

## Electrocatalytic Reduction of Carbon Dioxide on Sn-Pb Alloy Electrodes

Choi, Song Yi<sup>\*,\*\*</sup>, Jeong, Soon Kwan<sup>\*</sup> and Park, Ki Tae<sup>\*†</sup>

<sup>\*</sup>Greenhouse Gas Lab., Korea Institute of Energy Research,

<sup>\*\*</sup>TECHWIN Co., Ltd

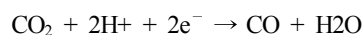
### ABSTRACT

Electrocatalytic reduction can produce useful chemicals and fuels such as carbon monoxide, methane, formate, aldehydes, and alcohols using carbon dioxide, the green house gas, as a reactant through the supply of electrical energy. In this study, tin-lead (Sn-Pb) alloy electrodes are fabricated by electrodeposition on a carbon paper with different alloy composition and used as cathode for electrocatalytic reduction of carbon dioxide into formate in an aqueous system. The prepared electrodes are measured by Faradaic efficiency and partial current density for formate production. Electrocatalytic reduction experiments are carried out at -1.8 V (vs. Ag/AgCl) using H-type cell under ambient temperature and pressure and the gas and liquid products are analyzed by gas chromatograph and liquid chromatograph, respectively. As results, the Sn-Pb electrodes show higher Faradaic efficiency and partial current density than the single metal electrode. The Sn-Pb alloy electrode which have Sn:Pb molar ratio=2:1, shows the highest Faradaic efficiency of 88.7%.

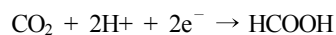
**Key words:** Carbon Dioxide, CCUS, Electrocatalytic Reduction, Formate

### 1. INTRODUCTION

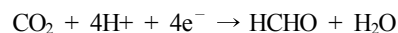
A certain level of electric potential should be applied between two separated electrodes to convert CO<sub>2</sub> into valuable chemicals through electrochemical reduction of CO<sub>2</sub> (Alvarez-Guerra *et al.*, 2014). Electrochemical reduction of CO<sub>2</sub> (ERC) provides a variety of attractive chemicals and fuels, such as methanol, formic acid, and other hydrocarbons (Ogura *et al.*, 2010). CO<sub>2</sub> is reduced on the cathode while the oxygen (O<sub>2</sub>) evolution reaction (OER) takes place on the anode. Half-reactions of the cathode for electrochemical CO<sub>2</sub> reduction into major products such as carbon monoxide, formate, methane, and ethylene are listed below (Jhong *et al.*, 2013). (pH 7 in aqueous solution vs. SHE(standard hydrogen electrode), room temperature, atmospheric pressure).



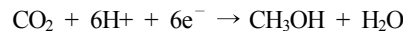
$$E^0 = -0.53 \text{ V (vs. SHE)}$$



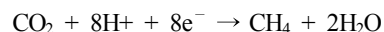
$$E^0 = -0.61 \text{ V (vs. SHE)}$$



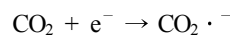
$$E^0 = -0.48 \text{ V (vs. SHE)}$$



$$E^0 = -0.38 \text{ V (vs. SHE)}$$



$$E^0 = -0.24 \text{ V (vs. SHE)}$$



$$E^0 = -1.90 \text{ V (vs. SHE)}$$

Among the number of products, conversion to formic acid/formate appears to have the best chance for the practical development of technically and economically viable processes (Oloman and Li, 2008). Accordingly, electrochemical reduction of CO<sub>2</sub> to formic acid/formate gas had special attention in the literature over the last years.

It has been found that the electrocatalytic activities for the electro-oxidation of organic compounds are changed dramatically by the presence of sub-monolayer ad-atoms at optimum surface compositions, and that synergistic action between surface atoms is obtained (Watanabe and Motoo, 1975). Watanabe

<sup>†</sup> Corresponding author: [ktpark@kier.re.kr](mailto:ktpark@kier.re.kr)

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*et al.* (1991) have already investigated the catalytic properties of various copper-based alloy electrodes. In some cases the catalytic activity of the electrode is improved, such as Cu-Ni, Cu-Sn or Cu-Pb alloys, but in other cases the catalytic aptitudes of the metals are diluted, as it happens for Cu-Ag and Cu-Cd electrodes. Kyriacou and Anagnostopoulos (1992) used Au-modified Cu electrodes and observed that the production of CH<sub>4</sub> falls when the surface contains more gold. The proportion of Au at the surface of the different electrodes did not exceed 7.2%. Christophe *et al.* (2012) used Cu-Au alloys with various Au contents (1~50%) and reported that Au<sub>50</sub>Cu<sub>50</sub> alloy appears to be the most efficient substrate for the conversion of CO<sub>2</sub> into CO.

In this study, the Sn-Pb alloys were synthesized for electrochemical reduction of CO<sub>2</sub> into formate in aqueous solution. The Sn-Pb alloy electrodes were obtained by electrochemical deposition with different compositions on a carbon paper. The oxidation and reduction behaviors of the electrodes were measured by cyclic voltammetry analysis. In addition, Faradaic efficiencies (FE) and partial current densities (PCD) for formate production on the alloy electrodes were obtained.

## 2. EXPERIMENTAL

### 2.1 Fabrication of Electrodes

Sn-Pb alloy electrodeposition is a typical binary co-deposition system. Pb<sup>2+</sup> and Sn<sup>2+</sup> can be reduced together at a lower overpotential, since their standard potentials are so close (−0.136 V for Sn and −0.126 V for Pb) without any additive agent [95]. Sn-Pb alloys as well as Sn and Pb electrodes were fabricated by electrodeposition on carbon paper as a substrate using conventional three electrode cell with a volume of 100 mL at 298 K under atmospheric pressure as shown in Fig. 1. The detailed procedure of the electrodeposition for the preparation of the alloy electrodes has been reported in our previous work (Choi, 2015; Choi *et al.*, 2016). The molar ratios of Sn<sup>2+</sup> to Pb<sup>2+</sup> in the electrolyte for the electrodeposition of tin-lead alloys were 1:1, 2:1, and 8:1. The total concentration of metal cation in electrolyte was 10 mM for all experiments. The compositions of electrolytes to fabricate Sn, Pb, and Sn-Pb alloy electrodes used in this study are given in Table 1.

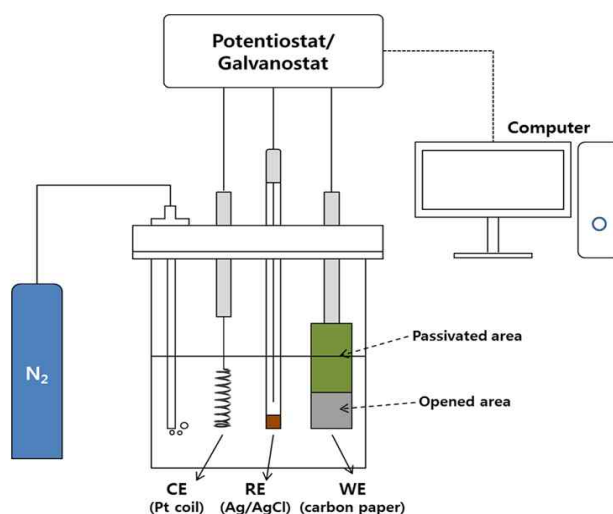


Fig. 1. Schematic diagram of the electrodeposition system.

Table 1. The compositions of electrolytes to fabricate electrodes used in this study

Electrode	Molar ratio of Sn : Pb	Concentration of metal cation (mM)	
		Sn <sup>2+</sup>	Pb <sup>2+</sup>
Sn	-	10.00	-
Sn-Pb (81)	8:1	8.89	1.11
Sn-Pb (21)	2:1	6.67	3.33
Sn-Pb (11)	1:1	5.00	5.00
Pb	-	-	10.00

Electroreduction experiments were carried out at potentiostatic conditions with potentiostat/galvanostat using an H-type two compartment cell. It was designed to be separated into the two compartments of cathode and anode chambers by an ion exchange membrane (Nafion<sup>®</sup> 115) and to keep the gas pressure of the cathode chamber equal to atmospheric pressure during the electrolysis. An Ag/AgCl electrode saturated with KCl was selected as the reference electrode along with a Pt coil as the counter electrode. The cathode potential was controlled by −1.8 V against the Ag/AgCl reference electrode. An aqueous solution 0.5 M KHCO<sub>3</sub> was used as catholyte, while 0.5 MKOH (Sigma Aldrich, 90%) was used as anolyte. A 0.5 MKHCO<sub>3</sub> aqueous solution was saturated with CO<sub>2</sub> by

bubbling CO<sub>2</sub> gas for 5 h before electrolysis. CO<sub>2</sub> gas at a flow rate of 30 mL · min<sup>-1</sup> was supplied continuously to the catholyte using glass sparger throughout the experiment, and the outlet gas stream was analyzed by gas chromatograph (GC; YL Instrument, 6500GC system), equipped with both thermal conductivity detector (TCD) and flame ionization detector (FID). Liquid samples were taken at 20 min intervals of operation time from the cathode chamber via a syringe septum, and analyzed using a high performance liquid chromatograph (HPLC; Thermo Scientific, Ultimate 3000) to determine the amount of produced formate.

The electroreduction performance of the electrodes was measured by Faradaic efficiency and the partial current density of formate production. The Faradaic efficiency for formate production was calculated using the following equation:

$$EF_{\text{formate}} = \frac{n_{\text{formate}} \times N \times F}{C} \quad (1)$$

Where  $n_{\text{formate}}$  is the number of moles of formate produced,  $N$  is the number of electrons for formate produced,  $F$  is the Faradaic constant, and  $C$  is the total charge of electrons passed across the electrode duration of electrolysis. The partial current density (PCD) for formate production was calculated:

$$\text{PCD} = \text{Total current density} \times EF_{\text{formate}} \quad (2)$$

### 3. RESULTS AND DISCUSSIONS

Potential screening test was performed using Sn, Pb, and Sn-Pb alloy electrodes with different reduction potentials at a potential range from -1.6 V to -2.2 V (vs. Ag/AgCl) at 0.2 V intervals to find out the optimum reduction potential. In all the cases, aqueous solutions of CO<sub>2</sub>-saturated 0.5 MKHCO<sub>3</sub> and 0.5 MKOH were used in a H-type cell as a catholyte and anolyte, respectively, during which CO<sub>2</sub> gas (99.999% (v/v)) was continuously bubbled into the catholyte solution, and the cell temperature was maintained at 298 K. The catholyte was analyzed using HPLC after electrolysis to determine the amount of formate produced. The electro reduction performances such as Faradic efficiency and partial current density of the electrodes can be calculated by equation (1) and (2), respectively. Fig. 2

shows the Faradaic efficiencies for the electrodes as a function of reduction potential. As shown in Fig. 2, the maximum Faradaic efficiency was obtained at -1.8 V (vs. Ag/AgCl) among the selected potential conditions for all the tested electrodes, and the Faradaic efficiency was decreased as the potential decreases further due to H<sub>2</sub> evolution reaction. We can see during the experiments that bubbles form and increase fast on the surface of working electrode, which can be certainly attributed to the enhancement of H<sub>2</sub> evolution at more negative potentials.

Electroreduction experiments were carried out under chronoamperometric conditions for 2 h at constant potentials of -1.8 V (vs. Ag/AgCl) in H-type cell. Fig. 3 shows the Faradaic efficiencies of the electrodes at -1.8 V (vs. Ag/AgCl). The Faradaic efficiency at 20 min was increased with tin content from 0% (Pb electrode) to 66.7% (Sn-Pb (21) electrode) and then started to decrease for electrodes with higher tin content than that of Sn-Pb (21) electrode (e.g. Sn-Pb (81) and Sn electrodes). The Sn-Pb (21) electrode showed the highest Faradaic efficiency of 88.7%, while the Pb electrode showed the lowest Faradaic efficiency (70.7%) among the tested electrodes. This result can be explained by the synergetic effect based on the high electric conductivity and the high electrocatalytic activity of Pb<sup>0</sup> content of the alloy electrodes. The surfaces of Sn-Pb alloy electrodes have higher electrical conductivity compared to Sn and Pb, and the conductivity of the electrode surface increased as tin content increases in the alloys (Choi *et al.*, 2016). In addition, they reported that the metallic lead

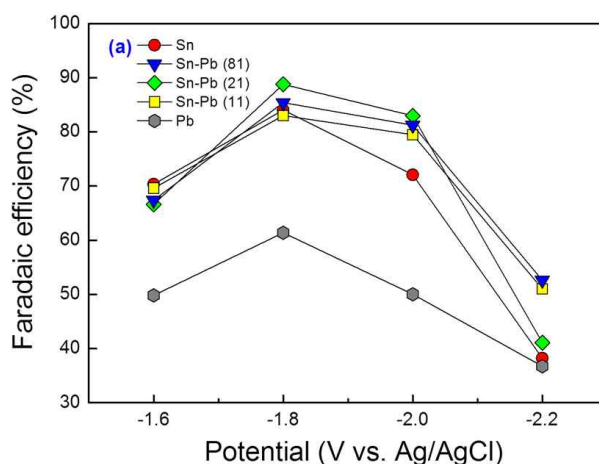


Fig. 2. Results of Faradaic efficiencies for the tested electrodes as a function of reduction potential.

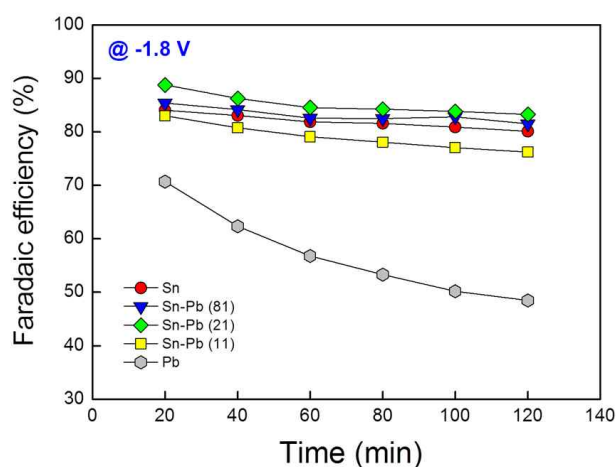


Fig. 3. Faradaic efficiencies of the tested electrodes for formate production at  $-1.8$  V (vs. Ag/AgCl).

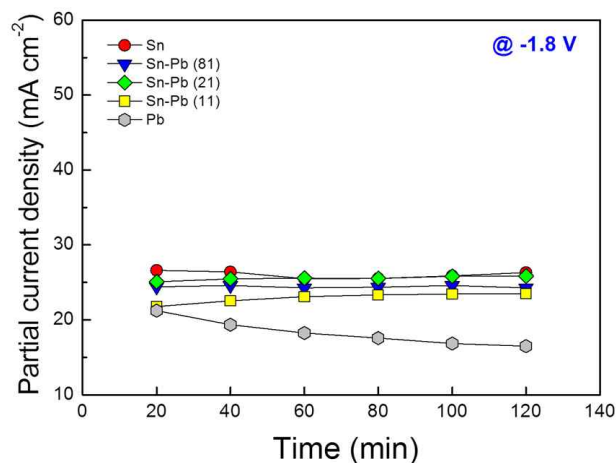


Fig. 4. Partial current densities of the electrodes with operation time at  $-1.8$  V (vs. Ag/AgCl).

( $Pb^0$ ), which have higher conductivity and catalytic activity than  $PbO$ , can exist by tin content in the alloys, because tin inhibits the formation of less conductive  $PbO$  film at the surface. On the contrary, the  $Pb$  electrode showed the lowest Faradaic efficiency, because it has no Sn content and has the lowest electrical conductivity due to less-conductive  $PbO$  film at the surface. Except for the  $Pb$  electrode, there was some decrease in Faradaic efficiency about 4% with operation time from 20 to 120 min, and the partial current densities were maintained stably over the operation time. In the case of  $Pb$  electrode, both the Faradaic efficiency and the partial current density were decreased by c.a. 22% at the same condition.

Fig. 4 shows the partial current densities of the electrodes at  $-1.8$  V (vs. Ag/AgCl). Generally, the partial current density was increased as the tin content increases, because the catalytic active area of the electrode increased with decreasing the  $PbO$  content at the surface. The Sn-Pb (21) showed the highest partial current density of  $25.1 \text{ mA} \cdot \text{cm}^{-2}$  among the alloy electrodes. It is considered that the relative high partial current density of the Sn-Pb (21) electrode comes from the high  $Pb^0$  content, which has high catalytic activity for electroreduction of  $CO_2$  into formate.

Gas products from the electroreduction of  $CO_2$  were analyzed by GC at 20 min intervals during operation time of 120 min. From the GC analysis, it was confirmed that the main products in gas phase are  $H_2$  and  $CO$ . Fig. 5 shows the Faradaic efficiencies for  $H_2$  evolution for the tested electrodes at

$-1.8$  V (vs. Ag/AgCl) over a period of 120 min. The Faradaic efficiencies were increased with operation time. In addition,  $Pb$  electrodes showed the highest Faradaic efficiencies for  $H_2$  evolution. The electroreduction of  $CO_2$  competes with  $H_2$  evolution reaction (HER) at the tested potentials, and the HER reduces the Faradaic current efficiency for formate production by consuming electrons. Therefore, the decrease of Faradaic efficiency for formate production is directly related to the increase of  $H_2$  evolution. When compare Fig. 5 with Fig. 3, the Faradaic efficiencies for  $H_2$  evolution and formate production show opposite tendency to the operation time and the composition of electrodes. Consequently, the increase of Faradaic

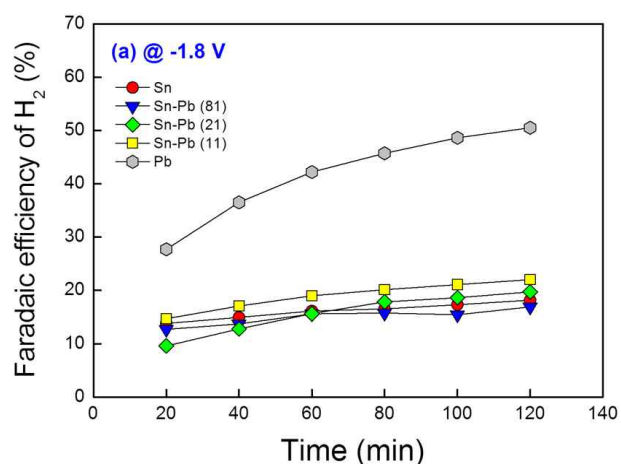


Fig. 5. Faradaic efficiencies of the tested electrodes for  $H_2$  evolution at  $-1.8$  V (vs. Ag/AgCl).

efficiency for H<sub>2</sub> evolution with operation time results in the decrease of Faradaic efficiency for formate production with operation time, and an electrode which showed high Faradaic efficiency for formate production has low Faradaic efficiency for H<sub>2</sub> evolution.

Fig. 6 shows the Faradaic efficiencies of the tested electrodes for CO production at  $-1.8$  V (vs. Ag/AgCl). The CO gas is also the conversion product from the electroreduction of CO<sub>2</sub> like a formate. Thus, the time behavior of Faradaic efficiencies for CO production was similar to that for formate production. However, the Faradaic efficiencies for CO production showed different tendency to the composition of electrode compared to those for formate production. Generally, a higher Faradaic efficiency for CO production was obtained from an electrode which has higher tin content. This result coincides well with the literature (Hori, 2008), which reported the order of CO selectivity of metals: Au > Ag > Cu > Zn >> Cd > Sn > In > Pb > Tl  $\approx$  Hg.

#### 4. CONCLUSION

Sn-Pb alloy electrodes were prepared by electrochemical deposition with different compositions on a carbon paper to use as the cathode for the electroreduction of CO<sub>2</sub> into formate. From the electroreduction experiment, the maximum Faradaic efficiency was obtained at  $-1.8$  V (vs. Ag/AgCl). Generally, the Sn-Pb alloy electrodes showed high Faradaic

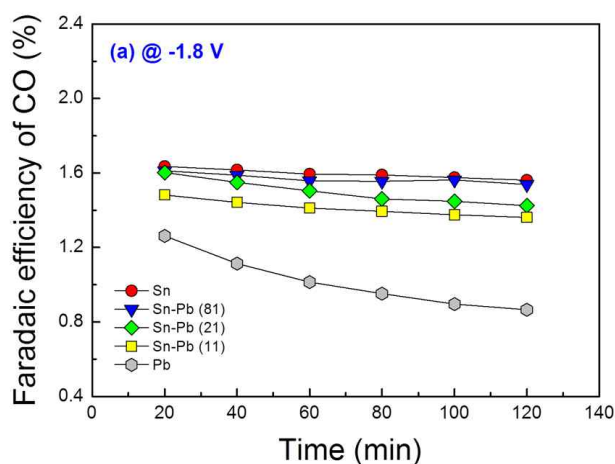


Fig. 6. Faradaic efficiencies of the tested electrodes for CO production at  $-1.8$  V (vs. Ag/AgCl).

efficiencies and high partial current densities compared to Sn and Pb electrodes. In addition, the Sn-Pb (21) electrode showed the highest Faradaic efficiency at  $-1.8$  V (vs. Ag/AgCl). Consequently, the Sn-Pb alloy electrodes are more favorable to produce formate from electroreduction of CO<sub>2</sub> than single metal electrodes (e.g. Sn and Pb electrodes) due to the high electrical conductivity, increased with tin content in the alloys, and the high electrocatalytic activity from the Pb<sup>0</sup> content in the alloys. Consequently, the best performances in electrochemical CO<sub>2</sub> reduction into formate such as Faradaic efficiency and PCD off or mate production were obtained on Sn-Pb (21) electrode at a reduction potential of  $-1.8$  V (vs. Ag/AgCl).

#### 5. ACKNOWLEDGEMENT

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#### REFERENCES

- Alvarez-Guerra M, Castillo AD, Irabien A. 2014. Continuous electrochemical reduction of carbon dioxide into formate using a tin cathode: Comparison with lead cathode. *Chem Eng Res Des* 92:692-701.
- Choi SY. 2015. A study on the electrochemical reduction of carbon dioxide into formic acid using Sn-Pb alloy electrocatalysts. Dissertation, Chungnam National University.
- Choi SY, Jeong SK, Kim HJ, Baek IH, Park KT. 2016. Electrochemical reduction of carbon dioxide to formate on tin-lead alloys. *ACS Sustainable Chem Eng* 4:1311-1318.
- Christophe J, Doneux T, Buess-Herman C. 2012. Electroreduction of carbon dioxide on copper-based electrodes: Activity of copper single crystals and copper-gold alloys. *Electrocatal* 3:139-146.
- Hori Y. 2008. Electrochemical CO<sub>2</sub> reduction on metal electrodes, in modern aspects of electrochemistry. Springer, New York, pp 89.
- Jhong HR, Ma S, Kenis PJA. 2013. Electrochemical conversion of CO<sub>2</sub> to useful chemicals: Current status, remaining challenges, and future opportunities. *Current Opinion in*

- Chemical Engineering 2:191-199.
- Kyriacou G, Anagnostopoulos A. 1992. Electrochemical reduction of CO<sub>2</sub> at Cu+ Au electrodes. *J Electroanal Chem* 328:233-243.
- Oloman C, Li H. 2008. Electrochemical processing of carbon dioxide. *Chem Sus Chem* 1:385-391.
- Ogura K, Ferrel III JR, Cugini AV, Smotkin ES, Salazar-Villalpando MD. 2010. CO<sub>2</sub> attraction by specifically adsorbed anions and subsequent accelerated electrochemical reduction. *Electrochim Acta* 56:381-386.
- Watanabe M, Motoo S. 1975. Electrocatalysis by ad-atoms: Part III. enhancement of the oxidation of carbon monoxide on platinum by ruthenium ad-atoms. *J Electroanal Chem* 60:275-283.
- Watanabe M, Shibata M, Katoh A, Sakata T, Azuma M. 1991. Design of alloy electrocatalysts for CO<sub>2</sub> reduction: Improved energy efficiency, selectivity, and reaction rate for the CO<sub>2</sub> electro reduction on Cu alloy electrodes. *J Electroanal Chem* 305(2):319-328.