                | 2.65            | 4.769                          |

Table 1. Terminal rising velocity of CO$_2$ bubbles.

Replacing the bubble stone with the atomizer reduces significantly the terminal rising velocity up to 30 times slower. In our 20 cm length reactor, retention time of the bubbles therefore will increase from 0.07 s to 2.40 s. Ideally, microbubbles size at 10 – 50 µm in diameter, which has terminal rising velocity of 4.075 mm/min, will provide much longer retention time at 49 min. To be noted, experiment conducted by Parkinson et al. shows higher terminal velocity of CO$_2$ bubble in pure water than ones predicted by the Stokes equation [12]. The effect is attributed to formation of boundary layer around the small bubble due to enhanced CO$_2$ solubility.

3.2. Effect of bubble size on electrolysis performance

Figure 3 shows effect of the bubble size and $D_e/D_t$ ratio to electrical current on the electrolysis system. The electrical current increases with decreasing of bubble size. As we know, the reaction rate is proportional to the current. It is supposed that increasing CO$_2$ gas in the electrolyte enhance the diffusion rate, move the reaction out from mass control region. Increasing the $D_e/D_t$ ratio means increase in
electrode spiral diameter. As the bubble generator was located in the bottom centre of the spiral, we supposed that wider diameter accommodates better distribution of bubble. With decreasing the spiral diameter, there are more bubble move to outside of the electrode spiral. It will reduce the contact between the bubble and electrode as well as the reaction rate.

![Figure 3](image1.png)

**Figure 3.** Effect of Bubble size and \(D_e/D_t\) ratio on performance of electrolysis.

![Figure 4](image2.png)

**Figure 4.** Infrared spectra of electrolysis products using Sn-Pb cathode with various bubble size and \(D_e/D_t\) ratio.

Figure 4 shows the IR spectra of the catholyte after 3 hours electrolysis. Peaks at the wavenumber of 1364, 1634 and 3328 cm\(^{-1}\) indicating the presence of -C=O, -C = O, and -OH groups, respectively. The spectra results are compared with the IR spectra of the possible by-products such as methanol and CO. The presence of the –C = O group at the wavenumber 1634 cm\(^{-1}\) indicates formic acid in the product.

Reduction of carbon dioxide into formic acid follows reaction in Equation 2 [13]. On the Pb-Sn electrode, the reduction reaction is intermediated by formation of CO\(_2^+\) radical [14, 15]. Theoretical amount of produced formic acid is then calculated using the Faraday’s law of electrolysis as shown in Equation 3.

\[
\text{CO}_2 + 2 \text{H}^+ + 2e^- \rightarrow \text{HCOOH} \quad E^0 = -0.12 \text{V/RHE} \quad (2)
\]

\[
m = \frac{\int I \, dt}{nF} \eta \quad (3)
\]
Using electric current ($I$) – total electrolysis time ($t$) data shown in Figure 3, Faraday constant ($F$) of 96485 C/mol, number of involved electron ($n$) of 2, and assuming 100% efficiency ($\eta$), the theoretical amount of produced formic acid ($m$) within 3 h electrolysis is about $9 \times 10^{-3}$ to $1.5 \times 10^{-2}$ mmol. In average, reducing the bubble size by 0.17 times increases amount of formic acid by 1.4 times. Further, a quantitative analysis is required to determine the actual electrolysis efficiency.

4. Conclusion and Future Works
Performance of CO$_2$ electrochemical reduction to formic acid is enhanced by decreasing of CO$_2$ bubble size. Infrared spectra indicate formic acid presence in the electrolysis product. Future work on quantitative analysis using High Performance Liquid Chromatography is being conducted to determine the current efficiency of electrolysis.

Acknowledgments
This work was funded by research, community service, and innovation (P3MI) program 2020, Institut Teknologi Bandung.

References
[1] Nitopi S, Bertheussen E, Scott S B, Liu X, Engstfeld A K, Horch S, Seger B, Stephens I E L, Chan K, Hahn C, Nørskov J K, Jaramillo T F, and Chorkendorff I 2019 Chem. Rev. 119 761
[2] Jitaru M 2007 J. the University of Chem. Tech. Met. 42 333
[3] Hori Y 2008 Modern Aspects of Electrochemistry vol 42. (New York: Springer) p 89
[4] de Salles Pupo M M and Kortlever R 2019 Chem. Phys. Chem. 20 2926
[5] Wu J., Risalvato, F and Zhou X D 2012 ECS Trans. 41 49
[6] Konig M, Vaes J, Klemm E, and Pant D 2019 iScience 19 135
[7] Kaneco S, Iiba K, Katsumata H, Suzuki T, and Ohta K 2007 J. Solid State Electrochem. 11 490
[8] Zimmerman W B, Tesar V, Butler S, Bandulasena H C H 2008 Microbubble Generation, Recent Patents on Engineering Vol. 2 (Sharjah: Bentham Science Publishers) p 1
[9] Agarwal A, Ng W J, and Liu Y 2011 Chemosphere 84 1175
[10] Takahashi, M.,Chiba K, and Li P 2007 J. Ohys. Chem. B 111 11443
[11] Stokes G G 1851 Cambridge Philos. Trans. 9 8
[12] Parkinson L, Sede R, Formasiiero D, and Ralston J 2008 J. Colloid and Interface Sci. 322 168
[13] Nitopi S, Bertheussen E, Scott S B, Liu X, Engstfeld A K, Horch S, Seger B, Stephens I E L, Chan K, Hahn C, Nørskov J K, Jaramillo T F, and Chorkendorff I 2019 Chem. Rev. 119 7610
[14] Sun Z, Ma T, Tao H, Fan Q, and Han B 2017 Chem 3 560
[15] Innocent B, Pasquier D, Ropital F, Hahn F, Leger J M, and Kokoh K B 2010 Appl. Catal. B 94 219