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Facilitated oxygen transport through a Nafion membrane containing cobaltporphyrin as a fixed oxygen carrier

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ABSTRACT

A Nafion membrane containing a cobaltporphyrin (CoP) complex as a fixed oxygen carrier was prepared with a view to facilitate oxygen transport through the membrane. The design concept of the CoP-loaded Nafion membrane was based on the CoP's modification to place the CoP complex in a hydrophobic domain of the microphase-separated structure, in order to facilitate the oxygen transport and to maintain proton conductivity. The oxygen permeability through the CoP-loaded Nafion membrane was higher than the nitrogen permeability, and significantly enhanced at relatively-low oxygen pressures of the upstream, indicating that the fixed CoP complex acted as an oxygen hopping site to facilitate the oxygen transport. The oxygen/nitrogen permselectivity increased with the content of CoP in the Nafion membrane. Electrochemical reduction of oxygen at a glassy carbon electrode, modified with a Pt/C catalyst and the CoP-loaded Nafion membrane, provided additional support for the facilitated oxygen transport by the membrane. Increased current for the reduction of oxygen on the modified electrode by loading CoP indicated that the CoP offered the oxygen hopping site in the Nafion membrane.

1. Introduction

A polymer electrolyte fuel cell (PEFC) is promising as an efficient electrical power generation, consuming hydrogen and oxygen gases and producing only H_2O. The efficiency of oxygen supply to the cathode is one of the important factors in determining the performance of PEFC [1,2]. Oxygen is reduced at the cathode in the three-phase boundary composed of the gas, the polymer electrolyte layer and the Pt/C catalyst [1,2]. A sufficient amount of the polymer electrolyte increases the active surface area of the catalyst, providing an adequate supply of protons. However, the polymer electrolyte layer could limit the mass transport of the oxygen gas because of the lower diffusivity within the layer, resulting in the suffocation of the cell. Thus, as far as operating PEFC with air, the reduction current can be frequently limited by the oxygen depletion [3–5]. Our previous report on an oxygen sensing material demonstrated that oxygen is indeed depleted at the end of gas-flow channel [2]. One way to enhance the oxygen reduction current is to apply pure oxygen to the cathode. However, the mixed loading of the fuel gas (i.e. hydrogen) and oxygen is undesirable in terms of safety. Furthermore, stored oxygen gas occupies much space, resulting in not only the enlargement but also increased complication of the entire system. A simple and safe oxygen enrichment process should promote the use of abundant air, which is advantageous from the viewpoint of cost and handling use.

The catalytic surface where oxygen reduction takes place is covered by a polymer electrolyte membrane, such as Nafion. The oxygen (air) in the gas-flow channel is dissolved into the polymer electrolyte membrane, and then reduced on the surface of catalyst. A proton conductive electrolyte membrane which also takes up oxygen from air and facilitates oxygen transport to the surface of catalyst is expected to enhance the oxygen supply to the catalyst, resulting in the larger current for the reduction of oxygen.

A number of polymer-blended, metal- and metal complex-loaded Nafion membranes have been reported for the improvement of proton conductivity, the suppression of methanol permeability and the catalytic applications [6–10]. However, no attempt has been made to enhance the oxygen permeability by introducing an oxygen carrier to the membrane. It may be noted that there are some studies where specific species were loaded into the Nafion membrane and distributed in the hydrophobic domain. Our group reported that the reversible oxygen binding on the cobaltporphyrin (CoP) can be used as the facilitated oxygen transport, allowing oxygen enrichment through a CoP-loaded solvent-free membrane [11,12]. Within the polymer membrane, a CoP–imidazole complex binds oxygen and releases it rapidly and reversibly, according to the equilibrated oxygen concentration. The CoP complex fixed in a polymer membrane facilitates the oxygen transport through the

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membrane, based on the fast kinetics of the oxygen hopping between the binding sites. A number of polymer matrices such as poly(alkylmethacrylate)s and their copolymers with vinyl imidazoles have been reported as axial ligands to fix CoP in the membrane [13–16].

In this study, we report on the attempt to facilitate the oxygen transport across the Nafion membrane, with a view to enhance the oxygen transport on the cathode surface of PEFC. The effect of the oxygen enrichment by the membranes was assessed, not only by gas permeation measurements but also by electrochemical techniques using modified electrodes.

2. Experimental part

2.1. Materials

Nafion solution (5 wt% in an 8:2 mixture of aliphatic alcohol and water, ion exchange capacity = 0.91 meq g^{-1}, Aldrich Co.), *meso*-tetraphenylporphyrinatocobalt (CoTPP, Chart 1, Aldrich Co.) and perchloric acid (60%, Kanto Chem. Co.) were used without further purification. *N*-Benzylimidazole (BIm, Aldrich Co.) was sublimated prior to use. *meso*-Tetrakis(pentafluorophenyl)porpyrinatocobalt (CoFPP, Chart 1) was prepared from the free-base porphyrin, according to the literature [17]. A platinum-embedded carbon powder (Pt/C) as a catalyst for the oxygen reduction was obtained from the Tanaka Kikinzoku Kogyo Co.

2.2. Preparation of a CoP-loaded Nafion membrane

CoP and BIm were dissolved in THF, followed by mixing with the Nafion solution. The conditions were fixed at a molar ratio of CoP and BIm = 1:2 and Nafion concentration in the solution = 1.5 g l^{-1}. The resulting homogeneous solution was cast on a Teflon plate and dried under vacuum to produce a reddish membrane with a 30 μm thickness. For gas permeation measurements the CoP-loaded Nafion solution was cast on a porous support membrane (polyacrylonitrile) using a barcoater, in order to obtain a high gas permeance. After removing the solvents, a CoP-loaded Nafion membrane was obtained with 150 nm thickness, which was estimated from the cross-sectional SEM image.

2.3. Preparation of samples for TEM observation

For TEM observations, the Nafion membranes were prepared on a Teflon plate. The membrane was fixed in an epoxy resin by Spurr's method. The fixed Nafion membranes were sliced to a 30 nm thickness using a microtome. The laminas of the Nafion membrane were collected onto electron microscope grids, followed by staining with RuO_4 solution for 40 min [18]. After staining, the samples were dried under vacuum for a day.

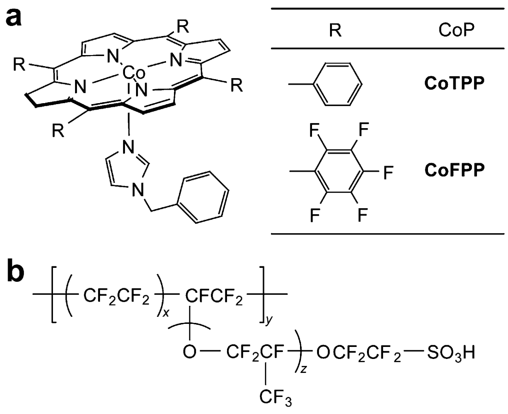


Chart 1. Chemical structures of cobaltporphyrins complexed with *N*-benzylimidazole (a) and Nafion (b).

2.4. Proton conductivity measurements

Proton conductivity of the membranes was measured using an Auto lab PGSTAT30 AC impedance analyzer (Eco Chemie Co.) over a frequency range from 1 Hz to 1 MHz. For conductivity measurements, the CoP-loaded Nafion membrane was directly formed on the gold disk with a 15 mm diameter. Before the measurement, the membranes on the gold disks were immersed in distilled water for at least a day.

2.5. Gas permeability measurements

The oxygen and nitrogen permeability coefficients (P_{O_2} and P_{N_2}) of the CoP-loaded Nafion membranes were measured with a permeation apparatus [19]. The gas permeability coefficient P (cm^3 (STP) cm/cm^2 s cm Hg) is defined as follows:

$$P = Rl\Delta p^{-1}A^{-1}$$

R, volumetric gas permeation rate (cm^3 s^{-1}); l, membrane thickness (cm); Δp, difference between the upstream and permeate side pressures (cm Hg) A, permeation area (cm^2).

The upstream pressure range was 77–152 cm Hg, while the permeate side pressure was atmospheric (76 cm Hg).

2.6. Preparation of modified electrodes

As a working electrode to evaluate oxygen permeability by electrochemical measurements, a glassy carbon electrode with a 6 mm diameter was modified with the membrane. Before the modification, the surface of the electrode was polished, followed by cleaning in distilled water with ultrasonic irradiation. The Pt/C (2 mg) powder was dispersed in 2-propanol (0.4 ml), and then a portion of the dispersion (10 μl) was transferred onto the glassy carbon electrode, which was dried in air. The CoP-loaded Nafion solution was prepared as described above with the conditions of the molar ratio of CoP and BIm = 1:2 and volumetric ratio of the Nafion solution and THF = 1:2. The CoP-loaded Nafion solution (8 μl) was carefully dropped onto the surface of the electrode to cover the Pt/C layer, followed by removing the solvents under vacuum. The thickness of the resulting Nafion layer was ca. 2.6 μm, which was calculated based on the amount of Nafion, the surface area of the electrode, and the density of Nafion (1.58 g cm^{-3}).

2.7. Electrochemical measurements

The modified glassy carbon electrode was used as the working electrode. A platinum ring was used as the auxiliary electrode. Ag/AgCl was used as the reference electrode, which was placed in the main cell compartment. An aqueous solution of $HClO_4$ (0.1 M) was used as the electrolyte. The standard potential for the four-electron reduction of oxygen to H_2O was 1.03 V (vs. Ag/AgCl) under acidic conditions [20]. All measurements were carried out using a PARSTAT 2263 Advanced Electrochemical System (Princeton Applied Research Co.) using an RRDE-1 rotator (NIKKO KEISOKU Co.).

3. Results and discussion

3.1. Characterization of the microphase-separated structure

In the preparation of the CoP-loaded Nafion membrane, hydrophobic porphyrins and *N*-benzylimidazole were employed.

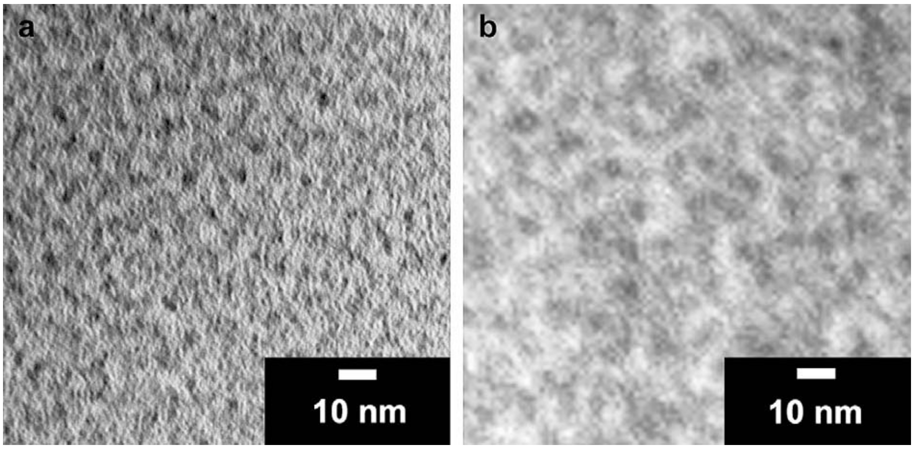


Fig. 1. TEM images for the Nafion membrane (a) and the CoP-loaded Nafion membrane (b). Both samples were stained with RuO_4.

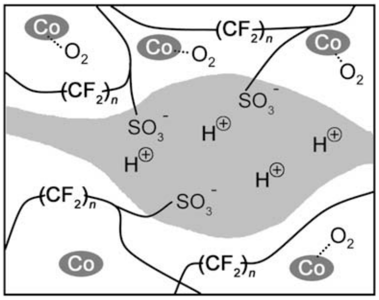
The hydrophilic species are anticipated to locate mainly in the hydrophilic domain of Nafion, which most likely decrease the proton conductivity of the membrane. Furthermore, the hydrophilic species will be eluted from the membrane by water. Hydrophobic CoTPP or CoFPP and *N*-benzylimidazole remained intact even after the prolonged immersion of the membrane in water. The CoP-loaded Nafion membrane was obtained as a reddish membrane. The UV–vis spectrum of the deoxy CoP ($\lambda_{max} = 412$ nm) in CH_2Cl_2 was changed into the spectrum with the absorption maximum at 429 nm assigned to the oxygen adduct (oxy) of CoP after the exposure to oxygen. The oxy–deoxy spectral change was reversible in response to the partial oxygen pressure of the atmosphere, with isosbestic points at 420 nm. The UV–vis spectrum of the CoP-loaded Nafion membrane ($\lambda_{max} = 413$ nm) indicated that, although the interior of the Nafion membrane has an acidic environment, most of the CoP complex was fixed in the hydrophobic domain of Nafion without irreversible oxidation of oxygen-binding Co(II) to inactive Co(III). Thus, the CoP complex fixed in the Nafion membrane was expected to act as an oxygen carrier after the fixation. Optimal conditions were tuned by employing the hydrophobic species, and the molar ratio of CoP and BIm = 1:2 to minimize the loss of BIm from the hydrophobic domain, in order to yield a five coordinated oxygen–philic complex preferentially. Control experiments using excess BIm resulted in a decrease in proton conductivity and gas permeability due to the dissolution of BIm into the hydrophilic domain.

The microphase-separated structure of the Nafion membranes was observed in the TEM images (Fig. 1). The TEM image of the Nafion stained with RuO_4 indicated the presence of the connected hydrophilic domain as the black round shaped area with a 5–7 nm diameter, as has been reported in the literature [18]. Observation of the microphase-separation of the unstained CoP-loaded membrane was unsuccessful. Reasoning that CoP was distributed not only in the hydrophobic domain but also in the hydrophilic part to some extent (vide infra), we turned to the observation of stained samples. For the stained CoP-loaded Nafion membrane, the similar black area with a distinct connectivity was observed. The image indicated that the incorporation of CoP did not break the microphase separation. A slight increase in the size of the unstained hydrophobic domain is considered to reflect the incorporation of the hydrophobic CoP.

The ratio of the CoP complex located inside the hydrophobic domain of the Nafion to the total loaded amount in the membrane was determined by the extraction experiments. The CoP-loaded Nafion membranes were immersed in conc. H_2SO_4 that most likely soaked into the hydrophilic domain of Nafion and dissolved the CoP out of the membrane, and was equilibrated for one day. The extract was diluted with purified H_2O for the UV–vis measurement. The amount of CoP in the diluted extract was calculated with the calibration curve. For the preparation of calibration curve, pre-determined amount of CoP was also dissolved in conc. H_2SO_4 and diluted with purified H_2O considering the demetallation from CoP by the strong acid. From the CoTPP-loaded Nafion membrane, 55% of the loaded complex was extracted, while the ratio for the more hydrophobic, fluorinated CoFPP-loaded Nafion membrane was only 15%. The result indicated that the incorporation of CoP could be caused by a hydrophobic interaction between CoP and the hydrophobic domain of Nafion, and that the fluorinated CoFPP, which is more hydrophobic than CoTPP for its fluoroalkyl group, was more likely incorporated into the hydrophobic domain of the Nafion membrane. Homogeneous incorporation of CoPs in the hydrophobic domain of Nafion would be supported by the following experiment using poly(vinylidene fluoride) (PVDF). The membrane cast from the THF solution of PVDF and CoP ([CoP] = 20 wt%) was homogeneously red-colored and did not any segregation of CoP.

The localization of the CoP in the hydrophobic domain is advantageous for use as an oxygen-enriching membrane at the electrode, because the presence of CoP may not interfere with the overall proton conductivity which takes place through the hydrophilic domain (vide infra) (Scheme 1).

The proton conductivity of the CoP-loaded Nafion membranes was evaluated by impedance analysis (Fig. 2). The proton conductivity of the pristine Nafion membrane ([CoP] = 0 wt%) was a little lower than the literature data (10^{-1}–10^{-2} S cm^{-1}), due to the omission of the conventional pretreatment process [21]. For both membranes containing CoTPP and CoFPP, the proton conductivity decreased with an increase in the CoP content, which suggested that the CoP and imidazole were located partially in the hydrophilic



Scheme 1. Schematic representation of the distribution of CoP in the microphase separated structure of Nafion.

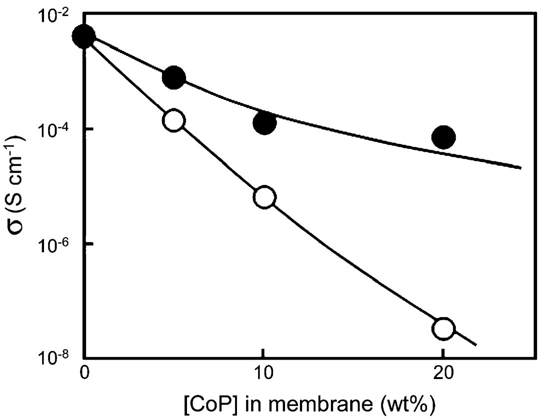


Fig. 2. Proton conductivity of the CoTPP-loaded (○) and CoFPP-loaded (●) Nafion membranes at 25 °C. RH = 100%.

domain of Nafion to hinder proton conduction through the membrane. However, the proton conductivity of the CoFPP-loaded Nafion membrane was not decreased as significantly as the CoTPP-loaded Nafion. The distribution of the CoFPP complex, located mainly in the hydrophobic domain, is considered to maintain the proton conductivity of the Nafion.

3.2. Gas permeability of CoP-loaded Nafion membranes

The oxygen and nitrogen permeability of the membranes were evaluated by the permeability measurements (Fig. 3). For the Nafion membrane without any complexes, both P_{O_2} and P_{N_2} were low as has been reported previously [22] and were independent of the upstream oxygen and nitrogen pressure. The oxygen/nitrogen permselectivity, defined as the value of P_{O_2}/P_{N_2} at an upstream pressure of 77 cm Hg, was 1.9. In the case of CoP-loaded Nafion membrane, the P_{O_2} was higher than that of the P_{N_2} and increased with a decrease in the upstream pressure, while the P_{N_2} was independent of the upstream nitrogen pressure. The P_{O_2} of a deactivated CoP-loaded Nafion membrane was also low and independent of the upstream oxygen pressure. These results indicated that the CoP complex facilitated the oxygen transport through the Nafion membrane (Table 1).

The oxygen/nitrogen permselectivity increased with the CoP content (Table 1). A membrane with higher oxygen permeability was obtained using CoFPP. In the study using the CoFPP, a high affinity for the fluorocarbon backbone of Nafion resulted in the localization of CoP in the hydrophobic domain. The CoFPP complex closely-localized in the hydrophobic domain effectively facilitated the oxygen transport by serving as the oxygen-binding and hopping site, allowing the rapid binding and release of oxygen diffusing across the membrane. The oxygen-binding affinity (p_{50}, defined as the partial oxygen pressure at which half of the CoP binds oxygen) of the CoFPP complexed with BIm was 17.9 cm Hg, which was lower than the value of the CoTPP [16]. The lower oxygen binding affinity of the CoFPP resulted in a significant increase in the oxygen/nitrogen permselectivity up to 14. The lifetime of the CoP was also longer for the CoFPP than that for the CoTPP as a result of the hydrophobic environment, which was desirable for the long-time use in the composite CoP-loaded membrane.

3.3. Electrochemical reduction of oxygen on the electrode modified with the CoP-loaded Nafion membranes

On the modified glassy carbon electrode, one could expect that the CoP-loaded Nafion membrane takes up oxygen near the surface of cathode through the reversible binding of oxygen, resulting in the increase in the oxygen reduction current. The oxygen reduction current on the modified electrodes was measured chronoamperometrically. The conventional Pt/C catalyst was employed to allow sufficiently rapid electron transfer for the oxygen reduction, allowing diffusion-limited reduction of oxygen at the electrode. Furthermore, the potential was fixed at a value of −0.1 V (vs. Ag/AgCl) where the oxygen reduction should proceed with a sufficiently large overpotential.

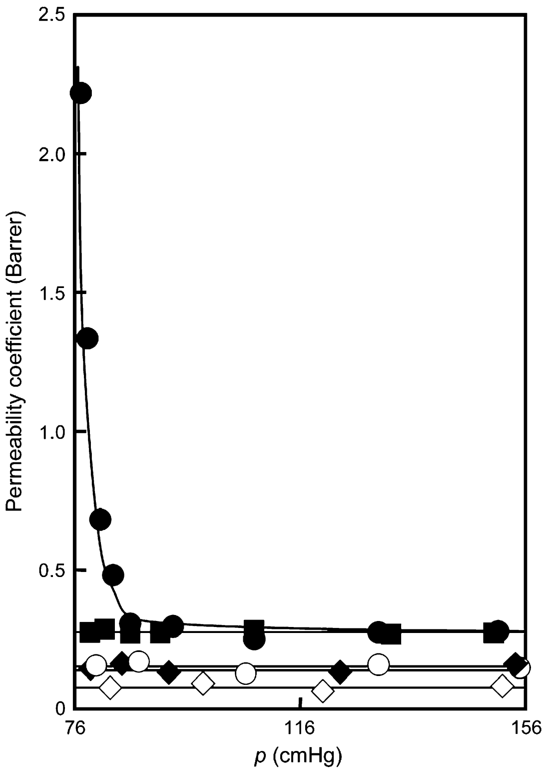


Fig. 3. Oxygen (P_{O_2}, closed plots) and nitrogen (P_{N_2}, open plots) permeability coefficients for the CoFPP-loaded Nafion (●), deactivated CoFPP-loaded Nafion (■) and Nafion (◆) membranes at 25 °C. [CoFPP] = 20 wt%.

The CoP complexes have been found to be stable even under the acidic conditions employed in this study. In the Nafion membrane, the complex located in the hydrophobic fluorocarbon domain persisted without degradation under the acidic conditions. In the case of the CoTPP, the binding and releasing of oxygen determined by laser flash photolysis are quite rapid with the rate constants of 1.3×10^9 M^{-1} s^{-1} and 1.7×10^8 s^{-1}, respectively [23]. The CoFPP also showed similar oxygen binding characteristics. These values suggest that the oxygen binding and releasing processes may not be the rate-determining step for the overall electrochemical reduction of oxygen.

The diffusion-limited behavior was demonstrated by the linearity of the Cottrell plots obtained for the reduction of oxygen (vide infra). The oxygen reduction current was recorded every 0.5 s after applying a potential pulse at $E = -0.1$ V vs. Ag/AgCl (Fig. 4). The

Table 1
Oxygen/nitrogen permselectivity (P_{O_2}/P_{N_2}) of the Nafion membranes with various contents of the CoP complex at 25 °C.

[CoP] (wt%)	CoTPP	CoFPP
0	2.1	2.1
5	3.2	5.0
10	6.5	10
20	8.5	14

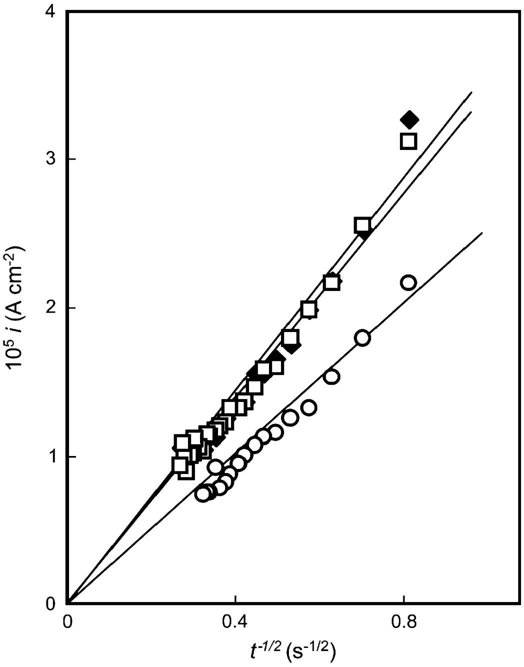


Fig. 4. Cottrell plot for the oxygen reduction on the modified glassy carbon electrodes after the application of a potential pulse at −0.1 V vs. SCE. The electrodes were coated with Nafion (○), CoTPP/Nafion (□), or CoFPP/Nafion (◆) membrane. [CoP] in membranes = 10 wt%. The electrolyte solution was saturated with air.

current was normalized with the active surface area of Pt on the electrode, which was evaluated by the charge consumed for the oxidation of the adsorbed hydrogen in the cyclic voltammograms, assuming a value of 220 μC cm^{-2} for the oxidation of the adsorbed hydrogen on the Pt surface [24].

During the measurement, the i - $t^{-1/2}$ (Cottrell) plots of all samples showed linear regions, which corresponded to the semi-infinite diffusion of oxygen in the membrane attached to the electrode. In the beginning of the measurement before the diffusion-limited region ($t < 1$ s) a large non-faradaic current was observed. Deviation from linearity was also obtained for electrolysis at the prolonged time of measurement ($t > 20$ s) which was ascribed to the effect of the finite diffusion of oxygen.

The oxygen diffusivity (D) through the Nafion membranes on the surface of electrode, and the local oxygen concentration (C) on the surface of electrodes are both reflected in the slope of the Cottrell plot expressed as $nFAC\pi^{-1/2}D^{1/2}$. A comparison of the slopes obtained from the electrodes equilibrated under air, modified with the Nafion and the CoP-loaded Nafion membrane, revealed that oxygen reduction current increased in the presence of CoP. In the CoP-loaded Nafion membrane, the CoP is considered to bind oxygen molecules and facilitate the oxygen dissolution into the membrane. Oxygen was accumulated near the surface of the electrode by CoP, resulting in the increase of oxygen reduction current. Furthermore, the slope of the Cottrell plots of the modified electrodes indicated that the oxygen diffusivity through the Nafion membrane, D, was likely to be enhanced slightly by the CoP-loading. The oxygen concentration on the surface of electrode, C, was able to be estimated as mentioned below, so that we could discuss the contribution of D and C separately.

Comparison of oxygen reduction current between those obtained in the presence and the absence of CoTPP on the modified electrodes revealed that the CoTPP-loaded Nafion enhanced the current up to ca. 130% vs. the pristine Nafion. The enhancement was ascribed to the accumulation of oxygen in the Nafion membrane, which is able to be calculated with the oxygen physical solubility of Nafion, and the molar amount of oxygen bound to the CoP-loaded into Nafion. Physically dissolved amount of oxygen within Nafion is calculated with the oxygen solubility coefficient [24] and the volume of Nafion membrane on the surface of the electrode (6.9×10^{-10} mol). The amount of oxygen bound to CoP is assessed by the product of the concentration of active CoP (defined as the CoP distributed into the hydrophobic domain of Nafion) in the membrane and the ratio of the oxygen-binding CoP to the total amount in the membrane. At 25 °C, the p_{50} of CoTPP is calculated as 930 cm Hg, so that the molar amount of oxygen bound to CoP was calculated to be 7.8×10^{-11} mol in atmospheric pressure. According to the calculation, the CoTPP-loaded in the Nafion membrane increased the inside oxygen concentration by 10%. The other 20% increase was likely to be attributed to the enhancement of oxygen diffusivity through the membrane with CoTPP loading. These results supported that the CoP-loaded into Nafion membrane acts as an oxygen binding and hopping sites.

The results on the modified electrode with different CoP species were compared. Both CoTPP and CoFPP indicated the similar value on the slope of Cottrell plots, however, CoFPP/Nafion membrane resulted in the higher permselectivity on gas permeability measurements. As noted above, the slope of Cottrell plots depends on D and C, which are evaluable with oxygen-binding affinity of CoPs. For the higher oxygen permselectivity indicated on the result of gas permeability measurements, D through the CoFPP-loaded Nafion membrane was considered to be higher than that of CoTPP-loaded membrane. In contrast, CoTPP-loaded membrane dissolves more oxygen than CoFPP-loaded one. The extent of C within membranes was evaluated relative to the concentration of active CoPs and the oxygen-binding affinity of CoPs. The concentration of active CoPs is approximately in the same order of magnitude (9.6×10^{-9} mol and 1.2×10^{-8} mol for CoTPP-Nafion and CoFPP-Nafion, respectively), so that C reflected mainly the oxygen-binding affinity of CoPs (9.3×10^{2} cm Hg and 1.3×10^{4} cm Hg for CoTPP and CoFPP at 25 °C, respectively). The compensation of D and C resulted in the similar slope of Cottrell plots. For more effective oxygen enrichment on the electrode, search for the oxygen carrier with higher oxygen-binding affinity which will increase C within the Nafion is one of the subjects of our ongoing research. Highly-fluorinated oxygen carrier will be also effective to enhance D, due to the dense distribution only in the hydrophobic domain of Nafion.

4. Conclusions

The Nafion membrane containing CoP complexes as a fixed oxygen carrier was prepared without irreversible oxidation. In the Nafion membrane, the fluorinated CoFPP complex was located mainly in the hydrophobic domain, due to the affinity to the fluorocarbon backbone of Nafion. The incorporation of CoP in the hydrophobic domain of Nafion successfully suppressed the decrease in the overall proton conductivity of the membrane. The P_{O_2} of the CoP-loaded Nafion membrane was increased with the decrease of the upstream pressure, while the P_{N_2} of the membrane was independent of the pressure. These results indicated that the CoP complex fixed in the Nafion membrane facilitated the oxygen transport through the membrane. On the glassy carbon electrode modified with the Pt/C catalyst and the CoP-loaded Nafion membrane, the oxygen reduction current on the electrode was enhanced due to the increase in the oxygen concentration within the membrane and the oxygen diffusivity. These results also supported that the CoP complex in the Nafion membrane acted as an oxygen enricher on the surface of catalyst at the cathode. In the fuel cell, especially at the end of the gas-flow channel, the partial oxygen pressure decreases due to the oxygen consumption. The membrane reported in this paper will supply oxygen rapidly to the surface of catalyst particularly at the end of gas-flow channel, where the partial oxygen pressure is decreased, results in increase of oxygen consumption efficiency.

Acknowledgements

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[21] The CoP-loaded Nafion membrane was incompatible to the pretreatment process, because all prepared membranes changed in size drastically during the process, and exfoliated from the gold plate for the proton conductivity measurement. To uniform the conditions for the membrane preparation, all measurements were performed using the membrane prepared without the pretreatment process. However, the observed qualitative trends (Fig. 2) sufficed to provide insights into the effect of CoP, based on the control experiments which showed the coincidence of the proton conductivity of the pristine membrane after the pretreatment process with that of the literature data.

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