Fuel Cells

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A Direct CO Polymer Electrolyte Membrane Fuel Cell**

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The reformation of natural gases, coal gases, and biomass-derived gases generates a considerable amount of CO. The ideal method for the generation of energy from CO would be the direct use of CO as a fuel in polymer electrolyte membrane fuel cells (PEMFCs). However, its use as a fuel is restricted, despite it being a strong reducing agent, because it is a strong poison for the Pt catalyst of PEMFCs. The presence of only 100 ppm CO results in the oxidation of H_2 on the Pt catalyst decreasing to 25 % of that without CO in.[1] Direct electrochemical oxidation of CO is very sluggish even at high temperatures;[2] hence the realization of a low-temperature direct CO fuel cell has been regarded as an impossible task.

Recently, a novel CO utilization system operating at low temperature was proposed.[3] In this system, CO is oxidized by a polyoxometalate with the aid of an Au catalyst, and the reduced polyoxometalate serves as a fuel for the PEMFC. This report demonstrated that CO could act as an energy source "indirectly". However, the system requires electron transfer from CO to the polyoxometalate, and hence is essentially equal to the water gas shift reaction (electron transfer from CO to H_2O).[4] Many different processes are needed for the use of CO, and, as a result, the system becomes complex. The performance of this cell is limited by the redox activity of the polyoxometalate, and irrespective of the strong reducing power of CO. The reported cell performance remains much lower than those of H_2-PEMFCs and direct methanol fuel cells.

Although systems for the conversion of CO into fuels (H_2, reduced polyoxometalate, and so on) have been reported,[3,4] a direct CO-PEMFC, in which neat CO is supplied to a membrane electrode assembly (MEA), has not yet been developed. The difficulty in the development of such a system is based on the fact that current noble-metal catalysts are strongly poisoned by CO, as mentioned above. However, certain kinds of metalloporphyrins can catalyze the electrochemical oxidation of CO.[5–7] We focused on a carbon-supported Rh porphyrin which has been reported to oxidize CO electrochemically.[5–7] In a previous study we demonstrated that carbon-supported Rh octaethylporphyrin ([Rh(oep)]) gave a steady-state current during the oxidation of CO at very low potentials.[7] On the basis of the high performance of the carbon-supported [Rh(oep)],[7] we planned to use this material as an anode catalyst for the oxidation of CO and to construct a direct CO-PEMFC.

Herein, we report for the first time a direct CO-PEMFC. The CO-PEMFC cell delivers a much improved performance than the previous PEMFC that used a fuel reduced by CO.[3] Our cell is very specific in that it can use neat CO without oxidation of H_2.

The performances of the PEMFC with [Rh(oep)]/C and a standard PEMFC with Pt/C as the anode catalyst are depicted in Figures 1 and 2 when CO and H_2 were used as the anode gases, respectively. Figure 1 A shows an *I–V* curve for a PEMFC in which the anode catalyst is [Rh(oep)]/C. Neat CO gas and neat O_2 gas were used as the anode and cathode gases, respectively. The cell delivered a good performance: the cell voltage at 96 mA cm^{-2} reached 0.47 V, and the maximum power exceeded 45 mW cm^{-2} at 80 °C. This is the first example of a direct CO-PEMFC. In typical PEMFCs with a Pt catalyst, the oxidation of H_2 by Pt is dramatically suppressed, even in the presence of 100 ppm CO,[1]. In fact, PEMFCs with a Pt/C anode catalyst generate virtually no power when neat CO is used as a fuel (Figure 1 B). In contrast, surprisingly, a cell with [Rh(oep)]/C can use neat CO very efficiently. The anode and cathode reactions are shown in Equations (1) and (2), respectively.

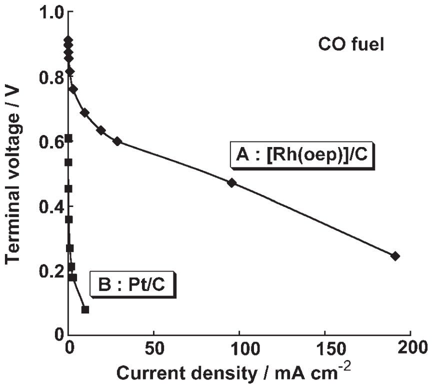

Figure 1. *I–V* curves for PEMFC with A) [Rh(oep)]/C and B) Pt/C (40 %, Johnson–Matthey) anode catalysts using neat CO as the anode gas. Neat O_2 was used as the cathode gas. The gases were supplied at a rate of 100 cm^3 min^{-1}. The cell operation and gas humidification were performed at 80 °C.

$$CO + H_2O \rightarrow CO_2 + 2\,H^+ + 2\,e^- \qquad (1)$$

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O \qquad (2)$$

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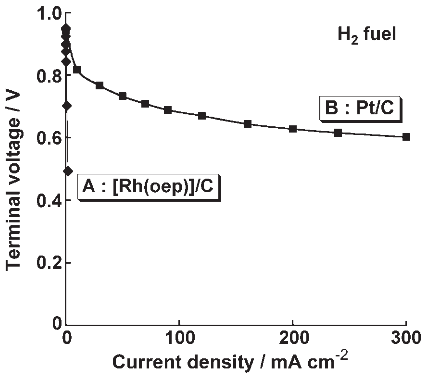

Figure 2. *I–V* curves for a PEMFC with A) [Rh(oep)]/C and B) Pt/C (40%, Johnson–Matthey) anode catalysts using neat H_2 as the anode gas. Neat O_2 was used as the cathode gas. The gases were supplied at a rate of 100 cm^3 min^{-1}. The cell operation and gas humidification were performed at 80°C.

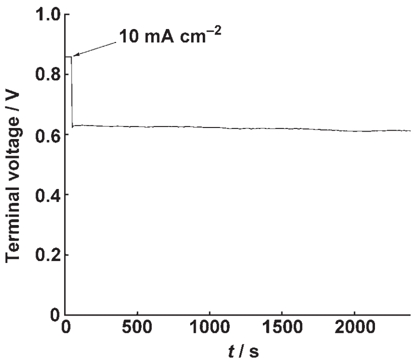

Figure 3. Time-courses of the voltage of the PEMFC with [Rh(oep)]/C using neat CO as the anode gas. The current density was changed from 0 to 10 mA cm^{-2} at $t = 50$ s. The other conditions were the same as in Figure 1.

While the cell performance is worse than that of a typical PEMFC (Figure 2B), it is much higher (by a factor of about 15) than that of the previous PEMFC in which a fuel reduced by CO is used.[3] The design of our cell with [Rh(oep)]/C is very simple and in contrast to previous systems that utilize CO, and furthermore it can be made by the same procedure as normal PEMFCs.

Evaluation of the performance of the PEMFC with [Rh(oep)]/C in which H_2 is used as an anode gas (Figure 2A) shows that only a small amount of power is generated using H_2. However, the power and performance are virtually zero compared to those obtained when CO is used as the fuel (Figure 1A). Thus, the PEMFC with [Rh(oep)]/C is unprecedented and very specific in that the cell uses CO in preference to H_2, while a normal PEMFC with a Pt/C anode catalyst uses H_2 in preference to CO. This contrast is clearly seen in Figures 1 and 2. A large amount of CO is generated concomitant with H_2 during the reformation of hydrocarbons. The PEMFC with [Rh(oep)]/C uses CO, while the PEMFC with a Pt/C anode uses H_2. When using the CO-PEMFC, it should be placed in the anode gas line upstream relative to the H_2-PEMFC. Ideally, the CO in the CO/H_2 gas mixture is consumed as a fuel by the CO-PEMFC. The resulting CO-free H_2 gas can then then used by the H_2-PEMFC. Thus, the CO-PEMFC can be used as an anode gas cleaner concomitant with generation of power. When the CO concentration decreases, the current generated would also decrease. However, only a small amount of current is required for the removal of a low concentration of CO. This situation would allow the possibility of using this cell for the removal of a low concentration of CO in hydrogen gas steams in PEMFCs.

The time-course of the potential at 10 mA cm^{-2} in the CO-PEMFC with [Rh(oep)]/C is shown in Figure 3. A steady-state power output is observed, thus indicating that power generation is stable over the time range of the measurement. However, for a prolonged use of this cell, the possibility that the Rh porphyrin could leak into the acidic electrolyte from the carbon should be taken into consideration. A long-term stability study on the CO-PEMFC is underway.

These novel characteristics of the CO-PEMFC with [Rh(oep)]/C are derived from the catalytic effect of [Rh(oep)]/C, which was examined in detail in our previous report.[7] The open circuit voltage (OCV) of the CO-PEMFC with [Rh(oep)]/C is 0.91 V (Figure 1A). This value is somewhat smaller than the theoretical cell voltage of CO-PEMFC (1.35 V). The difference (0.44 V) cannot be explained by cathode overpotential alone. In general, the cathode overpotential of Pt/C (40%) is estimated to be approximately 0.2–0.3 V. Thus the difference (ca. 0.14–0.24 V) reflects the overpotential of the anodic oxidation of CO. We have already demonstrated that an observable electrochemical oxidation of CO by [Rh(oep)]/C starts at a potential about 0.2 V higher than the redox potential of reaction (1).[7] The OCV of CO-PEMFC can be explained by the properties of the [Rh(oep)]/C catalyst.

In our previous study,[7] an almost diffusion-limited steady-state current was observed for the electrocatalytic oxidation of CO by [Rh(oep)]/C under electrode rotation conditions. The steady-state current of CO oxidation is a characteristic property of [Rh(oep)]/C. This catalytic effect of the [Rh(oep)]/C can explain the high current density (Figure 1A) and steady-state power output (Figure 3) of the CO-PEMFC with [Rh(oep)]/C.

The possible influences of impurities such as light alcohol (methanol), aldehyde (formaldehyde), and acid (formic acid) in the anode gas were examined using a rotating disk electrode. However, the effects of these gases on CO oxidation were negligible up to 0.1 mM. The level of impurities in the anode gas is thought to be much lower, and hence the effects of impurities on the CO-PEMFC would be negligible.

Many attempts have been made to use organic-based metal complexes as an anode catalyst. However, these complexes appear to be catalytically active only in alkaline solution.[8] In the acidic electrolyte of the PEMFC, their application is limited to being promoters for a Pt anode catalyst.[9] Hence, this report on a CO-PEMFC is the first example of the use of organic-based metal complexes as an anode catalyst for a PEMFC.

In conclusion, we have reported for the first time a direct CO-PEMFC. Surprisingly, the cell uses neat CO as a fuel, which is in contrast to the performance of PEMFCs with CO-tolerant Pt catalysts[10–19] which are dramatically suppressed even in the presence of a low concentration of CO. The success of this direct CO-PEMFC arose from the catalytic effect of [Rh(oep)]/C; the cell performance can be explained by the catalytic effect of the [Rh(oep)]/C system, which was examined in our previous study.[7]

[Rh(oep)]/C exhibits the best catalytic effect among other electrocatalysts for CO oxidation at 25 °C.[7] However, it is known that certain kinds of Ru catalysts have relatively high activity for the electrooxidation of CO.[20] Our design of a CO-PEMFC might lead to the development of various CO-PEMFCs with CO oxidation catalysts based on ruthenium.

A mixture of CO and H_2 is generated by the reformation of hydrocarbons. More CO is generated from biomass-derived gases and coal gases. Thus, the CO-PEMFC might make it possible to use biomass-derived gases and coal gases as a power source for PEMFCs.

Another prominent property of this cell is that it uses CO without effecting H_2 oxidation. This property, which is not observed in the conventional anode catalyst (Pt/C), may enable two important applications. One application is the assembly of an apparatus for the electrochemical removal of CO and the generation of power. Currently, selective oxidation catalysts as well as water gas shift catalysts are widely used to decrease the CO concentration in the anode gas.[4] However, the inevitable oxidation of H_2 by O_2 by selective oxidation processes lowers the efficiency of the PEMFC. An apparatus with a PtRu catalyst for the electrochemical removal of CO was developed by Maeda et al.[21] However, this apparatus requires an energy supply and, furthermore, oxidizes H_2 concomitantly. In marked contrast to this, the CO-PEMFC can eliminate CO selectively from a CO/H_2 gas mixture. Our CO-PEMFC does not require energy to drive electrochemical CO oxidation, and moreover, it can generate power from this reaction. The CO-PEMFC is more favorable as an apparatus for CO removal in that it does not need energy and O_2 to remove the CO, and has high selectivity. The other application is as a CO sensor, since the selectivity of the CO-PEMFC enables the detection of CO even in CO/H_2 mixtures.

Experimental Section

Full experimental details are described in the Supporting Information. Briefly, carbon-supported [Rh(oep)] was prepared as described in the literature.[7,22,23] Carbon-supported [Rh(oep)] or carbon-supported platinum (40 %, Johnson–Matthey Co. Ltd.) was used as the anode catalyst. Throughout the experiments, carbon-supported platinum (40 %, Johnson–Matthey Co. ltd.) was used as the cathode catalyst. Nafion solution (5 %, Aldrich) was added to the catalyst materials, and mixed thoroughly. The suspension was then made into a thin layer as described in the literature.[10,11] The thin layers of anode and cathode catalysts were hot-pressed on both sides of the pretreated nafion membrane to form the MEA. Nafion 117 was used for the electrolyte membrane unless otherwise stated. The cell performance was measured at 80 °C. Fully hydrated gases were supplied at a flow rate of 100 $cm^3 min^{-1}$ to MEA.

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