

Mass balance research for high electrochemical performance direct methanol fuel cells with reduced methanol crossover at various operating conditions

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Abstract

Mass balance research in direct methanol fuel cells (DMFCs) provides a more practical method in characterizing the mass transport phenomena in a membrane electrode assembly (MEA). This method can be used to measure methanol utilization efficiency, water transport coefficient (WTC), and methanol to electricity conversion rate of a MEA in DMFCs. First, the vital design parameters of a MEA are recognized for achieving high methanol utilization efficiency with increased power density. In particular, the structural adjustment of anode diffusion layer by adding microporous layer (MPL) is a very effective way to decrease WTC with reduced methanol crossover due to the mass transfer limitation in the anode. On the other hand, the cathode MPL in the MEA design can contribute in decreasing methanol crossover. The change of structure of cathode diffusion layer is also found to be a very effective way in improving power density. In contrast, the WTC of DMFC MEAs remains virtually constant in the range of 3.4 and 3.6 irrespective of the change of the cathode GDL. The influence of operating condition on the methanol utilization efficiency, WTC, and methanol to electricity conversion rate is also presented and it is found that these mass balance properties are strongly affected by temperature, current density, methanol concentration, and the stoichiometry of fuel and air.

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1. Introduction

The development of a polymeric proton-conducting membrane has opened new opportunities for alternative portable energy sources with great market potential [1,2]. The world's leading consumer electronics manufactures such as Sony, Toshiba, and Samsung are investing a good sum of resources for commercialization of portable fuel cell systems in the near future through research and development work on the direct methanol fuel cells (DMFCs) [2–4]. DMFCs, where the fuel methanol (CH₃OH) is fed directly to the cell, generate electrical power without any complex reforming process [5]. This gives

DMFC devices the advantage of smaller system volume and weight compared to other FC systems. DMFCs can also avoid complex thermal management problems including humidification which is an issue in polymer electrolyte membrane fuel cells (PEMFCs) since a dilute methanol/water mixtures is used [6].

In order to be economically viable the next-generation power sources for portable electronic devices need to be relatively cheap and while generating high energy densities. Methanol, theoretically, has a superior energy density (4.8 kWh cm⁻³), safe in term of handling, and can be cost-effectively sourced [7]. These characteristics mean longer operation times for portable electronic devices such as mobiles and laptops as well as quick and easy fuel cartridge replacement. However, the development of such FC systems is being impeded by a number of efficiency and performance challenges including slow methanol electro-oxidation kinetics, lack of high activity electrocatalysts

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for oxygen reduction, and methanol crossover across electrolyte membranes [8,9]. Furthermore, the concentrated effort in dealing with these challenges has meant that balance-of-plant (BOP) components such as fuel supply devices, air pumps, heat exchangers, and power control circuits are often overlooked. Therefore the developments of lightweight and efficient auxiliary equipments are critical to the creation of portable, reliable and compact FC systems.

Among development issues in fuel loss methanol crossover through the membrane is still a major challenge [10–13]. This results in reduced FC system efficiency because the crossovered methanol is converted into carbon dioxide at the cathode. Moreover, the formation of a mixed potential at the cathode causes additional losses [12]. Methanol crossover mainly results from both chemical diffusion and molecular transport caused by methanol permeability and electro-osmotic drag, respectively [13]. Additionally, unless a high stoichiometry of cathode air is supplied, flooding can occur on the cathode side due to water produced by the oxygen reduction, methanol oxidation reaction, and electro-osmotically dragged water molecules [14]. However, a high airflow rate makes it hard to design a small fuel cell system requiring a large capacity air pump with inevitable parasitic power loss. Furthermore, the air pump requirement will generate unwanted noise making the product less desirable to consumers. Finally, the operational stability of the FC system becomes considerably complex due to the necessity for a big capacity recycler and heat exchanger with a complicated control unit [15]. Therefore, better understanding of mass transport phenomena such as methanol crossover and water transport is crucial in developing a simple and cheap DMFC system with high energy density for market-driven products [16–20].

In this work, we present a practical way of characterizing the mass transport phenomena of membrane electrode assemblies (MEAs) through mass balance research in DMFC systems. The research on DMFC MEA design was performed with an aim to reduce methanol and water crossover maintaining high power characteristics. By varying material properties, the critical design parameters were identified for high methanol utilization improving power density through systematical experiments. Additionally, parametric investigations were performed to reveal the effects of operating conditions of FC systems such as methanol concentration, fuel/air stoichiometry, operating current, and cell temperature.

2. Experimental methods and materials

2.1. MEA preparation and electrochemical evaluation

The MEAs were prepared by several kinds of membrane products: Nafion-112, 1135, 115, and 117 (Dupont). The catalysts used were Pt/Ru black (HiSpec 6000, Johnson Matthey) and Pt black (HiSpec 1000, Johnson Matthey) for anode and cathode, respectively. The catalyst loading for the anode and cathode was 6 mg cm^{-2} and 6 mg cm^{-2} , respectively. The active area of MEAs was 25 cm^2 .

To see the effects of DMFC MEAs membrane thickness on the mass balance properties, the commercial carbon papers

34BA (SGL, Germany) and 25BC (SGL, Germany) were used as an anode and cathode gas diffusion layer (GDL), respectively. The GDL “BA” and “BC” in SGL means a 5 wt.% PTFE-treated hydrophobized substrate and 5 wt.% PTFE-treated hydrophobized substrate with microporous layer (MPL) on one side, respectively [21]. The experiments were conducted at a current density of 160 mA cm^{-2} and cell temperature of 70°C with 1 M methanol solution. The methanol and airflow rate were a stoichiometry of 3.

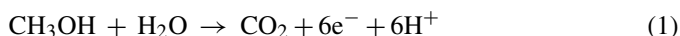
In investigating the operating condition influences on DMFCs, the mass balance properties of MEAs were investigated at various operating condition of current density (100, 160, 210 mA cm^{-2}), temperature (50, 70°C), methanol concentration (0.5, 1, 1.5 M), and fuel/air stoichiometry ((2, 2.5, 3, 3.5)/3 and 3/(2, 2.5, 3, 3.5)).

By combining different anode and cathode structures, eight types of MEAs with Nafion-1135 membrane were prepared and investigated to see the effect of the GDL on the mass balance properties. The commercial SGL carbon papers 25DA, 25BC, 35BA, and 25BC for the anode with 25BC for the cathode were used as backing layers. The GDL “DA” in SGL means a 20 wt.% PTFE-treated hydrophobized substrate [21]. For the study of the cathode GDLs, 21DA, 25BC, 21DC, and 24DC for the cathode with 35BA for the anode were used. The experiments were conducted at a current density of 160 mA cm^{-2} and cell temperature of 70°C .

All the electrochemical performances of the DMFCs were measured using the Fuel Cell Technologies, Inc. (USA) test station. The design of bipolar plates for the anode was the triple serpentine-type flow-field. All structures were 1 mm wide and 2 mm deep.

2.2. Mass balance measurement

From the mass change of the anode feed and anode effluent with the measured methanol concentration, water and methanol masses were calculated for a given time. Methanol utilization efficiency, η_f , is defined here as a percentage of the methanol flux consumed by oxidation reaction (Eq. (1)) in the anode over the total used methanol amount as suggested by Kang et al. [16].



$$\eta_f = \frac{f_{\text{current}}}{f_{\text{current}} + f_{\text{crossover}}} \times 100 \quad (2)$$

where f_{current} and $f_{\text{crossover}}$ is the amount of fuel used in current generation and the amount of fuel consumed by methanol crossover and other reactions, respectively.

The net water crossover flux, $N_{\text{H}_2\text{O}}$, is the combined outcome of the crossovered water by electro-osmotic drag and diffusion through the membrane, and permeation from hydraulic pressure gradient [19,20]. The water transport coefficient (WTC) can thus be measured as

$$\text{WTC} = \frac{N_{\text{H}_2\text{O}}}{N_{\text{H}^+}} = N_{\text{H}_2\text{O}} \frac{FA}{i} \quad (3)$$

where N_{H^+} , i , A , and F is the proton flux, current density, electrode area, and Faraday constant.

The energy efficiency, η_e , is defined as

$$\eta_e \text{ (kWh cm}^{-3}\text{)} = 4.8 \times C_{\text{fuel}} \times \eta_{\text{fuel}} \times V_{\text{fuel}} \times \eta_{\text{cell}} \quad (4)$$

where 4.8 is the theoretical energy density of the fuel (methanol), C_{fuel} is the fuel volumetric concentration, η_{fuel} is the fuel efficiency, V_{fuel} is the fuel volume, and η_{cell} is the cell voltaic efficiency. Thus, the fuel-to-electricity conversion ratio (FECR) can then be calculated as a percentage of the measured energy efficiency over the theoretical energy efficiency of methanol. Details on equipment fabrication and measurements were adopted from our previous work [16].

3. Results and discussion

3.1. Influence of membrane thickness

Mass balance properties of DMFC MEAs can be considerably varied by membrane thickness since the methanol/water diffusion across the membrane depends on an activity gradient, an electro-osmotic drag of proton, and a hydraulic pressure difference between the anode and the cathode [13,17,19,20]. Fig. 1 shows the methanol utilization efficiency and the FECR as a function of membrane thickness using Nafion-112, 1135, 115, and 117. The thickness of Nafion-112, 1135, 115, and 117 was 51, 89, 127, and 183 μm , respectively. As expected, the methanol utilization efficiency of the MEA in DMFCs was linearly increased from 57.6% to 63.7% with increasing membrane thickness. This could be due to the reduction of methanol crossover with increasing mass transfer resistance in the membrane as reported by Liu et al. [17,20]. The fuel-to-electricity conversion ratio (FECR) of DMFCs also showed similar trends

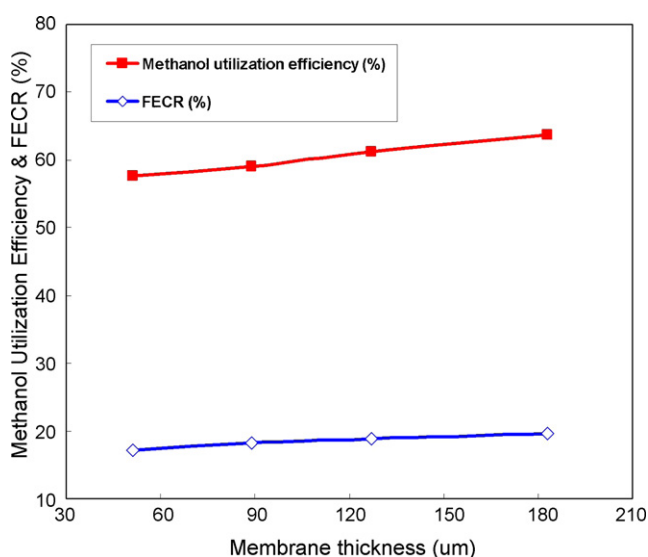


Fig. 1. The methanol utilization efficiency and the FECR as a function of membrane thickness using different membrane products of Nafion-112, 1135, 115, and 117 (test condition: 160 mA cm⁻², 70 °C, 1 M methanol, and a stoichiometry of 3 for fuel/air).

Table 1

The relative proportion of three electrochemical phenomena for cathode water balance at 160 mA cm⁻², 70 °C, 1 M methanol, and a stoichiometry of 3 for fuel/air

	NF 112	NF 1135	NF 115	NF 117	Average
ORR (%)	12.0	12.0	11.9	11.8	11.9
MOR (%)	4.8	4.5	3.5	2.4	3.8
Water crossover (%)	83.3	83.5	84.5	85.8	84.3

to that of the methanol utilization efficiency, which increased with increasing membrane thickness.

The methanol utilization efficiency of the DMFC was increased by around 7.2% with increasing membrane thickness from 51 to 183 μm , while the FECR was moderately increased by 2.5%. An increase of membrane thickness might lead to the decrease in cell performance due to increased cell resistance, in spite of decreasing methanol crossover. In Eq. (4), the FECR in DMFCs is a function of both power density and the amount of used fuel, which strongly depends on the methanol utilization efficiency. As a consequence, the increase in membrane thickness resulted in a small increase in the FECR after a trade-off between decreased cell performance and increased methanol utilization efficiency.

For the cathode water balance, three water-producing electrochemical phenomena are mainly considered. The first is the oxygen reduction reaction (ORR), the second is the methanol oxidation reaction (MOR) from combustion of crossoverd methanol, and the third is the water transport by electro-osmotic drag (EOD) of protons [19,20,22,23]. It is interesting to note that most of water produced at the cathode (on average of 84.3% in the tested membranes) was generated from crossoverd water through the membrane, as shown in Table 1 and Fig. 2. The average proportion of the water produced by ORR and MOR in DMFCs were 11.9% and 3.8%, respectively. Therefore, minimizing water crossover through the membrane is all-important for the system simplification required in portable DMFCs in respect to avoiding cathode flooding. Further, the increase of membrane thickness resulted in somewhat increasing percent of water crossover and decreasing percent of ORR and MOR,

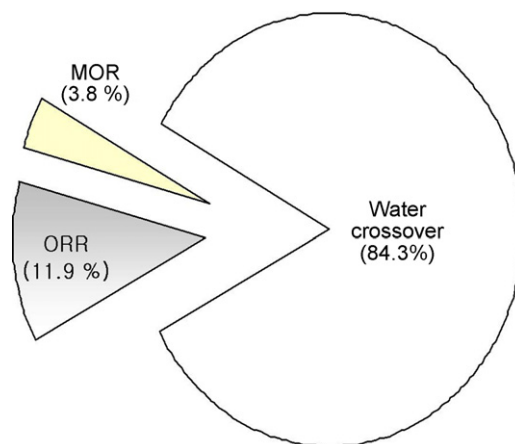


Fig. 2. The average relative proportion of three electrochemical phenomena at a current density of 160 mA cm⁻² and cell temperature of 70 °C.

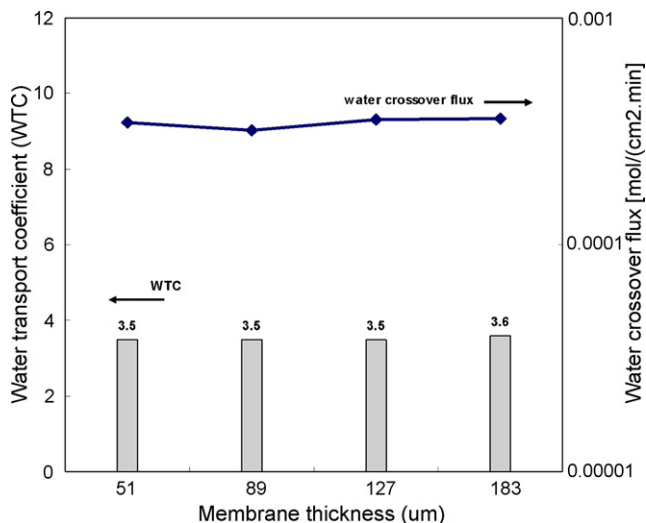


Fig. 3. The water crossover flux and the WTC at 160 mA cm^{-2} and 70°C as a function of membrane thickness.

as shown in Table 1. Fig. 3, however, shows membrane thickness had negligible effect on the water transport coefficient (WTC) in the tested MEA configuration. The average WTC at 160 mA cm^{-2} and 70°C was about 3.5 and nearly insensitive to the membrane thickness.

An ultimate goal in water management of DMFCs is to achieve the lowest WTC value since less water crossover leads to less flooding of catalyst, thus resulting in improved performance and durability. Although not investigated here, the use of hydrocarbon membrane in the MEA design parameter may be one possible solution for decreasing water transport as well as methanol crossover through the membrane. The introduction of MPLs for both electrodes may also enhance methanol utilization and decrease water crossover. This is because of the increased mass transfer resistance at the anode and the hydraulic pressure to promote the water back-flow on the cathode side, respectively [17,19,22]. We expand on this topic in Section 3.4.

3.2. Influence of current density and temperature

Fig. 4 shows the effects of current density on the mass balance properties of the DMFC MEAs. The methanol utilization efficiency of each different membrane thickness of MEAs increased more than 11% with increasing current density from 100 to 210 mA cm^{-2} . This was due to the decreased methanol crossover rate of DMFCs at high current densities. However, the FECR of DMFCs increased by approximately 2% with increasing current density owing to the reduced cell voltaic efficiency, η_{cell} in Eq. (4). The water flux to the cathode increased with increasing current density, as shown in Fig. 5. However, the WTC remained essentially constant in the range of 3.4 and 3.6 regardless of change in current density. This implies that the electro-osmotic drag is the major mechanism of water crossover at given operation conditions.

The effects of temperature on methanol utilization efficiency and FECR at current density of 160 mA cm^{-2} were also investigated (Fig. 6). The methanol utilization efficiency increased with decreasing temperature, which is due to the reduced methanol diffusivity at lower temperature. The methanol utilization efficiency of a MEA prepared by Nafion-117 membrane at 210 mA cm^{-2} current density was improved by 11.2% from 70% at 70°C to 81.2% at 50°C . However, the FECR of DMFCs was increased to only 0.5% with decreasing operating temperature. This may be attributed to significantly reduced cell performance at lower temperature. Thus, further work is required in order to enhance the power density of MEAs at lower temperature.

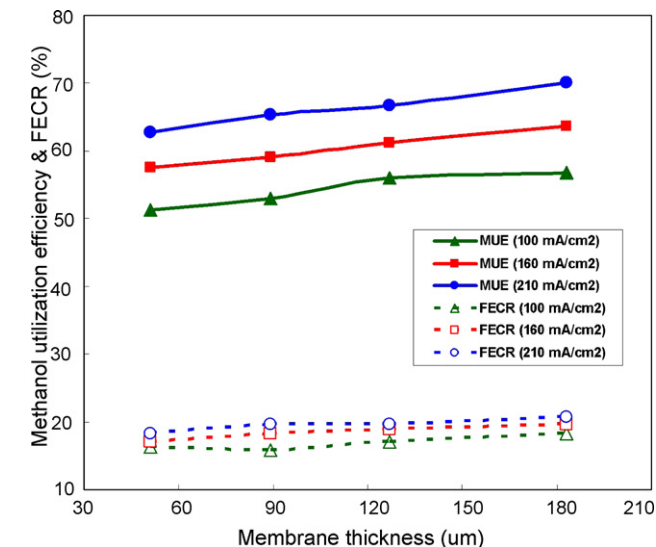


Fig. 4. The effect of current density on the methanol utilization efficiency (MUE) and the FECR of the DMFC MEAs.

Fig. 7 displays the WTC and water/methanol transport flux measured at different temperatures. High temperature resulted in increased water and methanol crossover flux. Furthermore, the WTC was increased from 2.9 at 50°C to 3.5 at 70°C at current density of 210 mA cm^{-2} . This could be attributed to promoted water removal rate in the cathode backing through the considerably increased water vapor saturation pressure at

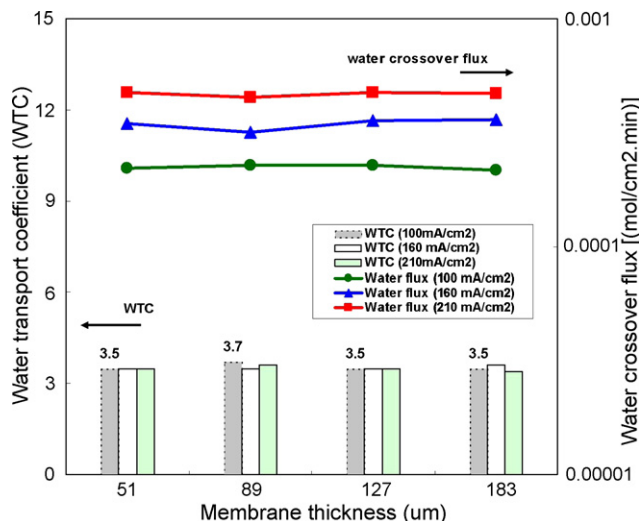


Fig. 5. The effect of current density on the WTC and the water crossover flux to the cathode at 70°C .

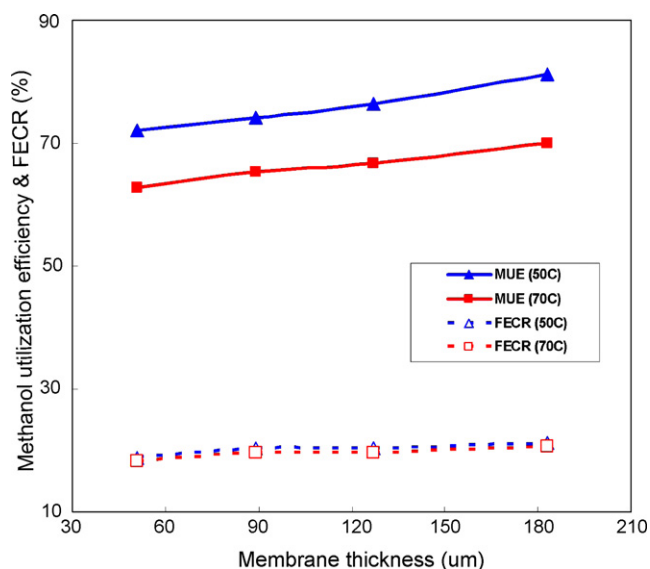


Fig. 6. The effect of temperature on the methanol utilization efficiency (MUE) and the FECR investigated at 210 mA cm⁻².

high temperature. Furthermore, the increased mobility of water molecules through the membrane with temperature may also contribute to the increased WTC at high temperature.

As a result, operating FC system at temperature below 50 °C is undesirable due to low power density, while temperature above 70 °C has also adversely effects the methanol utilization efficiency and WTC. Additionally, in the case of system operation at high current density levels, the overall system efficiency may be decreased due to parasitic power loss for BOP components, reduced voltaic efficiency, and a large volume recycler for significant produced water. Conversely, the low current density system operation needs a larger stack to produce sufficient power. For that reason, in order to design small volume of high energy efficient FC systems, the operating condition of the DMFC such as temperature and current density should be optimized with

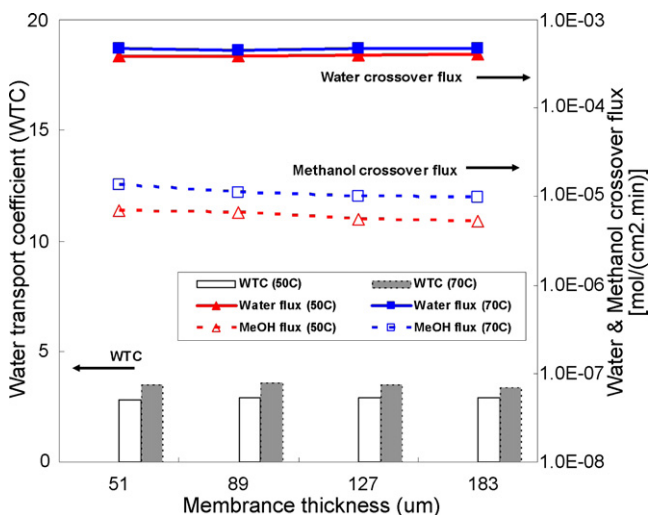


Fig. 7. The WTC and water/methanol transport flux measured at different temperatures and 210 mA cm⁻².

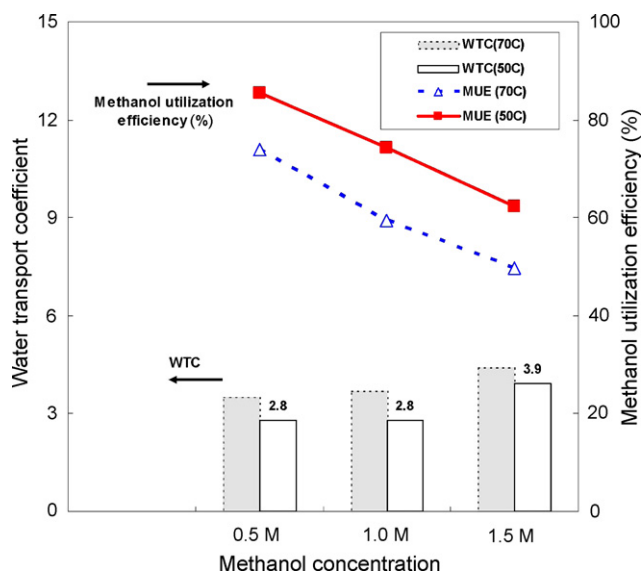


Fig. 8. The measured methanol utilization efficiency, power density, and WTC of DMFCs at 70 °C and 160 mA cm⁻² for various methanol concentrations.

due consideration to power density, FECR, and methanol/water crossover of MEAs.

3.3. Influence of methanol concentration and fuel/air stoichiometry

For this study MEAs were prepared by Nafion-1135 membrane with the commercial carbon papers 34BA and 25BC (SGL, Germany) for the anode and cathode, respectively. Fig. 8 shows the measured methanol utilization efficiency, power density, and WTC of DMFCs at 160 mA cm⁻² for various methanol concentrations. As expected a low methanol concentration resulted in higher methanol utilization efficiency of the DMFC due to relatively small methanol crossover. The highest methanol utilization efficiency of DMFCs was approximately 85.6% at 50 °C and 0.5 M for the thin Nafion 1135 membrane. In addition, the WTC of DMFCs increased from 3.3 at 0.5 M to 4.4 at 1.5 M methanol concentration. The reason for this phenomenon is unknown at this moment.

The stoichiometry effect of air and fuel on the methanol utilization efficiency and WTC is shown in Fig. 9. As exhibited, the methanol utilization efficiency increased with decreasing methanol and/or air feed rate. Noticeably an improvement in the methanol utilization efficiency was found in a stoichiometry of less than 2.5, similar for the methanol and air feed rate. On the other hand, the change of fuel stoichiometry had negligible influence on the WTC, while WTC showed a stronger dependence on air stoichiometry.

3.4. Influence of MPL in the anode and cathode GDL

By combining different anode and cathode structures, eight types of MEAs with Nafion-1135 membrane were prepared and investigated. The SGL carbon papers 25DA, 25BC, 35BA, and 25BC for the anode with 25BC for the cathode were used as a backing layer to investigate the effects of anode GDL on the

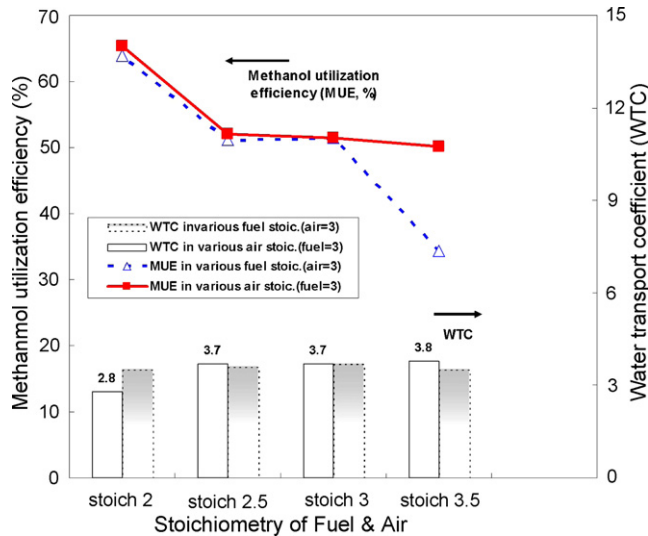


Fig. 9. The stoichiometry effect of air and fuel on the methanol utilization efficiency and WTC at 70 °C and 160 mA cm⁻².

mass balance properties. Fig. 10 compares the effects of anode GDLs on the methanol utilization efficiency at 160 mA cm⁻² and power density at 210 mA cm⁻² of DMFCs. It is seen that the methanol utilization efficiency of MEA prepared using SGL 25BC for the both electrodes, was improved significantly. In fact, the MPL in anode diffusion layer played a leading role in enhancing methanol utilization. However, the power density of the MEA having an anode MPL diminished because of the decreased mass transfer at the anode. It means that the MEA of this structure may be suitable for use at methanol concentrations of more than 1 M. Thus, the anode MPL in DMFC MEAs served as an additional resistance against diffusion of methanol, since a MPL which consists of a mixture of PTFE and carbon black has higher density than a plain backing layer. In contrast, the increase of PTFE in anode diffusion layer has unfavorable effects on both the methanol utilization efficiency and power density.

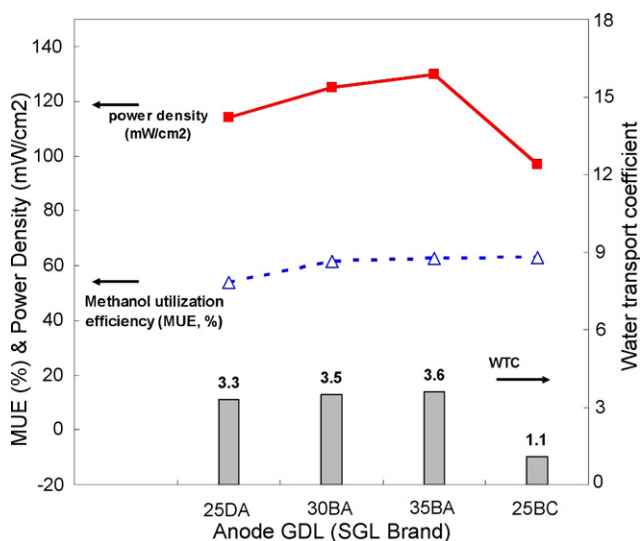


Fig. 10. The effect of anode GDLs (SGL, Germany) on the methanol utilization efficiency (MUE) and power density of DMFCs at 70 °C.

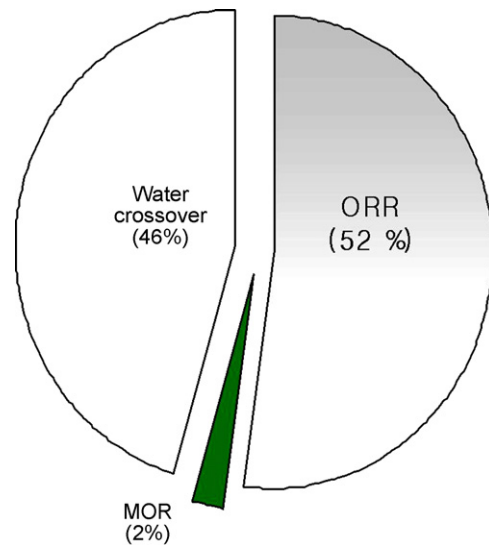


Fig. 11. The relative proportion of water produced by three electrochemical phenomena of DMFCs in anode MPL structures at 160 mA cm⁻² and 70 °C.

The MEA fabricated by 25DA (SGL, 20 wt.% PTFE) for the anode showed lower methanol utilization efficiency and power density than those of the 30BA and 35BA (SGL, 10 wt.% PTFE).

It is worthwhile to note that the introduction of a MPL in anode diffusion layer resulted in significantly decreased WTC, seen in Fig. 10. Surprisingly, the WTC of the MEA having an anode MPL was decreased from 3.5 (without the anode MPL) to 1.1 at 70 °C in the presence of 160 mA cm⁻² current density. Furthermore, in the case of MEA with the anode MPL, the proportion of the water produced by water crossover in DMFC MEAs significantly decreased from 84% to 46% (Fig. 11). This may be because the MPL acts as an efficient blocking layer for preventing water transport in the same way as it mitigates methanol diffusion when it is used in the anode diffusion layer. This is a good example where water transport characteristics can be improved by modified anode structure.

For the investigation of the cathode GDLs, 21DA, 25BC, 21DC, and 24DC for the cathode with 35BA for the anode were used. Fig. 12 shows the effect of cathode GDLs on the methanol utilization efficiency and power density of DMFCs. The cathode MPL in the MEA design was also responsible for decreasing methanol crossover. The methanol utilization efficiencies of MEAs prepared using 25BC, 24DC, and 21DC for the cathode were more than 61%, while the 21DA cathode GDL MEA (no MPL structure) showed only 49.5%. Another important design parameter in the cathode diffusion layer could be PTFE-content in the GDL. The existence of PTFE in the cathode GDL was indispensable for the rapid removal of water produced by the electrochemical reactions. However, too much PTFE-content in cathode GDLs led to decreased power density of DMFCs. This is attributed to increased mass transfer limitation by the low air permeability, as shown in Fig. 12. Furthermore, the change of the cathode GDL in this MEA structure did not reveal any appreciable difference in the WTC. The WTC of DMFC MEAs remained virtually constant in the range of 3.4 and 3.6 irrespective of the change of the cathode GDL. In this set of experiments,

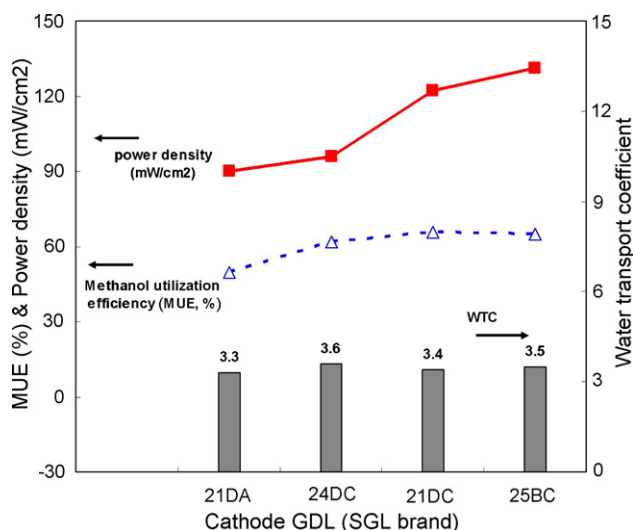


Fig. 12. The effect of cathode GDLs (SGL, Germany) on the methanol utilization efficiency, power density, and WTC of DMFCs at 70 °C.

the change of structure of cathode diffusion layer was found to be a very effective way in improving power density.

4. Conclusions

In order to provide a portable power source with high energy density, reduction of both methanol crossover and water exhaust on cathode must be achieved in the DMFC. This work demonstrated that the structure of the MEA and its mass balance properties such as methanol utilization, WTC, and FECR in the DMFC were strongly related. The methanol utilization efficiency of the MEA in DMFCs was improved with increasing membrane thickness in spite of decreasing power density. The MPL in anode diffusion layer also resulted in significantly decreased water transport to the cathode with increased methanol utilization efficiency. The WTC of the MEA having an anode MPL was decreased from 3.5 (in case without MPL) to 1.1 at 70 °C and 160 mA cm⁻². This may be because the MPL acts as the efficient blocking layer for preventing water transport in the same way as it mitigates methanol diffusion when it is used in the anode diffusion layer. However, the power density of the MEA having an anode MPL diminished because of the decreased mass transfer at the anode. On the contrary, the change of structure of cathode diffusion layer was found to be a very effective way in improving power density. Furthermore, the change of the cathode GDL in this MEA structure did not reveal any appreciable difference in the WTC.

In addition, as the structural parameters of a MEA to maximize the fuel efficiency in FC system, the effect of the Pt-based catalysts (carbon supported, black) and their loading on the methanol utilization and power density in DMFCs should be investigated. However, this topic is remained as a future work topic due to the present limited resources.

The mass balance properties in DMFCs were also sensitive to operational variables of the system, such as temperature, cell current, methanol concentration, and stoichiometry of fuel/air. The methanol utilization efficiency increased with decreasing temperature due to the reduced methanol permeability at lower temperature. Furthermore, a lower methanol concentration of 0.5 M at 50 °C resulted in higher methanol utilization efficiency of 85.6%. Additionally, the methanol utilization efficiency increased with decreasing methanol and/or air feed rate. Finally, the change of fuel stoichiometry had negligible influence on the WTC, while the WTC showed a strong dependence on air stoichiometry.

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