Power Generation Characteristics of a Polymer Electrolyte Fuel Cell by Feeding CO₂ and H₂: Dependence on the Cathodic Pt-Ru/C Catalyst Composition

Shofu MATSUDA, Kazutaka SATO, Yuuki NIITSUMA, and Minoru UMEDA*

Department of Materials Science and Technology, Graduate School of Engineering,
Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan

* Corresponding author: mumeda@vos.nagaokaut.ac.jp

ABSTRACT

To identify an electrocatalyst that can effectively generate power and reduce CO₂, we measured the power generation characteristics of a polymer electrolyte fuel cell fed with H₂ and CO₂ to the anode (Pt/C) and cathode (Pt_(1-x)Ru_x/C), respectively. The obtained power generation characteristics were compared to their corresponding CO₂ reduction characteristics. A trade-off relationship between the CO₂ reduction and power generation performances was observed. Overall, the Pt_{0.8}Ru_{0.2}/C electrocatalyst has the potential to be an efficient cathodic catalyst in a H₂-CO₂ fuel cell that reduces CO₂ while generating power.

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Keywords : H₂-CO₂ Fuel Cell, Pt-Ru/C, CO₂ Reduction

1. Introduction

Recently, CO₂ reduction has become a popular topic in the field of electrochemistry. Many reports regarding CO₂ electroreduction at various metal electrodes have been recently published. Hori et al. reported that hydrocarbons (CH₄ and C₂H₄) can be produced at a Cu electrode with a Faradaic efficiency of ~60%.^{1,2} When using Au, Ag, or Zn electrodes, CO is typically obtained as the major product with high selectivity.^{3–5} However, CO₂ reduction at Cu, Au, Ag, and Zn electrodes requires an overpotential as high as approximately 1 V.

CO₂ electroreduction is expected to contribute novel energy systems in the future, including power to gas devices.⁶ For practical applications of CO₂ electroreduction, the overpotential should be minimized. Importantly, Giner and we previously reported that CO₂ is reduced at a potential ranging between 0.0 and 0.4 V vs. RHE using Pt and Pt-Ru electrocatalysts^{7–9} and CH₄ production was also observed with both electrocatalysts.⁹ Comparisons to the CO₂/CH₄ standard redox potential can be expressed by the following equation:¹⁰

the CO₂ reduction reaction at the Pt and Pt-Ru electrocatalysts occurs at a potential close to the theoretical CO₂ reduction potential.

Considering that the potential of CO₂ reduction at the Pt and Pt-Ru electrocatalysts is more positive than that of H₂ oxidation, power generation is theoretically expected by combining the two reactions of Eqs. (1) and (2) as the cathode and anode reactions, respectively.

H₂-CO₂ fuel-cell power generation was previously observed by feeding H₂ and CO₂ to the anode and cathode, respectively, of a polymer electrolyte fuel cell (PEFC) with a membrane electrode assembly (MEA) containing the cathodic and anodic Pt/C electrocatalyst.¹¹ However, the cathodic products from the CO₂ reduction were not analyzed in detail.¹¹ On the other hand, H₂-CO₂ fuel cells containing cathodic Pt-Ru/C electrocatalysts generate power while producing CH₄ from CO₂ reduction. However, the fuel-cell tested only one composition of the Pt_{0.8}Ru_{0.2}/C electrocatalyst.⁹ Thus, it is

important to study the dependence of the power generation and CH₄ production from CO₂ reduction on the composition of the cathodic Pt-Ru/C catalyst.

This study compares the H₂-CO₂ fuel-cell power generation characteristics among five Pt-Ru/C cathodic electrocatalyst compositions. Pt/C, Pt_{0.8}Ru_{0.2}/C, Pt_{0.5}Ru_{0.5}/C, Pt_{0.33}Ru_{0.67}/C, and Ru/C electrocatalysts were used herein. An MEA with Pt/C and Pt_(1-x)Ru_x/C at the anode and cathode, respectively, was prepared and inserted into the PEFC for evaluation of the H₂-CO₂ fuel-cell ability. The optimum Pt_(1-x)Ru_x/C electrocatalyst composition for CO₂ reduction and power generation in the H₂-CO₂ fuel cell was determined.

2. Experimental

A PEFC was prepared using previously described methods.⁹ The different types of powder electrocatalysts were purchased from Tanaka Kikinzoku Kogyo (Tokyo, Japan). Briefly, 45.7 wt% Pt/C, 42.5 wt% Pt-Ru/C (0.8:0.2 atomic ratio Pt:Ru), 49.5 wt% Pt-Ru/C (0.5:0.5 atomic ratio Pt:Ru), 55.8 wt% Pt-Ru/C (0.33:0.67 atomic ratio Pt:Ru), and 28.0 wt% Ru/C were used as cathodic catalysts. Their XRD patterns correspond to the results reported in the literatures.^{8,12} In contrast, 45.7 wt% Pt/C was used as the anodic catalyst. An MEA was prepared with the cathodic and anodic catalysts using a Nafion 117 membrane (Dupont, Wilmington, DE, USA). The apparent electrode surface area was 9 cm² and the metal loading was 1.0 mg/cm². Finally, the prepared MEA was equipped with a polymer electrolyte fuel single cell (Miclab, Kanagawa, Japan).

The prepared PEFC was connected to a polymer electrolyte fuel cell power generation unit (FCG-20S, ACE, Inc., Kanagawa, Japan). The current-density/voltage (*I*-*V*) and current-density/power-density (*I*-*P*) characteristics of the prepared PEFCs were evaluated by supplying fully-humidified H₂ gas (purity: 99.999%) to the anode at a volume flow of 50 cm³/min and fully-humidified CO₂ gas (purity: 99.995%) to the cathode at 50 cm³/min. After the open circuit voltage (OCV) stabilized, a load current of 0.02 A was applied every minute from the OCV to 0.02 V at cell temperatures of 40, 60, and 80°C. The PEFC test was also conducted at 90°C for the cell with a

Figure 1. Schematic diagram of the PEFC setup used in this study.

Pt/C cathode. The instruments used in this study were an HA-310 galvanostat (Hokuto Denko, Tokyo, Japan) and HB-104 function generator (Hokuto Denko). A schematic diagram of the PEFC setup used in this study is shown in Fig. 1.

3. Results and Discussion

Figure 2 shows the I - V and I - P curves of a single PEFC when humidified H_2 and CO_2 were supplied to the anode and cathode, respectively. The data for the Pt/C catalyst, except for the results obtained at $90^\circ C$ and with the $Pt_{0.8}Ru_{0.2}/C$ catalyst were taken from the literature.⁹ Figure 2 shows that all the five $Pt_{(1-x)}Ru_x/C$ ($0 \leq x \leq 1$) catalyst compositions used in this study generated power in the H_2 - CO_2 fuel cell and the I - V and I - P behaviors depended on the catalyst composition and cell temperature. Except for the $Pt_{0.8}Ru_{0.2}/C$ catalyst (Fig. 2(b)), the generated cell voltage and power density was enhanced with increasing cell temperature. These trends, which were attributed to the increased reaction rate due to higher temperatures, corresponded well the previously reported H_2 - CO_2 fuel cell characteristic.¹¹ The power density at

Figure 3. Maximum power density (●) and m/z 16 signal intensity (□) at the temperature of $80^\circ C$ as functions of the composition of the cathodic catalyst. The data for the m/z 16 signal intensity was obtained from the literature.⁹

$60^\circ C$ was the highest for the $Pt_{0.8}Ru_{0.2}/C$ catalyst due to the efficient CH_4 production from CO_2 reduction. According to our previous report, the efficiency at $60^\circ C$ was higher than that at $80^\circ C$.⁹

To clarify the catalyst composition dependence, Fig. 3 shows the relationships between the intensity of the m/z 16 signal (from the literature⁹), the maximum power density (P_{max}) which was calculated by averaging three values before and after the maximum at the temperature of $80^\circ C$ from Fig. 2, and the catalyst composition, indicating that P_{max} increases with increasing Ru content in the catalyst. Each $P_{max} \pm$ its standard deviation was 0.639 ± 0.017 , 0.852 ± 0.023 , 0.886 ± 0.010 , 0.973 ± 0.021 , and 0.986 ± 0.010 mW/cm² for Pt/C, $Pt_{0.8}Ru_{0.2}/C$, $Pt_{0.5}Ru_{0.5}/C$, $Pt_{0.33}Ru_{0.67}/C$, and Ru/C, respectively. The Ru/C catalyst exhibited the highest power density and the intensity of the m/z 16 signal indicated the extent of CH_4 generation from the CO_2 electro-reduction.⁹ Interestingly, a trade-off relationship was observed between the intensity of the m/z 16 signal and P_{max} with changing

Figure 2. Voltage and power density as functions of current density for the various catalyst compositions: (a) Pt/C, (b) $Pt_{0.8}Ru_{0.2}/C$, (c) $Pt_{0.5}Ru_{0.5}/C$, (d) $Pt_{0.33}Ru_{0.67}/C$, and (e) Ru/C. The cell temperatures were $40^\circ C$ (black), $60^\circ C$ (red), $80^\circ C$ (blue), and $90^\circ C$ (green only for Pt/C). Open symbols represent voltages and closed symbols are power densities.

Pt-Ru composition. This relationship can be explained by the mechanism of fuel-cell power generation.

A fuel cell uses the chemical energy of H₂ supplied as the fuel to the anode for reduction of the compound supplied to the cathode. During this process, the remaining energy can be harnessed as electric power. Thus, the amount of available electric power depends on the nature of the reaction occurring at the cathode. Consequently, the relationship between the electrochemical generation of CH₄ from CO₂ and power generation from the excess energy exhibited a trade-off relationship. Less electrical energy can be harnessed as power with increasing activity at the cathode, while power generation increases with reduced activity. The results presented herein follow the same trend; less CH₄ generation resulted in higher $P_{\max}$ values. For the purpose of this study, a catalyst able to reduce CO₂ and work in a fuel cell to generate power is required, and Pt_{0.8}Ru_{0.2}/C was determined to be optimal for this purpose. This CO₂ reduction system is continuous type and can generate CH₄ at lower temperature compared to a batch-type catalytic methanation of CO₂ which requires the temperature of several hundred °C.¹³

4. Conclusions

Fuel-cell power generation tests were performed with a PEFC by feeding H₂ and CO₂ to the Pt/C-catalyst-containing anode and Pt_(1-x)Ru_x/C-containing cathode, respectively. All cathodic catalysts (Pt/C, Pt_{0.8}Ru_{0.2}/C, Pt_{0.5}Ru_{0.5}/C, Pt_{0.33}Ru_{0.67}/C, and Ru/C) functioned in the prepared H₂-CO₂ fuel cells with power generation characteristics that depended on their composition. The Ru/C catalyst exhibited the highest power density, but the amount of CH₄ generated was negligible. In contrast, the Pt_{0.8}Ru_{0.2}/C catalyst

exhibited a lower power density compared to that of Ru/C, but large amounts of CH₄ were generated. Hence, the Pt_{0.8}Ru_{0.2}/C was an ideal catalyst for use in the H₂-CO₂ fuel cell that reduces CO₂ while generating power.

Acknowledgment

This work was supported by the Japan Science and Technology Agency (JST) through the Advanced Catalytic Transformation Program for Carbon Utilization (ACT-C, Grant Number JPMJCR12Y4).

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