Oxygen Reduction Activity of Thermally Decomposed Tetraphenylporphyrin as Cathode Catalyst of DMFC

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DMFC has a serious technical problem, which is called "crossover". The crossover CH_3OH, which passes through the polymer electrolyte from the anode to cathode, usually adsorbs on the surface of the cathode catalyst (Pt black) that decreases the DMFC performance. In this study, tetraphenylporphine and tetraphenylporphyrin-metals (metals: Co, Mn and Ru) were thermally decomposed at 673-1173 K for 7.2 ks and the activity of the oxygen reduction of the product was investigated using a rotating disk electrode in order to develop a new cathode catalyst with CH_3OH tolerance. The thermally decomposed TPP-Co and TPP-Ru, which have no activity toward CH_3OH oxidation, are possible materials as the cathode catalyst of the DMFC, thus being a substitute for the Pt black.

Key Words : DMFC, Cathode Catalyst, Tetraphenylporphyrin-metals, Oxygen Reduction.

1. Introduction

The DMFC (Direct Methanol Fuel Cell) is a power generation system in which methanol is directly supplied to the anode. Initial research was for utilization in an electric vehicle using methanol. However, this fuel cell can be simplified and minimized because no fuel converter is necessary. Therefore, much attention has been paid to the mini-DMFC[1)2)] or micro-DMFC as a battery for a computer and a cellular phone used by the general population. Recently, some electronic companies have advertised a trial product. Although the products are still a long way off from perfection, the size of the product will be reduced for practical use sooner or later. Now, the DMFC has the following two technical problems: (1) Large overpotential at both the anode and cathode, and (2) Crossover of CH_3OH from the anode to cathode. Proton plays an important role as a charge carrier in the DMFC. However, some of the CH_3OH also passes through the polymer electrolyte membrane from the anode to cathode with the proton. This behavior is called "crossover". Pt black is usually used as the cathode catalyst for oxygen reduction. The crossover CH_3OH adsorbs on the surface of the Pt black that decreases the DMFC performance.

The purpose of this research is to develop a new cathode catalyst, which has CH_3OH tolerance. The tetraphenylporphyrin-metals (TPP-Mes) were selected as the new cathode catalyst[3)-5)]. There are two reasons for this selection as follows: (1) Although there is only a 2-electron pathway of oxygen reduction for the original TPP-Mes, the thermally decomposed TPP-Mes have a high activity for the 4-electron pathway. (2) The most important feature is that the thermally decomposed TPP-Me catalysts do not have any activity for CH_3OH oxidation. Okada et al.[6)] carried out a detailed study of the oxygen reduction characteristics of the cobalt-porphyrins heat-treated at various temperatures. On the other hand, Jiang and Chu[7)] reported the influence the mixing TPP-Mes on the oxygen reduction. However, a new cathode catalyst competent for the DMFC has not developed yet. In this research, several TPP-Mes were thermally decomposed at various temperatures to evaluate the catalytic activity of the oxygen. The oxygen reduction currents of the catalysts were measured in 0.50 kmol m^{-3} H_2SO_4 with or without 1.0 kmol m^{-3} CH_3OH using the rotating disk electrode method in order to understand the relation to the structural characteristics analyzed by X-ray diffraction. Finally, a mini-DMFC was made using a possible catalyst in order to reveal the important problems which confronted the practical use.

2. Experimental

2-1. Preparation of Catalyst

The starting materials were tetraphenylporphyrin (TPP) and tetraphenylporphyrin-metals (TPP-Mes, metal: Co, Mn and Ru), which were obtained from the Aldrich Chemical Company and used as received. They were weighed in an Al_2O_3 boat and thermally decomposed under an Ar atmosphere for 7.2 ks. The decomposition temperature was varied from 673 to 1173 K using an electric furnace. The decomposition products were analyzed by x-ray diffraction (JEOL, JDX-3530) with CuKα. The accelerating voltage and the emission current were 40 kV and 40 mA, respectively. The decomposition products were then used as the catalyst for the oxygen reduction.

2-2. Measurement of Oxygen Reduction Current

The catalyst, carbon powder (Valcan XC-72) and Nafion

solution were weighed in a glass mortar. They were mixed, ground and shaken in an ultrasonic bath. The suspension was then added as a drop on the glassy carbon (Tokai Carbon, GC20SS, diameter: 3.0 mm) of the working electrode by a micropipette. The surface of the glassy carbon was uniformly covered with the suspension. The working electrode was completed after its heat-treatment at 348 K for 300 s and the net loading of the catalyst was usually 0.40 mg cm^{-2}.

Figure 1 is the measurement system for the oxygen reduction current. The working electrode with a catalyst layer was attached to an electrode rotating system (Hokuto Denko, HR-200). The counter electrode and the reference electrode were a Pt spiral and an Ag/AgCl electrode in 3.30 kmol m^{-3} KCl, respectively. A separator was used in order to avoid the bad influence of chloride ions on the working electrode and all measured potentials were quoted with respect to the normal hydrogen electrode. The electrolyte solution was 0.5 kmol m^{-3} H$_2$SO$_4$ or 0.5 kmol m^{-3} H$_2$SO$_4$ with 1.0 kmol m^{-3} CH$_3$OH at 298 K, which was saturated with oxygen by the bubbling of high purity O$_2$. The working electrode was rotated from 400 to 2500 rpm and the cathodic polarization curve was measured using a potentiostat (Hokuto Denko, HZ-3000) in the potential range from +1.0 V to −0.2 V vs. NHE.

2-3. Preparation of Electrode Assembly

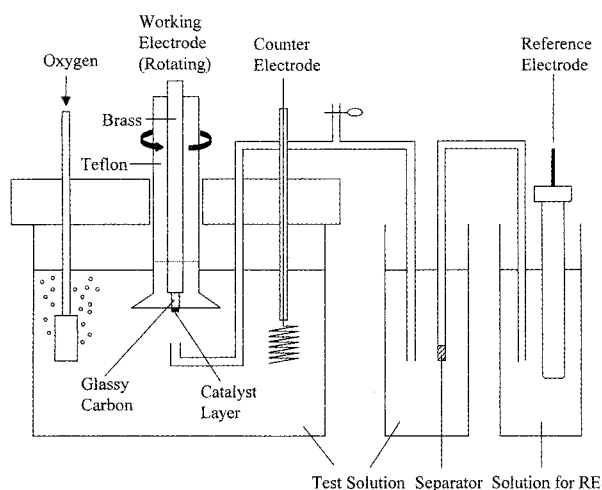The mini-DMFC was assembled by sandwiching a Nafion

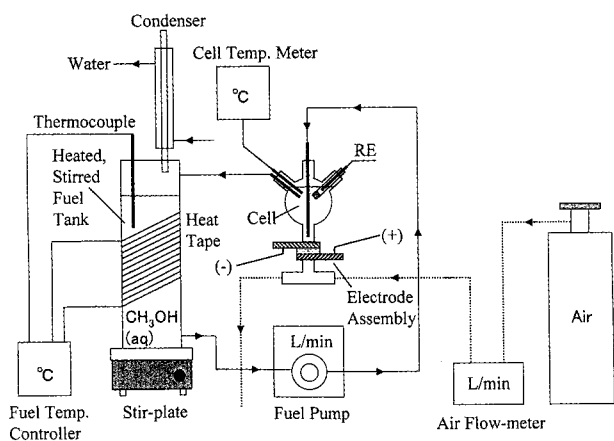Figure 1   Measurement system of oxygen reduction current.

Figure 2   Testing set-up of mini-DMFC performance.

membrane between two electrode chips with porous catalyst layers. First, carbon was coated on the electrode chip with gold current collector and the Pt-Ru alloy was electrodeposited as the anode catalyst on it. On the other hand, a new cathode catalyst or thermally decomposed TPP-Me was coated on the Nafion membrane by spraying. After coating of oxygen diffusion layer on cathode catalyst, the electrode chip with anode catalyst, the Nafion membrane with cathode catalyst and the another electrode chip with gold current collector were laminated in a sandwich construction, and then hot-pressed to make an electrode assembly at a pressure of about 30 psi at 443 K for 600 s.

2-4. Testing of mini-DMFC Performance

Figure 2 is the testing set-up of mini-DMFC performance. The set-up consisted: a glass cell, an electrode assembly, a heated, stirred fuel tank with condenser, a fuel circulation pump and an air flow-meter. The new cathode catalyst in the electrode assembly was the mixture of TPP-Co and TPP-Ru, which was thermally decomposed at 1073 K for 7.2 ks. The concentration of CH$_3$OH in the electrolyte of 0.05 kmol m^{-3} H$_2$SO$_4$ was changed from 0.5 to 17.0 kmol m^{-3} and the temperature was kept at 296, 333, 347 and 363 K. In this testing, the cell voltage was swept form the open circuit voltage to zero to measure the current using a potentiostat (EG&G, 175). The anode potential versus a saturated calomel electrode (SCE) was measured by a voltmeter (KEITHLEY, 175A) and the cathode potential was calculated from the sum of the cell voltage and the anode potential.

3.   Results and Discussion

3-1.   Oxygen Reduction of Pt Black and Glassy Carbon

Figure 3 shows the polarization curves of Pt black and glassy carbon measured (a) in 0.5 kmol m^{-3} H$_2$SO$_4$, and (b) in 0.5 kmol m^{-3} H$_2$SO$_4$+1.0 kmol m^{-3} CH$_3$OH at 298 K. The current density of the Pt black obviously increases with the increasing rotation rate of the electrode. However, the current density of the glassy carbon is independent of the rotation rate and very small regardless of the presence of CH$_3$OH. Therefore, it can be confirmed that the glassy carbon has no activity for oxygen reduction. In the polarization curves of Pt black in the solution of 0.5 kmol m^{-3} H$_2$SO$_4$ without CH$_3$OH, there are characteristic current peaks at 0.07, 0.21 and 0.73 V vs. NHE. Moreover, these peaks could be observed not only in the solution saturated with oxygen but also in the solution saturated with Ar gas. Therefore, the current peaks at 0.07 and 0.21 V are probably associated with the hydrogen adsorption. The characteristic current peaks at 0.73 V can be interpreted as the reduction of the Pt surface oxide[8]. However, the oxygen reduction activity of Pt black significantly decreases in the presence of CH$_3$OH. To correctly explain this decline, there is a large anodic current for the methanol oxidation at a potential higher than 0.45 V vs. NHE. The starting potential shifts from 1.0 V to about 0.5 V and the cathodic current overall decreases due to the presence of CH$_3$OH. These changes must be the essence of the "crossover" in the DMFC.

3-2.   Oxygen Reduction of Thermally Decomposed TPP-Mes

Figure 4 shows the polarization curves of various TPP-Mes substrates, which were thermally decomposed at 873 K for 7.2 ks, in 0.5 kmol m^{-3} H$_2$SO$_4$ (a) without, and (b) with 1.0 kmol m^{-3} CH$_3$OH. The electrode was rotated at 900 rpm. There is a significant difference in the activity of the methanol oxidation between Pt black and the thermally decomposed TPP-Mes. Although a

large anodic current due to the methanol oxidation can be observed in the polarization curve of Pt black in 0.5 kmol m^{-3} H$_2$SO$_4$ with 1.0 kmol m^{-3} CH$_3$OH, the thermally decomposed TPP-Mes have no activity for the methanol oxidation. As a result of the activity, the cathodic polarization curves of the TPP-Mes are not influenced by the presence of CH$_3$OH, contrary to the behavior of Pt black. In addition, TPP-Co and TPP-Ru can maintain a good activity for oxygen reduction in the solution with CH$_3$OH. However, the current densities of TPP and TPP-Mn are insufficient as a catalyst for the oxygen reduction regardless of CH$_3$OH. Consequently, the thermally decomposed TPP-Co and TPP-Ru were selected as the possible catalysts and the activities of the oxygen reduction were investigated in detail.

Figure 5 (a) is the cathodic polarization curves of various TPP-Co substrates, which were thermally decomposed at 673-1173 K for 7.2 ks, in 0.5 kmol m^{-3} H$_2$SO$_4$ + 1.0 kmol m^{-3} CH$_3$OH at 298 K. The starting potential of the cathodic current is not influenced by the decomposition temperature and it is approximately 0.95 V vs.

NHE. On the other hand, the current density increases with the increasing temperature in the range of 673-873 K. However, the current density is significantly decreased by the thermal decomposition in the range of 973-1173 K. Figure 5 (b) shows the changes in the current densities at 0.2 V and 0.6 V vs. NHE as a function of the decomposition temperature. The change in the current density at 0.6 V is more remarkable than that at 0.2 V vs. NHE. As a whole, the catalysts obtained by the thermal decomposition at 773 and 873 K have a high activity for oxygen reduction without regard to the presence of CH$_3$OH.

Figure 6 (a) shows the influence of the decomposition temperature on the cathodic polarization curves of TPP-Ru in 0.5 kmol m^{-3} H$_2$SO$_4$ + 1.0 kmol m^{-3} CH$_3$OH at 298 K. Although the TPP-Ru substrates obtained by the thermally decomposition at 773 and 873 K for 7.2 ks do not have a high activity, the decomposition at 973-1073 K can activate the oxygen reduction. However, the cathodic polarization curve declines again by the thermal decomposition at 1173 K. Figure 6 (b) is the changes in the current densities at 0.2
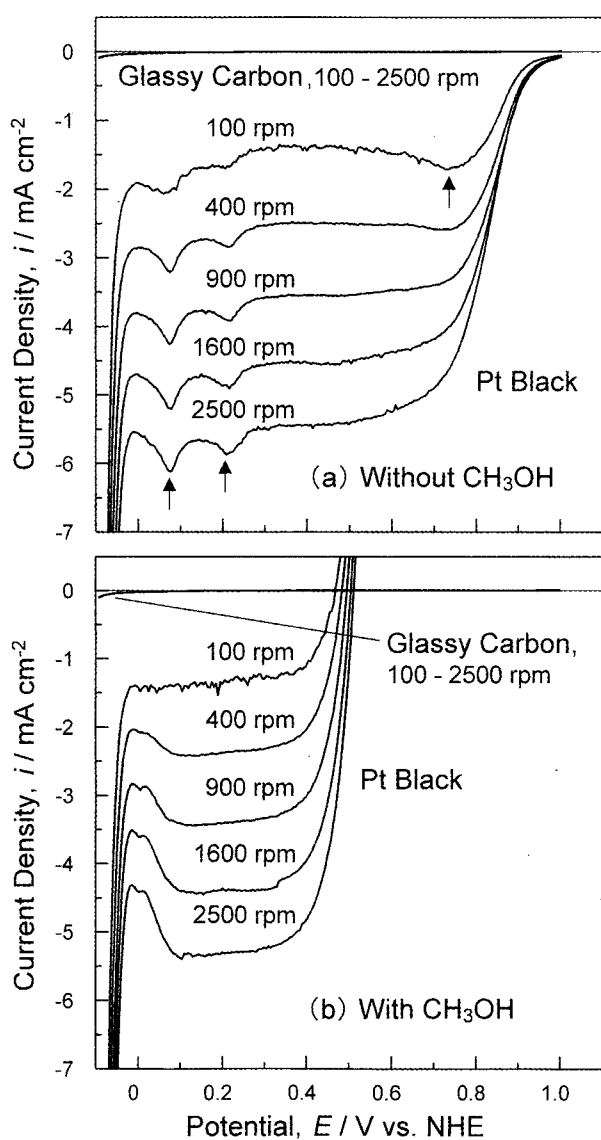

Figure 3   Polarization curves of Pt black and glassy carbon (a) in 0.5 kmol m^{-3} H$_2$SO$_4$, and (b) in 0.5 kmol m^{-3} H$_2$SO$_4$ + 1.0 kmol m^{-3} CH$_3$OH at 298 K. The electrode was rotated from 100 to 2500 rpm.
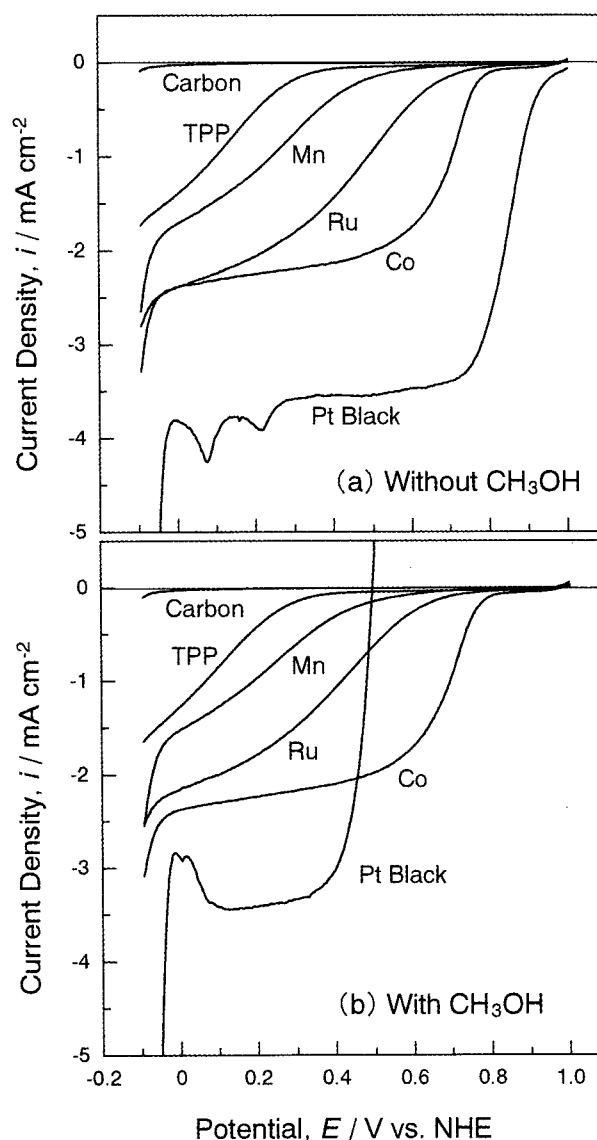
Figure 4   Polarization curves of various TPP-Mes thermally decomposed at 873 K for 7.2 ks (a) in 0.5 kmol m^{-3} H$_2$SO$_4$, and (b) in 0.5 kmol m^{-3} H$_2$SO$_4$ + 1.0 kmol m^{-3} CH$_3$OH at 298 K. The rotation rate of electrode was 900 rpm.

144   Masami TAGUCHI et. al.

and 0.6 V vs. NHE as a function of the decomposition temperature. This shows that the thermal decomposition at 973-1073 K can achieve a maximum efficiency for improvement of the oxygen reduction current of the TTP-Ru not only at 0.6 V, but also at 0.2 V vs. NHE.

3-3. Influence of Structure of Thermally Decomposed TPP-Co and TPP-Ru on Activity of Oxygen Reduction

Figure 7 shows the x-ray diffraction spectra (a) of the TPP-Co and (b) of the TPP-Ru, which were thermally decomposed at 673-1173 K for 7.2 ks. The spectrum of the TPP-Co thermally decomposed at 673 K was quite similar to that of the chemical agent without heat-treatment. No sharp diffraction peaks are observed for the thermal decomposition products of the TPP-Co at 773 and 873 K. However, three sharp peaks, which correspond to β-Co, appear in the background of the decomposition products of the TPP-Co at 973, 1073 and 1173 K. Figure 5 shows that the thermal decomposition at 773 and 873 K produces good activity during the

oxygen reduction of the TPP-Co. The decomposition at 973, 1073 and 1173 K also causes a significant decline in the oxygen reduction activity. Therefore, the thermal decomposition of TPP-Co would occur at temperatures of 773 K or higher. It may also be concluded that the electrocatalytic activity of TPP-Co begins to decline if the decomposition leads to the formation of β-Co particles. That is to say, a medium temperature, which promotes the decomposition, but does not produce the metallic Co particles yet, is preferable in this case. Okada et al.[6] found that the oxygen reduction characteristics of the cobalt porphyrin complexes largely depended on the heat-treatment conditions. They also reported that the decline in the catalytic activity of the oxygen reduction was deeply related to the further decomposition of the Co-N_4 chelates.

On the other hand, the most suitable decomposition temperature for the TPP-Ru is about 200 K higher than that for the TPP-Co. Figure 6 shows that a high reduction current can be observed at the decomposition temperatures of 973-1073 K but the value declined
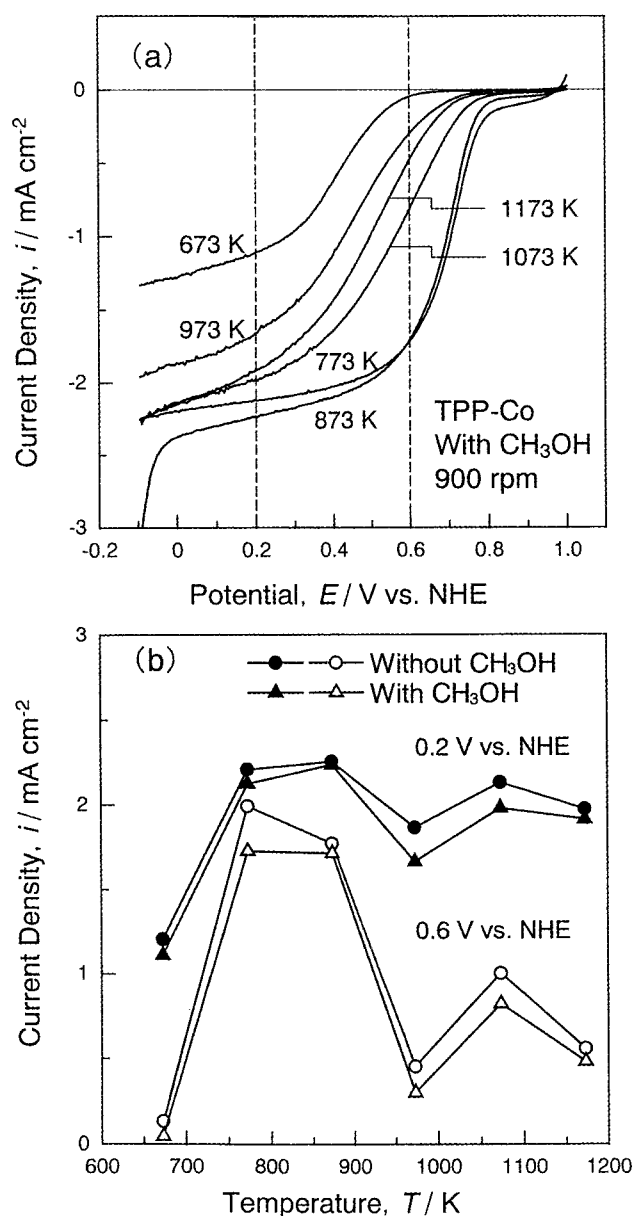

Figure 5   Influence of decomposition temperature on polarization curves of TPP-Co
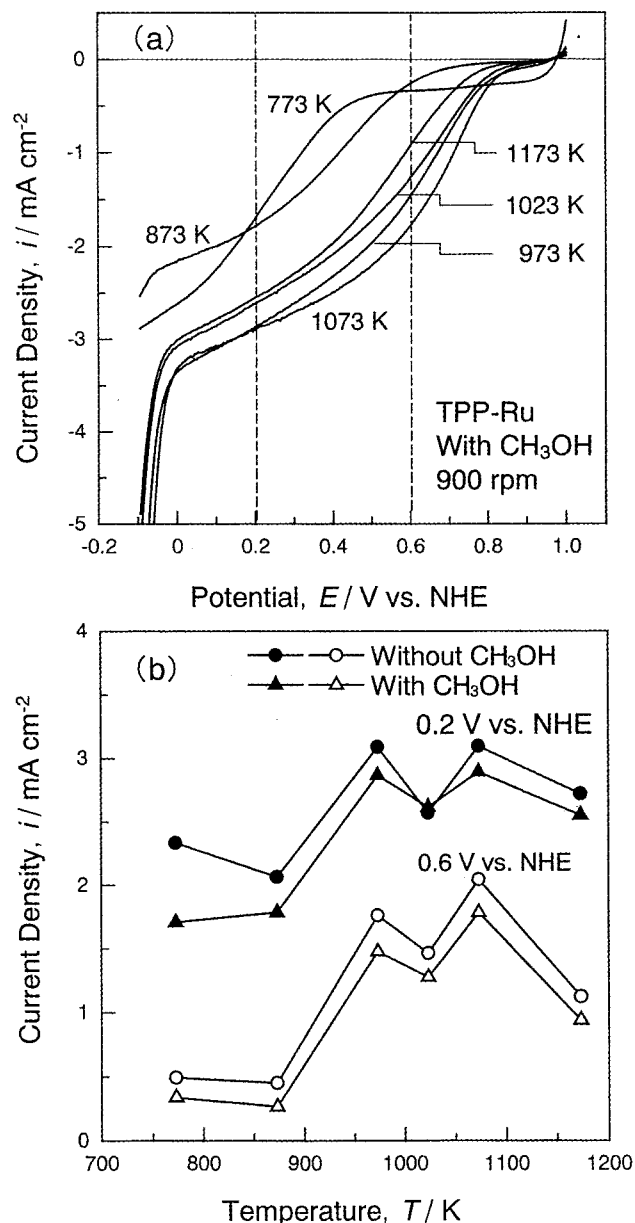

Figure 6   Influence of decomposition temperature on polarization curves of TPP-Ru

at 1173 K. No sharp peaks are observed in the x-ray diffraction spectra of the TPP-Ru thermally decomposed at 773-1173 K. However, two broad peaks, which correspond to metallic Ru, appear at 973-1173 K. Therefore, the improvement of the electrocatalytic activity of the TPP-Ru must be concerned with the appearance of the metallic Ru. Besides, the decline in the activity might be caused by the change in the dispersion of the metallic Ru particles, for example, the growth of the particle.

3-4. Influence of Mixing TPP-Mes on Oxygen Reduction

The activity of the TPP-Mes mixture is sometimes superior to that of a single TPP-Mes. Jiang et al.[7] studied the influence of the mixing TPP-Mes on the oxygen reduction. They reported that the catalytic activity of the thermally decomposed binary metalloporphyrin catalyst was better than that of a thermally decomposed single metalloporphyrin. Figure 8 shows the polarization curves of TPP-Co, TPP-Ru and the mixture of both TPP-Mes, which were thermally decomposed at 873 K or 1073 K for 7.2 ks. For the mixture, the TPP-Co and the TPP-Ru were mixed in the ratio 1:1 by weight and then thermally decomposed. At 873 K, the oxygen reduction current of the TPP-Co is higher than that of the

TPP-Ru. The activity of the mixture of TPP-Co and TPP-Ru (Co/Ru Mixture) is between those of the single TPP-Mes. On the other hand, the oxygen reduction of the TPP-Co is lower than that of the TPP-Ru prepared at the decomposition temperature of 1073 K. The polarization curve of the mixture of TPP-Co and TPP-Ru is also between the curves of TPP-Co and TPP-Ru. That is to say, the oxygen reduction activity of the mixture is in the middle between those of each single TPP-Mes without regard to the decomposition temperature. Therefore, the mixing of TPP-Mes cannot necessarily produce a better oxygen reduction activity than that of the single TPP-Me.

3-5. Kinetics of Oxygen Reduction of Thermally Decomposed TPP-Co and TPP-Ru

It is postulated that the oxygen reduction on the catalyst proceeds via the direct 4-electron pathway or the peroxide one.
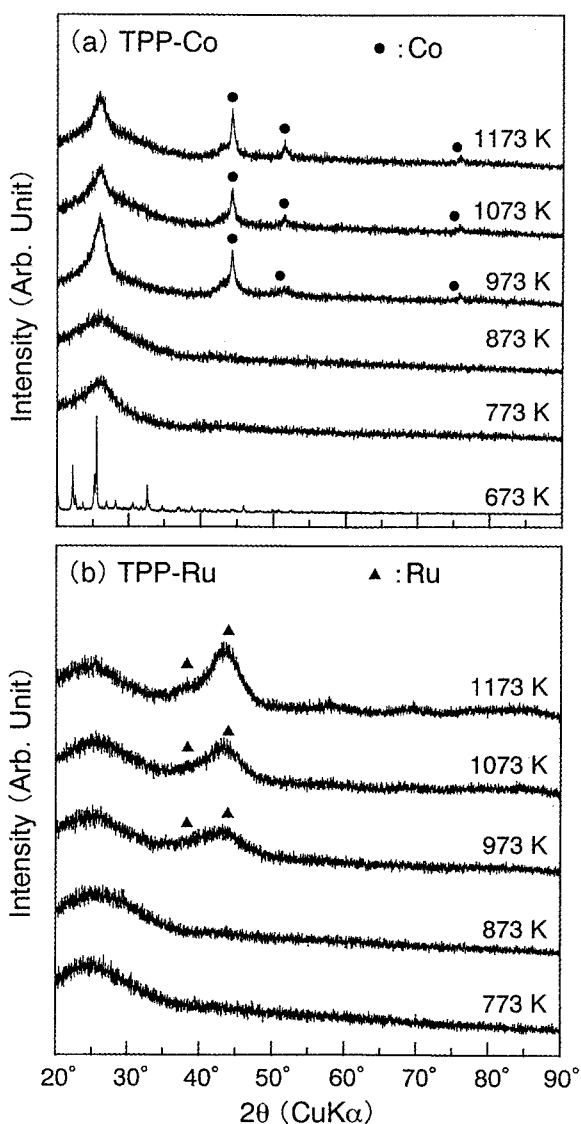

Figure 7 X-ray diffraction spectra (a) of the TPP-Co, and (b) of the TPP-Ru thermally decomposed at 673-1173 K for 7.2 Ks.
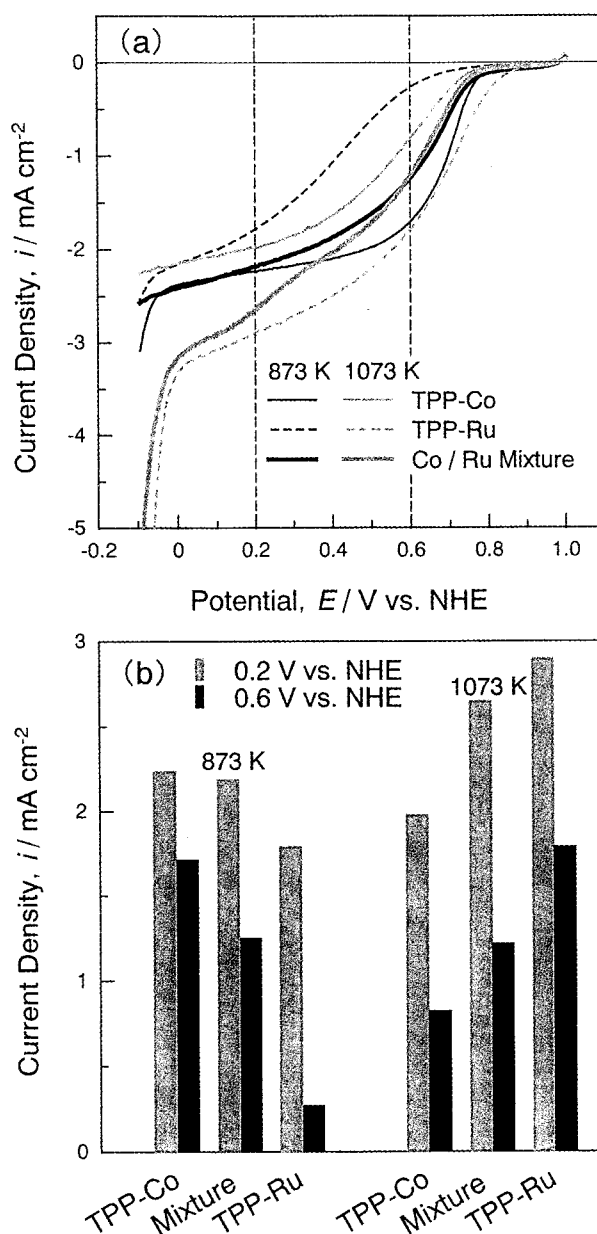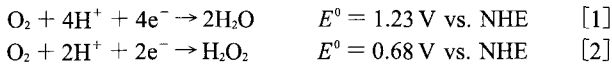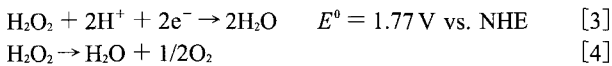

Figure 8 Polarization curves of TPP-Co, TPP-Ru and the mixture of the TPP-Mes, which were thermally decomposed at 873 K or 1073 K for 7.2 Ks.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^0 = 1.23 \text{ V vs. NHE} \qquad [1]$$
$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E^0 = 0.68 \text{ V vs. NHE} \qquad [2]$$

Two consecutive reactions after reaction [2] can also proceed.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E^0 = 1.77 \text{ V vs. NHE} \qquad [3]$$
$$H_2O_2 \rightarrow H_2O + 1/2O_2 \qquad\qquad [4]$$

Although reaction [4] is not electrochemical, reaction [3] would affect the efficiency of the electrochemical oxygen reduction on the catalyst. That is to say, both reactions [2] and [3], which can proceed the 2+2 electron reduction, play an important role in the oxygen reduction in acidic solutions.

When the reaction is controlled by mass-transport, the limiting current of the oxygen reduction, i_L, can be analyzed using the Levich equation[9].

$$i_L = 0.62 \, n \, F \, A \, D_0^{2/3} \, \nu^{-1/6} \, C_0 \, \omega^{1/2} \qquad [5]$$

where n is the number of electrons related to the oxygen reduction, F is Faraday's constant, A is the surface area of the working electrode, D_0 is the diffusion coefficient of oxygen in the solution, ν is the kinematic viscosity of the solution, C_0 is the concentration of dissolved oxygen in the solution, and ω is the rotation rate of the working electrode. If the reaction has mixed control, the activation current, i_{ac}, and the mass-transport controlled current combine to yield the total current as the sum of the reciprocals.

$$1/i = 1/i_{ac} + 1/(B\omega^{1/2}) \qquad [6]$$
$$B = 0.62 \, n \, F \, A \, D_0^{2/3} \, \nu^{-1/6} \, C_0 \qquad [7]$$

The current, i, under mixed control can be analyzed using equations [6] and [7], namely Koutecky-Levich equation[9]. In this research, we used the following values for the calculation: $D_0 = 1.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $C_0 = 1.3 \times 10^{-6} \text{ mol cm}^{-3}$, which are based on the literature[10-12], and $\nu = 9.6 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, which was measured using the Ubbelode viscometer.

Figure 9 shows the Koutecky-Levich plots of the oxygen reduc-
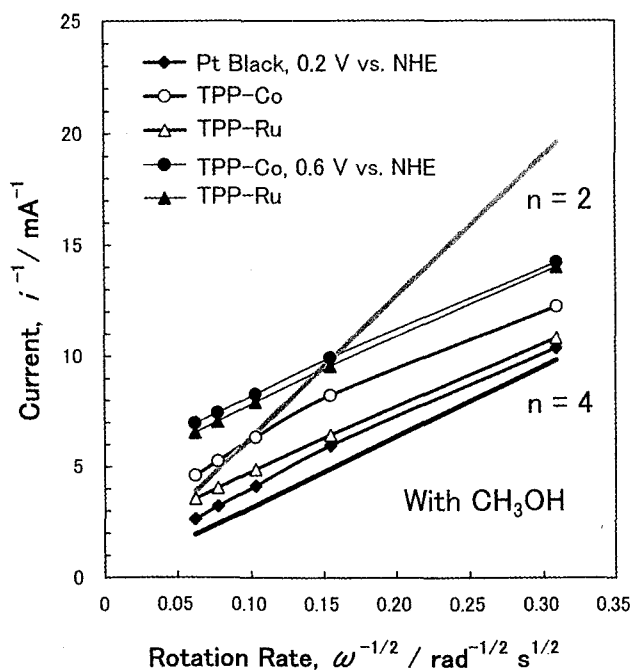
tion current for the Pt black, and thermally decomposed TPP-Co and TPP-Ru. The TPP-Co and TPP-Ru were thermally decomposed at 873 and 1073 K for 7.2 ks, respectively. The resulting graph should be a straight line with the slope of $1/B$. In this figure, the theoretical straight lines marked for $n = 2$ and 4, which indicate that the charge transfer is determined by a 2-electron reduction or 4-electron one, were drawn. The slopes of all the straight lines of Pt black, TPP-Co and TPP-Ru are almost equal to that of the line for $n = 4$. This means that the oxygen reduction on the catalyst is under mixed control and a 4-electron reduction or 2+2 electron one participates in the charge transfer on not only Pt black, but also for the tetraphenylporphyrin-metals. Moreover, the reciprocal of the oxygen reduction current, i^{-1}, for TPP-Ru is smaller than that for TPP-Co. In other words, the reduction current of TPP-Ru is greater than that of the TPP-Co and it is close to the Pt black regarding the oxygen reduction activity.

3-6. Discharge Performance of mini-DMFC using Thermally Decomposed TPP-Mes as Cathode Catalyst

Figure 10 is the discharge performance of mini-DMFC using the mixture of TPP-Co and TPP-Ru as cathode catalyst. The mixture was thermally decomposed at 1073 K for 7.2 ks. The discharge current increases with the increasing temperature in the fuels of (a) 0.5 and (b) 5.0 kmol m^{-3} CH$_3$OH, while the concentration of CH$_3$OH hardly affect the discharge performance. However, the discharge current is significantly lowered by heightening the

Figure 9   Koutecky-Levich plots of oxygen reduction current for the Pt black, thermally decomposed TPP-Co and TPP-Ru.
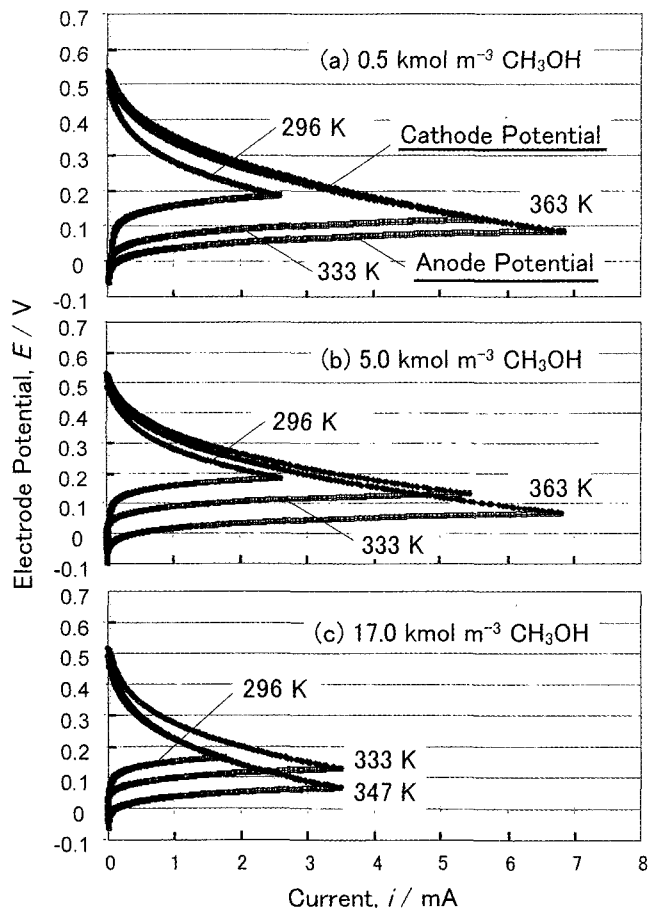

Figure 10   Discharge performance of mini-DMFC using the mixture of TPP-Co and TPP-Ru as cathode catalyst. The mixture was thermally decomposed at 1073 K for 7.2 Ks.

concentration of CH_3OH to (c) 17.0 kmol m^{-3}. The higher both the operation temperature and the concentration of CH_3OH in the fuel, the larger the amount of the crossover CH_3OH in DMFC. As mentioned earlier, the new cathode catalysts or the thermally decomposed TPP-Mes have CH_3OH tolerance on the activity of the oxygen reduction. Therefore, there is no influence of the concentration of CH_3OH on the discharge performance of the mini-DMFC in the range of 0.5-5.0 kmol m^{-3}. On the other hand, the reason why the discharge current is significantly lowered in the fuel of 17.0 kmol m^{-3} CH_3OH may be due to several degradations, which include the decrease of the activity of the oxygen reduction. By the way, the decrease of the cathode potential is greater than that of the anode potential in the discharge performance of the mini-DMFC. This result suggests that the DMFC performance is controlled by the cathode property rather than the anode one. Moreover, the discharge performance of the mini-DMFC is insufficient for the practical use, even though the polarization measurement of Sec. 3-2 shows that the oxygen reduction current of the new catalyst is enough. The temperature of the hot-pressing for the mini-DMFC production is as high as 443 K, while the rotating disk electrode for the measurement of oxygen reduction current is prepared at temperatures of 348 K or less. Therefore, it is possible that the higher treatment temperature has a bad influence upon the mini-DMFC performance. At present, the improvement for the preparation of the electrode assembly is planed in order to get a good performance for the practical use.

4. Conclusions

The catalytic activity of the oxygen reduction of Pt black is severely decreased by the presence of CH_3OH. However, the activity of the thermally decomposed TPP-Mes is not affected by the CH_3OH. Although the application requires some improvements on the preparation of the electrode assembly, the thermally decomposed TPP-Co and TPP-Ru are potential materials as the cathode catalyst of the DMFC with CH_3OH tolerance. The most suitable temperature for the thermal decomposition of TPP-Co is 773-873 K. The XRD analysis also showed that the occurrence of a metallic Co at 973 K or above was not desirable for the catalytic activity. On the other hand, the thermally decomposed TPP-Ru had a high catalytic activity at 973-1073 K, in which metallic Ru appeared as the decomposition product. The oxygen reduction on the catalysts is under mixed control of diffusion and charge transfer, and a 4 electron reduction or $2+2$ electron one probably participates in the charge transfer process.

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