Electroreduction of CO₂ to CH₄ without overpotential using Pt-black catalysts: Enhancement of faradaic efficiency

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Summary
The use of metal electrocatalysts (Cu, Au, and Ag) is the mainstream in primary CO₂ reduction systems, but their large overpotential induces a decrease in energy conversion efficiency. Recently, it has been discovered that carbon-supported Pt can make a game change to reduce CO₂ to CH₄ electrocatalytically without overpotential; however, its faradaic efficiency remains only 12.3% thus far. One approach is to investigate the role of carbon supports for improving the efficiency. In this study, improved CO₂ reduction was carried out by employing a Pt-black electrocatalyst without a carbon support in a polymer electrolyte membrane electrolyzer cell. When supplying CO₂ diluted by Ar gas at CO₂ concentrations of 4-7 vol.%, the efficient CH₄ generation was observed. The reason behind the improved production of CH₄ occurs by a Langmuir-Hinshelwood mechanism associated with adsorbed CO (COads) and H (Hads) on the Pt electrocatalyst. Moreover, a high-density COads environment (surface) can be created at the Pt-black catalyst, achieving CH₄ generation with a faradaic efficiency of 23.2% at 0.18 V vs RHE. Therefore, this study succeeded in improving the faradaic efficiency of CH₄ production from CO₂ reduction without overpotential using a Pt-black electrocatalyst.

1 | INTRODUCTION

CO₂ electroreduction and fixation are central issues to the prevention of global warming. The products of CO₂ reduction strongly depend on the metal used as the electrode.¹⁻⁵ This phenomenon is explained by the fact that during CO₂ reduction, CO (a reduction intermediate) interacts with the metal electrode.⁶,⁷ When gold, silver, and zinc are used, CO is obtained because of its weak adsorption to the metal surface.¹,⁴ In the case of copper electrodes, hydrocarbons are obtained because of the existence of moderate interactions, where the faradaic efficiency for hydrocarbon generation exceeds 60%.⁸ In spite of these notable features, those electrodes require a high overpotential to obtain the desired products, which results in low production selectivity and low stability. Conversely, the Pt electrode exhibits completely different characteristics for CO₂ reduction.

The reaction between CO₂ and the Pt electrode has long been studied. In 1963, the first report in this regard revealed that CO₂ is electrochemically reduced at approximately 0 V vs the reversible hydrogen electrode (RHE), to generate “reduced CO₂.”⁹ Subsequently, with the help of in situ infrared (IR) studies, the “reduced CO₂” was found to be CO adsorbed on Pt (COads).¹⁰,¹¹ Hoshi et al. found that the reduction rate of CO₂ → COads at a Pt electrode is faster than that at the electrodes of other Pt group metals.¹² Hara et al. reported a 38.8% CH₄
generation efficiency at −1.9 V vs Ag/AgCl and 20 atm CO₂. However, the experiment conducted at 1 atm CO₂ showed that small amounts of CH₄ and CH₃OH were obtained at −1.5 V vs RHE. According to these reports, CO₂ is reduced to CO_ads at the Pt electrode with an infinitesimal overpotential; the CO_ads is not reduced further, even when a high overpotential is applied to the related aqueous systems.

Previously, we reported that a small amount of CH₃OH and CH₄ can be obtained without overpotential by employing a carbon-supported platinum electrocatalyst (Pt/C) in a polymer electrolyte membrane electrolyzer cell (PEMEC). However, its faradaic efficiency was as low as 0.4%. Recently, using the same electrocatalyst, we developed a new technique in which diluted CO₂ (below 10 vol.%) was fed to the Pt/C, resulting in an improved faradaic efficiency. The mechanism that led to this improved efficiency was considered to control the molecular ratio of CO_ads and adsorbed H (H_ads) on the Pt, which were both formed around the theoretical potential and also participated in CH₄ generation. As a result, CH₄ was generated at 0.16 V without H₂ evolution, and its faradaic efficiency was dramatically enhanced to 12.3%.

Despite this, more than 85% of the total current did not contribute to CH₄ generation. Therefore, it is necessary to clarify the source of the current consumption, and mitigate it to increase the CH₄ production efficiency. In Ag-based electrocatalysts, the faradaic efficiency for CO production is reported to be improved more than 10 times by removing the carbon support for CO₂ reduction at a certain overpotential, although the detailed mechanism is still uncertain. However, this suggests a new approach for CO₂ reduction using Pt catalysts, where the carbon support may have a special role in the reduction reaction.

An efficient way to demonstrate this is by using a Pt-black catalyst without carbon particles. The objectives of this study were to elucidate the influence of the carbon support on CO₂ electroreduction and to increase the faradaic efficiency of CH₄ generation based on the considered mechanism. In this experiment, the CO₂ reduction characteristics of the Pt-black electrocatalyst were investigated and compared with those of Pt/C electrocatalysts with different Pt:C weight ratios. This was done to better understand the extent of their influence on the CO₂ reduction process.

2 | EXPERIMENTAL PROCEDURE

A PEMEC was prepared by a method described in our previous papers, using a Nafion-based membrane electrode assembly containing 96.4 wt.% Pt-black (TEC90300 from Tanaka Kikinzoku Kogyo Co., Ltd.) and 46.2 wt.% Pt/C (TEC10E50E from Tanaka Kikinzoku Kogyo Co., Ltd.) as the working and counter electrodes (WE and CE), respectively. A RHE was also incorporated into the cell. The amount of Pt in the WE was 9 mg/9 cm². Fully humidified H₂ and Ar/CO₂ gases at CO₂ concentrations of 0, 4, 7, 10, 20, 50, and 100 vol.% were supplied to the CE and WE, respectively. A fully humidified environment was employed to maintain high H⁺ conductivity and H⁺ diffusion coefficient of a Nafion membrane. H₂ was supplied to the CE so that the voltage applied to the entire cell becomes lower. The cell temperature was maintained at 40°C. Cyclic voltammetry (CV) was conducted in a potential range from 0.03 V to 1.0 V vs RHE at a scan rate of 10 mV/s. For the potential step experiment, the WE potential was stepped 13 times in the range from 0.40 V to 0.03 V vs RHE, in the negative direction every 2 minutes at a 4 vol.% CO₂. In addition, the WE potential was stepped down from 0.40 V to 0.18 V vs RHE, held there for 300 seconds, then stepped down further to 0.03 V vs RHE. During these electrochemical experiments, in-line mass spectrometry (MS) with an ionization energy of 23 eV was performed for the quantitative and qualitative evaluation of the products of CO₂ reduction. The instruments used were an HA-310 potentiostat (Hokuto Denko Co.), an HB-104 function generator (Hokuto Denko Co.), and a JMS-Q1050GC (JEOL Ltd.) mass spectrometer.

3 | RESULTS AND DISCUSSION

3.1 | CO₂ concentration dependence of CO₂ reduction on the Pt-black electrocatalyst

In-line MS results during CV for the prepared PEMEC (which had a Pt-black electrocatalyst as a WE) at 4 vol.% CO₂ are shown in Figure 1A, where cyclic voltammogram and MS signals of m/z 2 (corresponding to H₂ evolution) and m/z 15 (representing a CH₃⁺ from CH₄ fragmentation) are shown. These are the data from the third cycle of CV with in-line MS. On the cyclic voltammogram, the oxidation currents (A) at approximately 0.60 V vs RHE and (B) in the range 0.05-0.35 V vs RHE are derived from the oxidative desorption of CO_ads (CO₂ generation) and H_ads (H⁺ generation), respectively. The CO_ads and H_ads are formed when the reduction current (C) in the range 0.40-0.10 V vs RHE is observed. This information is supported by reports from literature. With a rapid increase in the reduction current (D) at a potential lower than 0.10 V vs RHE, an
An increase in $m/z$ 2 signal (indicating $H_2$ generation) was observed. Notably, the $m/z$ 15 signal was detected not only at potentials below 0.10 V vs RHE but also at potentials in the range 0.20-0.10 V vs RHE. Figure S1 shows the mass spectra at approximately 0.10 V vs RHE during the cathodic scan shown in Figure 1A and that of standard $CH_4$ gas. Both trends are consistent, revealing that $CH_4$ generation from $CO_2$ reduction occurs at the standard electrode potential (0.169 V). Also, it has been elucidated that the $CH_4$ really comes from $CO_2$ reduction at Pt electrocatalyst by a test using isotopically labeled $CO_2$ ($^{13}CO_2$) gas. Therefore, it is clear that when a Pt-black electrocatalyst is used, $CH_4$ is produced without overpotential.

The faradaic efficiency for $CH_4$ generation from $CO_2$ reduction ($CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$) was calculated based on the molar quantity estimated from the integrated $m/z$ 15 signal intensity in the range 0.20-0.10 V vs RHE and the faradaic current measured simultaneously. Figure 1B shows the faradaic efficiencies plotted as a function of $CO_2$ concentration. Although the efficiency at 100 vol.% $CO_2$ was low, a clear improvement in $CH_4$ production efficiency was observed particularly when supplying 4-7 vol.% $CO_2$. This observation is similar to that made for $CO_2$ reduction ($CH_4$ generation) over Pt/C and Pt$_{0.8}$Ru$_{0.2}$/C electrocatalysts.

Regarding the reaction mechanism of $CH_4$ generation at Pt electrocatalyst, it has been experimentally evidenced that $CH_4$ production reaction proceeds by a Langmuir-Hinshelwood mechanism associated with $CO_{ads}$ and $H_{ads}$, as represented in the following equation:

$$CO_{ads} + 6H_{ads} \rightarrow CH_4 + H_2O + 7\ast,$$  \hspace{1cm} (1)

where $\ast$ represents the active sites on the Pt catalyst. When the concentration of $CO_2$ supplied becomes low, $H_{ads}$ is efficiently formed and the $CH_4$ production reaction proceeds. The similar phenomenon is suggested to occur at Pt-black electrocatalyst. It should be noted that in the $CH_4$ generation mechanism, $H_{opd}$, which is the $H_{ads}$ located at atop sites, would be involved in the reaction, and the $H_{opd}$ formation requires a large overpotential for $CH_4$ generation. Significantly, the $H_{opd}$ formation occurs near the standard electrode potential of $CO_2$/$CH_4$ redox reaction when using Pt electrocatalyst.

Therefore, $CH_4$ generation from $CO_2$ reduction can take place without overpotential at Pt (including Pt black) electrocatalyst because the onset potential of $H_{opd}$ formation and the equilibrium potential of $CH_4$ production coincidentally match. On the other hand, in the potential range where the overpotential is much larger, the coverage of $H_{opd}$ increases and $H_2$ evolution reaction occurs preferentially as shown in Figure 1A.

### 3.2 | $CO_2$ reduction at stationary potential

Suitable $CO_2$ concentrations for the formation of $CH_4$ were determined using potentiodynamic experiments. To
discuss the electrode potential dependence of CH₄ generation, a potentiostatic experiment was conducted. Figure 2 shows the MS intensity results along with faradaic charges at the 14-level potential steps, at 4 vol.% CO₂ concentration. The applied potential program is shown in Figure S2. The maximum intensity for the m/z 15 peak was observed at 0.18 V vs RHE. The potential for CH₄ generation and H₂ evolution did not overlap significantly. CH₄ production occurs at a more positive potential than H₂ evolution. According to the CH₄ generation mechanism associated with Hopd, the coverage of Hopd formed at a Pt electrocatalyst is suggested to influence on the realistic potentials difference between H₂ evolution and CO₂ reduction to CH₄. Consequently, CH₄ is maximally and selectively obtained by setting the electrode potential to 0.18 V vs RHE.

We then investigated the CH₄ generation efficiency when the WE potential was stepped down to 0.18 V vs RHE directly in order to discuss continuous CH₄ production. The results are shown in Figure 3. A potential step-down from 0.40 V vs RHE (where no reduction current was observed, see Figure 1A), to 0.18 V vs RHE resulted in the selective production of CH₄. Notably, the detected m/z 15 signal remained almost constant for 5 minutes. When the potential was stepped down further to 0.03 V vs RHE, CH₄ generation occurred only momentarily, but the main reaction was H₂ evolution. Figure S3 shows the results of the same experiment as in Figure 2, using a PEMEC with an incorporated Pt/C cathode with a 78.5 wt.% Pt ratio (TEC10E80HPM from Tanaka Kikinzoku Kogyo Co., Ltd.). Its CO₂ reduction characteristics closely resembled those of Pt black. Based on these results, the faradaic efficiency for CH₄ generation under steady state was calculated and plotted as shown in the upper panel of Figure 4 with the addition of

![Figure 2](image_url)  
**Figure 2** Potential dependence of faradaic charge and relative MS intensities of m/z 2 and m/z 15 signals at each potential, held for 2 minutes at a CO₂ concentration of 4 vol.%

![Figure 3](image_url)  
**Figure 3** Potential program applied to the WE and in-line MS signals of m/z 2 and m/z 15 at a CO₂ concentration of 4 vol.%

![Figure 4](image_url)  
**Figure 4** Faradaic efficiency for CH₄ generation (top left vertical axis), ECSA (top right vertical axis), and CO₉ads to H₉ads molar ratio (bottom left axis) as functions of the Pt weight ratio in the catalyst. The faradaic efficiency was calculated using data from potentiostatic measurements. Data of faradaic efficiency and the CO₉ads/H₉ads ratio of 46.2 wt.% Pt/C from our previous reports.¹⁷,2¹
46.2 wt.% Pt/C along with their electrochemical surface areas (ECSAs). Notably, the ECSAs were obtained from the cyclic voltammograms in an Ar atmosphere, as shown in Figure S4, following the hydrogen adsorption method. Remarkably, the faradaic efficiency of Pt black was determined to be 23.2%, which is the highest among the three electrocatalysts and almost twice as high as that of 46.2 wt.% Pt/C (12.3%). The faradaic efficiency for 78.5 wt.% Pt/C was 16.1%, such that increasing the Pt weight ratio increased the CH₄ generation efficiency. Conversely, the ECSA decreased as the Pt weight ratio increased. Hence, a trade-off relationship was observed between the faradaic efficiency and ECSA. This can be ascribed to the molar balance between COads and Hads on the electrocatalyst surface. According to Equation (1), CH₄ production probably proceeds most efficiently when the COads to Hads molar ratio is \( \frac{1}{6} \). Here, the COads to Hads molar ratio for Pt black and 78.5 wt.% Pt/C were investigated based on the calculation method shown in Figure S5 (using Equation S1). The results obtained for the two catalysts were \( \frac{1}{10} \) and \( \frac{1}{15} \), respectively. The COads to Hads molar ratio for 46.2 wt.% Pt/C was reported to be \( \frac{1}{20} \), making the ratio for Pt black the closest to the theoretical value (\( \frac{1}{6} \)) among the three (see the lower panel in Figure 4). Based on these results, the COads to Hads density on the Pt catalyst’s surface was found to have a strong, direct relationship with the faradaic efficiency, as shown in Figure 4.

In order to investigate the electrocatalytic stability, the retention rate of the MS signal of \( m/z \) 15 after 5-minute potential holding was calculated for Pt black from the data of Figure 3. As a result, the retention rate for Pt black was as high as 92.2%. When the result was compared to those obtained using Pt/C with Pt weight ratios of 78.5 wt.% and 46.2 wt.%, the rate for Pt black was the highest as shown in Figure S6. This can be because the electrochemical corrosion of carbon supports occurred at Pt/C electrocatalysts. Hence, the catalytic activity of Pt black is stable, and the high stability should be obtained because there was also little influence of poisoning by COads at Pt black.

Figure 5 summarizes the difference in CH₄ generation efficiency on Pt electrocatalysts with and without a carbon support, via CO₂ reduction. Although the presence of a carbon support enhances the ECSA of the Pt electrocatalyst, the molar ratio of COads: Hads on the catalyst surface is altered, resulting in a lower faradaic efficiency for CH₄ production. The increase in the COads to Hads ratio may stem from the difference in the reaction rates for the formation of COads and Hads. Because the rate of formation of COads is slower than that of Hads, Hads can be found in excess on the carbon-supported Pt electrocatalyst when the ECSA is large. In other words, the elimination of the carbon support increases the COads density on the Pt surface and removes excess Hads that does not contribute to CH₄ production. When the onset potential of COads formation at Pt-black electrocatalyst was investigated as shown in Figure S7, the onset potential was determined to be 0.375 V vs RHE. It should be noted that the onset potential of COads formation at 46.2 wt.% Pt/C electrocatalyst was reported to be 0.35 V vs RHE. Therefore, COads formation is more preferable to occur at Pt black than at Pt/C electrocatalyst, which strongly supports the consideration that a high-density COads environment (surface) can be created at Pt black. It is possible that the increase in the COads to Hads molar ratio is also connected to the spillover phenomenon. This phenomenon is more likely to occur in substances with smaller mass numbers; there have been reports of H spillover from the Pt catalyst to the carbon. Based on the aforementioned discussion, we conclude that modifying the COads and Hads molar ratio can be efficiently used to enhance the faradaic efficiency toward the production of CH₄ on Pt-black electrocatalysts.

**FIGURE 5** Schematic representation of CO₂ reduction on Pt electrocatalysts with and without a carbon support at 4 vol.% CO₂. Abundant Hads is not shown in the figure.

**4 | CONCLUSION**

This study focused on investigating the CO₂ reduction properties of a Pt-black electrocatalyst without a carbon support. Based on the results obtained from electrochemical measurements in combination with in-line MS, CH₄ generation improved at low CO₂ concentrations (4-7 vol. %), and maximum production was observed at 0.18 V vs RHE without H₂ evolution. The faradaic efficiency for CH₄ production using Pt black was determined to be 23.2%, which exceeded the efficiencies for Pt/C with Pt weight ratios of 78.5 wt.% and 46.2 wt.%. Hence, it was
elucidated that decreasing the carbon content of the Pt/C catalyst improved the CH4 generation efficiency. This is because the molar ratio of COads to Hads (the intermediates of the CH4 generation reaction) differs depending on the amount of carbon support. Overall, CO2 was selectively and efficiently reduced to CH4 without overpotential using a Pt-black electrocatalyst. The findings of this study will be useful for the design of catalysts for CO2 electrolytic methanation in the future.

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CONFLICT OF INTEREST
There are no conflicts of interest to declare.

DATA AVAILABILITY STATEMENT
All data that support the findings of this study are available from the corresponding author upon request.

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