Effect of anode micro-porous layer on species crossover through the membrane of the liquid-feed direct methanol fuel cells

Xiao-Yue Li, Wei-Wei Yang, Ya-Ling He, Tian-Shou Zhao, Zhi-Guo Qu

1. Introduction

The direct methanol fuel cell (DMFC) has been regarded as a leading contender to compete with the conventional batteries for power supply due to its advantages of simple structure, fast refueling and high energy density of liquid fuel. Although significant progress has been made over the past decade, the performance of the DMFC currently has not reached the expected level for powering the most energy-hungry electronic devices [1–5].

Technically, besides the sluggish kinetics of methanol oxidation reaction at the DMFC anode [6], the permeation of methanol through the membrane to the cathode, known as methanol crossover, is another barrier that limits the cell performance [7]. Methanol crossover not only causes the cathode mixed potential, decreasing the cell voltage, but also leads to the waste of fuel, lowering the fuel efficiency. As a result, the rate of methanol crossover has to be suppressed to minimize its detrimental impact. Conventionally, to alleviate the problem of methanol crossover, a diluted liquid methanol solution has to be fed to the DMFC anode such that the cell performance can be maximized. Although it can yield decent cell performance, the use of highly diluted methanol solution drastically reduces the specific energy of the fuel cell system. In addition, it also results in high rate of water crossover to the cathode, which further causes the two problems. First, the high rate of water crossover causes water loss from the anode and thus making up water to the anode is required. Second, it exacerbates the problem of cathode flooding, deteriorating the cell performance and operating stability. Therefore, it is also critical to suppress the rate of water crossover. To achieve these, it is essential to gain a deep understanding of the mechanisms of methanol and water transport through the membrane electrode assembly (MEA) and their dependence on the designs of the MEA.

During the past decade, great efforts have been paid to investigating the effects of operating conditions [8–10] and the structure designs of the MEA [11–17] on methanol crossover. To reduce methanol crossover, the mass transport resistance of methanol through the anode has to be increased by properly designing the anode gas diffusion layer, such as making the anode diffusion layer more hydrophobic, increasing the diffusion layer thickness and reducing the diffusion layer permeability [11–15]. In addition, it is proven that coating a fine micro-porous layer (MPL) to the anode diffusion layer also plays an important role in controlling methanol transport through the anode. For an example, the study by Shao et al. [16] indicated that the MPL with smaller carbon powders with higher surface area, such as Black Pearl 2000, could greatly enhance the mass transport of methanol, thus helping limit the rate of methanol crossover.

In addition to the study of methanol crossover, the problem of water crossover [17–31] has also been studied extensively. Xu and...
Zhao [20] proposed an approach that enables the in-situ measurement of water crossover in a liquid-feed DMFC and investigated the mechanisms of water crossover and its dependence on various design variables of the MEA and operating conditions. It was indicated that the rate of water crossover was dominated by water diffusion through the membrane. The effects of the cathode backing layer and cathode MPL on the transport behaviors of both water and oxygen were also investigated [21,22]. The results suggested that the optimal design of the cathode diffusion layer is crucial to suppress water crossover. In addition, novel designs of the MEA were proposed to achieve low rate of water crossover in the DMFCs [23–27]. The key idea in those designs is built up a high cathode liquid pressure to enhance the water backflow to the anode by increasing the hydrophobic level and reducing the pore size of the cathode MPL, such that the total rate of water crossover can be reduced. Relatively, few [28–31] revealed the role of the anode porous layers in reducing water crossover. Liu and Wang [28] examined the effects of the design variables of the anode MPL on water crossover. It was shown that as compared with a hydrophilic anode MPL, a hydrophobic anode MPL could lead to a significant reduction in the rate of water crossover. A similar study was also performed by Li et al. [29]. Recently, Wu et al. [31] experimentally investigated the effects of the designs of the anode back layer and MPL on water crossover. The results indicated that increasing the PTFE loading in the backing layer and introducing a crack-free MPL could greatly decrease the rate of water crossover.

Our literature review indicated that most previous studies focused on either exploring the effects of anode porous layers on the rate methanol crossover or investigating the effects of the cathode porous layers on the rate of water crossover. Relatively, few examined the influence of the anode porous layers on both the rates of methanol and water crossover. Especially, the roles of the anode MPL in simultaneously managing methanol and water transport through the MEA are less understood. In this work, we numerically explore the dependence of the rates of methanol and water crossover on the design parameters of the anode MPL in a liquid-feed DMFC.

2. Mathematical model

As illustrated in Fig. 1, the 2-D domain consists of an anode diffusion layer (ADL), an anode micro-porous layer (AMPL), an anode catalyst layer (ACL), a membrane (MEM), a cathode catalyst layer (CCL), a cathode micro-porous layer (CMPL) and a cathode diffusion layer (CDL), representing a typical geometry of a membrane electrode assembly, sandwiched between two parallel flow field plates. In view of the symmetrical conditions of the model geometry, only a half-rib width and a half-channel width are considered in present model to save the computing cost. Also, since liquid and gas phases coexist in the constituent components of the DMFC under typical operating conditions, a two-phase mass transport model as outlined below, is employed to investigate the methanol and water transport processes through the DMFC. Details on model development can be found elsewhere [22,32–35].

2.1. Governing equations

2.1.1. Anode porous region (From ADL to ACL)

Referring to Fig. 1, on the DMFC anode, methanol supplied in the anode channel transfers through the diffusion medium to the anode CL where part of methanol is electrochemically oxidized to form gas carbon dioxide and current. The produced carbon dioxide will transfer back through the diffusion layer to the flow channel. The two-phase mass transport behaviors in the anode porous region are related to four major variables, including anode liquid pressure \( (p_{l,a}) \), anode gas pressure \( (p_{g,a}) \), the liquid methanol concentration \( (C_{M,L}) \), and the methanol vapor concentration \( (C_{M,V}) \). The corresponding governing equations for the steady-state, isothermal two-phase mass transport in the porous anode the DMFC are presented below

\[
\nabla \cdot \left( \frac{-K_{l,a}}{\mu_l/\rho_l} \nabla p_{l,a} \right) = \dot{m}_{l,a} \\
\n\nabla \cdot \left( \frac{-K_{g,a}}{\mu_g/\rho_g} \nabla p_{g,a} \right) = \dot{m}_{g,a} \\
\n\n\nabla \cdot \left[ \left( -\frac{K_{l,a}}{\mu_l} \nabla p_{l,a} \right) C_{M,L} \right] = \nabla \cdot \left( D_{M,L}^{\text{eff}} \nabla C_{M,L} \right) + \dot{R}_{M,L} \\
\n\n\n\nabla \cdot \left[ \left( -\frac{K_{g,a}}{\mu_g} \nabla p_{g,a} \right) C_{M,V} \right] = \nabla \cdot \left( D_{M,V}^{\text{eff}} \nabla C_{M,V} \right) + \dot{R}_{M,V} 
\]

Note that the difference between liquid and gas pressures is balanced by the capillary pressure. In a hydrophobic porous medium, the capillary pressure is given by [36]

\[
p_c = p_g - p_l = \sigma \cos \theta / \mathcal{L} (1.417s - 2.120s^2 + 1.263s^3)
\]

where \( s \) is the liquid saturation, representing the volume fraction of liquid water filled pores in a porous medium.

2.1.2. Cathode porous region (From CDL to CCL)

On the DMFC cathode, oxygen transfers from the channel through the diffusion medium to the catalyst layer and is reduced electrochemically to form water. Some of the produced water, in
the liquid phase, transfers back through the diffusion layer to the flow channel. In cathode porous region, four key variables are considered, including liquid phase pressure in the cathode \((p_l,c)\), gas phase pressure in the cathode \((p_g,c)\), the concentration of gas oxygen in the cathode \((C_{O_2,g})\), and the concentration of water vapor in the cathode \((C_{WV,g,c})\). The corresponding governing equations for the steady-state, isothermal two-phase mass transport in the porous cathode can be, respectively, written as

\[
\nabla \cdot \left( - \frac{K_{fq}}{l_i} \nabla p_{l,c} \right) = m_{l,c}
\]

(6)

\[
\nabla \cdot \left( - \frac{K_{fq}}{l_g} \nabla p_{g,c} \right) = m_{g,c}
\]

(7)

\[
\nabla \cdot \left( - \frac{K_{fq}}{l_g} \nabla C_{O_2,g} \right) = \nabla \cdot \left( D_{O_2,g} \nabla C_{O_2,g} \right) + \dot{R}_{O_2}
\]

(8)

\[
\nabla \cdot \left( - \frac{K_{fq}}{l_g} \nabla C_{WV,g,c} \right) = \nabla \cdot \left( - D_{WV,g} \nabla C_{WV,g,c} \right) + \dot{R}_{WV}
\]

(9)

2.1.3. Electrolyte regions (ACL to CCL)

In the polymer electrolyte of the CL and the membrane, transport of liquid phases (dissolved methanol and water) needs to be considered only, as the membrane is usually regarded as a gas insulator. Two variables including the dissolved methanol concentration \((C_{M,N})\) and the dissolved water concentration \((C_{W,N})\) are involved. Generally, both the mass transports of the dissolved methanol and the dissolved water through the membrane depend on the electroosmotic drag due to the proton migration, the molecular diffusion due to the water concentration gradient, and the hydraulic convection due to the hydraulic pressure gradient. The flux of the dissolved methanol transported through the membrane and the conservation of the dissolved methanol in the membrane can, respectively, be written as

\[
N_M = -D_{M}^{eff} \nabla C_{M,N} + n_d M \frac{1}{F} (\frac{K}{l_f} \nabla p_l) C_{M,N} \nabla N_M = 0
\]

(10)

And, the flux of the dissolved water transport through the membrane and the conservation of dissolved water in the membrane can be written as

\[
N_W = -D_{W,N} \nabla C_{W,N} + n_w M \frac{1}{F} \frac{\rho_l}{M_{W}} K_{fq} \nabla p_l \nabla N_W = 0
\]

(11)

Usually, the concentration of dissolved water \((C_{W,N})\) in the membrane is valued by the term of water content in the membrane \((\lambda)\), which is given by

\[
\lambda = \frac{C_{W,N}}{C_{fixed}}
\]

(12)

with \(C_{fixed}\) denoting the concentration of the fixed charge sites in the membrane.

In the CLs, it is assumed that the dissolved water in the polymer electrolyte is in thermodynamic equilibrium with the liquid water and water vapor saturated gas in the pores of the CLs. As such, the water content in the polymer electrolyte of the CLs can be given by

\[
\lambda_{CL} = (1-s)\lambda_{eq}^{WV} + 5s\lambda_{eq}^{WV}
\]

(13)

with \(\lambda_{eq}^{WV}\) and \(\lambda_{eq}^{WV}\) representing the equilibrium water contents when the polymer electrolyte is in phase equilibrium with the water vapor saturated gas [21] and liquid water, respectively.

All above governing equations describe the two-phase mass transport in the porous regions as well as the membrane of a DMFC. To make those governing equations closed, some constitutive correlations and definitions are required, which are listed in Table 1.

2.2. Boundary conditions

1. At the channel/diffusion layer interface

The interfaces between the diffusion layers and the channels, as indicated in Fig. 1, represent the inlets of the reactant supply and outlets of the product removal. At these interface, the value of the variables is specified to be the inlet/outlet conditions as listed in Table 2.

2. At the rib/diffusion layer interface

Since the rib collector is impermeable to mass and species, the fluxes of mass/species normal to this boundary are set to be zero.

3. At the midlines of the channel and rib

Considering the symmetrical conditions at the middle lines of the channel and the rib, the gradients of all the variables normal to this boundary are set to be zero.

4. At the internal interface between adjacent functional layers

The conditions at all the internal interfaces between the functional layers are decided based on the principle that the continuity and mass/species flux balance are required at each interface to satisfy the general mass and species conservation.

2.3. Reaction kinetics

At the anode, simply, a Tafel-like expression is employed to indicate the reaction kinetics of the methanol oxidation reaction (MOR). The volumetric current density of the anode MOR can be written as

\[
j_a = A_s a_0^{ref} \left( \frac{C_M}{C_M^{ref}} \right)^\gamma \exp \left( \alpha_1 \frac{RT}{h} \eta_a \right)
\]

(14)

where \(\gamma\) is the reaction order, which is assumed to be zero when methanol concentration is higher than a reference value [36]. Otherwise, the first-order reaction is specified.

As for the oxygen reduction reaction (ORR) at the cathode, a modified first-order Tafel-like kinetics that takes into account the influence of liquid water and the agglomeration in the cathode CL is applied [37], which gives

\[
j_c = (1-s) A_s a_0^{ref} \left( \frac{C_{O_2}}{C_{O_2}^{ref}} \right) \exp \left( \alpha_2 \frac{RT}{h} \eta_c \right) E
\]

(15)

Note that in Eq. (15), the term \((1-s)\) is a correction factor in view of the adverse impact of the liquid water in the cathode CL, and the term \(E\) is the correction factor in consideration of the addition mass transport resistance of oxygen in the agglomerate.

2.4. Cell current density and parasitic current density

The protons and electrons generated by the anode MOR move to the cathode through the membrane and the external circuit,
respectively. Simply, the mean cell current density can be calculated by

$$I_{\text{cell}} = \frac{\int \int j_c \, dx \, dy}{0.5 w_c + 0.5 w_r} \quad \text{(16)}$$

At the cathode, it is assumed that both the cell current produced by the anode MOR and the parasitic current of the oxidation of the permeated methanol in the cathode CL, which represents the equivalent current of methanol crossover, are completely consumed by the cathode ORR. Mathematically, it can be written as

$$I_{\text{cell}} + I_{\text{para}} = \frac{\int \int j_c \, dx \, dy}{0.5 w_c + 0.5 w_r} \quad \text{(17)}$$

where $I_{\text{para}}$ represents the equivalent current of the methanol crossover, which is given by

$$I_{\text{para}} = \frac{6F}{0.5 w_c + 0.5 w_r} \int N_M \, dx \quad \text{(18)}$$

with $N_M$ representing the molar flux of methanol crossover as given in Eq. (10).

### 2.5. Water crossover

As aforementioned, the water transport through the membrane depends on diffusion, electroosmotic drag and convection. The water diffusion flux and the electroosmotic drag (EOD) flux are, respectively, given by

$$N_{W, \text{diff}} = \int \left(- \frac{D_W}{R} \frac{\partial C_{W,N}}{\partial y} \right) \, dx \quad \text{mol m}^{-2} \text{s}^{-1}$$

$$0.5 w_c + 0.5 w_r$$

and

$$N_{W, \text{EOD}} = \int j_w \, dx \quad \text{mol m}^{-2} \text{s}^{-1}$$

$$0.5 w_c + 0.5 w_r$$
The anode MPL thickness is varied from 20 to 80 μm with other parameters remaining unchanged. Fig. 2a shows the distributions of the anode liquid saturation for different MPL thicknesses at the current density of 100 mA cm$^{-2}$. As can be seen, an increase in the MPL thickness leads to a decrease in the mean liquid saturation level in the anode CL because both the resistance for liquid water transported from the channel to the anode CL and the resistance for gas CO$_2$ transported from the anode CL to the channel are enhanced. The reduction in the liquid saturation in the anode CL lowers the water content in the membrane and its gradient across the membrane as indicated in Fig. 2b, thus weakening the water diffusion through the membrane. The variations of water crossover flux due to each mechanism and the total rate of water crossover with the anode MPL thickness are displayed in Fig. 3. As can be seen in the figure, the diffusion flux of water crossover is reduced from 3.26 to 2.54 μmol cm$^{-2}$ s$^{-1}$ when the anode MPL thickness is increased from 20 to 80 μm. With respect to the EOD flux and backflow, they are almost unchanged. Overall, the total rate of water crossover is decreased by 13% with increasing the anode MPL thickness from 20 to 80 μm. Generally, it can be concluded that water crossover can be suppressed by thickening the anode MPL, which can be achieved by increasing the carbon material loading in the MPL [31]. Besides, the effects of the anode MPL thickness on the liquid methanol concentration distribution across the porous anode and the membrane at the current density of 100 mA cm$^{-2}$ are shown in Fig. 4. It is clear that the concentration of liquid methanol in the anode CL decreases with the increase in the anode MPL thickness due to the increased mass transport resistance of methanol. The decrease in the methanol concentration of the anode CL consequently lowers the rate of methanol crossover. As indicated in Fig. 5, at the current density of 100 mA cm$^{-2}$, the rate of methanol crossover is reduced by 58% with increasing the anode MPL thickness from 20 to 80 μm.

### 3. Results and discussion

The above-mentioned governing equations subjected to specific boundary conditions, along with the constitutive correlations as listed in Table 1, the geometric and operating parameters as listed in Table 2, and the physicochemical properties as listed in Table 3, are numerically solved with a home-written code basing on the SIMPLE algorithm with Finite-Volume-Method. Details on the model validation can be found elsewhere [35]. In the following, we examine the effects of the structural properties of the anode MPL (i.e., thickness, permeability and hydrophobicity) on both methanol and water transport across the MEA in detail.

#### 3.1. Effect of anode MPL thickness

In this section, the effects of the anode MPL thickness on both methanol and water transport through the MEA are investigated.

### Table 3

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbols</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity, permeability</td>
<td>ADL</td>
<td>$s_{adl}$, $K_{adl}$</td>
<td>$0.75, 1.0 \times 10^{-12}$</td>
</tr>
<tr>
<td>AMPL</td>
<td>$s_{ampl}$, $K_{ampl}$</td>
<td>$0.35, 2.0 \times 10^{-13}$</td>
<td>m$^{-2}$</td>
</tr>
<tr>
<td>ACL</td>
<td>$s_{acl}$, $K_{acl}$</td>
<td>$0.35, 5.0 \times 10^{-14}$</td>
<td>m$^{-2}$</td>
</tr>
<tr>
<td>MEM</td>
<td>$s_{mem}$, $K_{mem}$</td>
<td>$0.3, 2.0 \times 10^{-18}$</td>
<td>m$^{-2}$</td>
</tr>
<tr>
<td>CCL</td>
<td>$s_{ccl}$, $K_{ccl}$</td>
<td>$0.35, 5.0 \times 10^{-14}$</td>
<td>m$^{-2}$</td>
</tr>
<tr>
<td>CMPL</td>
<td>$s_{cmpl}$, $K_{cmpl}$</td>
<td>$0.35, 2.0 \times 10^{-13}$</td>
<td>m$^{-2}$</td>
</tr>
<tr>
<td>Diffusivities</td>
<td>MeOH in water</td>
<td>$D_{MeOH}$</td>
<td>$10^{-5} \times 4,653 \times 3.18 \times 10^{-10}$</td>
</tr>
<tr>
<td>MeOH in Nafion</td>
<td>$D_{MeOH,N}$</td>
<td>$4.9 \times 10^{-15} \times 3.18 \times 10^{-10}$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Methanol vapor</td>
<td>$D_{MeOH,vap}$</td>
<td>$-6.954 \times 10^{-6} + 4.9586 \times 10^{-10} + 9.4919 \times 10^{-11} + 7 \times 10^{-12}$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>O$_2$ in gas</td>
<td>$D_{O_2,g}$</td>
<td>$1.775 \times 10^{-5} + 0.1837$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Water vapor</td>
<td>$D_{Water,vap}$</td>
<td>$2.56 \times 10^{-5} + 2 \times 10^{-14}$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>Viscosity of liquid and gas phases</td>
<td>$\mu_W, \mu_L$</td>
<td>$2.03 \times 10^{-3}, 4.05 \times 10^{-4}$</td>
<td>kg m$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>Electroosmot drag coefficients</td>
<td>$n_{H_2O}, \nu$</td>
<td>$25.2/22$</td>
<td>kg m$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>Condensation rate constant for water</td>
<td>$k_l$</td>
<td>$5.0 \times 10^{-3}$</td>
<td>mol atm$^{-1}$ s$^{-1}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Evaporation rate constant for water</td>
<td>$k_d$</td>
<td>$5.0 \times 10^{-3}$</td>
<td>atm$^{-1}$ s$^{-1}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Henry law constant for methanol</td>
<td>$K_{g,n}$</td>
<td>$0.096 \times 1.0451(T + 273)$</td>
<td>atm$^{-1}$ s$^{-1}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Interfacial transfer rate constant for methanol</td>
<td>$h_{in}$</td>
<td>$0.001$</td>
<td>m$^{-1}$</td>
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<td>Specific interfacial area between liquid and gas</td>
<td>$A_{in}$</td>
<td>$1.0 \times 10^{5}$</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>The saturation pressure of water vapor</td>
<td>$P_{sat,Water}$</td>
<td>$2.1974 + 0.2095(T + 273) - 9.1837 \times 10^{-3}(T + 273)^2 + 1.4454 \times 10^{-5}(T + 273)^3$</td>
<td>atm</td>
</tr>
<tr>
<td>The saturation pressure of methanol vapor</td>
<td>$P_{sat,MeOH}$</td>
<td>$K_{methanol}$</td>
<td>atm</td>
</tr>
<tr>
<td>Transfer coefficient of anode</td>
<td>$\alpha_a$</td>
<td>$0.5$</td>
<td>atm$^{-1}$ s$^{-1}$ cm$^{-3}$</td>
</tr>
<tr>
<td>Transfer coefficient of cathode</td>
<td>$\alpha_c$</td>
<td>$1.0 \times 10^{5}$</td>
<td>A m$^{-3}$</td>
</tr>
<tr>
<td>Anode exchange current density</td>
<td>$A_{ex,MeOH}$</td>
<td>$1.14 \times 10^{3}$</td>
<td>A m$^{-3}$</td>
</tr>
<tr>
<td>Cathode exchange current density</td>
<td>$A_{ex,Water}$</td>
<td>$100$</td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>Cathode reference concentration</td>
<td>$C_{ref,Water}$</td>
<td>$0.52$</td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>Surface tension</td>
<td>$\sigma$</td>
<td>$0.0644$</td>
<td>N m$^{-1}$</td>
</tr>
<tr>
<td>Fixed charge concentration in the membrane</td>
<td>$C_{fixed}$</td>
<td>$1200$</td>
<td>mol m$^{-3}$</td>
</tr>
</tbody>
</table>
In summary, it is indicated that both the rates of water and methanol crossover can be simultaneously limited by increasing the anode MPL thickness.

3.2. Effect of anode MPL permeability

In this section, the effect of anode MPL permeability is examined by varying its value from $4.0 \times 10^{-13}$ to $0.2 \times 10^{-13}$ m$^2$ with other parameters remaining unchanged.

Fig. 6a shows the profiles of anode liquid saturation with different anode MPL permeabilities at the current density of 100 mA cm$^{-2}$. As shown in the figure, on average, the liquid saturation in the anode CL decreases from about 0.4 to about 0.25 when the anode MPL permeability is decreased from $4.0 \times 10^{-13}$ to $0.2 \times 10^{-13}$ m$^2$ because of the increased mass transport resistance of liquid water from the channel to the anode CL. The decreased liquid saturation in the anode CL inevitably lowers the mean water content in the membrane and its gradient across the membrane. As indicated in Fig. 6b, with decreasing the anode MPL permeability from $4.0 \times 10^{-13}$ to $0.2 \times 10^{-13}$ m$^2$, the water content in the membrane near the anode CL lowers from about 14.9 to about 13, while the water content in the membrane near the cathode CL remains almost unchanged. Consequently, the water content difference on both sides of the membrane is lowered from about 3.5 to about 2.1.

Fig. 2. Effects of anode MPL thickness on distributions of (a) anode liquid saturation and (b) water content in the membrane.

Fig. 3. Variations of water crossover with anode MPL thickness.

Fig. 4. Effects of anode MPL thickness on distributions of liquid methanol concentration.

Fig. 5. Variations of methanol crossover with anode MPL thickness at different current densities.
indicating a large reduction in the water content gradient across the membrane. The decrease in the water content and its gradient across the membrane reduces both the diffusion flux of water crossover and the EOD flux of water crossover. As clearly shown in Fig. 7, the diffusion flux of water crossover decreases by a factor of almost 2 when the anode MPL permeability is changed from $4.0 \times 10^{-13}$ to $0.2 \times 10^{-13}$ m$^2$. The electroosmotic drag flux is also slightly decreased with reducing the anode MPL permeability. Totally, the overall rate of water crossover is lowered by 42% with reducing the anode MPL permeability from $4.0 \times 10^{-13}$ to $0.2 \times 10^{-13}$ m$^2$. The result indicates that the rate of water crossover can be effectively suppressed by lowering the anode MPL permeability, which can be achieved by reducing the mean pore size of the anode MPL and avoiding the formation of mud cracks in the anode MPL.

Fig. 8 also presents the profiles of liquid methanol concentration across the MEA for different anode MPL permeabilities. Clearly, the methanol concentration in the anode CL is decreased with lowering the anode MPL permeability. This is due to the reason that with the decrease in the anode MPL permeability, the mean liquid saturation in the anode porous region is lowered as indicated in Fig. 6a, thus decreasing the effective diffusion coefficient of methanol through the anode porous region. As a result, the mean methanol concentration in the anode CL is decreased due to the increased overall mass transport resistance of methanol from channel to the anode CL. As can be seen in the figure, when the
The anode MPL permeability is lowered from $4.0 \times 10^{-13}$ to $0.5 \times 10^{-13}$ m², the liquid methanol concentration at the anode CL/membrane interface decreases from about 313 to 86 mol m⁻³. The decrease of the methanol concentration in the anode CL consequently lowers the rate of methanol crossover. As shown in Fig. 9, the rate of methanol crossover is greatly reduced with decreasing the anode MPL permeability. For example, at the current density of 100 mA cm⁻², the parasitic current density decreases by a factor of almost 4.7 when the anode MPL permeability is decreased from $4.0 \times 10^{-13}$ to $0.5 \times 10^{-13}$ m².

In summary, it is indicated that decreasing the anode MPL permeability by reducing the mean pore diameter or avoiding the formation of relatively large cracks in fabricating the MPL can help suppress both the rates of water and methanol crossover, thus benefiting the improvement of the cell performance.

3.3. Effect of anode MPL contact angle

In this section, we examine the effect of anode MPL contact angle on water and methanol transport through the MEA by varying its value from 110° to 150°. Fig. 10a shows the distributions of anode liquid saturation for different anode MPL contact angles at the current density of 100 mA cm⁻². It is found that with the increase in the anode MPL contact angle, the liquid saturation in the anode MPL is slightly reduced whereas the liquid saturation in the anode CL as well as the anode DL is almost unchanged. Consequently, the water content the rate of methanol crossover is greatly reduced with decreasing the anode MPL permeability. For example, at the current density of 100 mA cm⁻², the parasitic current density decreases by a factor of almost 4.7 when the anode MPL permeability is decreased from $4.0 \times 10^{-13}$ to $0.5 \times 10^{-13}$ m².

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the rate of methanol crossover is greatly reduced with decreasing the anode MPL permeability. For example, at the current density of 100 mA cm⁻², the parasitic current density decreases by a factor of almost 4.7 when the anode MPL permeability is decreased from $4.0 \times 10^{-13}$ to $0.5 \times 10^{-13}$ m².

In summary, it is indicated that decreasing the anode MPL permeability by reducing the mean pore diameter or avoiding the formation of relatively large cracks in fabricating the MPL can help suppress both the rates of water and methanol crossover, thus benefiting the improvement of the cell performance.

3.3. Effect of anode MPL contact angle

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In summary, it is indicated that decreasing the anode MPL permeability by reducing the mean pore diameter or avoiding the formation of relatively large cracks in fabricating the MPL can help suppress both the rates of water and methanol crossover, thus benefiting the improvement of the cell performance.
level and its gradient across the membrane are unchanged with the change of anode MPL contact angle as indicated in Fig. 10b. Accordingly, as shown in Fig. 11, the water fluxes by all three mechanisms remain the same for different anode MPL contact angles. As the value of contact angle represents the hydrophobic level of the MPL which is mainly decided by the PTFE loading in the MPL. Thus, it is suggested that the PTFE loading in the anode MPL exhibit little impact on water crossover. This result is in well agreement with the experimental results in Ref. [31].

Additionally, Fig. 12 shows the profiles of liquid methanol concentration across the MEA for different anode MPL contact angles at the current density of 100 mA cm–2. Clearly, the liquid methanol concentration in the anode CL is reduced with increasing the anode MPL contact angle as the result of the decreased liquid saturation in the anode MPL. Correspondingly, the variations of methanol crossover with anode MPL contact angle at different current densities are plotted in Fig. 13. As indicated in the figure, the parasitic current density is significantly decreased with increasing the contact angle from 100° to 150°, despite that the rate of water crossover is nearly independent on the anode MPL contact angle.

In summary, it is shown that although enhancing the anode MPL hydrophobicity exhibits little impact on water crossover, it can help alleviate the problem of methanol crossover.

4. Conclusion

In this work, a two-phase mass transport model is developed to investigate the effects of designing variables of the anode MPL on both methanol and water transport through the MEA of the DMFC. The salient findings are as follows:

1. Increasing the anode MPL thickness by improving the carbon loadings in the MPL can limit both the rates of water and methanol crossover because of the increased mass transport resistance.
2. Decreasing anode MPL permeability can help reduce the diffusion flux and electroosmotic drag flux of water crossover as a result of the decreased water content and its gradient across the membrane, thus suppressing the total rate of water crossover. Also, it is also shown that the rate of methanol crossover can also be greatly limited by decreasing in the anode MPL permeability.
3. The increase in the anode MPL contact angle can significantly reduce the rate of methanol crossover, whereas it exhibits little impact on water crossover.

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References


Nomenclature

Ae: specific surface area of the active reaction sites, m2 m–3
C: molar concentration, mol m–3
D: diffusivity, m2 s–1
F: Faraday constant, 96,478 C mol–1
ιc: cell current density, A m–2
ιpar: parasitic current resulting from methanol crossover, A m–2
ιc: exchange current density, A m–2
ιa: anode current density, A m–2
\( j_c \): cathode current density, \( \text{A m}^{-2} \)
\( k_r \): relative permeability
\( K \): permeability of porous material, \( \text{m}^2 \)
\( m \): source term in mass conservation equation, \( \text{kg m}^{-3} \text{s}^{-1} \)
\( M \): molecular weight, \( \text{kg mol}^{-1} \)
\( N \): mol flux, \( \text{mol m}^{-2} \text{s}^{-1} \)
\( n_e \): electroosmotic drag coefficient
\( p_c \): capillary pressure, \( \text{Pa} \)
\( p_g \): gas phase pressure, \( \text{Pa} \)
\( p_l \): liquid phase pressure, \( \text{Pa} \)
\( R \): gas constant, \( \text{J mol}^{-1} \text{K}^{-1} \)
\( R_s \): source term in species conservation equation, \( \text{mol m}^{-3} \text{s}^{-1} \)
\( s \): liquid saturation
\( T \): temperature, \( \text{K} \)
\( w_c \): channel width, \( \text{m} \)
\( w_r \): rib width, \( \text{m} \)
\( x \): coordinate, \( \text{m} \)
\( y \): coordinate, \( \text{m} \)

**Greek**

\( \alpha_a \): anode transfer coefficient at anode
\( \alpha_c \): cathode transfer coefficient at cathode
\( \gamma \): reaction order
\( \delta \): thickness of porous layer, \( \text{m} \)
\( \lambda \): porosity of porous medium
\( \lambda_s \): water content

\( \eta \): overpotential, \( \text{V} \)
\( \mu \): viscosity, \( \text{kg m}^{-1} \text{s}^{-1} \)
\( \rho \): density, \( \text{kg m}^{-3} \)
\( \sigma \): interfacial tension, \( \text{N m}^{-1} \)

**Subscript**

\( a \): anode
c: cathode
coc: convection
diff: diffusion
eod: electroosmotic drag
g: gas
l: liquid
M: methanol
MV: methanol vapor
N: Naflon
para: parasitic
tot: total
W: water
WV: water vapor

**Superscript**
eq: equilibrium
ref: reference