

Conversion of Carbon Dioxide to Methanol

G. Rahman and Y. H. Chung*

*Hallym University, Chuncheon, Gangwon-do, Korea, yhchung@hallym.ac.kr

ABSTRACT

Carbon dioxide has been converted to methanol by means of electrochemical reduction using electrodes of metal oxides. The electrodes used in the conversion of CO₂ consisted of Ru/Ir/Co oxides in the atomic ratios of Ru/Ir/Co of 5.4:3.6:1, 3:2:1, and 4.7:3.1:1. The typical electrolyte employed in the study was 0.8 M NaHCO₃ solutions with CO₂ saturation. The cyclic voltammetric result indicates that the electrode of Ru/Ir/Co (4.7:3.1:1) oxides appeared to be more efficient for the reduction of CO₂ to methanol than the other two.

Keywords: carbon dioxide, methanol, cyclic voltammetry

1 INTRODUCTION

Carbon dioxide is a long-lived greenhouse gas and major contributor to global warming [1]. Its atmospheric concentration has been rising since the Industrial Revolution in the mid 18th century. Mauna Loa Observatory instrument record for atmospheric carbon dioxide starting in 1958 shows that its annual rate of increase has been rising drastically from 0.86 ppm during 1960-1969 to 1.92 ppm during 2000-2009 as its concentration increased from 315.71 ppm during March of 1958 to 388.59 ppm during November of 2010 [2,3]. Many developing countries strive to improve their standards of living through vigorous industrialization burning fossil fuels. Moreover, deforestation for livestock industry in the Amazon rainforest has been rather persistent, leading to releasing more carbon dioxide along with methane that is more potent than carbon dioxide at warming the planet. A higher carbon dioxide concentration would exacerbate global warming, leading to catastrophic climate change.

In order to handle carbon dioxide emission, various researches have been performing in fields such as green energy technology, carbon capture and sequestration, and energy efficiency [4]. Concurrently, electrochemical reduction of carbon dioxide has been studied by many researchers and would be one of viable reactions to alleviate global warming [5,6]. The reduction products depend on electrode materials and experimental conditions [7-12]. One of the reduction products is methanol that is of great use in fuel cells [13-15]. The reduction of carbon dioxide to methanol can solve the issues related to the global warming and energy shortage.

Various electrodes have been developed and studied during the last decade. One of them was electrodes with ruthenium oxide deposited on Ti support [7,16] or boron-

doped diamond [9]. The adherence of ruthenium oxide film on Ti was reported to be rather weak. Different adatoms added to ruthenium oxide electrodes were reported to improve the electrode efficiency in CO₂ reduction [17].

In the present work electrochemical properties of electrodes of various composite oxides of ruthenium, iridium and cobalt are reported. Concurrently their preliminary results of carbon dioxide reduction are compared to find an electrode that can be used in reducing CO₂ on a large scale in the future.

2 EXPERIMENT

Electrodes of 3 cm² total surface area were prepared by depositing a thin layer of various composite oxides of Ru, Ir and Co on 0.5mm thick Ti plates. Ti plates used for the electrode were sand-blasted, treated in boiling 10% oxalic acid for 3-10 minutes, washed and rinsed with triply distilled water, and then dried in air [16].

The required amounts of RuCl₃, IrCl₃ and CoCl₂ were dissolved in 20% HCl and dried by gentle heating to result in their corresponding oxide residues whose atomic ratios of Ru, Ir and Co were 5.4:3.6:1, 4.7:3.1:1 and 3:2:1. The oxide residues were dissolved in isopropanol to their corresponding limpid solutions, which were brushed onto the Ti supports and dried at 350°C in an oven [12]. The resulting electrodes were annealed at 400°C for 2-4 hours. A typical oxide film thickness was estimated to be ca. 1 mg/cm².

Electrochemical properties of the electrodes were measured by cyclic voltammetry (Electrochemical analyzer; CHI605B) in 0.8M NaHCO₃ solutions with and without saturation of CO₂. Typical saturation time was 40-50 minutes. Electrochemical reduction of CO₂ was carried out in an electrolytic cell consisting of three standard electrodes. A saturated calomel electrode (SCE) and Pt wire were used for the reference electrode and counter electrode, respectively.

The electrolysis was performed with the working electrode of 2 cm² surface area in 0.8M NaHCO₃ solution with CO₂ saturation. The CO₂ flow rate was set around 15-40 cc/min. All the experiments were performed at room temperature and atmospheric pressure. The stability of the working electrodes was checked by cyclic voltammetry before and after electrolysis. Methanol produced in the reduction of CO₂ was analyzed by GCMS (Focus Polaris Q/ Focus DSQ, USA).

3 RESULTS AND DISCUSSION

The voltammetric characterizations of two-component oxide electrodes studied in the previous work [17] are shown in Figure 1, where the atomic ratios of Ru and Ir are

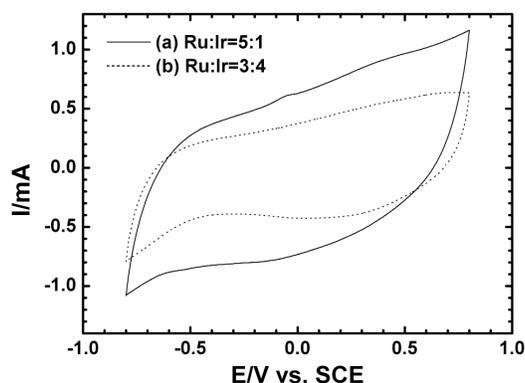


Figure 1. Cyclic voltammetric curves in 0.8M NaHCO₃ solutions with CO₂ saturation for the electrodes of oxides of Ru and Ir in two atomic ratios taken from Ref. [17]. Sweep rate 0.05 V/s.

5:1 and 3:4. Voltammetric curves of three oxide electrodes with opening of the same 5.8mm diameter obtained in 0.8 M NaHCO₃ solutions are shown in Figure 2. The atomic ratios of Ru, Ir and Co of the electrode are 5.4:3.6:1, 3:2:1, and 4.7:3.1:1, respectively. As shown in Figure 2, the electrode of Ru/Ir/Co (4.7:3.1:1) oxides delivers much higher currents than the other two, while that of Ru/Ir/Co (5.4:3.6:1) oxides the current flow significantly diminishes.

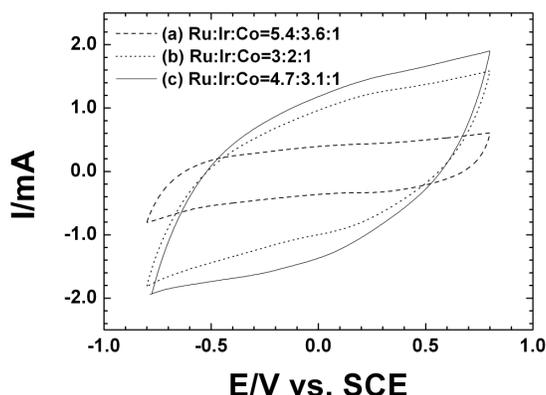


Figure 2. Cyclic voltammetric curves in 0.8M NaHCO₃ solutions with CO₂ saturation for the electrodes of oxides of Ru, Ir and Co in three atomic ratios. Sweep rate 0.1 V/s.

The current flows observed in the electrodes (a) and (b) in Figure 2 appear to enhance much better than two-component oxide electrodes in Figure 1. This observation indicates that an optimal atomic ratio of Ru, Ir and Co could be searched to further improve current flow.

In order to check the uniformity of electrode oxide layers before the reduction of CO₂, ten local points in both

sides A and B of each electrode were compared using their corresponding voltammetric curves. The five local points in Side A are denoted as LLA, ULA, CA, LRA and URA shown in Figure 3, while similarly those in Side B as

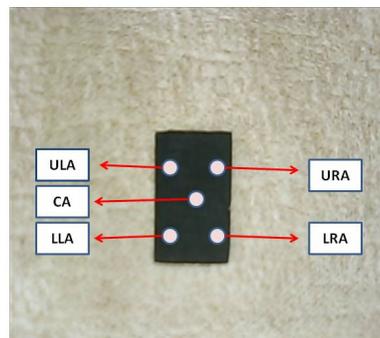


Figure 3. Five local points of Side A of the electrode for cyclic voltammetry. LLA refers to lower left; ULA to upper left; CA to center; LRA to lower right; URA to upper right.

LLB, ULB, CB, LRB and URB. Typical results are shown in Figure 4 measured for LLA and Figure 5 for LRB.

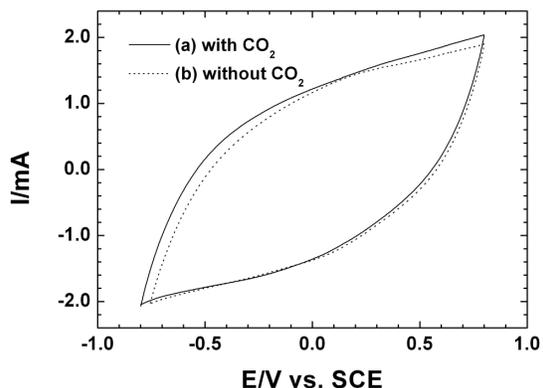


Figure 4. Cyclic voltammetric curves for LLA of the Ru/Ir/Co (4.7:3.1:1) oxide electrode in 0.8M NaHCO₃ solutions (a) with CO₂ saturation and (b) without CO₂. Sweep rate 0.1 V/s.

As shown in Figures 4 and 5, the voltammetric curves for two sides of the electrode are reasonably similar regardless of CO₂ saturation even though the currents for Side A appear slightly higher than for Side B. This implies that the oxide layers of the electrode are reasonably uniform. The other electrodes were measured to behave similarly.

The same local points of each electrode were concurrently examined before and after the CO₂ reduction. Typical results are shown in Figures 6 and 7. As shown in Figure 6, the oxide layers of the electrode holds its uniformity before the CO₂ reduction. However, as shown in Figure 7, its electrochemical behavior appears to be altered right after the reduction, implying that it might undergo a

partial change in the oxidation state of its metal oxides

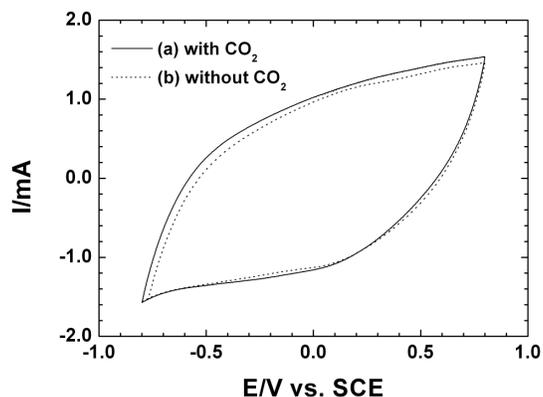


Figure 5. Cyclic voltammetric curves for LRB of the Ru/Ir/Co (4.7:3.1:1) oxide electrode as described in Figure 4.

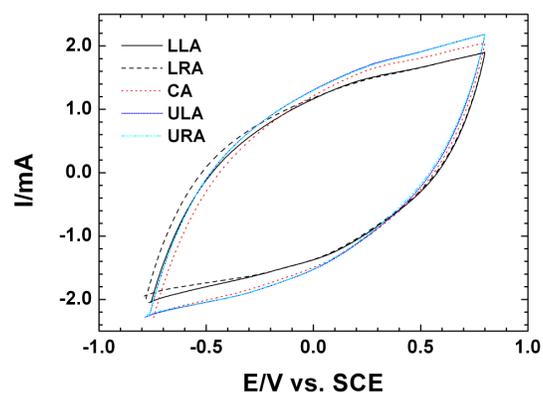


Figure 6. Cyclic voltammetric curves for five local points of Side A of the Ru/Ir/Co (4.7:3.1:1) oxide electrode before CO₂ reduction as described in Figure 4.

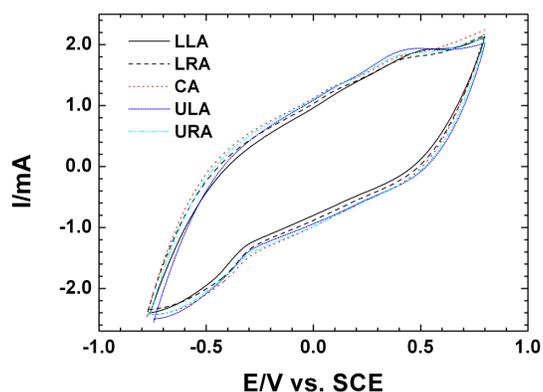


Figure 7. Cyclic voltammetric curves for five local points of Side A of the Ru/Ir/Co (4.7:3.1:1) oxide electrode after CO₂ reduction as described in Figure 4.

even though it kept its uniformity. This trend was observed in the other electrodes. Further study is needed to fully understand this observation.

The reduction of CO₂ has been performed at the potential hold of E=-0.8V for 12 hours with the electrode of Ru/Ir/Co (4.7:3.1:1) oxides. The amount of methanol detected was estimated to be in the vicinity of 100 ppm.

4 SUMMARY

The electrochemical reduction of CO₂ was studied for the electrodes of Ru/Ir/Co oxides in the atomic ratios of Ru/Ir/Co of 5.4:3.6:1, 3:2:1, and 4.7:3.1:1 in 0.8 M NaHCO₃ solutions with CO₂ saturation. For the reduction of CO₂ to methanol the electrode of Ru/Ir/Co (4.7:3.1:1) oxides appeared to be most efficient since it induced significantly higher current density than those used in the previous study. With a solar cell providing the power needed for the electrochemical reduction, CO₂ can be converted to methanol without any cost of energy. The reduction process will alleviate global warming and produce energy resource for fuel cells. Further research is needed to find an optimal composition of electrode metal oxides and consequently perform the electrochemical reduction of CO₂ with the electrodes of interest leading to substantially produce methanol used for fuel cells.

ACKNOWLEDGEMENTS

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