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Effects of anode microporous layers made of carbon powder and nanotubes on water transport in direct methanol fuel cells

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ABSTRACT

The effects of the design parameters of the anode diffusion layer (DL), including the PTFE loading in the backing layer (BL), and the carbon and PTFE loading in the microporous layer (MPL), on water transport through the membrane and the performance of a liquid-feed direct methanol fuel cell (DMFC) are experimentally investigated. The results indicate that increasing the PTFE loading in the BL and introducing a MPL could decrease water crossover through the membrane without sacrificing cell performance when the feed methanol concentration is increased. It is also found that changing the PTFE loading in the MPL has little effect on water crossover, whereas increasing the carbon loading in the MPL could noticeably decrease the water-crossover flux. Nevertheless, the ability of the MPL to reduce water crossover is limited by the presence of a number of mud cracks. To reduce further the water-crossover flux, a crack-free MPL made of multi-walled carbon nanotubes (MWCNTs) and PTFE is proposed. Tests indicate that the DMFC with the nanotube MPL results in a much lower water-crossover flux than a conventional carbon-powder MPL. More importantly, the use of the nanotube MPL allows the DMFC to be operated with a higher methanol concentration, and thereby increases the fuel cell system energy density.

1. Introduction

The direct methanol fuel cell (DMFC) has been recognized as one of the most promising next-generation power sources for portable electronic devices due to its unique advantages such as high energy-conversion efficiency, simple structure, and convenient delivery and storage of liquid fuel [1–3]. Unfortunately, however, commercialization of DMFC technology is still hindered by several technical problems, among which water management is one of the most important [4–10]. In the DMFC, excessive water, along with methanol, can be transported through the Nafion membrane to the cathode. This process is termed water crossover causing two challenging issues for DMFCs. First, it results in water loss from the anode, and hence replenishment is needed as water is the essential reactant for the anode electrochemical reaction; such make-up complicates the fuel cell system. Second, a high rate of water crossover may exaggerate water flooding problems at the cathode and thereby limit electrode performance [11–15]. Thus, suppressing water crossover is important not only to simplify the DMFC system but also to improve cell performance.

Extensive studies of water crossover through the membrane in DMFCs have been conducted over the past decade [6–26]. Peled et al. [8] added a liquid water-barrier layer to the DMFC cathode to build up a high liquid pressure to drive water flow back to the anode. They showed that the design of the water-barrier layer greatly influenced the rate of water crossover. With an optimized water-barrier layer, water loss at the anode could be minimized and even water-neutral operation could be achieved in a passive DMFC. Similarly, Lu et al. [12] reported a novel design of membrane electrolyte assembly (MEA) that consisted of a thin membrane and a backing layer (BL) coated with a highly hydrophobic microporous layer (MPL). The build up in liquid pressure in the cathode, due to the large contact angle and the small pore size of the MPL, created the back-flow flux of water to the anode and substantially reduced the rate of water crossover. Liu et al. [14] also investigated the effects of MEA fabrication processes and operating conditions on water transport through the membrane. It was found that membrane thickness, cathode BL and MPL play important roles in water transport through the membrane. Recently, Xu and Zhao [24] and Xu et al. [26] measured water-crossover flux through the membrane in a DMFC and examined the influence of various designs and geometric parameters as well as operating conditions such as the properties of the cathode diffusion layer (DL), membrane thickness, cell current density, cell temperature, methanol concentration and oxygen flow rates on water crossover through the membrane and cell performance in a DMFC. It was concluded that PTFE loading in the cathode BL should be as low as possible to maintain an acceptable water-crossover rate without blocking oxygen transport. An MPL consisting of 40 wt.% PTFE with a 2.0 mg cm^{-2} carbon loading was found to exhibit relatively low water-crossover rate and the best cell performance.

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A review of the literature indicates that most of previous studies focused on investigating the effects of cathode DL design on water crossover through the membrane and cell performance. Although the influence of the anode DL on water crossover has been investigated by a few investigators [24,27,28], the role of the anode DL in reducing water crossover is still unclear. In this work, the effects of PTFE loading in the anode BL and in the MPL, as well as the carbon loading in the MPL on both cell performance and water crossover in a DMFC are investigated. In addition, a MPL made of multi-walled carbon nanotubes (MWCNTs) and PTFE is proposed to reduce water crossover in a DMFC.

2. Analytical

As illustrated in Fig. 1, water transport through the membrane depends on three transport mechanisms, namely, diffusion due to a water concentration gradient, electro-osmotic drag due to proton transport, and convection due to a hydraulic pressure gradient. The water flux by diffusion, J_{diff}, can be expressed as:

$$J_{\mathrm{diff}} = D_{\mathrm{eff}} \frac{c_{\mathrm{la}} - c_{\mathrm{lc}}}{\delta_{\mathrm{m}}} \quad (1)$$

where D_{eff} is the effective diffusivity of water in the membrane, δ_{m} is the membrane thickness, c_{la} and c_{lc} represent liquid water concentrations at the anode catalyst layer (CL)|membrane interface and cathode CL|membrane interface, respectively. According to the phase equilibrium between the dissolved water in the polymer and the water in the free pores in CL [21], c_{la} can be determined by the water saturation in the anode CL, which is influenced by the generation rate of CO_2 in the anode CL (or the current density) and by the removal rate of CO_2 from the anode DL. Hence, the magnitude of c_{la} depends on the properties of the anode DL, the flow-field design as well as operating conditions. Increasing the PTFE loading in the anode BL and the addition of a hydrophobic MPL in the anode DL not only can increase the mass transport resistance of water, but also can increase the gas saturation in the anode CL that lowers c_{la} and thus depresses the water diffusion flux.

The water flux by electro-osmotic drag, J_{eo}, can be determined from:

$$J_{\mathrm{eo}} = n_{\mathrm{d}} \frac{i}{F} \quad (2)$$

where n_{d} is the electro-osmotic drag coefficient in the membrane, i is the cell current density and F is the Faraday's constant.

Another important contribution to water crossover is the water flux by convection, J_{bc}, which depends on the difference in liquid pressure across the membrane and can be expressed as:

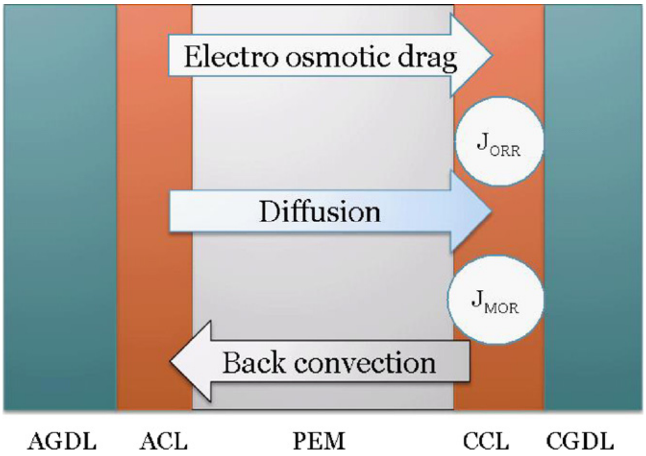

Fig. 1. Schematic representation of water transport through a polymer electrolyte membrane.

$$J_{\mathrm{bc}} = \frac{K\rho(p_{\mathrm{la}} - p_{\mathrm{lc}})}{\mu M_{\mathrm{H_2O}} \delta_{\mathrm{m}}} \quad (3)$$

where K is the permeability through the membrane, ρ is the density of water, μ is the viscosity of liquid water, and $M_{\mathrm{H_2O}}$ is the molecular weight of water. The terms p_{la} and p_{lc} represent liquid water pressure at the anode CL|membrane interface and cathode CL|membrane interface, respectively. Clearly, the back-flow flux caused by convection can be enhanced by increasing p_{lc} and decreasing p_{la}. Usually, increasing p_{lc} can be achieved by employing a highly hydrophobic MPL [12–15,26] or a similar functional layer in the cathode DL [6,8]. Moreover, a highly hydrophobic MPL in the anode DL can also help decrease p_{la}, as the MPL lowers the permeability of the DL and thereby increases the pressure drop of liquid from the anode channel to the anode CL.

In summary, the total water-crossover flux through the membrane, J_{wc}, is determined by summing the above three transport mechanisms, i.e.,

$$J_{\mathrm{wc}} = J_{\mathrm{diff}} + J_{\mathrm{eo}} + J_{\mathrm{bc}} \quad (4)$$

The foregoing analysis indicates that reducing the diffusion flux by decreasing the liquid saturation in the anode CL, and enhancing the back-convection flux by increasing the liquid pressure in the cathode CL and lowering the liquid pressure in the anode CL, can depress water crossover through the membrane.

3. Experimental

3.1. Direct methanol fuel cell

The in-house fabricated DMFC consisted of a MEA (active area of 2.0 cm × 2.0 cm) that was sandwiched between two bipolar plates, which were fixed by two plates. The MEA consisted of a Nafion 112 membrane and two electrodes. The cathode electrode was a single-side ELAT® electrode from E-TEK, which used carbon cloth (E-TEK, type A) with 30 wt.% PTFE wet-proofing treatment as the backing layer. 4.0 mg cm^{-2} unsupported HP Pt was used as the cathode catalyst. At the anode, the CL was fabricated in-house by the decal method [30]. The catalyst ink was prepared by a method reported elsewhere [30] and then sprayed on a Teflon blank. The anode CL was then transferred to the membrane by hot pressing the catalyst-coated Teflon blank and the cathode electrode on the two sides of the membrane at 135 °C and 4.0 MPa for 3 min. The anode catalyst loading was about 2.4 mg cm^{-2} using unsupported Pt/Ru (1:1, *a*/*o*) from E-TEK. The content of Nafion ionomer in the anode CL was maintained at about 20 wt.%. The decal method for preparing the anode ensured that the effect of anode DL can be investigated by using different anode DLs for the same anode CL and the same membrane and cathode. To study the effect of anode BL, Toray-090 carbon papers treated with different PTFE loadings were tested without the MPL. Then the untreated BLs coated with MPLs of different PTFE loadings and carbon loadings were tested to study the effect of the anode MPL. Finally, a novel MPL, consisting of MWCNTs with a loading of about 5.0 mg cm^{-2} and 30 wt.% PTFE, was compared with a conventional MPL made of Vulcan XC-72 carbon powder of the same amount of PTFE and the same carbon loading.

For the convenience of temperature control, both the anode and cathode fixture plates were made of stainless-steel blocks. Single serpentine flow-fields, with 0.8 mm channel width, 1.2 mm rib width and 0.8 mm depth, were formed in the fixture plates for both the anode and cathode sides.

3.2. Measurement instrumentation and test condition

The experiments were carried out in the test rig detailed elsewhere [4]. At the anode, 1.0 M aqueous methanol solution at the flow rate of 1.0 ml min^{-1} was fed by a digital HPLC micro-pump (series III). At the cathode, high-purity oxygen (99.7%) at a flow rate of 100.0 sccm was supplied without humidification. A mass-flow meter (Omega FMA-7105E), along with a multiple-channel indicator (Omega FMA-5876A), was used to control and measure the flow rate of oxygen. The experiments were performed at a temperature of 60.0 °C. An Arbin BT2000 (Arbin Instrument) electro-load interfaced with a computer was employed to control the cell operation and measure voltage–current (polarization) curves.

3.3. Determination of water-crossover flux

A water trap filled with Drierite® (anhydrous $CaSO_4$) was connected to the exit of the cathode channel to collect the water. The water was collected while maintaining a constant current density for about 0.5–3 h. Fifteen minutes were usually needed to achieve stabilization of the operating point at each water-collecting point. To eliminate the influence of back pressure on water transport through the membrane, the respective back pressures on the anode and cathode compartments were kept to the atmosphere pressure. More details about the determination of J_{wc} can be found elsewhere [24].

4. Results and discussion

4.1. Effect of the PTFE loading in the BL

Fig. 2 shows the effect of PTFE loading in the BL without a MPL on the water-crossover flux at different current densities. It is seen that the water-crossover flux increases with the current density; more importantly, the water-crossover flux decreases with increasing PTFE loading, especially at high current densities. For instance, the water-crossover flux at a current density of 240 mA cm^{-2} is lowered by about 40% as the PTFE loading is increased from 0 to 40 wt.%. The reason for the reduction in water crossover with high PTFE loading in the anode BL is explained as follows: first, it is understood that during wet-proof treatment, the PTFE is prone to form films on the surface of the BL, blocking the pores in the BL. A higher PTFE loading in the anode BL results in more pores covered by PTFE films, leading to a smaller permeability of the BL and thereby a higher mass-transfer resistance of water from the flow channel to the anode CL. Second, a higher PTFE loading may increase the hydrophobicity of the BL such that the generated CO_2 can readily accumulate in the BL, as a result of the more hydrophobic surfaces, and thereby reduce the mass transport paths for the liquid phase. As a result, the mass-transfer resistance of water from the flow channel to the anode CL is further intensified. In summary, increasing the PTFE loading in the anode BL may reduce the water concentration in the CL as a result of the increased mass-transfer resistance of water from the flow channel to the CL caused by pore blockage and more hydrophobic surfaces, which decreases the water flux J_{diff} due to the diffusion and thus lowers the total water-crossover flux.

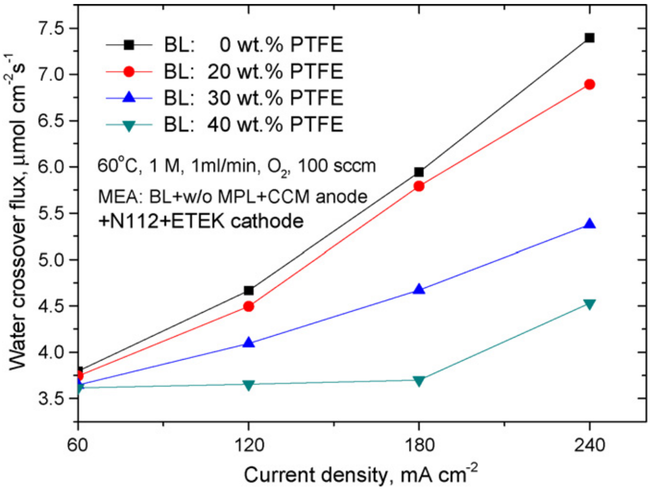

Fig. 2. Effect of PTFE loading in anode BL on water-crossover flux.

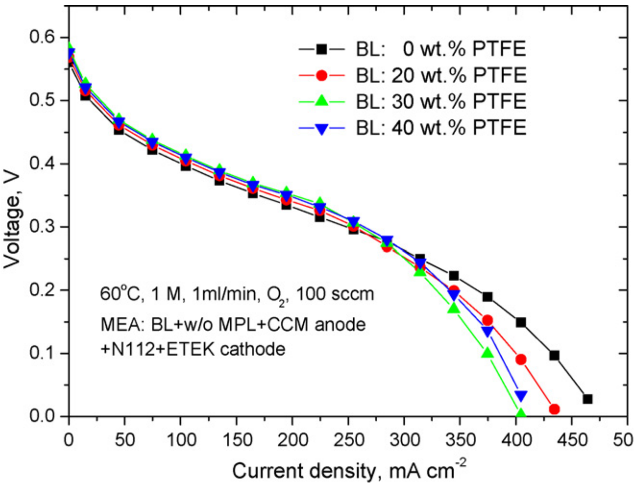

Fig. 3. Effect of PTFE loading in anode BL on cell performance with 1.0-M methanol operation.

The effect of the PTFE loading in the BL on the cell performance with a 1.0-M methanol concentration operation is shown in Fig. 3. It is seen that at low current densities (<50 mA cm^{-2}), a higher PTFE loading in the anode BL yields higher voltages than does a lower one, but at high current densities (>50 mA cm^{-2}) the cell performance decreases with increasing the PTFE loading. This is because increasing the PTFE loading in the anode BL not only increases the mass-transfer resistance of water but also increases the mass-transfer resistance of methanol from the flow channel to the anode CL. At low current densities, increasing the mass-transfer resistance of methanol results from the increased PTFE loading in the anode BL and leads to a decrease in the methanol concentration in the anode CL, that, in turn, lowers methanol crossover and the cathode mixed-potential. Hence, the cell voltage increases with increasing PTFE loading in the anode BL. At high current densities however, the demand of the methanol transfer rate for the anode reaction is increased. In this case, the increased mass-transfer resistance of methanol in the anode BL with a high PTFE loading results in an inadequate methanol concentration in the anode CL, leading to a larger concentration loss. As such, the cell performance decreases with increasing PTFE loading in the anode BL at high current densities. Nevertheless, it should be recognized that adequate methanol concentration can be achieved by increasing the feed methanol concentration. To demonstrate this point, experiments were performed with the feed methanol concentration increased from 1.0 to 2.0 M. The results are given in Fig. 4 and shows that cells with different PTFE loadings in the anode BL yield almost the same performance. This observation indicates that the increased mass-transfer resistance of methanol at the anode due to a higher PTFE loading in the anode BL, is actually not a problem. By contrast, an increase in the feed methanol concentration can raise the energy density of the fuel cell system. Hence, a high PTFE loading in the anode BL can not only suppress water crossover, reducing the anode water loss and alleviating cathode flooding, but

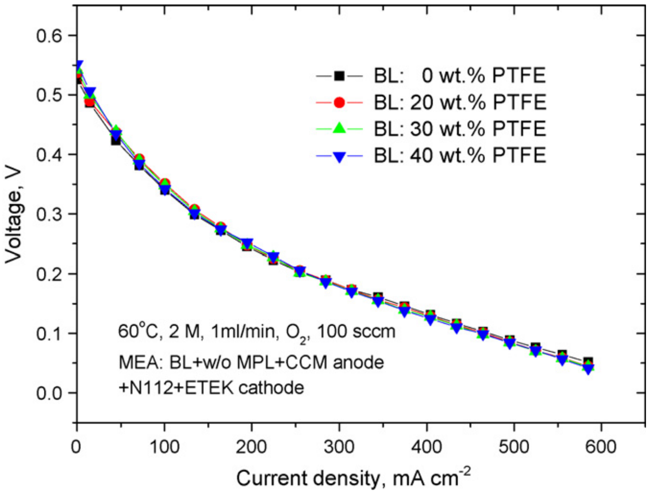

Fig. 4. Effect of PTFE loading in anode BL on cell performance with 2.0-M methanol operation.

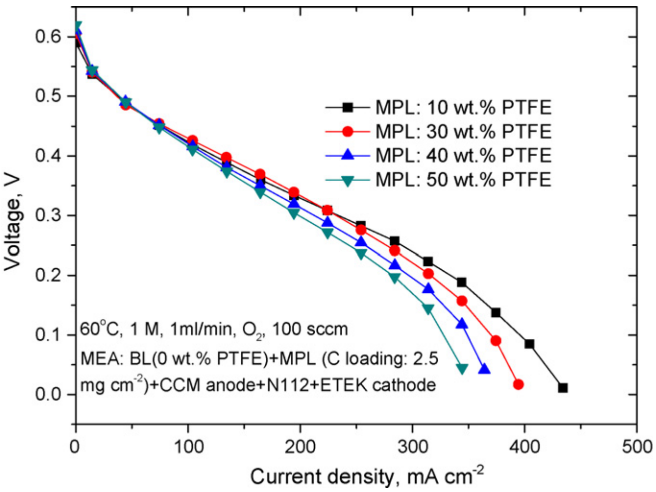

Fig. 6. Effect of PTFE loading in anode MPL on cell performance with 1.0-M methanol operation.

also allow the DMFC to be operated at a relatively high methanol concentration.

4.2. Effect of the PTFE loading in the MPL

First the effect of PTFE loading in the anode MPL on water crossover and cell performance was investigated with the same cathode and anode BL. As-received untreated carbon paper that is slightly hydrophobic was used as the anode BL and the carbon loading was maintained at 2.5 mg cm^{-2}. The influence of the hydrophobic MPL was also examined by comparing the water-crossover flux with different anode DLs that had carbon papers with and without a MPL. The experimental results are shown in Figs. 5–7.

It is seen from Fig. 5 that the water-crossover flux is markedly reduced after adding the hydrophobic MPL to the anode BL, particularly at high current densities. This is because the added MPL can significantly increase the water transfer resistance from the flow channel to the anode CL, thus lowering the water concentration in the anode CL. As a result, the water flux due to diffusion is reduced, lowering the water-crossover flux. The result reveals that the hydrophobic MPL plays a dominant role in the water transport and can help to reduce significantly the water crossover. It is also interesting to note that anode DLs with different PTFE loadings in the MPL show almost the same water-crossover flux. This suggests that the effect of PTFE loading in the anode MPL on water crossover is rather small. This finding is different from the results regarding the effect of the PTFE loading in the anode BLs, i.e., an increase in PTFE loading may significantly reduce the water-crossover flux. The cause of the above phenomena is complicated. First, as discussed earlier, increasing the amount of PTFE in the MPL can decrease the water-crossover flux as a result of the increased hydrophobicity of the anode DL. In addition, an increase in the PTFE loading in the MPL may reduce the porosity, resulting in a higher mass-transfer resistance of water and thus a lower water-crossover flux. However, the water-crossover flux not only depends on the surface property but also the permeability of the MPL. It has been recognized that during the fabrication process of the MPL, the formation of some macropores (between 2 and 20 μm), or so-called mud cracks [29,31,32], is difficult to avoid. Further, the more the PTFE loading in the MPL, the greater the tendency for mud cracks to form. These relatively larger mud cracks can lead to an increase in the permeability of the MPL, thereby increasing the water-crossover flux through the membrane. Subsequently, the reduced water flux as a result of the increased hydrophobic level is compensated by the increased water flux due to the increased permeability so that there is almost the same total water-crossover flux through the membrane. Therefore,

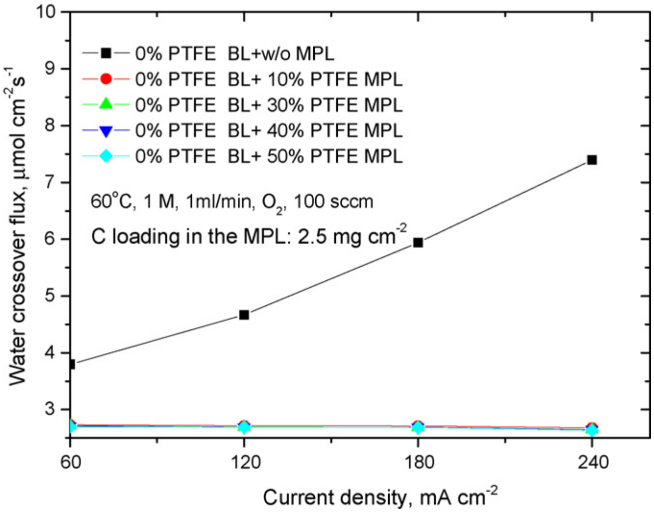

Fig. 5. Effect of PTFE loading in anode MPL on water-crossover flux.

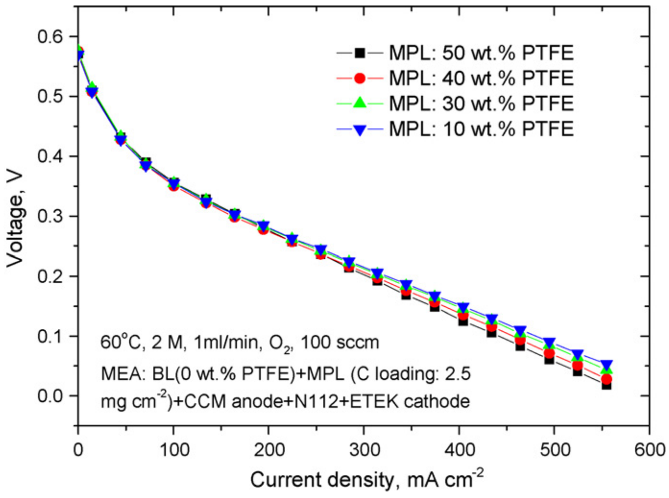

Fig. 7. Effect of PTFE loading in anode MPL on cell performance with 2.0-M methanol operation.

the presence of these mud cracks in the MPL mainly accounts for the negligible effect of PTFE loading in the MPL on the water-crossover flux. Accordingly, reducing the pore size and the number of mud cracks is a key issue in reducing water crossover through the membrane.

Although the effect of PTFE loading in the MPL on water crossover is negligible, its influence on cell performance is substantial, as shown in Fig. 6. When increasing the PTFE loading in the MPL from 10 to 50 wt.% with 1.0-M methanol operation, the higher mass-transfer resistance of methanol as a result of the enhanced hydrophobic level results in an inadequate methanol concentration in the anode CL, that, in turn increases the mass transport loss and thereby lowers the cell performance. As mentioned earlier, however, adequate methanol concentration in the anode CL can be achieved by increasing the feed methanol concentration. The cell performance with different PTFE loadings in the anode MPL with 2.0-M methanol operation is shown in Fig. 7. The difference in performance with different PTFE loadings becomes much smaller. It is believed that if the methanol concentration is further increased, a cell with a high PTFE loading in the anode MPL may yield better performance as a result of the higher mass-transfer resistance of methanol, lowering the mixed-potential at the cathode. Operation at a high methanol concentration can increase the energy density of fuel cell system. Therefore, the increased mass-transfer resistance of methanol on the anode as a result of the higher PTFE loading in the MPL is actually not a problem. On the contrary, it can reduce methanol crossover such that the DMFC can be operated at a high methanol concentration.

4.3. Effect of carbon loading in MPL

In addition to the PTFE loading in the MPL, the effect of carbon loading in the MPL on water crossover and cell performance has also been investigated. It is found that water-crossover flux decreases with increasing the carbon loading in the MPL, as shown in Fig. 8. For instance, when the carbon loading is increased from 1.5 to 5.0 mg cm^{-2}, the water-crossover flux at 180 mA cm^{-2} decreases from 2.81 to 2.34 μmol m^{-2} s^{-1}, i.e., a reduction of about 17%. This is because a higher carbon loading increases the thickness of the MPL, which increases the water-transfer resistance from the flow channel to the anode CL and lowers the water concentration in the anode CL. As a result, the water flux due to diffusion is decreased, thereby reducing the total water-crossover flux. It should be noted, however that a thicker MPL may result in more mud cracks, which increase the permeability of the MPL. Consequently, further increasing the carbon loading may not be effective in reducing the water-crossover flux. As shown in Fig. 8, the water-crossover fluxes are almost the same when the carbon loading in the MPL is increased from 3.5 to 5.0 mg cm^{-2}. Therefore, to achieve a low rate of water crossover through the membrane, minimizing the number of mud cracks in the MPL is of great importance.

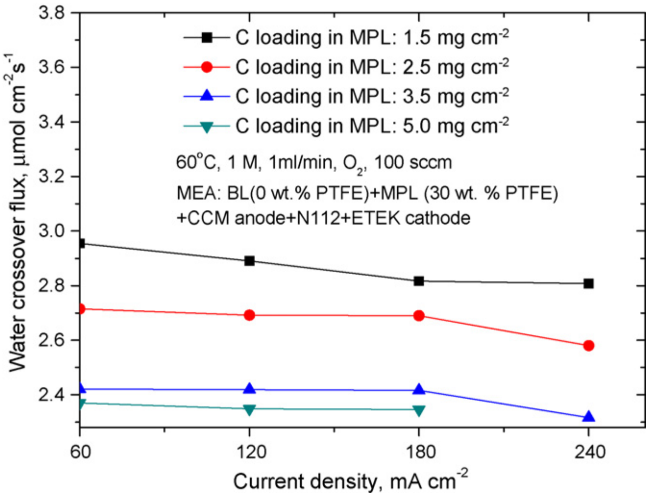

Fig. 8. Effect of carbon loading in anode MPL on water-crossover flux.

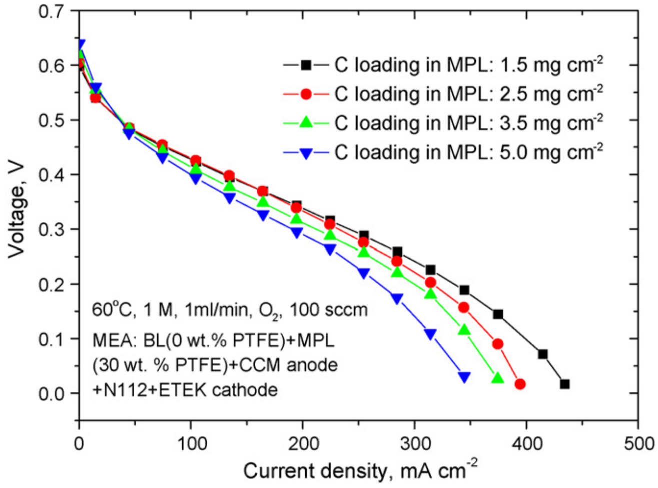

Fig. 9. Effect of carbon loading in anode MPL on cell performance with 1.0-M methanol operation.

The effect of carbon loading in the MPL on cell performance with 1.0- and 2.0-M operation has also been examined. For 1.0-M operation the data in Fig. 9 show that increasing the carbon loading from 1.5 to 5.0 mg cm^{-2} leads to a sharp decrease in the limiting current density. This feature can be attributed to the increased mass-transfer resistance of methanol, which is similar to the water transport. A high carbon loading makes the MPL thicker such that the transport path of methanol is longer and thus increases the mass-transfer resistance of methanol. As a consequence, the methanol concentration in the anode CL becomes inadequate for operation at low methanol concentrations and the limiting current density is decreased. This adverse effect of high carbon loading on methanol transport can be resolved by increasing the feed methanol concentration. As shown in Fig. 10, cells with different carbon loadings exhibit almost the same performance when the methanol concentration is increased to 2.0 M, indicating that a higher carbon loading in the MPL allows the DMFC to be operated

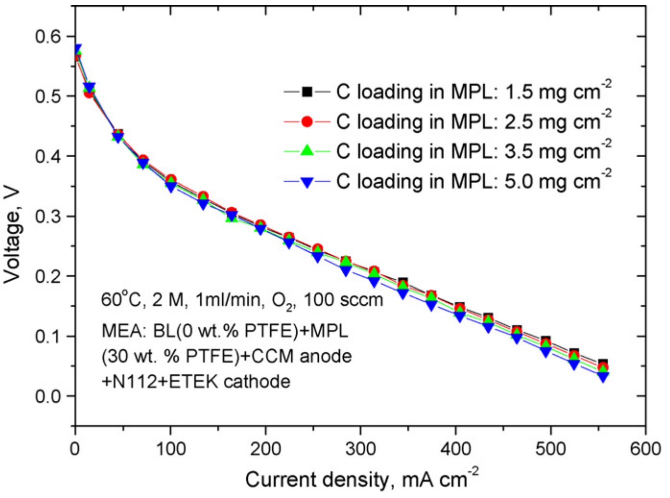

Fig. 10. Effect of carbon loading in anode MPL on cell performance with 2.0-M methanol operation.

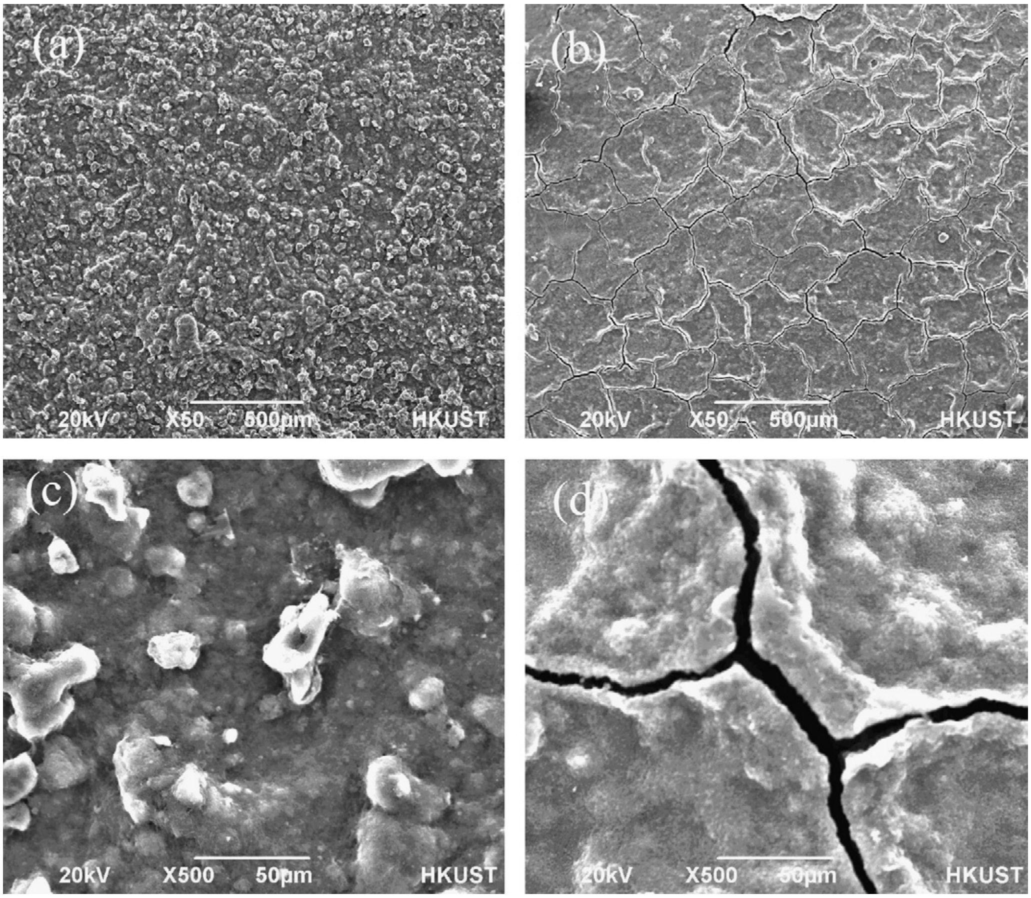

Fig. 11. Surface morphologies of various anode MPLs: (a) and (c) nanotube MPL; (b) and (d) carbon-powder MPL.

at a relatively high methanol concentration. In summary, increasing the carbon loading in the anode MPL can significantly reduce the water-crossover flux and permit operation at high methanol concentration. Meanwhile, when the carbon loading is too high, reducing the number of mud cracks during MPL preparation is essential.

4.4. MPL made of MWCNTs

As mentioned above, the conventional MPL made of Vulan XC-72 carbon powder and PTFE is prone to forming mud cracks across the whole surface of the MPL, particularly at high loadings of PTFE and carbon. These mud cracks may increase the permeability of the anode DL, thereby enhancing the water-crossover flux. Therefore, it is essential to remove mud cracks in the MPL. In this work, it is proposed to form the MPL with MWCNTs and PTFE. The surface morphologies of the nanotube and carbon-powder MPLs are shown in Fig. 11. From these SEM images, it is seen that the nanotube MPL is free of macro-cracks, but a large number of mud cracks with a width of about 10 μm is formed on the surface of the carbon-powder MPL. The change in the physical properties of the MPLs, including porosity, hydraulic permeability, pore-size distributions and hydrophobicity, may influence the liquid–gas two-phase flow behaviour and thus water-crossover flux through the membrane.

Fig. 12 compares the effect of the nanotube and carbon-powder MPLs on the water-crossover flux at different current densities. It can be seen that the water-crossover flux is significantly reduced by using the nanotube MPL. For example, at a current density of 180 mA cm^{-2}, the flux of water crossover is decreased from 2.35 to 1.93 μmol m^{-2} s^{-1} with the nanotube MPL. This behaviour can be explained as follows: the nanotube MPL shows no cracks and exhibits higher hydrophobicity, leading to a lower liquid saturation level in the anode MPL as well as the anode CL. As a result, the water flux due to diffusion is reduced, lowering the total water-crossover flux. In addition, the use of the nanotube MPL also influences the mass transport of methanol from the channel to the anode CL, consequently affecting cell performance.

The cell performance of a DMFC with different anode MPLs is presented in Fig. 13. For 1.0-M operation, the DMFC with a nanotube MPL has a smaller limiting current density than that

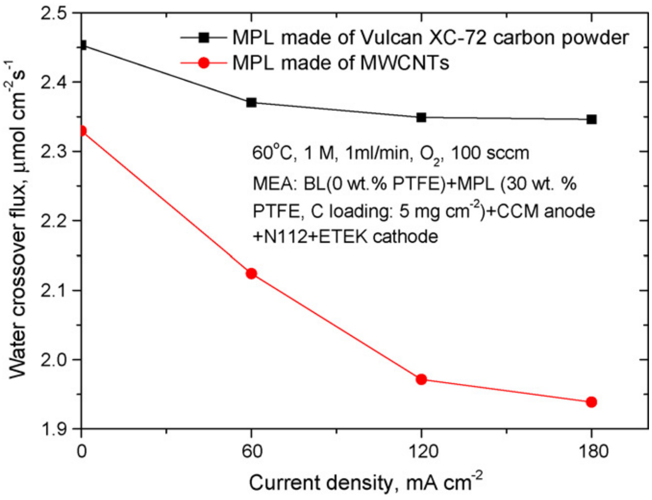

Fig. 12. Comparison in water-crossover flux between carbon-powder and nanotube MPLs.

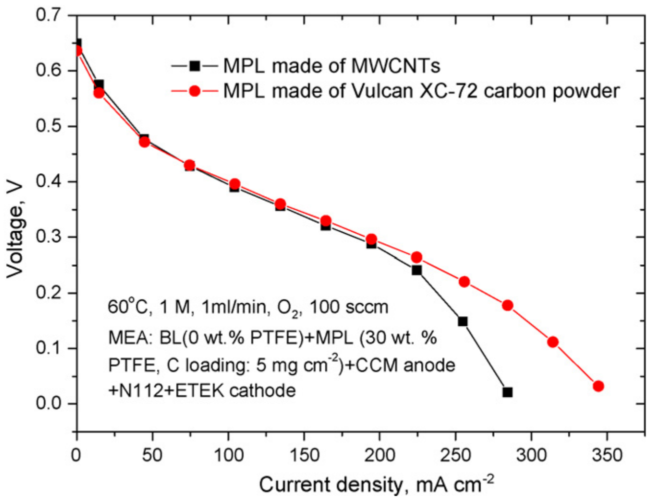

Fig. 13. Comparison in cell performance between carbon-powder and nanotube MPLs with 1.0-M methanol operation.

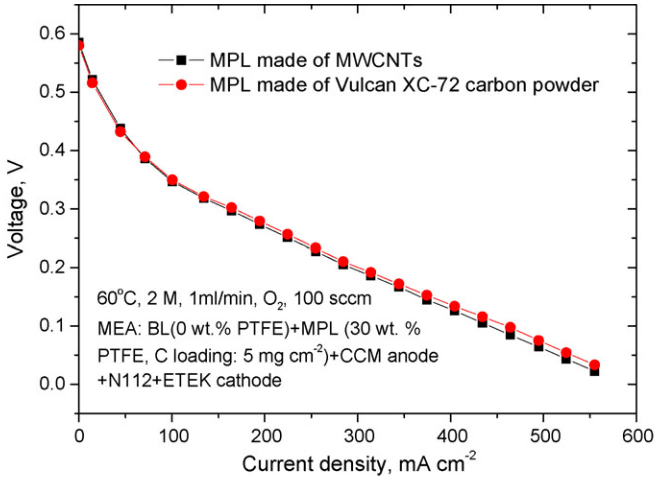

Fig. 14. Comparison in cell performance between carbon-powder and nanotube MPLs with 2.0-M methanol operation.

with a conventional MPL. The lowered limiting current density is primarily attributed to the higher mass-transfer resistance of methanol in the nanotube MPL as a result of its crack-free morphology and high hydrophobic level. Although the nanotube MPL showed higher methanol transport resistance, the adverse impact of the higher transport resistance can be minimized by increasing the feed methanol concentration. As shown in Fig. 14, when 2.0-M methanol solution is fed, the cell performance is nearly the same for the DMFCs with different MPLs. This suggests that methanol transport from anode channel to anode CL is no longer a limiting factor that controls cell performance as aforementioned. Also, the use of a high concentration methanol increases the overall energy density of the DMFC system. Therefore, the MPL made of MWCNTs and PTFE can not only reduce water crossover but also can increase the energy density of the fuel cell system.

5. Conclusions

Minimizing water crossover from the anode to cathode is an important aspect of water management in DMFCs. Hence, it is crucial to understand the effect of structure design and material properties of the anode DL on water transport behaviour in DMFCs. This work, presents an experimental investigation of the effects of anode BLs treated with different loadings of PTFE, conventional carbon-powder MPLs with different PTFE and carbon loadings, as well as a novel MPL made of MWCNTs and PTFE on both water crossover and cell performance. The salient findings that are of use for the optimal design of DMFCs are summarized as follows:

(1) The water-crossover flux through the membrane decreases significantly with increasing the PTFE loading in the BL due to the increased hydrophobic level and the reduced permeability of the BL. Therefore, to reduce water crossover, the anode BL in the DMFC should be treated with a higher PTFE loading.

(2) In the presence of a hydrophobic MPL, water loss from anode CL is found to decline by about 40% as a result of increased hydrophobicity and reduced permeability. On the other hand, the PTFE loading in the MPL has little effect on the water-crossover flux owing to its mud cracks which increase the permeability of the MPL, and compensate the increased hydrophobicity. By contrast, increasing the carbon loading in the MPL is a more effective means of decreasing water crossover. Further thickening the MPL may, however create a number of mud cracks, which increase the permeability.

(3) MWCNT is found to be a promising material for fabricating crack-free MPLs, which can substantially reduce water crossover through the membrane, and hence the DMFC with the nanotube MPL can gain a better water balance level.

(4) The above structure designs, including increasing the PTFE loading in the BL, increasing the PTFE and carbon loading in the MPL and the application of a nanotube MPL, can lower the cell limiting current density when the fuel cell is fed with the same methanol concentration as that used before modification of the MEA. This adverse effect can be minimized, however, when a higher methanol concentration is used. Thus, the measures for modifying the MEA design proposed in this work not only can reduce the water loss from the anode to the cathode, but also can facilitate the use of higher methanol concentrations to increase the energy density of the fuel cell system.

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