Characteristics of water transport through the membrane in direct methanol fuel cells operating with neat methanol

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Abstract
The water required for the methanol oxidation reaction in a direct methanol fuel cell (DMFC) operating with neat methanol can be supplied by diffusion from the cathode to the anode through the membrane. In this work, we present a method that allows the water transport rate through the membrane to be in-situ determined. With this method, the effects of the design parameters of the membrane electrode assembly (MEA) and operating conditions on the water transport through the membrane are investigated. The experimental data show that the water flux by diffusion from the cathode to the anode is higher than the opposite flow flux of water due to electro-osmotic drag (EOD) at a given current density, resulting in a net water transport from the cathode to the anode. The results also show that thinning the anode gas diffusion layer (GDL) and the membrane as well as thickening the cathode GDL can enhance the water transport flux from the cathode to the anode. However, a too thin anode GDL or a too thick cathode GDL will lower the cell performance due to the increases in the water concentration loss at the anode catalyst layer (CL) and the oxygen concentration loss at the cathode CL, respectively.

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1. Introduction
Direct methanol fuel cells (DMFCs) have been regarded as a competitive candidate for next-generation power sources primarily because of its attractive features such as using low-cost fuel, convenience in fuel storage and transportation, environmental friendliness and high specific energy [1–8]. Conventionally, DMFCs have to be fed with diluted methanol solution (i.e., 2.0–5.0 M) to limit the so-called methanol crossover and its detrimental effects, namely the mixed-potential at the cathode and fuel loss. Although DMFCs can achieve a decent performance in such low-concentration operation, this will lead to an unfavorable penalty in the specific energy of the fuel cell system. Moreover, since state-of-the-art membranes used for conducting protons are also permeable to water, the low-concentration operation leads to a high rate of water permeation from the anode to the cathode, thereby aggravating the problem of cathode water flooding. Thus, it is desirable to operate the DMFC with concentrated methanol solution and even neat methanol to eliminate such inherent drawbacks of the low-concentration operation.

As direct feeding concentrated fuel to the DMFC with the conventional design will result in severe methanol crossover, modifying and developing new anode structures to control the methanol delivery rate are of great significance. Pan [9] used four Nafion 117 membranes as methanol transport barriers to depress methanol crossover. A peak power density of 40 mW cm⁻² was
achieved at 50 °C with feeding 10.0 M methanol solution. Zhang et al. [10] developed an integrated anode flow field with small porosity to reduce methanol permeation. Their experimental data showed that this new flow field significantly improved the cell performance at the high-concentration operation. Nakagawa et al. [11,12] employed a hydrophobic porous carbon plate with a high mass-transfer resistance between the fuel reservoir and the anode flow field. By optimizing the structure of the porous plate, their passive DMFC can run with 22.0 M methanol solution without dramatically sacrificing cell performance. Rather than adding a new layer to the DMFC, Wu and Zhao et al. [13] developed a novel micro-fluidic flow field that enabled the passive DMFC to operate with highly concentrated methanol solution. The basic idea of the micro-fluidic flow field was to utilize evaporation from the small meniscus in each flow passage to create an extremely large interfacial mass-transfer resistance so that the methanol delivery to the anode catalyst layer (CL) was under control. With this micro-fluidic flow field, they showed that as high as 18.0 M methanol solution can be fed to the passive DMFC and a good performance was still maintained. In an attempt to use neat methanol, other investigators [14–17] proposed the use of a pervaporation (permeation and evaporation) membrane that allowed the methanol concentration from the neat in the fuel reservoir to be declined to an appropriate level in the anode CL. By using the pervaporation membrane, Xu et al. [17] demonstrated that their passive DMFC can yield a maximum power density of 34 mW cm⁻².

Although the methanol-crossover rate can be dramatically reduced with the above proposed anode structures, the performance of the DMFC operating with neat methanol is still lower than that in the low-concentration operation, which is primarily attributed to the water problem. Since no water is provided in the fuel reservoir with the neat-methanol operation, the water that takes part in the anode methanol oxidation reaction (MOR) needs to be passively supplied from the cathode through the membrane by diffusion. Under this circumstance, the anode performance becomes dependent of not only the water transport flux from the cathode to the anode but also the water concentration in the anode CL. Therefore, understanding the mechanism and characteristics of water transport through the membrane under the neat-methanol operation is critically important for upgrading the cell performance. However, only few works [18–22] have been reported with regard to the water transport behavior in the DMFC fed with neat methanol. Liu et al. [18] developed a novel membrane electrode assembly (MEA) structure that consisted of a Nafion 112 membrane and a compact microporous layer (MPL) on both the anode and the cathode to increase the water transport flux from the cathode to the anode. Masdar et al. [20] found that the water transport flux from the cathode to the anode in the neat-methanol operation was enhanced by fixing a hydrophobic air filter to the cathode. Wu and Zhao et al. [21] added a thin layer that consists of nanosized SiO₂ particles and Nafion ionomer onto each side of the membrane to enhance the water concentration level within the MEA. Their results showed that the MEA with the water retention layers yielded a much higher power density than did the MEA without water retention layers. Although the above mentioned measures can somewhat improve the water management in the neat-methanol operation, but the water transport behavior through the membrane and its influence on the cell performance of the DMFC are still far from understood. In this work, a facile method to measure the water transport flux through the membrane with the neat methanol operation is proposed. With the help of the present method, we investigate the water transport flux from the cathode to the anode in an in-house fabricated DMFC with various MEA design parameters and under different operating conditions, and show how these parameters affect the transport of water and the cell performance of the DMFC under the neat-methanol operation.

2. Analytical

Consider a DMFC system that can operate with neat methanol. As illustrated in Fig. 1, the system consists of a fuel reservoir (FR), a pervaporation membrane (PM), a perforated plate (PP) to control the evaporation area, a gas gap (GG), an anode flow field (AFF), a MEA, and a cathode flow field (CFF). The MEA is composed of five layers: an anode gas diffusion layer (GDL), an anode CL, a proton-exchange membrane (PEM), a cathode CL and a cathode GDL. On the anode, neat methanol stored in the fuel reservoir can permeate through the pervaporation membrane and be evaporated into vapor on the other side. The small open area of the perforated plate and the small interfacial mass-transfer rate constant of methanol allow the methanol concentration from the neat in the fuel reservoir to decrease to an appropriate concentration in the gas gap. The methanol vapor then diffuses through the gas gap, the anode flow field, and the anode GDL to the anode CL, where methanol reacts with water to produce CO₂, protons and electrons. On the cathode, dry oxygen is fed to the cathode flow field at an extremely low flow rate. The oxygen in the flow channel then diffuses through the cathode GDL to the cathode CL, where it reacts with the protons and electrons to generate water. As water is produced at the cathode CL but consumed at the anode CL, a water concentration gradient across the membrane is created, as illustrated in Fig. 1. Such a water distribution can drive water to diffuse from the cathode to the anode; the diffusion flux, ̇J₀, can be expressed by Fick’s law:

\[ ̇J_0 = D_M^C (C_{CCL} - C_{ACL}) / \delta_M \]  

(1)

where \(C_{CCL}\) and \(C_{ACL}\) represent the water concentration at the cathode CL and anode CL, respectively; \(D_M^C\) is the effective diffusivity of water through the membrane; \(\delta_M\) denotes the thickness of the membrane. Eq. (1) indicates that the diffusion flux depends on the water concentration level at each side of the membrane and the membrane properties including thickness, water uptake characteristics, and effective diffusivity of dissolved water. Generally, \(C_{CCL}\) is influenced by the water production flux at the cathode that is related to cell current density and the methanol-crossover flux, the structure of the cathode gas diffusion layer (GDL) including the PTFE loading in the GDL and its thickness, the cathode flow field design, the operating temperature and the relative humidity of the cathode gas. The water concentration at the anode CL, \(C_{ACL}\), can be affected by the water consumption flux at the anode that is related to the cell current density and the design of the anode GDL such as its thickness and porosity. In
Summary, the magnitudes of \( C_{\text{CL}} \), \( C_{\text{ACL}} \) and the \( J_D \) all depend on the designs of the MEA and the flow field as well as the operating conditions.

Simultaneously, the water at the anode CL can also be dragged by protons from the anode to the cathode; the water flux by EOD drag, \( J_E \), can be determined from:

\[
J_E = n_d i F
\]  

where \( n_d \) stands for the EOD coefficient of water; \( i \) is the cell current density; \( F \) denotes the Faraday’s constant. Clearly, the EOD flux depends on the cell current density and \( n_d \), which is related to the water content in the membrane. Under the neat-methanol operation, we assume \( n_d = 1.59 \), corresponding to the case that the membrane is in equilibrium with saturated water vapor [23].

In summary, the total water transport flux through the membrane, \( J \), can be obtained by summing up Eqs. 1 and 2 to give:

\[
J = J_D - J_e = D_{\text{diff}} \frac{C_{\text{CL}} - C_{\text{ACL}}}{\delta_{\text{mem}}} - n_d i F
\]  

Eq. (3) indicates that the net water transport flux through the membrane is influenced by all the parameters that affect \( J_D \) and \( J_e \) such as the geometric dimensions and physical properties of the membrane, GDLs and flow fields. It should be noted that to meet the minimal requirement of the water for the anode MOR, \( J \) should be larger than the value of \( \frac{i}{F} \) at a given operating current density \( i \). This suggests that under the neat-methanol operation, the MEA and the operating conditions should be properly designed to give a sufficiently high \( J \).

With the net water transport flux through the membrane given by Eq. (3), we now consider the water transport from the cathode CL to the ambient. Under steady states, the water removal flux from the cathode, \( J_C \), can be written as:

\[
J_C = J_{\text{ORR}} + J_{\text{MOR}} - J
\]  

where \( J_{\text{ORR}} \) and \( J_{\text{MOR}} \) represent, respectively, the molar flux of water due to the oxygen reduction reaction (ORR) and MOR of the permeated methanol at the cathode, which are given by:

\[
J_{\text{ORR}} = \frac{i}{2F}
\]  

and

\[
J_{\text{MOR}} = \frac{iC_3}{3F}
\]

with \( i_C \) stands for the equivalent methanol-crossover current density. As the methanol crossover through the membrane is dominated by molecular diffusion when the current density and the methanol concentration in the anode CL are not too high, \( i_c \) can be determined from [24]:

\[
i_c = i_{\text{OCV}} \left( 1 - \frac{i}{i_{\text{lim}}} \right)
\]

where \( i_{\text{OCV}} \) is the equivalent methanol-crossover current density under the open circuit condition and \( i_{\text{lim}} \) denotes the anode limiting current density caused by the limitation of the methanol transport.

Combining Eqs. 4–7, we obtain:

\[
J = \frac{i}{2F} + \frac{i_{\text{OCV}}}{3F} \left( 1 - \frac{i}{i_{\text{lim}}} \right) - J_c
\]  

Eq. (8) indicates that once the equivalent methanol-crossover current density under the open circuit condition, \( i_{\text{OCV}} \), and the limiting current density of methanol, \( i_{\text{lim}} \), are known, the net water transport flux from the cathode to the anode in a DMFC can be in-situ determined by measuring the water removal flux from the cathode, \( J_c \), at a given cell current density.

Generally, the water removal flux \( J_c \) depends on the cathode operating modes: the active or passive operation. Since the passive operation can minimize the water loss from the cathode so as to improve the anode MOR performance and
generate no parasitic power loss by the peripheral devices such as gas blowers/compressors, the passive operation is more favorable for the DMFC operating with neat methanol. However, with a passive cathode, it is rather difficult to determine $J_c$. In order to make it possible to determine $J_c$, we designed the active cathode shown in Fig. 1. As discussed above, if the oxygen flow rate is sufficiently low with the active cathode, the difference in the water flux $J_c$ between the active and passive cathode will be small.

Let us consider how the mass-transfer coefficient, $h_m$, at the cathode GDL/flow field interface changes when the passive cathode is changed to the active one. With the passive cathode, the mass-transfer coefficient of oxygen at the cathode GDL surface can be determined from the Sherwood number:

$$Sh = \frac{h_m L}{D}$$

where $L$ and $D$ represent the characteristic length and the diffusivity of oxygen in the air, respectively. For the gas flow, the Sherwood number can be determined by its analogy to the Nusselt number [25]:

$$\frac{Sh}{Nu} = 1$$

For a heated plate that is oriented vertically, the natural-convection Nusselt number is given by [26]:

$$Nu = 0.68 + \frac{0.67Ra_l^{1/4}}{1 + (0.492/Pr)^{9/16}}$$

where $Ra_l$ is the Rayleigh number ($Ra_l = \frac{2\pi \rho g \Delta T L^4}{\mu^2}$) and $Pr$ is Prandtl number ($Pr = \frac{v}{\alpha}$). With Eqs. 9–11 and the geometric dimensions as well as the physical properties listed in Table 1, we can calculate the mass-transfer coefficient of oxygen, $h_m$, with the passive cathode to be $h_m = 5.21 \times 10^{-3}$ m/s at 30 °C.

With the active cathode, as oxygen is supplied with the parallel flow field at rather low rate (10 sccm), the transport of oxygen through the cathode GDL is dominated by molecular diffusion. Thus, the molar flux of oxygen to the cathode CL, $N_{O_2}$, can be determined from:

$$N_{O_2} = \frac{i}{4F} = \frac{C_{O_2}^{lim} - C_{O_2}^{avg}}{h_m \frac{\delta_{BL}}{D_{BL}} + \frac{\delta_{MPL}}{D_{MPL}}}$$

where $C_{O_2}^{avg}$ and $C_{O_2}^{avg}$ denote, respectively, the average oxygen concentrations in the cathode flow field and in the cathode CL; $\delta_{BL}$, $\delta_{MPL}$, $\delta_{BL}$, and $\delta_{MPL}$ represent the thicknesses of the backing layer (BL) and MPL, and the porosities of the BL and MPL, respectively. When the limiting current caused by the limitation of oxygen transport is reached ($i = \frac{J_c}{4F}$), the oxygen concentration in the cathode CL decreases to zero, i.e., $C_{O_2}^{avg} = 0$. Therefore, Eq. (12) reduces to

$$\frac{C_{O_2}^{lim}}{4F} = \frac{1}{h_m \frac{\delta_{BL}}{D_{BL}} + \frac{\delta_{MPL}}{D_{MPL}}}$$

Eq. (13) indicates that the mass-transfer coefficient of oxygen at the cathode GDL surface, $h_m$, can be determined by measuring the limiting current density of the oxygen once the geometric dimensions and the physical properties of the cathode GDL and MPL are known. As an approximation, we use the value of $\frac{C_{O_2}^{lim}}{4F}$ measured in the H_{2}/O_{2} proton-exchange membrane fuel cell (PEMFC) [28] that was operated at 80 °C and fed with air at a flow rate of 50 sccm to estimate $h_m$. With Eq. (13) and the data from Reference [28], we found $h_m = 6.53 \times 10^{-3}$ m/s, which is very close to $5.21 \times 10^{-3}$ m/s with the passive cathode, although the flow rate and the operating temperature in Ref. [28] were much higher than the values in the present work. Therefore, the water removal flux $J_c$ determined with the active cathode in the present work is approximately the same as that with the passive cathode.

### Table 1 – Geometric dimensions, physical properties and operating conditions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbols</th>
<th>Values</th>
<th>Unit</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristic length</td>
<td>L</td>
<td>$2 \times 10^{-2}$</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>Diffusivity of oxygen in the air at 30 °C</td>
<td>D</td>
<td>$2.15 \times 10^{-5}$</td>
<td>m²/s</td>
<td>[27]</td>
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<tr>
<td>Diffusivity of oxygen in the air at 80 °C</td>
<td>D</td>
<td>$2.84 \times 10^{-5}$</td>
<td>m²/s</td>
<td>[27]</td>
</tr>
<tr>
<td>Gravitational acceleration</td>
<td>g</td>
<td>9.8</td>
<td>m/s²</td>
<td></td>
</tr>
<tr>
<td>Thermal expansion coefficient of air at 30 °C</td>
<td>$\beta$</td>
<td>$3.3 \times 10^{-3}$</td>
<td>1/K</td>
<td></td>
</tr>
<tr>
<td>Temperature difference between the heated wall and the ambient</td>
<td>$T_w - T_u$</td>
<td>6</td>
<td>K</td>
<td>Estimated</td>
</tr>
<tr>
<td>Kinematic viscosity of air at 30 °C</td>
<td>$\nu$</td>
<td>$1.6 \times 10^{-5}$</td>
<td>m²/s</td>
<td></td>
</tr>
<tr>
<td>Thermal diffusivity of air at 30 °C</td>
<td>$\alpha$</td>
<td>$2.25 \times 10^{-5}$</td>
<td>m²/s</td>
<td></td>
</tr>
<tr>
<td>Thickness of the BL</td>
<td>$\delta_{BL}$</td>
<td>$3.5 \times 10^{-4}$</td>
<td>m</td>
<td>[28]</td>
</tr>
<tr>
<td>Thickness of the MPL</td>
<td>$\delta_{MPL}$</td>
<td>$1 \times 10^{-4}$</td>
<td>m</td>
<td>[28]</td>
</tr>
<tr>
<td>Porosity of the BL</td>
<td>$e_{BL}$</td>
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<td></td>
<td>Estimated</td>
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<tr>
<td>Porosity of the MPL</td>
<td>$e_{MPL}$</td>
<td>0.3</td>
<td></td>
<td>Estimated</td>
</tr>
<tr>
<td>Limiting current density caused by oxygen transport</td>
<td>$i_{lim}$</td>
<td>450</td>
<td>mA/cm²</td>
<td>[28]</td>
</tr>
<tr>
<td>Average oxygen concentration in the cathode flow field</td>
<td>$C_{O_2}^{avg}$</td>
<td>2.28</td>
<td>Mol/m³</td>
<td>Calculated from [28]</td>
</tr>
<tr>
<td>Faraday's constant</td>
<td>F</td>
<td>96,485</td>
<td>C/Mol</td>
<td></td>
</tr>
</tbody>
</table>

### 3 Experimental

#### 3.1. Membrane electrode assembly

Commercially available electrodes from Johnson Matthey® were used as the anode and cathode electrodes. On the anode, the CL was made of carbon supported Pt–Ru (50 wt. % Pt 25 wt.

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% Ru) catalysts with a loading of 4.0 mg cm\(^{-2}\). While the cathode electrode consisted of 2.0 mg cm\(^{-2}\) carbon supported Pt (60 wt. % Pt) catalysts. Unless mentioned otherwise, both the anode and cathode GDL were Toray\(^{\circledR}\)-090 carbon papers with a thickness of 275 \(\mu\)m and 15 wt. % polytetrafluoroethylene (PTFE) treatment. Three membranes, Nafion\(^{\circledR}\) 112, 115 and 117, were employed in the present work to study the effect of the membrane thickness. The MEA with an active area of 4.0 cm\(^2\) was fabricated by hot pressing the anode and cathode electrode on the two sides of the membrane at 135 °C and 4.0 MPa for 3 min. More detailed information about the MEA fabrication can be found elsewhere [29].

### 3.2. Single cell fixture

As shown in Fig. 1, the MEA used in this work was sandwiched between an anode and a cathode flow field. The anode flow field was made of perforated 316L stainless steel plates with an open ratio of 47.8% and a thickness of 1.0 mm, while a parallel flow field, having 1.4 mm channel width, 0.9 mm rib width and 1.4 mm depth, was used in the cathode. Unlike the conventional DMFCs, the DMFC used in this work consisted of a 10-mm gas gap, a CO\(_2\) venting hole of 0.01 mm\(^2\), a perforated plate with an open ratio of 15% and a pervaporation membrane with a thickness of 28 \(\mu\)m. The entire cell setup was then held together between an organic glass anode fixture with a 5.0-ml flow field, having 1.4 mm channel width, 0.9 mm rib width and 4.0 MPa for 3 min. More detailed information about the MEA fabrication can be found elsewhere [29].

### 3.3. Determination of the water transport flux from the cathode to the anode

According to Eq. (8), the water transport flux from the cathode to the anode, \(J_w\), can be determined by measuring the values of \(i_{\text{lim}}\), \(i_{\text{OCV}}\) and \(J_c\). In our experiments, the limiting current density caused by the limitation of methanol transport, \(i_{\text{lim}}\), was determined to be the maximum current density during the polarization test because we found that the maximum current density remained unchanged with an increased or a decreased oxygen flow rate. The methanol-crossover flux under the open circuit condition, \(i_{\text{OCV}}\), was measured by the voltammetric method described elsewhere [30]. To conduct this measurement, liquid water, at the flow rate of 1.0 mL min\(^{-1}\), was fed into the cathode to create an inert atmosphere. A positive voltage of 0.85 V was applied on the cathode to ensure that the penetrated methanol from the anode was fully oxidized at the cathode CL. By recoding the current of the circuit I, the limiting current density for methanol crossover, \(i_{\text{lim}}\), can be determined from:

\[
i_{\text{lim}} = \frac{I}{A}
\]

where \(A\) was the area of the MEA. With the measured \(i_{\text{lim}}\), the methanol-crossover current density at the open circuit condition, \(i_{\text{OCV}}\), can be attained by correcting \(i_{\text{lim}}\) with the electro-osmotic effect [30]:

\[
i_{\text{OCV}} = \frac{i_{\text{lim}} \cdot 6nFCT_m}{\ln(1 + 6nFCT_m)}
\]

where \(T_m\) was the mole fraction of methanol in the anode CL, which was determined by the Agilent 6890N gas chromatography equipped with the Agilent DB-WAX 7033 capillary column. To measure the \(J_c\), a water trap filled with Drierite\(^{\circledR}\) (anhydrous CaSO\(_4\)) was connected to the exit for the cathode flow channel to collect the water. The water was collected while maintaining a constant current density for about 6.0–10.0 h. The back pressure of the cathode electrode was kept at the atmosphere pressure to eliminate the influence of back pressure on the water transport.

### 3.4. Electrochemical instrumentation and test conditions

An Arbin BT2000 electrical load interfaced to a computer was employed to control the condition of discharging and record the current–voltage (I–V) curves. For each discharging current point along the I–V curve, a 60 s waiting time was used to obtain the stable voltage. 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. All the performance tests and the measurement of water were performed with feeding 10 sccm 99.95% dry oxygen to the cathode and the cell temperature was control in the range from 30 °C to 60 °C. Prior to the performance test, the MEA was installed in an active cell fixture and activated for 24 h at 60 °C. During the activation period, 2.0 M methanol was fed at 1.0 mL min\(^{-1}\), while dry air was supplied under atmospheric pressure at a flow rate of 100 mL min\(^{-1}\). To ensure that the DMFC was running at neat methanol, the MEA was dried at ambient temperature for 24 h before each test to remove the water that initially existed inside the membrane.

### 4. Results and discussion

#### 4.1. General behavior

Fig. 2 shows the variations in the water production flux at the cathode, the water transport flux from the cathode to the anode, and the water consumption flux for the anode MOR with current density at 30 °C. The MEA used in this measurement consisted of a Nafion 112 membrane and 15 wt. % PTFE-treated carbon papers as the anode and cathode GDL. It is seen from Fig. 2 that the water production flux increases with current density. This behavior can be understood by combining Eqs. 5–7 to give the total water production flux at the cathode, \(J_w\), as:

\[
J_w = J_{\text{ORR}} + J_{\text{MOR}} = \left(1 - \frac{i_{\text{OCV}}}{3Ft_{\text{lim}}} \right) + \frac{i_{\text{OCV}}}{3Ft_{\text{lim}}}
\]

(16)

Since \(i_{\text{OCV}} < i_{\text{lim}}\), the term \(\left(1 - \frac{i_{\text{OCV}}}{3Ft_{\text{lim}}} \right)\) is always positive. As a result, \(J_w\) increases with current density. Meanwhile, it is found from Fig. 2 that the water transport flux from the cathode to the anode is always positive and increases with cell current density, indicating that the net water transport through the membrane with the neat-methanol operation is indeed from the cathode to the anode. The reason why the water transport flux increases with current density is attributed to the fact that the water concentration in the anode CL decreases, whereas it increases at the cathode CL with current density. Moreover, it is interesting to see that the water transport flux from the cathode to the anode is much higher...
than the water consumption flux at the anode at a given current density. Take 90 mA cm\(^{-2}\) as an example, the water transport flux from the cathode is about two times of the water consumption flux for the anode MOR at this current density. This fact suggests that the water transport flux from the cathode to the anode is high enough to meet the minimal requirement of the anode MOR with the MEA and flow field design under the operating conditions.

To gain a deep understanding of the water transport through the membrane under the neat-methanol operation, let us look at the diffusion flux and the EOD flux through the membrane shown in Fig. 3. As expected, both the diffusion and EOD fluxes increase with an increase in the current density. More importantly, it is observed from Fig. 3 that the EOD flux is significantly high. For instance, At 90 mA cm\(^{-2}\), the EOD flux is 1.483 µmol cm\(^{-2}\) s\(^{-1}\), which is 81.6% of the diffusion flux. The fact suggests that a large portion of water driven by diffusion from the cathode to the anode can be moved back to the cathode by EOD, resulting in a smaller net water flux to the anode, as shown in Fig. 3. Hence, the MEA should be designed to create a sufficiently large water concentration gradient across the membrane to offset such a high EOD flux to ensure a sufficiently great water flux for the anode MOR.

4.2. Effect of the anode GDL

The effect of the anode GDL thickness on the water transport flux from the cathode to the anode was investigated by doubling and tripling the single GDL used for the data presented in Section 4.1; the results are shown in Fig. 4. It is noticed that an increase in the anode GDL thickness leads to a decrease in the water transport flux from the cathode to the anode. For instance, at 90 mA cm\(^{-2}\), \(J_c\) with a single anode GDL is 24.4% higher than that with the tripled GDL. The anode GDL affects the water transport flux in two aspects. First, a thicker anode GDL will increase the mass-transfer resistance of methanol through the anode, resulting in a smaller methanol-crossover flux, which tends to reduce the water production flux at the cathode \(\left(J_P\right)\), thereby reducing the water transport flux. Secondly, a thicker anode GDL also increases the mass-transfer resistance of water from the cathode CL to the anode fuel reservoir, preventing the water from being transported to the anode and thus increasing \(J_c\), which also reduces the water transport flux from the cathode to the anode. It should be recognized that a change in the anode structure will affect not only the water transport flux from the cathode to the anode, but also the methanol-crossover flux from the anode to cathode, which in turn will change the water production flux as indicated in Eq. (16). In order to reflect the changes in both \(J\) and \(J_P\) as a result of a change in the anode structure, we introduce a parameter \(J/J_P\). The effect of the anode GDL thickness on the ratio of \(J/J_P\) is shown in Fig. 5. It can be seen that \(J/J_P\) decreases with an increase in the anode GDL thickness. This trend is similar to that observed in Fig. 4; at 90 mA cm\(^{-2}\), the ratio of \(J/J_P\)
is 50.2% with a single anode GDL while it decreases to 42.2% with the tripled GDL. Such a behavior arises from the fact that the change in the water production flux by the permeated methanol at the cathode CL is rather small; the values of $i_{\text{C,OCV}}$ with the single, doubled, and tripled anode GDL are, respectively, 162.1 mA cm$^{-2}$, 154.4 mA cm$^{-2}$ and 148.9 mA cm$^{-2}$. Consequently, the trend of $J/J_p$ remains the same as that of $J$.

The results shown in Figs. 4 and 5 imply that the anode GDL has a great impact on the water transport through the membrane and the MEA with a thinner anode GDL can increase the water transport flux from the cathode to the anode. The effect of the anode GDL thickness on cell performance is presented in Fig. 6. At low current densities, the voltages are almost the same, suggesting the anode GDL thickness has little effect on the methanol-crossover flux and thus the mixed-potential at the cathode. At high current densities, however, the MEA with the doubled anode GDL achieves the highest power density of 44.9 mW cm$^{-2}$. This result is somehow different from what it is expected because the MEA with a single anode GDL is supposed to achieve the best performance based on the fact that the water transport flux from the cathode to the anode is the highest as shown in Fig. 4. Nevertheless, it should be recognized that with the neat-methanol operation, the performance of the anode MOR depends not only on the water transport flux from the cathode but also the water concentration at the anode CL. A thicker anode GDL results in a larger mass-transfer resistance of water, reducing the water loss from the anode CL to the fuel reservoir and thereby increasing the water concentration at the anode CL. Hence, both the doubled and tripled anode GDL yield a better performance than the single anode GDL does. However, it should be pointed out that a too thick GDL can lead to a decrease in the limiting current density caused by the methanol transport, as can be observed from Fig. 6, where the tripled anode GDL results in a smaller limiting current density.

$\textbf{4.3. Effect of the membrane thickness}$

The effect of the membrane thickness on the water transport flux from the cathode to the anode was investigated by changing the membrane from Nafion 112 to 115 and 117, while keeping the same anode GDL and cathode GDL. The results are shown in Fig. 7. It can be seen that the water transport flux through the thicker membrane is much lower than through the thinner one. For example, at 90 mA cm$^{-2}$, the water transport flux from the cathode to the anode is reduced from about 0.361 to 0.286 µmol cm$^{-2}$ s$^{-1}$ when Nafion 112 is replaced with the Nafion 117 membrane. The membrane thickness affects the water transport flux in two ways: i) a thicker membrane reduces the water flux from the cathode to the anode as a result of the increased resistance; and ii) a thicker membrane also reduces the methanol-crossover flux and thus reducing the water production flux, $J_p$. Hence, the water transport flux from the cathode to the anode reduces with an increase in the membrane thickness. The effect of the membrane thickness on the ratio of $J/J_p$ is shown in Fig. 8. It can be seen that $J/J_p$ decreases with an increase in the thickness of the membrane; $J/J_p$ is decreased from 50.2% to 39.5% with the increase in the
membrane thickness from 50 μm to 175 μm. To understand this phenomenon, let us pay attention to the variation in the methanol-crossover flux with the membrane thickness; the values of $i_{c,OCV}$ with Nafion 112, 115 and 117 are 162.1 mA cm$^{-2}$, 152.1 mA cm$^{-2}$ and 144.4 mA cm$^{-2}$, respectively. These results indicate that the change in the water production flux with various membranes is rather small so that $J/J_p$ exhibits a similar trend as $J$. In summary, the water transport flux through the membrane is enhanced by using a thinner membrane.

The effect of the membrane thickness on the cell performance is shown in Fig. 9a. It is noticed that the cell performance decreases with an increase in the membrane thickness; the peak power density decreases from 40.7 mW cm$^{-2}$ to 33.1 mW cm$^{-2}$ when the membrane changes from the Nafion 112 to Nafion 117. One of the reasons leading to the improved performance of the MEA with a thinner membrane is that a thinner membrane can lower the internal resistance, thereby reducing the ohmic loss. Another reason is that a thinner membrane leads to a smaller mass-transfer resistance of water through the membrane, which helps to increase both the water transport flux from the cathode to the anode, $J$, and the water concentration level at the anode $c_{ACL}$. With the increases in both $J$ and $c_{ACL}$, the performance of the anode MOR gets improved. This point is supported by the polarization curves with I-R correction in Fig. 9b, which shows that the MEA with a thinner membrane still yields a better performance than that with a thicker one. The above performance test results suggest that a thin membrane or a membrane with a lower mass-transfer resistance of water is beneficial for the DMFC operating with neat methanol.

### 4.4. Effect of cathode GDL

The effects of the cathode GDL thickness on the water transport through the membrane and the cell performance are investigated by doubling and tripling cathode GDL while keeping the same anode and membrane as well as other operating conditions; the results are shown in Fig. 10. It can be seen in Fig. 10 that an increase in the thickness of the cathode GDL results in a higher water transport flux through the membrane. For instance, the water flux through the membrane with the tripled cathode GDL is about 30% higher than that with a single cathode GDL at 60 mA cm$^{-2}$. An increase in the thickness of the cathode GDL can increase the mass-transfer resistance of water through the cathode, limiting the removal of water from the cathode and thus leading to a smaller $J_C$. Therefore, the water transport flux through the membrane, $J$, is enhanced with a thicker cathode GDL installed in the cathode as indicated in Eq. (4). We now turn our attention to the effect of the cathode GDL on the ratio of $J/J_p$, which is presented in Fig. 11. It can be found that the ratio of $J/J_p$ increases with an increase in the thickness of the cathode GDL. This trend is similar to that of the water transport flux from the cathode to the anode because the total generation of water at the cathode, $J_p$, is the same for different cathode structures. The above results indicate that thickening the cathode GDL significantly increase the mass-transfer resistance of the cathode GDL, thus facilitating water transport from the cathode to the anode.
The effect of the cathode GDL on the cell performance of a DMFC in the neat-methanol operation is shown in Fig. 12. It is seen that replacing the single cathode GDL with the doubled one leads to an improved cell performance; but tripling the cathode GDL in turn lowers the cell performance. The DMFC with the doubled cathode GDL exhibits the best performance with a peak power density of 46.5 mW cm$^{-2}$. Thickening the cathode GDL can lead to an increased mass-transfer resistance, which results in a higher water transport flux through the membrane as shown in Fig. 10 and helps build up the water within the MEA to increase the anode water concentration level. These increases in both $J$ and $C_{ACL}$ result in an improvement in the anode MOR and thus the cell performance of the DMFC. Nevertheless, a too thick cathode GDL will render a too large mass-transfer resistance of oxygen, thereby aggravating the oxygen concentration loss of the ORR at the cathode. Hence, the cell performance becomes poorer when the DMFC equipped with the tripled cathode GDL. In summary, in general increasing the mass-transfer resistance of the cathode GDL can reduce the anode water concentration loss, but the mass-transfer resistance should not be too high to avoid severe oxygen concentration polarization at the cathode.

4.5. Effect of cell temperature

To investigate the effect of temperature on the water transport flux through the membrane, experiments were conducted with the MEA consisting of a Nafion 112 membrane, an anode GDL and a cathode GDL at three different temperatures (i.e., 30, 45, 60 °C); the results are shown in Fig. 13. It is seen that the water transport flux from the cathode to the anode increases substantially with temperature: when the cell temperature rises from 30 to 60 °C, the $J$ increases from 0.292 to 0.663 μmol cm$^{-2}$ s$^{-1}$ at the current density of 60 mA cm$^{-2}$. Such an increase in the water transport flux through the membrane can be attributed to a higher water production flux caused by the permeated methanol at the cathode and...
a bigger effective diffusion coefficient of water through the membrane at elevated temperatures. It should be noted that as the performance of the anode MOR may be limited by the water transport flux from the cathode to the anode in the neat-methanol operation, the enhanced transport of water to the anode at elevated temperature is favorable for improving the cell performance.

We now present the results of cell performance tests at various cell temperatures in Fig. 14. It is found that the performance of the DMFC operating with neat methanol improves significantly with an increase in the cell temperature; the peak power density at 60 °C reaches 69.5 mW cm\(^{-2}\), nearly 70.7% higher than that at 30 °C. The improved performance at a higher operating temperature is mainly attributed to the reductions in the activation losses of the anode MOR and cathode ORR as well as the decrease in the mass transport losses associated with methanol, water and oxygen.

5. Conclusions

Operating the DMFC with neat methanol is beneficial to the increases in the specific energy of the fuel cell system and the extension of its runtime. To achieve the neat-methanol operation, sufficient water needs to be transported from the cathode through the membrane to the anode to compensate the anode MOR. Thus, it is critical to gain a deeper understanding of the mechanism of water transport across the membrane in this type of fuel cell. In this work, we have demonstrated that the water transport flux from the cathode to the anode with the neat-methanol operation can be in-situ determined by measuring the water removal flux from the cathode. With this method, we experimentally investigated the water transport flux through the membrane in a DMFC with various MEA designs and under different operating conditions. Salient findings and conclusions are summarized as follows:

1. In the neat-methanol operation, the net water transport through the membrane is due to diffusion from the cathode to the anode and the offset flux by electro-osmotic drag in the opposite direction. With a typical MEA and flow filed design, the diffusion flux is higher than the EOD flux, resulting in a net water flux from the cathode to the anode. It is also found that the water transport flux through the membrane increases with the current density due to the enhanced diffusion flux at higher current densities.

2. Increasing the thickness of the anode GDL results in a smaller water transport flux from the cathode to the anode due to the decrease in the water production flux by the permeated methanol and the increase in the mass-transfer resistance of water through the anode GDL. Nevertheless, the MEA with a thicker anode GDL can increase the water concentration at the anode CL, thus slightly improving the cell performance.

3. It is found that a thin membrane (such as Nafion 112) can enhance the water transport from the cathode to the anode and increase the water concentration at the anode CL owing to its low mass-transfer resistance of water. Therefore, a thin membrane is favorable for the DMFC operating with neat methanol.

4. The increase in the thickness of the cathode GDL helps built up the water within the cathode CL such that more water is driven from the cathode to the anode by diffusion to reduce the water concentration loss of the anode MOR. However, the mass-transfer resistance should not be too high to avoid severe oxygen concentration loss of the cathode ORR.

5. The water transport flux through the membrane is markedly increased with the operating temperature because of a larger production flux of water at the cathode and an increased effective diffusivity of water through the membrane at elevated temperature. In the meantime, it is found that the cell performance is boosted at a higher operating temperature mainly due to the improved kinetics of MOR and ORR as well as the enhanced transport of methanol, water and oxygen.

It should be mentioned that although the above conclusions were made with the active cathode, they are also applicable to passive DMFCs due to the fact that the oxygen flow rate in the active cathode was rather small.

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