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

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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 Pt0.8Ru0.2/C electrocatalyst has the potential to be an efficient cathodic catalyst in a H2-CO2 fuel cell that reduces CO2 while generating power.

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.3 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.4 For practical applications of CO2 electroreduction, the overpotential should be minimized. Importantly, Giner and we previously reported that CO2 reduction at Cu, Au, Ag, and Zn electrodes requires an overpotential as high as approximately 1 V.5 However, CO2 reduction at Cu, Au, Ag, and Zn electrodes requires an overpotential as high as approximately 1 V.6

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CO2-electrocatalysts were used herein. An MEA was prepared with Pt and Pt-Ru electrocatalysts, and CH4 production was also observed with both electrocatalysts. Comparisons to the CO2/CH4 standard redox potential can be expressed by the following equation:10

\[
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- = \text{CH}_4 + 2\text{H}_2\text{O} \quad (E^\text{c} = 0.169 \text{ V vs. SHE}) \tag{1}
\]

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.

\[
2\text{H}^+ + 2\text{e}^- = \text{H}_2 \quad (E^\text{c} = 0.000 \text{ V vs. SHE}) \tag{2}
\]

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 Pt0.8Ru0.2/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, Pt0.5Ru0.5/C, Pt0.5Ru0.5/C, Pt0.3Ru0.7/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 literature.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 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
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 H₂ and CO₂ were supplied to the anode and cathode, respectively. The data for the Pt/C catalyst, except for the results obtained at 90°C and with the Pt₀.₈Ru₀.₂/C catalyst, were taken from a previous study.9 Figure 2 shows that all the Ptₓ₁₋ₓRuₓ/C (0 ≤ x ≤ 1) catalyst compositions used in this study generated power in the H₂-CO₂ fuel cell and the I-V and I-P behaviors depended on the catalyst composition and cell temperature. Except for the Pt₀.₈Ru₀.₂/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 to the previously reported H₂-CO₂ fuel cell characteristic. The power density at 60°C was the highest for the Pt₀.₈Ru₀.₂/C catalyst due to the efficient CH₄ production from CO₂ reduction. According to our previous report, the efficiency at 60°C was higher than that at 80°C.⁹

To clarify the catalyst composition dependence, Fig. 3 shows the relationships between the intensity of the m/z 16 signal (from the literature), the maximum power density (P_max) which was calculated by averaging three values before and after the maximum at the temperature of 80°C from Fig. 2, and the catalyst composition, indicating that P_max increases with increasing Ru content in the catalyst. Each P_max± 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, Pt₀.₈Ru₀.₂/C, Pt₀.₆Ru₀.₄/C, Pt₀.₃₃Ru₀.₆₇/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 CH₄ generation from the CO₂ 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 1. Schematic diagram of the PEFC setup used in this study.

Figure 2. Voltage and power density as functions of current density for the various catalyst compositions: (a) Pt/C, (b) Pt₀.₈Ru₀.₂/C, (c) Pt₀.₆Ru₀.₄/C, (d) Pt₀.₃₃Ru₀.₆₇/C, and (e) Ru/C. The cell temperatures were 40°C (black), 60°C (red), 80°C (blue), and 90°C (green only for Pt/C). Open symbols represent voltages and closed symbols are power densities.

Figure 3. Maximum power density (•) and m/z 16 signal intensity (♦) at the temperature of 80°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
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 Pₘₐₓ 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 Pt₀.₈Ru₀.₂/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 Pt₁₋ₓRuₓ/C-containing cathode, respectively. All cathodic catalysts (Pt/C, Pt₀.₈Ru₀.₂/C, Pt₀.₅Ru₀.₅/C, Pt₀.₃₃Ru₀.₆₇/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 Pt₀.₈Ru₀.₂/C catalyst exhibited a lower power density compared to that of Ru/C, but large amounts of CH₄ were generated. Hence, the Pt₀.₈Ru₀.₂/C was an ideal catalyst for use in the H₂-CO₂ fuel cell that reduces CO₂ while generating power.

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