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# Electrochemical Reduction of CO<sub>2</sub> in Methanol with the Aid of the Oxidation of CH<sub>3</sub>COOH

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**Abstract**— The simultaneous electrochemical reduction of CO<sub>2</sub> and electrochemical oxidation of acetic acid was studied on Sn and Ag cathode and at Pt anode. The experimental studies were performed in 0.15 M NaCl catholyte and in various types of acetate (Li, Na and K) in methanol or water based anolyte at different applied positive voltages (1.5–1.8 V). The main product by electrochemical reduction of CO<sub>2</sub> with Sn cathode was methyl formate, whereas the main product with Ag cathode was carbon monoxide, and on the contrary in acetic acid oxidation with Pt anode the products were methane and ethane. The maximum Faraday efficiencies of Sn and Ag electrodes were obtained in NaCl methanol solution with 75% HCOOCH<sub>3</sub> and 58% CO, respectively. Maximum oxidation of acetate for Sn and Ag cathodes with Pt anode were 32 and 24% in CH<sub>3</sub>COONa electrolyte methanol solution. It was observed that as applied voltages increased Faradaic efficiency decreased and CH<sub>3</sub>COOH oxidation increased. These results reveal the simultaneous CO<sub>2</sub> reduction to HCOOCH<sub>3</sub> and CO, and the generation of hydrocarbon as fuels. The proposed process may assist to develop new ideas in order to improve the simultaneous reduction of CO<sub>2</sub> to products electrochemically (RCPE) with acetate oxidation.

**Index Terms**— Electrochemical reduction of CO<sub>2</sub>, Electrochemical oxidation of acetate, Methanol.

## I. INTRODUCTION

At the same time as reducing CO<sub>2</sub>, it is possible to solve energy problems by generating useful chemicals. It is very effective that it can selectively produce fuel gas such as hydrocarbon from biomass acetic acid and at the same time reduces CO<sub>2</sub>. Metal catalysts are categorized into four groups based on their main reduction products, as observed by Hori et al.: HCOOH (Pb, Tl, Hg, Sn, In, Cd), ii) CO (Au, Ag, Pd, Ga, Zn), iii) CH<sub>4</sub>/C<sub>2</sub>H<sub>4</sub> (Cu), and iv) H<sub>2</sub> (Pt, Ni, Fe, Ti). These product trends are supported by consistent and extensive observation of these categorical trends in many studies, suggesting dissimilar reaction mechanisms and different surface affinities for CO<sub>2</sub> reduction intermediates. The catalytic activity of metals depends on their intrinsic atomic properties and their surface characteristics such as roughness and surface area to volume ratios, both of which affect the plane edges exposed at the surface [1-3]. However, there is little information on the electrochemical oxidation of organic pollutants combined with the electrochemical reduction of CO<sub>2</sub> in methanol. Therefore, the present work has dealt with the electrochemical reduction of CO<sub>2</sub> in methanol with the aid of the electrochemical oxidation of acetic acid.

## II. METHODS

The electrochemical system was operated using a potentiostat (HA-3001A, Hokutodenko Co. Ltd.) under ambient pressure and temperature. The 0.15 M NaCl in methanol solution was used as catholyte and various types of acetate salts (Li, Na and K) in methanol or water based electrolyte solutions were used as anolytes. The experiment was performed in a standard three-electrode H-type cell equipped with Sn and Ag wires or Pt plate as cathode and Pt plate as the anode and an Ag Q.R.E. as reference electrode (Fig. 1). The Pt foils were polished with alumina powder emulsion (Baikalox, 0.05 μm), and electrochemically activated in concentrated phosphoric acid. Sn electrode was immersed in 10% hydrochloric acid for 60 seconds, and Ag electrode was immersed in concentrated sulfuric acid for 20 seconds. Then, they were rinsed with distilled water and ethanol. Aldrich Nafion 117 ion exchange membrane was used as the diaphragm between anode and cathode. After CO<sub>2</sub> gas was bubbled into the methanol catholyte for 2 hours, the CO<sub>2</sub> saturated solution was reduced electrolytically, and the acetate solution was oxidized.

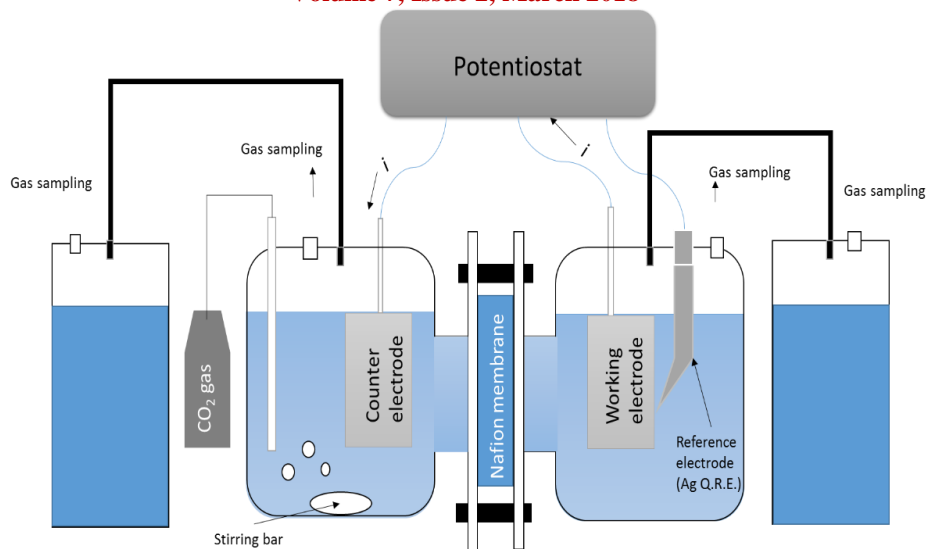


Fig. 1 Schematic illustration for the electrochemical reduction of CO<sub>2</sub> with H-type cell using 3 electrodes.

The gaseous products obtained during CO<sub>2</sub> reduction and acetate oxidation were collected in individual gas collectors and were analyzed by gas chromatography. The soluble products in the catholyte were analyzed by using high performance liquid chromatography (HPLC). The relative Faradaic efficiency was determined by calculating the charge used for products divided by the total charge passed through the system (1).

$$f = \frac{nzF}{Q} \quad (1)$$

where n is the amount of reduction products and oxidation products; z is the number of electrons needed to form CO, HCOOCH<sub>3</sub> from CO<sub>2</sub> and holes needed to form ethane and methane, F is Faraday's constant whose value is 96485 C mol, and Q is total charge during the experiment. [4]

### III. RESULTS AND DISCUSSION

The experiments were performed using an anode Pt and cathode Pt electrodes for CH<sub>3</sub>COOH oxidation. In order to investigate the effect of salts on the formed oxidation products from acetates, the various cations in methanol and water were checked for the electrochemical oxidation of acetate (Fig. 2). The Faradaic efficiencies are obtained at a potential of 1.7 V (vs. Ag Q.R.E) for 20 C. In all of conditions, the products were only methane and ethane. In the case of both the water solution and methanol solution electrolyte, the efficiencies increased with the order of Na, Li and K salts. The Faradaic efficiencies in the methanol solution were better relative to those obtained in the aqueous solution.

In order to investigate the influence of the potential, a potential was applied from 1.6 V to 1.8 V (vs. Ag Q.R.E.) using sodium acetate methanol solution as anolyte (Fig. 3). The results showed that the amounts of hydrocarbons increased as the potential increased.

In order to investigate the influence of concentration of sodium acetate, the concentration of acetate (0.1, 0.5, 1.0 and 1.2 M) was checked in methanol (Fig. 4). The products were only methane and ethane, but there were hardly effects on the formation product. Therefore, the anolyte in the simultaneous electrochemical reduction of CO<sub>2</sub> and oxidation of CH<sub>3</sub>COOH was fixed with 1.0 M sodium acetate.



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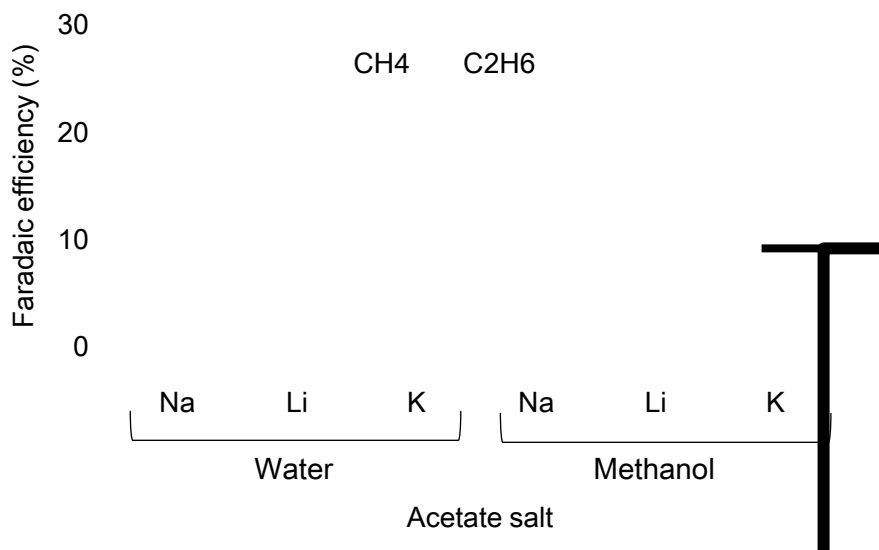


Fig. 2 Effect of salts on Faradaic efficiencies of the products by electrochemical oxidation of acetate. Anode: Pt, cathode: Pt, potential: 1.7 V, catholyte: 0.1 M NaCl in methanol.

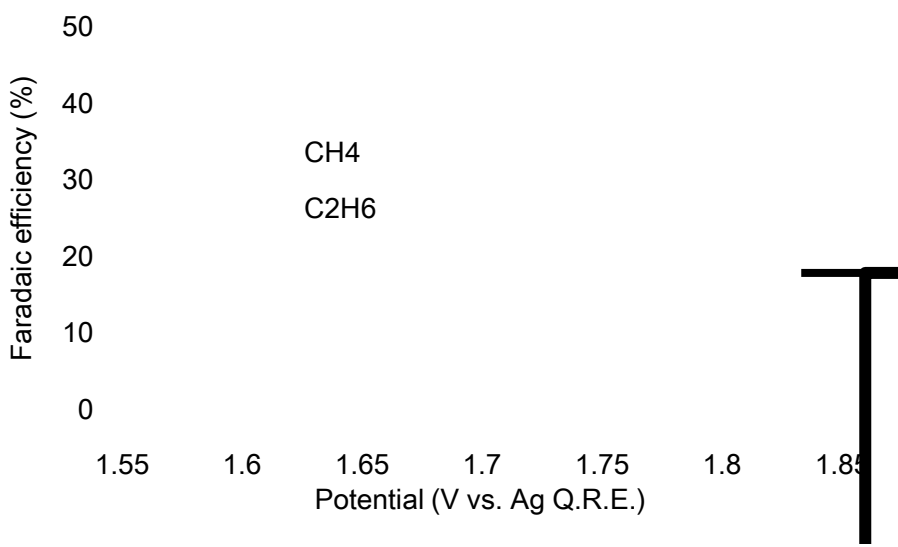


Fig. 3 Effect of potential on Faradaic efficiencies of the products by electrochemical oxidation of CH<sub>3</sub>COONa. Anode: Pt, cathode: Pt, anolyte: 1.0 M CH<sub>3</sub>COONa in methanol, catholyte: 0.1 M NaCl.

The experiments were conducted using an anode (Pt) and cathode (Sn and Ag) electrodes for CO<sub>2</sub> reduction and CH<sub>3</sub>COOH oxidation. Different applied potentials of 1.5 ~ 1.75 V vs. Ag Q.R.E. for Sn cathode and 1.5 ~ 1.8 V vs. Ag Q.R.E. for Ag cathode were used.

The electrochemical reduction of CO<sub>2</sub> in 0.15 M NaCl solution and the electrochemical oxidation of 1.0 M CH<sub>3</sub>COONa in methanol were carried out. The reduction products by electrochemical reduction of CO<sub>2</sub> with Sn cathode were methyl formate, carbon monoxide. The oxidation products with Pt electrode were methane and ethane. The main product by electrochemical reduction of CO<sub>2</sub> with Sn cathode was methyl formate, whereas the main product with Ag cathode was carbon monoxide at all potentials. The results for simultaneous electrochemical reaction studies in NaCl methanol catholyte and anolyte were shown in Figs. 5 and 6. Maximum formation efficiency of methyl formate was 75.2% at 1.75 V; on the other hand, maximum formation efficiency of ethane was 32.2%.

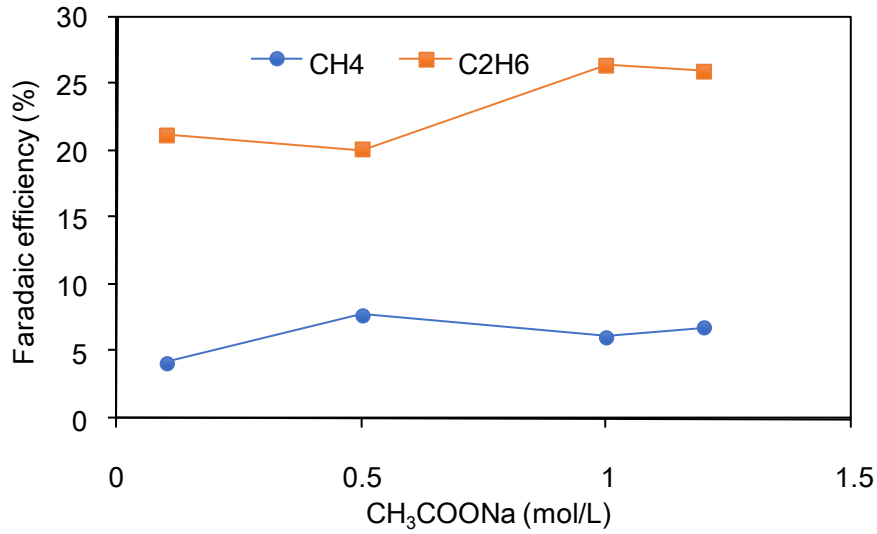


Fig. 4 Effect of concentration on Faradaic efficiencies of the products by electrochemical oxidation of CH<sub>3</sub>COONa. Cathode: Pt, Anode: Pt, potential: 1.7 V.

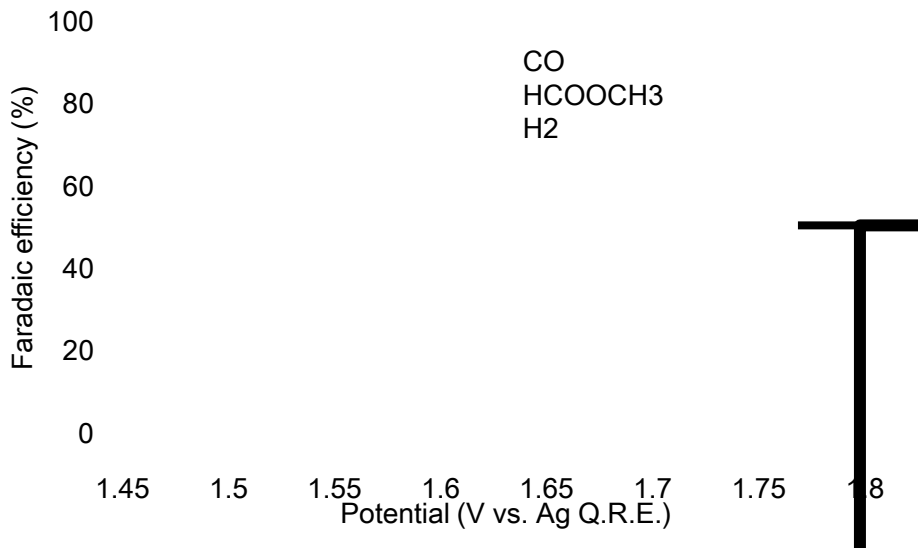


Fig. 5 Effect of potential on Faradaic efficiencies of the products by electrochemical reduction of CO<sub>2</sub>. Anode: Pt, cathode: Sn, anolyte: 1.0 M CH<sub>3</sub>COONa in methanol, catholyte: 0.15 M NaCl in methanol.

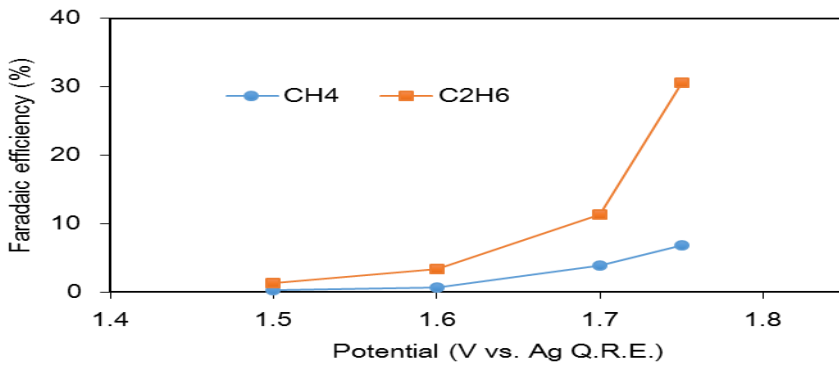


Fig. 6 Effect of potential on Faradaic efficiencies of the products by electrochemical oxidation of CH<sub>3</sub>COONa. Anode: Pt, cathode: Sn, anolyte: 1.0 M CH<sub>3</sub>COONa in methanol, catholyte: 0.15 M NaCl in methanol.

The results for simultaneous studies in NaCl methanol solution catholyte and anolyte were shown in Fig. 7 and 8. The main product by electrochemical reduction of CO<sub>2</sub> at Ag cathode was carbon monoxide at all potentials (1.5, 1.6, 1.7 and 1.8 V). Maximum formation efficiency of carbon monoxide was 58.2% at 1.7 V, on the other hand maximum formation efficiency of ethane was 32.2% at 1.8V.

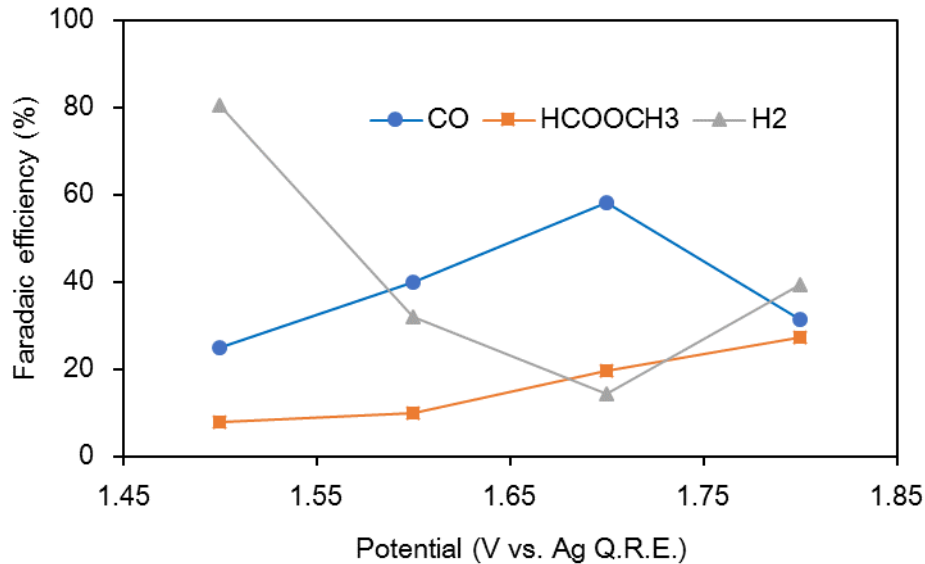


Fig. 7 Effect of potential on Faradaic efficiencies of the products by electrochemical reduction of CO<sub>2</sub>. Anode: Pt, cathode: Ag, anolyte: 1.0 M CH<sub>3</sub>COONa in methanol, catholyte: 0.15 M NaCl in methanol.

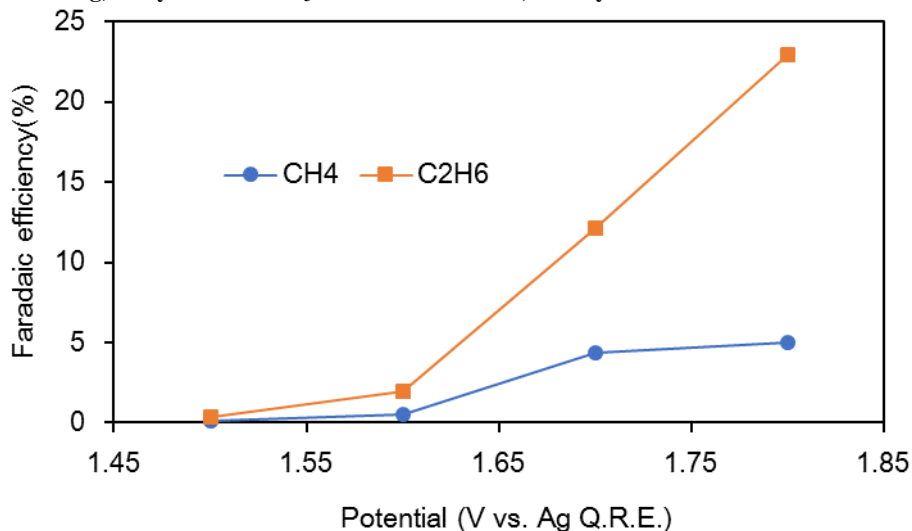


Fig. 8 Effect of potential on Faradaic efficiencies of the products by electrochemical oxidation of CH<sub>3</sub>COONa. Anode: Pt, cathode: Ag, anolyte: 1.0 M CH<sub>3</sub>COONa in methanol, catholyte: 0.15 M NaCl in methanol.

#### IV. CONCLUSION

The main product by electrochemical reduction of CO<sub>2</sub> at Sn cathode was methyl formate, on the other hand, the main product at Ag cathode was carbon monoxide (CO). The different reduction products could be obtained by changing the cathode electrode. As the applied voltages increased, Faradaic efficiency for the reduction of CO<sub>2</sub> decreased and CH<sub>3</sub>COOH oxidation efficiency increased.

By using methanol anolyte and catholyte, both the reduction and oxidation efficiencies with high efficiency could be realized. The oxidation products were ethane and methane, and an increase in efficiency could be observed by



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increasing the potential. Main reduction products from  $\text{CO}_2$  were  $\text{HCOOCH}_3$  and  $\text{CO}$  for Sn and Ag electrodes, respectively. Therefore, the selectivity differs, for Sn;  $\text{HCOOCH}_3$  and for Ag;  $\text{CO}$  with high current efficiency. Oxidation efficiencies for hydrocarbons at low potential is very low. However, at relatively negative potential, it is possible to the simultaneous electrochemical Reduction of  $\text{CO}_2$  in Methanol with the aid of the oxidation of  $\text{CH}_3\text{COOH}$ . The present system seems to be one of promising methods for the electrochemical reduction of  $\text{CO}_2$ .

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#### REFERENCES

- [1] A. Januszewska, R. Jurczakowski, P.J. Kulesza, "CO<sub>2</sub> electroreduction at bare and Cu-decorated Pd pseudomorphic layers: catalyst tuning by controlled and indirect supporting on Au (111)", *Langmuir* Volume 30 (2018) 14314–14321.
- [2] M. Azuma, K. Hashimoto, M. Hiramoto, Electrochemical reduction of carbon dioxide on various metal electrodes in low-temperature aqueous  $\text{KHCO}_3$  media, *J. Electrochem. Soc.* 137 (1990) 1772–1778.
- [3] J. Wu, F. Risalvato, X. Zhou, Electrochemical reduction of Carbon Dioxide I. effects of the electrolyte on the selectivity and activity with Sn electrode, *ECS Trans.* 41 (2012) 49–60.
- [4] W. Lv, R. Zhang, P. Gao, L. Lei, Studies on the faradaic efficiency for electrochemical reduction of carbon dioxide to formate on tin electrode, *J. Power Sources* 253 (2014) 276–281.

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