A fuel cell with selective electrocatalysts using hydrogen peroxide as both an electron acceptor and a fuel

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Abstract

We have realized a novel hydrogen peroxide fuel cell that uses hydrogen peroxide (H_2O_2) as both an electron acceptor (oxidant) and a fuel. H_2O_2 is oxidized at the anode and reduced at the cathode. Power generation is based on the difference in catalysis toward H_2O_2 between the anode and cathode. The anode catalyst oxidizes H_2O_2 at a more negative potential than that at which the cathode catalyst reduces H_2O_2. We found that Ag is suitable for use as a cathode catalyst, and that Au, Pt, Pd, and Ni are desirable for use as anode catalysts. Alkaline electrolyte is necessary for power generation. The performance of this cell is clearly explained by cyclic voltammograms of H_2O_2 at these electrodes. This cell does not require a membrane to separate the anode and cathode compartments. Furthermore, separate paths are not needed for the fuel and electron acceptor (oxidant). These properties make it possible to construct fuel cells with a one-compartment structure.
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Keywords: Hydrogen peroxide; Fuel cell; One compartment; Alkaline electrolyte; Silver cathode

1. Introduction

Present fuel cells have very complicated structures. The anode and cathode compartments must be separated by a membrane and a seal to suppress the reaction between the fuel and electron acceptor (oxidant). Furthermore, the paths for the fuel and electron acceptor must be independent. When gaseous compounds are used as fuels or electron acceptors, fuel cells require complex electrode structures for smooth gas diffusion. These structural restrictions greatly increase the cost of fuel cells. A one-compartment fuel cell without a membrane or a seal should help to significantly simplify the cell structure.

Many researchers have made much effort to simplify the fuel cell structure. One-compartment fuel cells and mixed-reactant fuel cells, in which a mixture of fuel and electron acceptor is supplied [1–4], have been studied intensively. However, it is very difficult to realize a one-compartment structure in present fuel cell systems. For example, in a proton exchange membrane

fuel cell (PEMFC), the anode and cathode platinum catalysts are separated by an electrolyte membrane. Without separation of the fuel and an electron acceptor in a PEMFC, the fuel would be oxidized at the platinum cathode and the electron acceptor would be reduced at the platinum anode. In a PEMFC, the cross-reactions not only reduce the cell performance but also lead to dangerous conditions. The lack of selective electrocatalysts has prevented the realization of a one-compartment fuel cell.

Several one-compartment (membraneless) bio-fuel cells have recently been described [5–7]. Enzymes, which are the most selective catalysts, are used in these bio-fuel cells. The high selectivity of enzyme catalysis enables bio-fuel cells to have a one-compartment structure. Among these bio-fuel cells, a fructose–oxygen bio-fuel cell exhibits much higher performance than other one-compartment bio-fuel cells [5].

While one-compartment bio-fuel cells give simplifier fuel cell structures, the one-compartment structure also causes problems concerning dissolution and diffusion of oxygen. The current in one-compartment fuel cells is often restricted by oxygen depletion. Within this context, we sought to make a one-compartment fuel cell using an electron acceptor that exists at a high concentration in electrolyte. We intended to use hydrogen peroxide
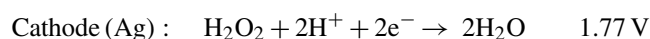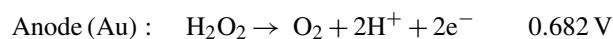

(H_2O_2) as an electron acceptor in a one-compartment fuel cell. We also tried to use H_2O_2 as a fuel as well as an electron acceptor. If H_2O_2 could act as both a fuel and an electron acceptor, the cell structure would be much simpler.

Hasegawa et al. has reported a H_2O_2 fuel cell in which H_2O_2 functions as both a fuel and an electron acceptor [8]. The cell uses Pt catalysts in both the anode and cathode. Part of the power might be generated by the difference in pH between the anode and cathode (i.e. concentration cell) due to the lack of selectivity of the electrocatalysts; hence, an acid/alkaline bipolar electrolyte is required. They successfully used a microchemical channel to keep the bipolar structure stable [8,9]. While this fuel cell uses H_2O_2 as both a fuel and an electron acceptor, it is not a one-compartment H_2O_2 fuel cell.

To construct a one-compartment H_2O_2 fuel cell, we focused on H_2O_2 oxidation/reduction by *selective* anode and cathode catalysts. These selective catalysts enable non-bio-fuel cells to adopt a one-compartment structure. If H_2O_2 is selectively oxidized on one electrode and selectively reduced on the other electrode, electric power might be generated from H_2O_2 oxidation/reduction.

Although, to the best of our knowledge, one-compartment H_2O_2 fuel cells have not yet been reported, Mallouk and coworkers showed that a micro-scale flow could be derived from H_2O_2 oxidation/reduction [10–13]. However, this is not a fuel cell, but rather a micro-pump. They observed micro-flow between different metals, e.g. Au–Pt and Au–Ag, in H_2O_2 solution. They emphasized the importance of the difference in catalytic activities toward H_2O_2 between several metals in micro-pumps. They demonstrated that H_2O_2 is oxidized on one metal, and is reduced on the other metal. They pointed out that these reactions could generate a driving force based on a difference in the redox potentials of H_2O_2 oxidation/reduction, as follows [10,12,13]:

Anode (Au) :　$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$　　　0.682 V

Cathode (Ag) :　$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$　　　1.77 V

They observed pattern-generation caused by the driving force. We sought to apply this H_2O_2 oxidation/reduction to one-compartment fuel cells.

In this report, we describe a one-compartment fuel cell using H_2O_2 as both a fuel and an electron acceptor. This cell is very unique in that electric power is generated from a single compound (H_2O_2) based on the difference in activity between the anode and cathode catalysts. This cell does not need a membrane or a seal. We clarified the relationship between electric power and selective catalysis by performance tests and cyclic voltammetry. Electric power was generated in alkaline electrolyte. We demonstrated that Ag is a special catalyst for H_2O_2 reduction, and a Ag cathode is necessary for significant power generation.

2. Materials and methods

2.1. Materials

All chemicals were purchased and used as received. Metal wires (0.5 mm Φ) and metal plates (1.5 cm × 2.5 cm), which

were used as electrodes for the fuel cells, were obtained from Nilaco Co. Water used in this study was purified using an Organo Puric-MX system unless otherwise stated.

2.2. Evaluation of the performance of a H_2O_2 fuel cell

H_2O_2 solution (300 mM) was placed in a two-compartment or a one-compartment electrochemical cell. In the two-compartment cell, the compartments are separated by a glass filter. Two wires of different metals were immersed in the H_2O_2 solution in each compartment. In the one-compartment cell, Au and Ag plates were immersed in the H_2O_2 solution. Ag|AgCl|KCl (sat.) electrodes were occasionally used as reference electrodes to evaluate polarization of anode and cathode. The reference electrodes were immersed near anode and cathode. Cell performance was evaluated by a galvanostat (Hokuto Co.). Measurements were performed at 25 °C in deaerated 1 M NaOH solution and 0.1 M phosphate buffer solution (pH 7.0). The surface areas of the wires and plates in the electrolyte solution were fixed at 0.253 cm^2 and 2.4 cm^2, respectively.
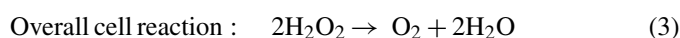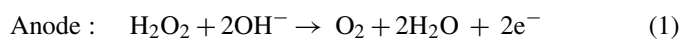
2.3. Electrochemical behavior of H_2O_2

The electrochemical behavior of H_2O_2 at several electrodes was examined using an ALS electrochemical analyzer. Ag|AgCl|KCl (sat.) and platinum electrodes were used as reference and counter electrodes, respectively. Disk electrodes of several metals were used as working electrodes. The surface area of Pt and Au electrodes was 0.0707 cm^2. The area of Ag and Pd electrodes was 0.0201 cm^2, and the area of a Ni electrode was 0.0177 cm^2. The measurements were performed at 25 °C under a nitrogen atmosphere in 1 M NaOH solution and 0.1 M phosphate buffer solution (pH 7.0).

3. Results and discussion

3.1. H_2O_2 fuel cell

We constructed a H_2O_2 fuel cell using an H-type electrochemical cell and examined its performance. The H-type cell is separated into two compartments by a glass filter (Fig. 1). We tested neutral and alkaline electrolytes. Possible electrochemical reactions in the H-type cell are as follows (in alkaline electrolyte):

Anode :　$H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e^-$　　　(1)

Cathode :　$H_2O_2 + 2e^- \rightarrow 2OH^-$　　　(2)

Overall cell reaction :　$2H_2O_2 \rightarrow O_2 + 2H_2O$　　　(3)

Initially, we used a Au wire as an anode and a Ag wire as a cathode, respectively, based on a past study [10]. Oxygen was removed by passing nitrogen gas to eliminate the effect of oxygen reduction.

Fig. 2(a) shows the performance of a H_2O_2 fuel cell with a Au anode, a Ag cathode, and an alkaline electrolyte (1 M NaOH).
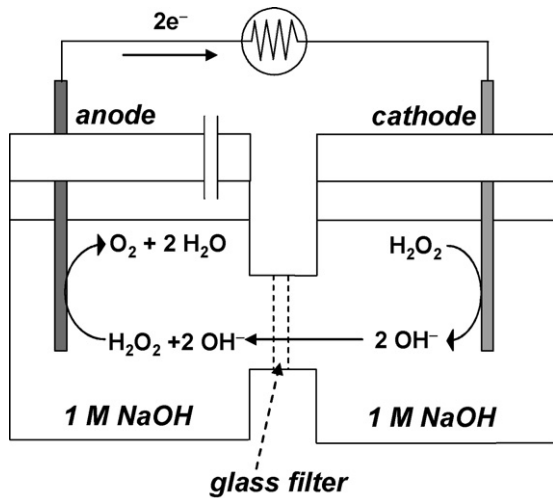
Fig. 1. Scheme of a H_2O_2 fuel cell.

The open-circuit potential (OCP) reached 0.12 V, and the maximum current density exceeded 1.5 mA cm^{-2}. This result is very interesting in that electric power is generated from a single compound (H_2O_2) based on the difference in activity between the anode and cathode catalysts.

Two reference electrodes (Ag|AgCl|KCl (sat.)) were used to evaluate polarization of Au anode and Ag cathode. One electrode is immersed in the anode compartment, and the other in cathode compartment. The electrodes were placed near Au anode and Ag cathode. The anode and cathode potentials vs. Ag|AgCl|KCl (sat.) were measured. Under open-circuit conditions, the difference between the Au-reference potential and Ag-reference potential coincided the OCP of the cell. At current density of 1.2 mA cm^{-2}, anode polarization (the deviation of anode from OCP) was 16 mV, and cathode polarization was

almost zero, indicating that polarization of anode is more significant than that of cathode. The drop of the cell voltage not by the polarization of anode and cathode is attributed to the *IR* drop. It exceeds 40 mV. The large resistance would be derived from the resistance of the glass filter.

A H_2O_2 cell using phosphate buffer solution (pH 7.0) as an electrolyte virtually did not produce electric power (maximum current density <1 μA cm^{-2}). Mallouk and coworkers reported that a driving force of micro-particles is generated from the oxidation/reduction of H_2O_2 in neutral solution. This apparent contradiction can be attributed to the difference in observed current densities between this work (mA cm^{-2}) and the past work (μA cm^{-2}) [12].

We also examined combinations of metals other than Au anode–Ag cathode. Combinations of Au anode and Pt, Fe, Cu, and Pd cathodes were tested. The cells exhibited little current (<0.2 mA cm^{-2}). Thus, a Ag cathode was proved to be necessary for the generation of substantial power. Combinations of Pt, Ni, Cu, Fe, and Pd anodes and Ag cathode were also tested. H_2O_2 cells with a Pt anode–Ag cathode, Pd anode–Ag cathode, and Ni anode–Ag cathode showed high performance. The results are summarized in Fig. 2. The maximum current density increases in the order: Pt–Ag > Pd–Ag > Au–Ag > Ni–Ag. The open-circuit potentials of these cells are similar.

To determine the mechanism of power generation, we added H_2O_2 to only the anode compartment or only the cathode compartment, and tested the performance of the cell. In both cases, the cell produced virtually no power (maximum current density <20 μA cm^{-2}). The results indicate that power generation in the H_2O_2 fuel cell is caused by the reactions expressed in Eqs. (1) and (2). Possible anode dissolution did not occur.

Bubbles were observed at the anode and cathode metals even under open-circuit conditions. The rate of bubble-generation decreased in the order: Ag > Pd > Pt ≫ Au > Ni. A significant amount of bubbles were generated immediately when Ag and Pd were immersed into alkaline electrolyte containing H_2O_2. In contrast, bubble-generation was scarcely seen on Ni. The bubbles should be due to the generation of oxygen by H_2O_2 decomposition on the anode and cathode metals. This decomposition of H_2O_2 on one electrode does not participate in power generation; hence, it would be desirable to suppress the generation of bubbles. Ni and Au are suitable for use as an anode electrocatalyst from this viewpoint, although in this case the electrocatalyst has less activity toward H_2O_2 electro-oxidation than Pt and Pd (Fig. 2).

The H_2O_2 fuel cell has interesting properties, which are not observed in conventional fuel cells. H_2O_2 functions as both a fuel and an electron acceptor. H_2O_2, which is usually classified as an electron acceptor, can act as a fuel in this cell. Power generation is based on the difference in the reactivity toward H_2O_2 between the anode and cathode catalysts. The lines that supply the fuel and electron acceptor can be combined. More importantly, neither a membrane nor a filter is needed due to the selectivity of the electrocatalysts. A one-compartment fuel cell can be realized based on this system (described in Section 3.3).
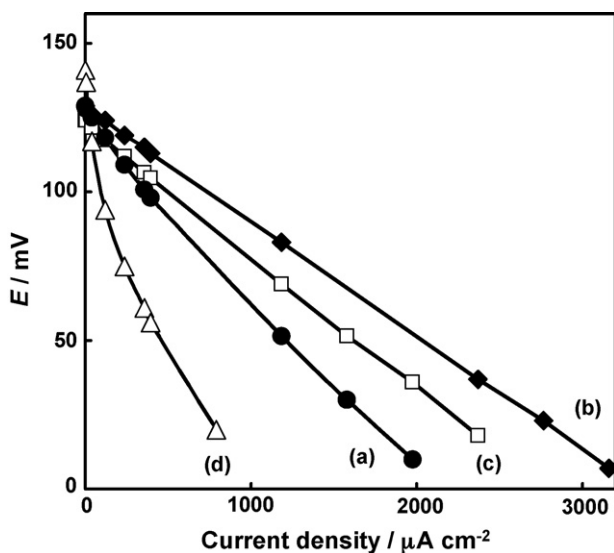

Fig. 2. *I–V* curves of H_2O_2 fuel cells with (a) Au anode–Ag cathode, (b) Pt anode–Ag cathode, (c) Pd anode–Ag cathode, and (d) Ni anode–Ag cathode. Performance tests were conducted in deaerated 1 M NaOH solution containing 300 mM H_2O_2. The electrode surface areas are fixed at 0.253 cm^2.

3.2. Electrochemical behavior of H_2O_2

To obtain further information on power generation, we intended to compare the electrochemical behaviors of H_2O_2 on Au, Ag, Pt, Pd, and Ni. These behaviors have already been extensively investigated [14–21]. However, the reported experiments were performed under different conditions, which prevent us from comparing the electrochemical behavior of H_2O_2 on these metals. Therefore, we investigated its electrochemical behavior under the identical conditions (1 M NaOH).

Fig. 3 shows cyclic voltammograms (CVs) of H_2O_2 at these electrodes. On Au, Ag, Pt, and Pd electrodes, both oxidation and reduction currents increased upon the addition of H_2O_2. At a Ni electrode, only oxidation current increased. The onset potential for H_2O_2 reduction on a Ag electrode (ca. −0.05 V, Fig. 3(B, line b)) was highest among the electrodes tested. The onset potentials for H_2O_2 oxidation on Au, Pt, Pd, and Ni electrodes are lower than the onset potential for H_2O_2 reduction on a Ag electrode. This indicates that H_2O_2 oxidation by these four electrodes with H_2O_2 reduction by Ag can produce electric power. The power generation by Au–Ag, Pt–Ag, Pd–Ag, and Ni–Ag is consistent with the results of CV.

Honda et al. analyzed the electrochemical behavior of H_2O_2 at Ag electrode in alkaline solution [14]. They attributed the peaks in the absence of H_2O_2 to the generation/reduction of surface oxide of Ag. In this paper, H_2O_2 was reduced below the potential region at which the generation/reduction of surface oxide occurred. Our results are in accordance with this past result. They stated that the one-electron H_2O_2 reduction and oxidation process are the rate-determining steps in the overall cathode and anode reaction, respectively. Our comparison

among five metals suggests that Ag requires the least potential for one-electron H_2O_2 reduction, or the largest potential for one-electron H_2O_2 oxidation.

Ni electrode is unique in that it catalyzed only electrochemical H_2O_2 oxidation. Electrochemical H_2O_2 behavior at Ni electrode was examined by Bagotzky et al. [20]. According to their results, the onset potential for H_2O_2 reduction is much lower than that for H_2O_2 oxidation. This would be a main reason why H_2O_2 reduction was not observed in the potential range in Fig. 3. At Ni electrode, H_2O_2 oxidation easily occurs rather than H_2O_2 reduction, in contrast to Ag electrode. Pt and Pd electrodes exhibited high activity toward both H_2O_2 oxidation and reduction. Prabhu et al. suggested that oxygen generated by H_2O_2 decomposition is reduced electrochemically on a Pt electrode in apparent electrochemical H_2O_2 reduction [21]. The participation of intermediate oxygen would be partly responsible for the high activity toward both reactions.

A Ag electrode gives H_2O_2 reduction current below ca. −0.05 V (Fig. 3(B, line b)). H_2O_2 oxidation by these four electrodes in the potential region is meaningful for the H_2O_2 fuel cell. We compared H_2O_2 oxidation current at −0.075 V among these four electrodes. Pd, Pt, and Au electrodes gave higher currents than a Ni electrode, and the order was consistent with the order of the power of H_2O_2 cells (Fig. 2).

We also examined the electrochemical behavior of H_2O_2 in neutral solution. Fig. 4 shows CVs of H_2O_2 at Au (Fig. 4(A)) and Ag (Fig. 4(B)) electrodes in 0.1 M phosphate buffer solution (pH 7.0). Several peaks were observed without H_2O_2 (Fig. 4, line a). These peaks are attributed to surface oxide formation and its reduction, as discussed in past studies [14,22]. The increase in oxidation and reduction currents upon the addition of H_2O_2 is
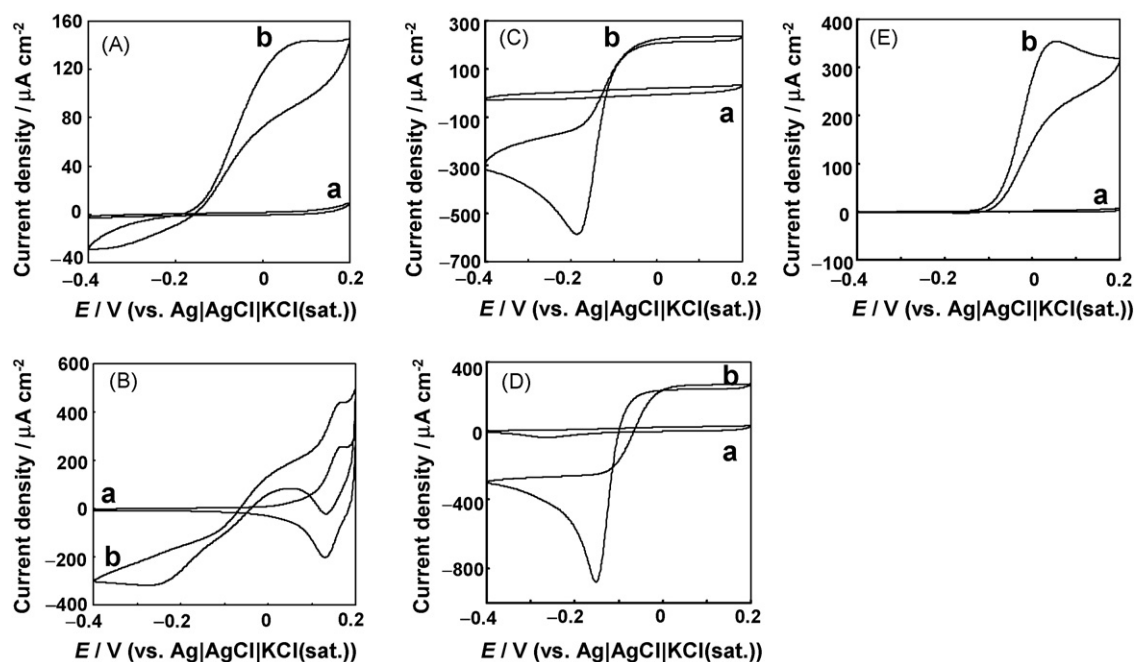

Fig. 3. Cyclic voltammograms of H_2O_2 on (A) Au, (B) Ag, (C) Pt, (D) Pd, and (E) Ni electrodes. Lines (a) and (b) indicate voltammograms in the absence and presence of H_2O_2, respectively. The measurements were performed in 1 M NaOH solution under a nitrogen atmosphere. The concentration of H_2O_2 was fixed at 3 mM.
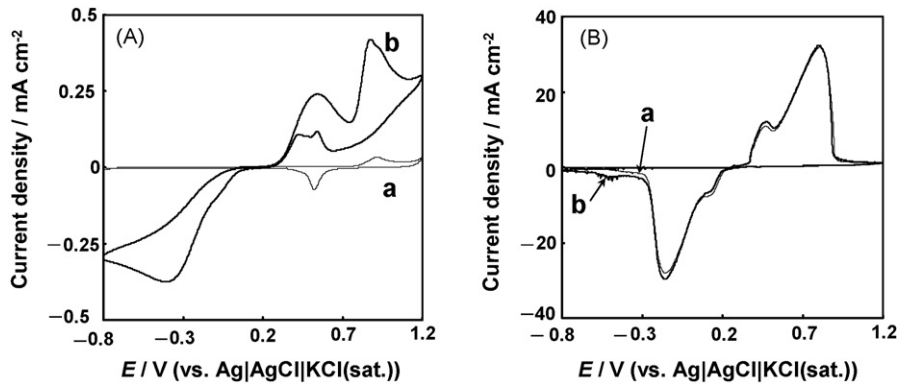
Fig. 4. Electrochemical behavior of (A) Au and (B) Ag electrodes. Lines (a) and (b) indicate voltammograms in the absence and presence of H_2O_2, respectively. The measurements were performed in 0.1 M phosphate buffer solution (pH 7.0) under a nitrogen atmosphere. The concentration of H_2O_2 was fixed at 3 mM.

clearly observed at a Au electrode (Fig. 4(A, line b)). A slight increase in reduction currents below −0.3 V is observed in Ag electrode (Fig. 4(B, line b)). The onset potential for H_2O_2 oxidation (ca. 0.25 V) by the Au electrode is higher than that for H_2O_2 reduction (−0.3 V) by the Ag electrode under neutral conditions, in contrast to the situation in alkaline solution. The overpotential for H_2O_2 reduction by the Ag electrode increased with a decrease in pH. The upset of the potentials of H_2O_2 oxidation and reduction is responsible for the fact that electric power is virtually not generated in neutral solutions.

The observed current in Fig. 3 is the subtraction of intrinsic reduction current from oxidation current. The potential at which net current is zero is called as the mixed potential. When current lines cross the potential axis almost vertically, both oxidation and reduction occur at a significant rate in a potential region near the mixed potential. This indicates that both electrochemical H_2O_2 oxidation and reduction occur on the same electrode (Fig. 5(a)). The overall reaction is H_2O_2 decomposition, which does not produce electric power. The bubble-generation at Au, Ag, Pt, and Pd electrodes under open-circuit conditions should

be partly attributed to the electrochemical H_2O_2 decomposition. The mechanism of electrochemical H_2O_2 decomposition at a Ag electrode was emphasized in the literature [14]. It is possible that simple chemical H_2O_2 decomposition (Fig. 5(b)) is partly responsible for the bubble-generation under open-circuit conditions. However, this cannot be determined from CVs.

The voltammograms in Fig. 3 indicate that both H_2O_2 oxidation and reduction near the mixed potential easily occur on Pd, Pt, and Ag. In contrast, the reduction currents of H_2O_2 on Ni and Au are very small; hence, electrochemical H_2O_2 decomposition (Fig. 5(a)) would occur less on Ni and Au. This is consistent with the finding that the Ni electrode shows the least bubble-generation under open-circuit conditions.

3.3. One-compartment fuel cell

We constructed a one-compartment H_2O_2 fuel cell using Au and Ag plates. Au and Ag plates were immersed in a
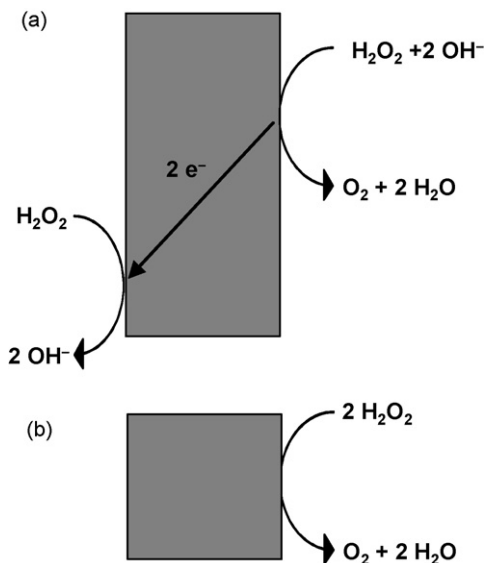

Fig. 5. Two mechanisms of chemical H_2O_2 decomposition: (a) local electrochemical cell mechanism and (b) mere chemical decomposition mechanism.
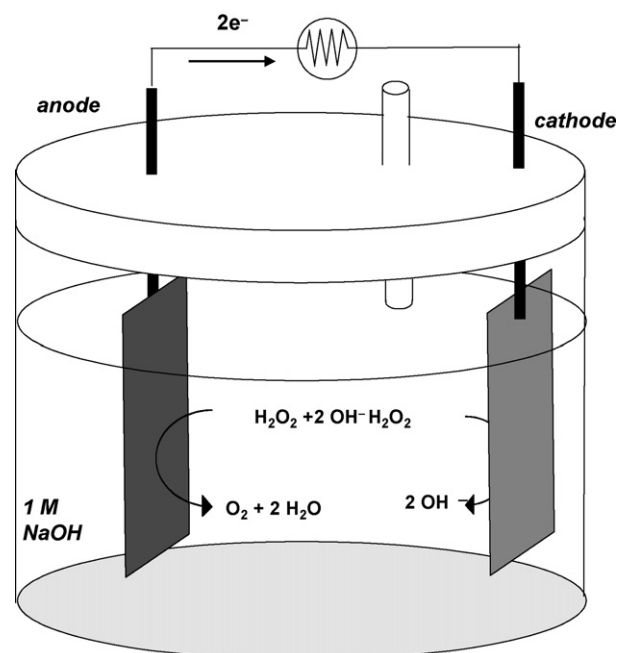

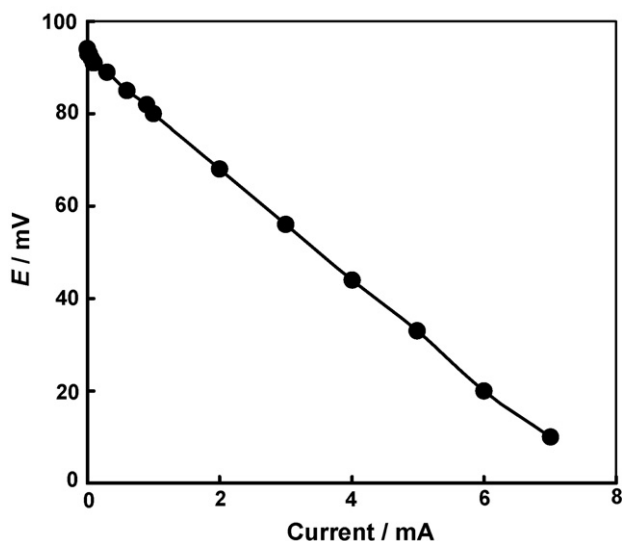Fig. 6. Scheme of a one-compartment H_2O_2 fuel cell.

Fig. 7. *I–V* curve of a one-compartment H_2O_2 fuel cell with Au anode–Ag cathode. Performance tests were conducted in 1 M NaOH solution containing 300 mM H_2O_2. The electrode surface areas are fixed at 2.4 cm^2.

one-compartment electrochemical cell, and H_2O_2 solution was injected into the cell (Fig. 6). The results are summarized in Fig. 7. The one-compartment cell also generates electric power. The maximum current density of this cell (2.9 mA cm^{-2}) is somewhat larger than that of the cell in Fig. 2. This indicates that a H_2O_2 fuel cell can adopt a one-compartment cell structure, as predicted by its mechanism. Reference electrodes were also used to measure polarization of anode and cathode. At current density of 1 mA cm^{-2}, the anode and cathode polarizations were 15 mV and 9 mV, respectively. The anode overpotential was also higher than the cathode overpotential in the system of Fig. 6. The *IR* drop was almost zero in the one-compartment cell, suggesting that the glass filter (Fig. 1) is responsible for the large *IR* drop observed in the two-compartment system.

The maximum current exceeds 7 mA in the cell using metal plates, while the current of the cell using metal wires is more than the order of 0.1 mA. An increase in the electrode surface areas tends to increase not only the current but also H_2O_2 decomposition, which does not generate electric power. It is possible that an increase in surface area does not significantly increase current. The results in Figs. 2 and 7 show that the current was successfully increased by an increase in the surface area.

4. Conclusions

We have demonstrated that electric power is generated from electrochemical H_2O_2 oxidation/reduction in alkaline electrolyte. CVs of H_2O_2 on several metals revealed that H_2O_2 is easily oxidized by Au, Pt, Pd, and Ni electrodes and is easily reduced by a Ag electrode. Power generation is based on the selectivity of electrocatalysts toward H_2O_2. Since the anode potential (H_2O_2 oxidation) is lower than cathode potential (H_2O_2 reduction) in alkaline electrolyte, electric power can

be generated in alkaline solution. We have also realized a one-compartment fuel cell and successfully increased the current by scaling up. The one-compartment cell does not contain either a membrane or a seal. Both the fuel and electron acceptor are liquid, which are dissolved at high concentration in electrolyte. The cell is free from problems that involve the supply of an electron acceptor or a fuel. Thus, this cell is dramatically different from other one-compartment fuel cells in this regard.

Unfortunately, the performance of H_2O_2 cells is still low. In particular, the voltage does not reach 200 mV. The redox potentials of H_2O_2 reduction (Eq. (1)) and H_2O_2 oxidation (Eq. (2)) at a given pH are 0.73 V and −0.36 V vs. Ag|AgCl|KCl (sat.), respectively. CVs of H_2O_2 oxidation/reduction clearly indicate that the onset potential (ca. −0.05 V) for H_2O_2 reduction by Ag is far from the thermodynamic value (0.73 V). The main subject of future research should be the decrease in cathode overpotential. H_2O_2 decomposition without power generation (Fig. 5) is also an obstacle to be overcome. The development of selective catalysts for H_2O_2 oxidation and reduction is needed to improve the efficiency of H_2O_2 fuel cells.

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