



Water vapor exchange system using a hydrophilic microporous layer coated gas diffusion layer to enhance performance of polymer electrolyte fuel cells without cathode humidification

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HIGHLIGHTS

- ▶ A water vapor exchange system installed in PEFC was developed to enhance PEFC performance without cathode humidification.
- ▶ The hydrophilic MPL coated GDL at the cathode exchange area is effective to promote water transport from the cathode to anode.
- ▶ The GDL without the MPL at the anode exchange area is effective to enhance PEFC performance.

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ABSTRACT

Polymer electrolyte fuel cells (PEFCs) generally have external humidifiers to supply humidified hydrogen and oxidant gases, which prevents dehydration of the membrane. If a PEFC could be operated without humidification, then external humidifiers could be removed, which would result in a simplified PEFC system with increased total efficiency and reduced cost. A water vapor exchange system installed in the PEFC was developed to enhance the performance without cathode humidification. A gas diffusion layer (GDL) coated with a hydrophobic microporous layer (MPL) was used at the active reaction area. A GDL coated with a hydrophilic MPL consisting of polyvinyl alcohol (PVA) and carbon black was used at the cathode water vapor exchange area to promote water transport from the cathode outlet wet gas to the anode inlet dry gas. This is effective for reducing the IR overpotential, which enhances the PEFC performance. Appropriate enhancement of hydrophilicity by increasing the PVA content in the MPL to 20 mass% is effective to increase water transport from the cathode to anode. At the anode water exchange area, a GDL without the hydrophilic MPL is effective to promote water transport from the water exchange area to the active reaction area, which enhances the PEFC performance.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) with high efficiency and low environmental impact have been developed in recent years. However, further improvements in performance and reliability, as well as a reduction in production cost, are required to ensure that PEFCs constitute a larger proportion of future power generation devices. In order to enhance PEFC performance, an appropriate water balance between the conservation of membrane humidity and the discharge of water produced in the cell is essential. Loss of water content in the membrane decreases ionic conductivity, which increases the internal resistance of the PEFC.

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PEFC systems generally have external humidifiers to supply humidified fuel and oxidant gases, which prevents dehydration of the membrane electrode assembly (MEA). Several humidification methods have been adapted to PEFC systems [1–5]. For a sparge-type humidification method, the reactant gases are humidified by bubbling them through a temperature controlled water bottle. A membrane humidification method has been widely used that consists of a dry gas channel and a humid gas channel separated by a water permeable membrane. The water vapor penetrates through the membrane from the humid gas channel to the dry gas channel due to the humidity gradient across the membrane, which results in humidification of the dry inlet gas [6]. Injecting liquid water directly into a PEFC has also been used for external humidification [7]. For internal humidification, the MEA is directly humidified using porous graphite plates with a cooling water flow and wicks to supply water by capillary action.

Nomenclature

C_a	average water vapor concentration of anode inlet and outlet gas (kg m^{-3})
C_c	average water vapor concentration of cathode inlet and outlet gas (kg m^{-3})
i	current density (A m^{-2})
M	water vapor flow rate (kg s^{-1})
R	total water transport resistance between the anode gas and cathode gas (s m^{-3})
$R_{h,a}$	mass transfer resistance between anode gas and GDL (s m^{-3})
$R_{h,c}$	mass transfer resistance between cathode gas and GDL (s m^{-3})
$R_{\text{GDL},a}$	water diffusion resistance of anode GDL (s m^{-3})
$R_{\text{GDL},c}$	water diffusion resistance of cathode GDL (s m^{-3})
R_{PEM}	water diffusion resistance of membrane (s m^{-3})
U	gas velocity in separator gas channel (m s^{-1})
V_{eff}	output voltage (V)
$W_{\text{in},a}$	water content in anode inlet gas (kg s^{-1})
$W_{\text{in},c}$	water content in cathode inlet gas (kg s^{-1})
$W_{\text{out},a}$	water content in anode outlet gas (kg s^{-1})
$W_{\text{out},c}$	water content in cathode outlet gas (kg s^{-1})
W_{prod}	amount of product water (kg s^{-1})
θ	contact angle (deg)
φ	discharge water ratio from the cathode outlet gas
η_{IR}	IR overpotential (V)

However, these humidification methods require additional equipment, which makes the PEFC system complex, thereby reducing the overall system efficiency. If a PEFC could be operated without humidification, then external humidifiers could be removed, which would result in a very simplified PEFC system with increased total efficiency and reduced cost. One of most important issues to advance the commercial viability of PEFCs is to develop high performance PEFCs that can operate without humidification. A self-humidification method has been developed to remove external humidification requirements. In this method, platinum catalyst particles and water absorbent additives such as silica (SiO_2) and titania (TiO_2) are added to the membrane [8]. Hydrogen and oxygen diffuse into the membrane from the anode and cathode sides and react due to the catalytic effect, generating water and maintaining membrane hydration.

The humidification requirements of the anode and cathode are different. At the anode, humidified hydrogen gas can be introduced using the water generated during the reforming process in fuel production. Furthermore, humidified pure hydrogen gas that is not used for the electrochemical reaction can be recirculated in the PEFC system. It is therefore possible to remove external humidification at the anode. In contrast, at the cathode, air is usually exhausted without recirculation, so that humidified air is generally supplied using an external humidifier. Therefore, it is important to find a method to enhance the PEFC performance without cathode external humidification. The authors have reported that the influence of anode gas recirculation on the PEFC performance without cathode humidification [9,10]. A gas diffusion layer (GDL) coated with a hydrophilic and hydrophobic double microporous layer (MPL) was developed to enhance the PEFC performance without cathode humidification [11]. For the double MPL coated GDL, the hydrophilic layer is effective to conserve humidity at the catalyst layer, while the hydrophobic intermediate layer between the hydrophilic layer and the substrate prevents the removal of water in the hydrophilic layer via dry air in the gas channel.

In the present study, a water vapor exchange system installed in a PEFC was developed to enhance the performance without cathode humidification, while maintaining a very low relative humidity of 20% at the anode. A GDL coated with a hydrophobic MPL, which is effective to prevent dehydration of the MEA, was used at the active reaction area. A GDL coated with a hydrophilic MPL consisting of polyvinyl alcohol (PVA) and carbon black was used at the cathode water vapor exchange area to promote water transport from the cathode outlet wet gas to the anode inlet dry gas. The influence of the PVA content in the hydrophilic MPL coated GDL used for the water exchange area on the PEFC performance was evaluated.

2. Experimental

2.1. PEFC with water vapor exchange system and performance tests

Fig. 1 shows a schematic diagram of the water vapor exchange system installed in a PEFC. The separator has a triple serpentine flow channel configuration. Anode and cathode gases were supplied in a counter-flow orientation. The GDL coated with a hydrophilic MPL consisting of polyvinyl alcohol (PVA) and carbon black was used at the water vapor exchange area to promote water transport from the cathode outlet wet gas to the anode inlet dry gas. The active reaction area of the MEA (PRIMEA® 5580) was 4.2 cm^2 , while the water vapor exchange area was 1.2 cm^2 . A polymer electrolyte membrane (PEM) without a catalyst layer was used at the water vapor exchange area. Both the MEA and PEM were sandwiched between the anode and cathode GDLs and separators, which were assembled using clamp screws. The catalyst layer was not spread on the PEM at the water vapor exchange area,

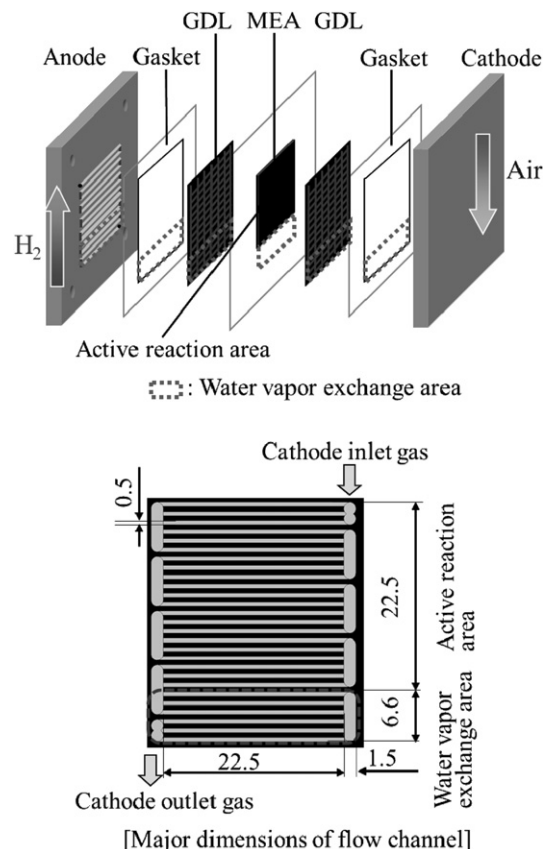


Fig. 1. Schematic diagram of water vapor exchange system installed in a PEFC.

so that there was a gap of approximately 10 μm between the PEM and GDL. In the assembled PEFC, the 240 μm thick porous GDL could easily be deformed due to the clamp loading. This deformation of the GDL was sufficiently large to cover the gap between the PEM and GDL, preventing gas leaks at the water vapor exchange area.

PEFC performance tests with the water vapor exchange area were conducted at a cell temperature of 75 °C. PEFC performance tests without the water vapor exchange area were also conducted using the same PEFC in which the water vapor exchange area was sealed with gasket sheets to prevent gas leaks. The flow rates of the supplied gases were controlled using mass flow controllers. The utilization of hydrogen and air at the anode and cathode, respectively, was set at 60%. The relative humidity (RH) of the cathode inlet gas was set at 0%, while maintaining a very low RH of 20% at the anode inlet. The back pressure of the supplied gases was set to zero. In the polarization curves of the PEFC with and without the water vapor exchange area, the current density was defined as the current divided by the active area (4.2 cm²) of the MEA. The IR overpotential (η_{IR}), or ohmic loss, was measured using the current-interruption method [12]. The water contents in the anode and cathode outlet gases were measured using RH sensors, as shown in Fig. 2.

2.2. Gas diffusion layers

Fig. 3 shows the GDLs used at the active reaction area and the water vapor exchange area. The anode GDL used at the active reaction area was a commercial carbon paper (SGL SIGRACET® 24BA) without the MPL, which was treated by 5 mass% polytetrafluoroethylene (PTFE) loading to impart hydrophobicity [13]. The 24BA GDL had a thickness of 190 μm, an areal weight of 54 g m⁻², 84% porosity and a mean flow pore diameter [14] of 42 μm. The cathode GDL used at the active reaction area was a 24BA GDL coated with a hydrophobic MPL consisting of 20 mass% PTFE and 80 mass% carbon black [14]. The GDLs used at the water vapor exchange area were a 24BA GDL, a hydrophobic MPL coated GDL and a hydrophilic MPL coated GDL. The hydrophilic MPL consisting of PVA and carbon black was coated on the 24BA GDL [11], with the PVA content varying between 5 and 40 mass%.

Fig. 4 shows the contact angles [14] obtained with the hydrophobic MPL and hydrophilic MPL coated GDLs. When the PVA content in the hydrophilic MPL was increased from 5 to 40 mass%, the contact angle was reduced from 49° to 35°, which represents an increase in the hydrophilic properties of the MPL.

Fig. 5 shows scanning electron microscopy (SEM) micrographs of the surface and cross-section of the 24BA and the hydrophilic

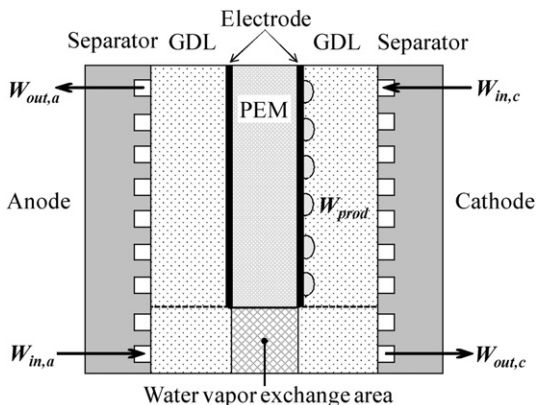


Fig. 2. Water vapor amount measurements in the inlet and outlet gases at the anode and cathode.

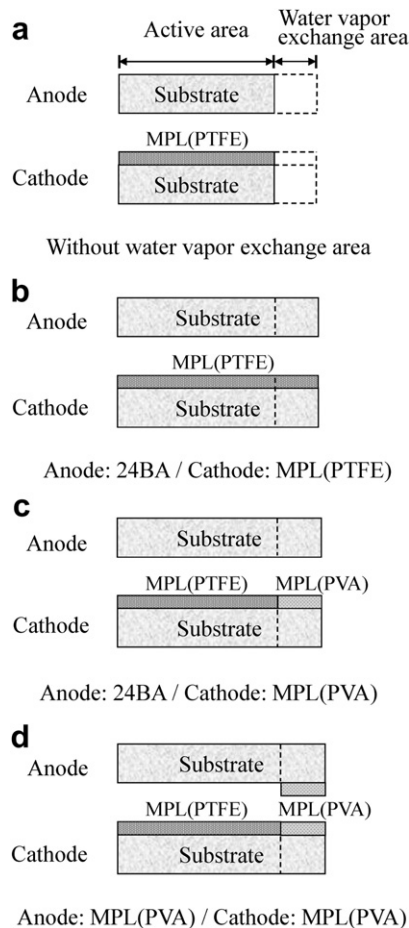


Fig. 3. GDLs used at the active reaction area and water vapor exchange area.

MPL (PVA 20 mass%) coated GDLs. For both the hydrophobic and hydrophilic MPLs, the mean flow pore diameter was set at 5 μm. The cross-sectional view of the MPL coated GDL shows that the MPL is not simply coated on the substrate surface, but penetrates into the porous substrate. The average MPL thickness considering the penetration into the substrate [14] for both the hydrophobic and hydrophilic MPLs was set at 90 μm. The total thickness of all hydrophobic and hydrophilic MPL coated GDLs was set at 240 μm.

3. Results and discussion

3.1. Influence of water vapor exchange area on PEFC performance

Fig. 6 shows the influence of the water vapor exchange area on the PEFC performance without cathode humidification. The 24BA

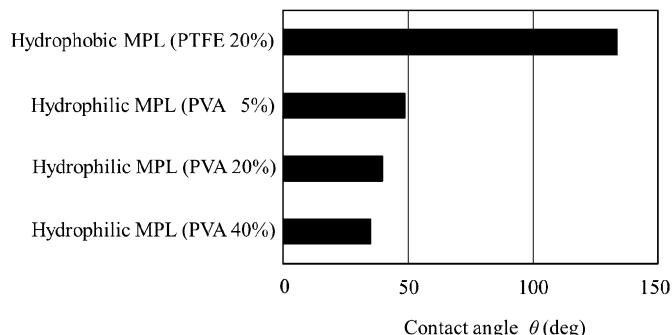


Fig. 4. Contact angles of hydrophobic and hydrophilic MPLs.

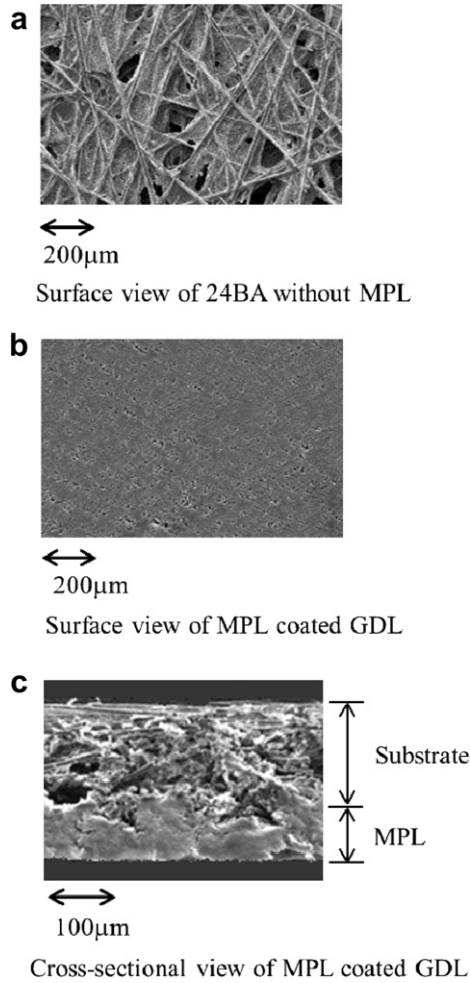


Fig. 5. Surface and cross-sectional SEM images of the 24BA and hydrophilic MPL coated GDLs.

GDL without the MPL was used at the anode water exchange area. Either the hydrophobic MPL (PTFE 20 mass%) or the hydrophilic MPL (PVA 20 mass%) coated GDLs were used at the cathode water exchange area. The IR overpotential obtained with the hydrophilic MPL coated GDL employed at the water exchange area was lower than that without the water exchange area, which indicates that the water exchange area is a factor influencing the PEFC performance without cathode humidification. However, no significant enhancement of the PEFC performance was obtained when using the hydrophobic MPL coated GDL at the cathode water exchange area, which indicates that the PEFC performance is dependent on the hydrophilic and hydrophobic properties of the GDL used at the cathode water exchange area.

Fig. 7 shows the relative humidity (RH) of the anode and cathode outlet gases measured at a constant current density of 0.8 A cm^{-2} . Even when the RH of the cathode inlet gas is 0%, water is transported into the MEA from the humidified hydrogen gas by electroosmotic drag, also in addition to production by the electrochemical reaction at the cathode catalyst layer. The RH of the cathode outlet gas increases to about 60%, which is affected by the hydrophilic and hydrophobic properties of the GDL used at the water exchange area.

In order to evaluate the degree of water recovery in the cathode outlet gas, the ratio of water content discharged from the cathode $W_{\text{out,c}}$ to the water introduced inside the PEFC, which is the sum of the water content in the anode inlet gas $W_{\text{in,a}}$ and the product water W_{prod} , was calculated using Eq. (1):

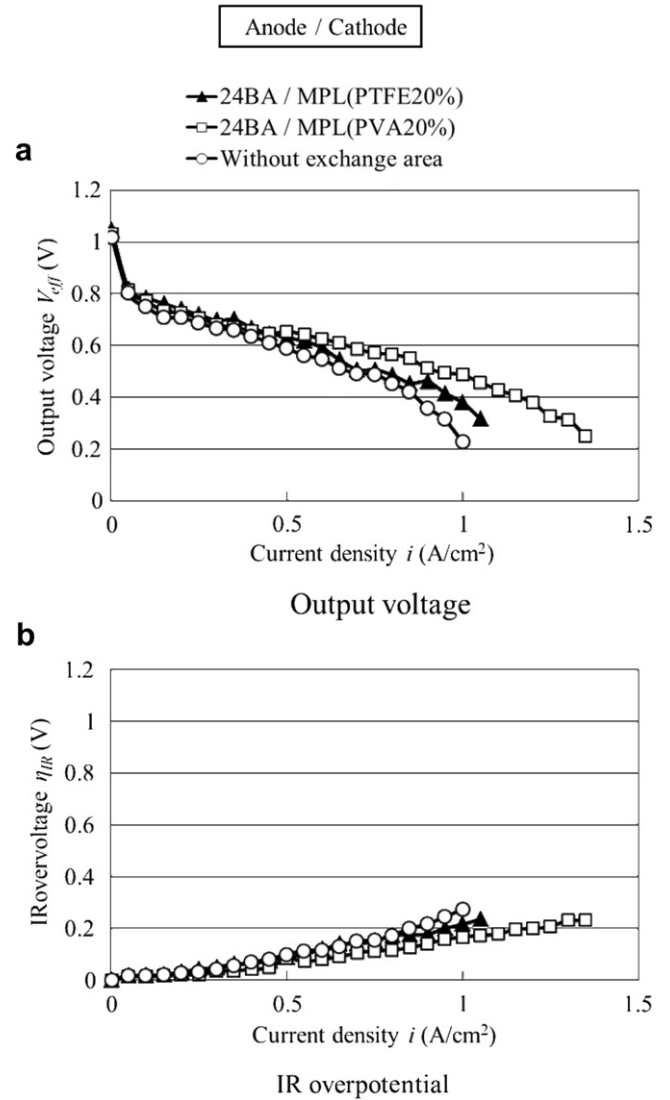


Fig. 6. Influence of water vapor exchange area on PEFC performance.

$$\varphi = \frac{W_{\text{out,c}}}{W_{\text{in,a}} + W_{\text{prod}}} \quad (1)$$

Fig. 8 shows the influence of the types of the water vapor exchange area on the discharge water ratio from the cathode outlet gas. The discharge water ratio was 94% when the water vapor exchange area was not used, and was reduced to 88% when the water exchange area with the hydrophilic MPL coated GDL was used at the cathode. However, the decrease in the discharge water ratio was not significant when the water exchange area with the hydrophobic MPL coated GDL was used, compared to that with the hydrophilic MPL coated GDL. This result indicates that the water vapor exchange area with the hydrophilic MPL coated GDL used at the cathode is effective to enhance the water absorption, increasing the recovery of water contained in the cathode outlet gas. As result, the humidity gradient through the PEM at the water vapor exchange area is increased, which promotes water transport from the cathode to the anode inlet dry gas. This is effective for the prevention of membrane dehydration, which reduces the IR overpotential and thereby enhances the PEFC performance, as shown in Fig. 6. However, in the case of the water vapor exchange area with the hydrophobic MPL coated GDL, the recovery of water in the

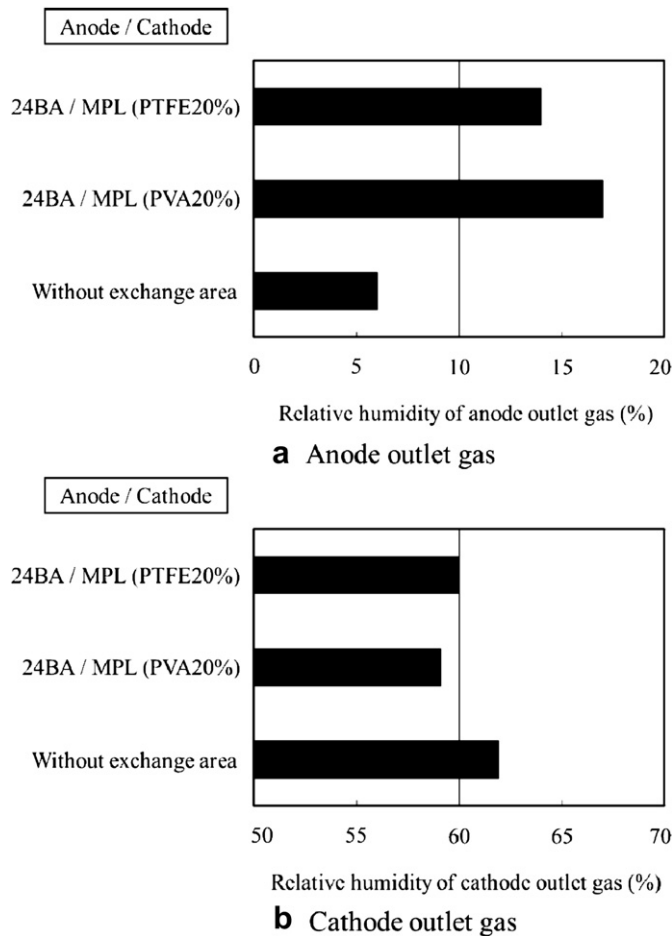


Fig. 7. Relative humidity measured at the anode and cathode outlet gases.

cathode outlet gas cannot be enhanced, compared to that with the hydrophilic MPL coated GDL. As a result, dehydration of the membrane cannot be avoided, which lowers the PEFC performance.

3.2. Influence of the hydrophilic MPL coated GDL used at both the anode and cathode water vapor exchange areas on PEFC performance

Fig. 9 shows the influence of the hydrophilic MPL coated GDL used at both the anode and cathode water vapor exchange areas on

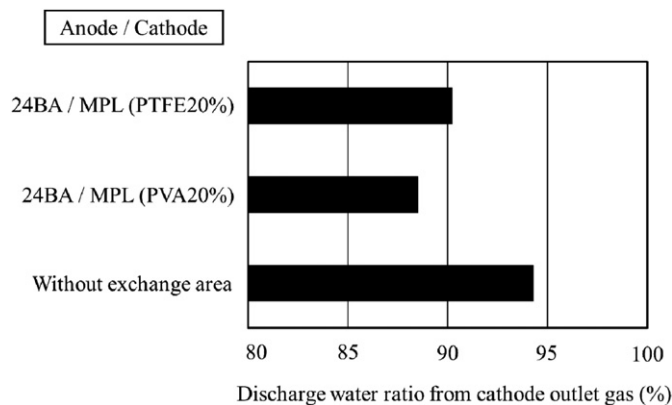


Fig. 8. Influence of water vapor exchange area on discharge water ratio from cathode outlet gas.

the PEFC performance without cathode humidification. The IR overpotential obtained with the hydrophilic MPL coated GDL used at both the anode and cathode water exchange areas was higher than that obtained with the hydrophilic layer used only at the cathode water exchange area. At the anode water exchange area, the GDL without the hydrophilic MPL was effective for enhancing the PEFC performance.

The test results shown in Figs. 6 and 9 indicate that the GDLs used at the anode and cathode water exchange areas significantly influence the water transport from the cathode to the anode. To evaluate the water transport properties in the water vapor exchange area, the water vapor diffusion resistance [15,16] was measured using the same PEFC, in which all active reaction areas except the water vapor exchange area were sealed by gasket sheets.

Fig. 10 shows a schematic model of the water transport in the water exchange area. The cell temperature was set at 75 °C. The RH of the hydrogen supplied at the anode inlet was set at 20% and that of the air supplied at the cathode inlet was set at 60%, which is similar to the RH of the cathode outlet gas during actual PEFC operation, as shown in Fig. 7(b). Under steady-state conditions, the amount of water vapor M , transported due to the concentration gradient between the cathode and anode gas can be described as:

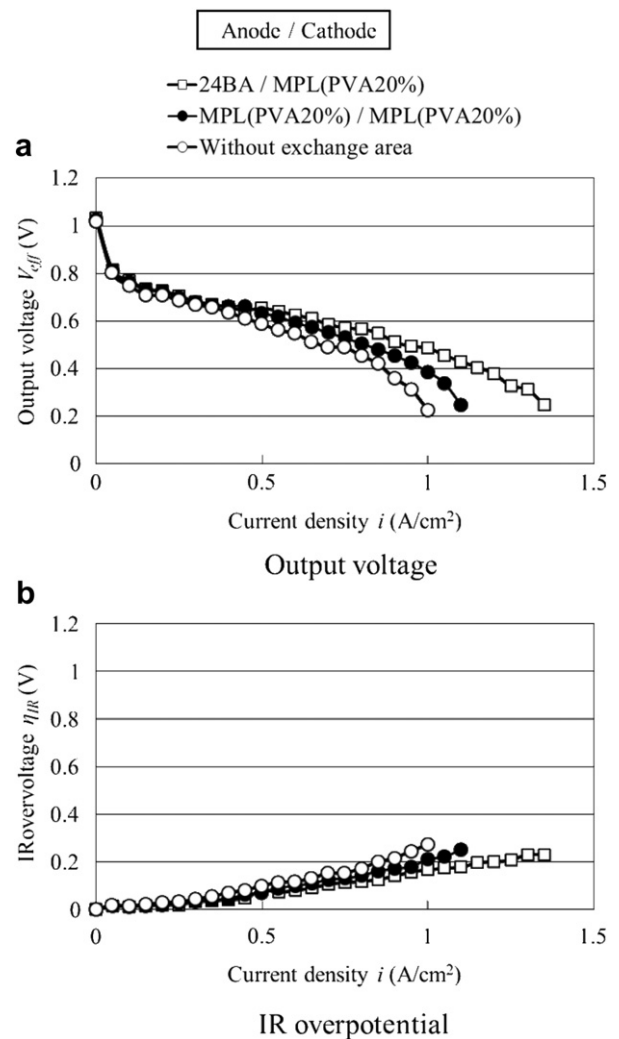


Fig. 9. Influence of hydrophilic MPL coated GDL used at the anode and cathode water exchange areas on PEFC performance.

$$M = \frac{C_c - C_a}{R} \tag{2}$$

where C_a and C_c are the averaged water vapor concentrations of the inlet and outlet gases at the anode and cathode, respectively. The total water transport resistance R is expressed by:

$$R = R_{h,a} + R_{GDL,a} + R_{PEM} + R_{GDL,c} + R_{h,c} \tag{3}$$

where $R_{h,a}$ and $R_{h,c}$ are the mass transfer resistances at the interface between the GDLs and the gas in the anode and cathode separator channels, respectively. R_{PEM} , $R_{GDL,a}$ and $R_{GDL,c}$ are the diffusion resistances of PEM, the anode and cathode GDLs, respectively. M from the cathode gas to the anode gas in the water vapor exchange area was obtained using the measured values of RH of the inlet and outlet gases at the cathode and anode. Therefore, R could be calculated from the values of C_a , C_c and M .

Fig. 11 shows the typical variation in the total water transport resistance R with an increase in the supplied gas velocity U in the water vapor exchange area when using the 24BA GDL at the anode and the hydrophilic MPL (PVA 20 mass%) coated GDL at the cathode. The gas velocity was defined as the flow rate divided by the cross-sectional area of the separator gas channel. Under low velocity conditions, R is relatively high, because $R_{h,a}$ and $R_{h,c}$ at the interface between the GDL and the gas in the separator channel are high. $R_{h,a}$ and $R_{h,c}$ decrease significantly as U increases. The diffusion resistances of both the GDL and the PEM (R_{GDL} and R_{PEM}) are almost the same, even when U increases. When U increases to more than 4 m s^{-1} , R becomes almost constant, because $R_{h,a}$ and $R_{h,c}$ become negligible. This representative water transport resistance, obtained at a gas velocity of 4 m s^{-1} , is considered to be the water transport resistance between the cathode and anode GDLs through the PEM in the water vapor exchange area.

Fig. 12 shows the influence of the GDL used for the water vapor exchange area on the water transport resistance measured at a gas velocity of 4 m s^{-1} . The 24BA GDL and the hydrophilic MPL (PVA 20 mass%) coated GDL were used at the anode. The hydrophobic MPL (PTFE 20 mass%) and the hydrophilic MPL (PVA 20 mass%) coated GDLs were used at the cathode. The water transport resistance varies significantly depending on the GDLs used at the anode and cathode, and is relatively low when using the hydrophilic MPL coated GDL at the cathode and the 24BA GDL without the MPL at the anode. However, when the hydrophilic MPL coated GDL was used at both the anode and cathode, because the ability of the hydrophilic MPL at the anode to retain water is enhanced significantly, the water transport resistance from the cathode to the anode is increased.

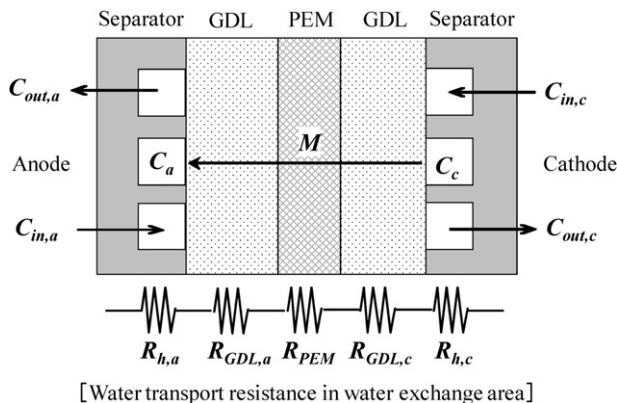


Fig. 10. Schematic model of water transport from cathode to anode in the water vapor exchange area.

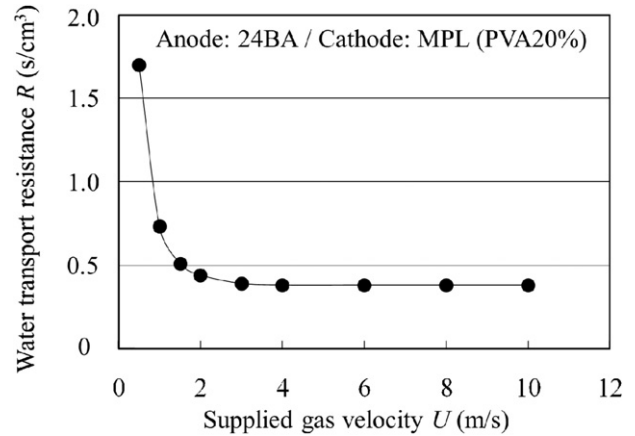


Fig. 11. Typical variation in water transport resistance with gas velocity in the water vapor exchange area.

These results demonstrate that the water transport from the cathode outlet wet gas to the anode inlet dry gas is increased by using the hydrophilic MPL coated GDL at the cathode water exchange area. At the anode water exchange area, the GDL without the hydrophilic MPL is effective to promote water transfer from the anode water exchange area to the active reaction area, thereby enhancing PEFC performance.

3.3. Influence of PVA content in the hydrophilic MPL coated GDL used at the cathode water vapor exchange area on PEFC performance

Fig. 13 shows the influence of the PVA content in the hydrophilic MPL coated GDL used at the cathode water exchange area on the PEFC performance without cathode humidification. The 24BA GDL without the MPL, which results in excellent performance as shown in Fig. 9, was used at the anode water exchange area. The PEFC performance varies depending on the PVA content in the hydrophilic MPL. When the PVA content is increased from 5 to 20 mass%, the IR overpotential is reduced, thereby enhancing the PEFC performance. However, when the PVA content is too high, such as at 40 mass%, the PEFC performance tends to decrease.

Fig. 14 shows the influence of the PVA content in the hydrophilic MPL coated GDL on the water transport resistance measured at a gas velocity of 4 m s^{-1} . When the PVA content is increased from 5 to 20 mass%, the water transport resistance is reduced. Appropriate

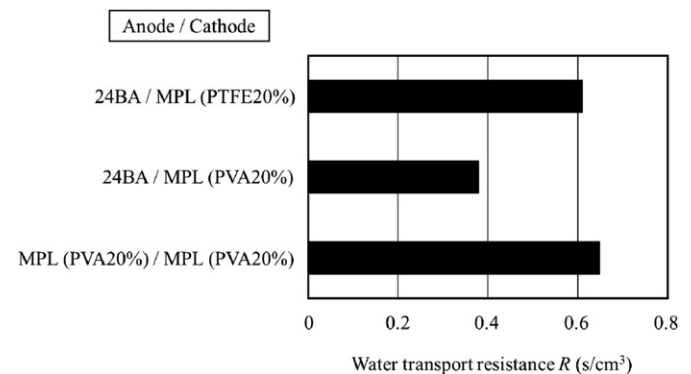


Fig. 12. Influence of anode and cathode GDLs used at the water vapor exchange area on water transport resistance.

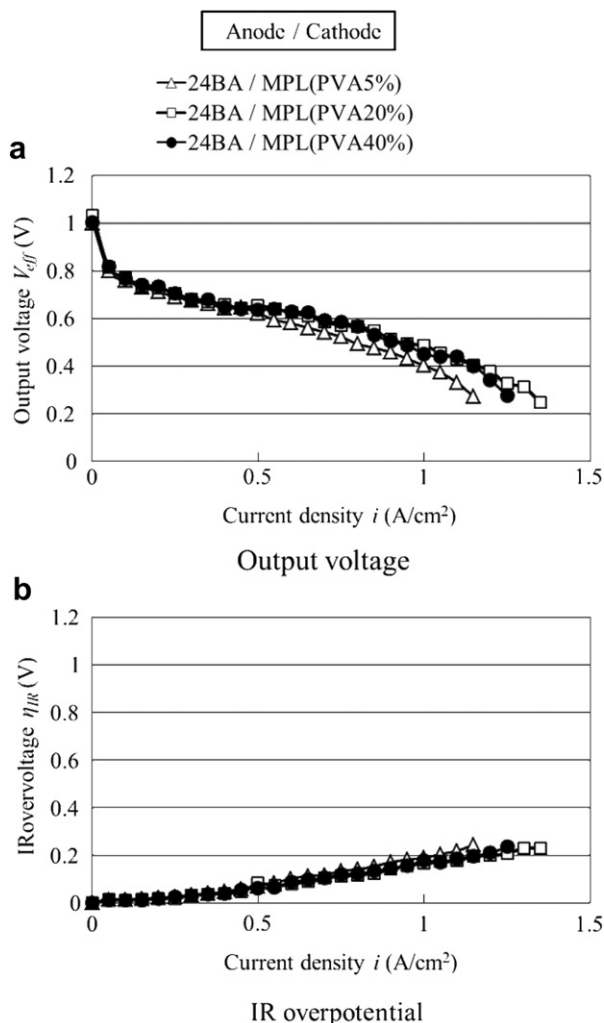


Fig. 13. Influence of PVA content in hydrophilic MPL coated GDL used at the cathode water vapor exchange area on PEFC performance.

enhancement of the hydrophilicity by increase of the PVA content in the hydrophilic MPL to 20 mass% is effective to promote water transport from the cathode to the anode. This effectively reduces the IR overpotential, and thereby enhances the PEFC performance,

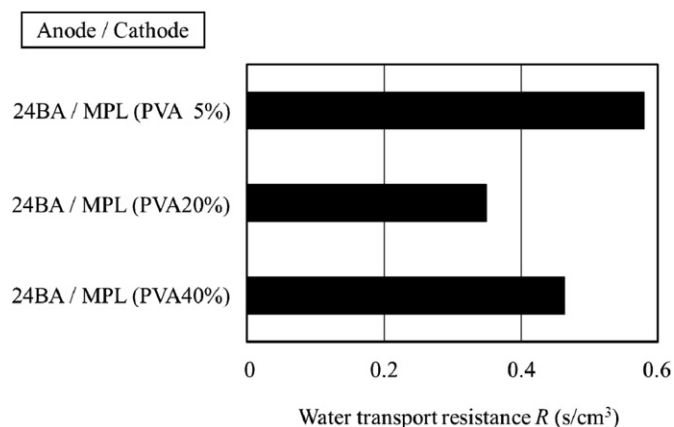


Fig. 14. Influence of PVA content in hydrophilic MPL coated GDL used at the cathode water vapor exchange area on water transport resistance.

as shown in Fig. 13. However, when the PVA content is too high (40 mass%), the water transport resistance from the cathode to anode tends to increase, because the ability of the hydrophilic MPL at the cathode to retain water is enhanced. This increases the IR overpotential, thereby lowering the PEFC performance.

4. Conclusions

A water vapor exchange system installed in the PEFC was developed to enhance performance without cathode humidification, while maintaining a very low humidity at the anode. The influence of the GDLs used at the anode and cathode water exchange areas on the PEFC performance was investigated and the following conclusions were obtained.

- (1) At the cathode water exchange area, appropriate enhancement of the hydrophilicity by increasing the PVA content in the hydrophilic MPL coated GDL to 20 mass% is effective to increase water transport from the cathode outlet wet gas to the anode inlet dry gas, which prevents membrane dehydration. This reduces the IR overpotential, and thereby enhances the PEFC performance. However, when the PVA content is too high, the PEFC performance tends to decrease, because the water transport resistance from the cathode to anode is increased.
- (2) At the anode water exchange area, the hydrophilic MPL coated GDL increases the ability to retain the water at the anode MPL, which increases the water transport resistance from the cathode to anode. The GDL without the hydrophilic MPL is effective to promote water transfer from the anode water exchange area to the active reaction area, thereby enhancing the PEFC performance.

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