Numerical study of the effect of the GDL structure on water crossover in a direct methanol fuel cell

Ya-Ling Hea,*, Zheng Miaoa, Tian-Shou Zhaob, Wei-Wei Yanga

aKey Laboratory of Thermo-Fluid Science and Engineering of MOE, Xi’an Jiaotong University, Xi’an, Shaanxi 710049, PR China
bDepartment of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

Abstract

A two-dimensional two-phase non-isothermal mass transport model is developed to numerically investigate the behavior of water transport through the membrane electrode assembly (MEA) of a direct methanol fuel cell. The model enables the visualization of the distribution of the liquid saturation through the MEA and the analysis of the distinct effects of the three water transport mechanisms: diffusion, convection and electro-osmotic drag, on the water-crossover flux through the membrane. A parametric study is then performed to examine the effects of the structure design of the gas diffusion layer (GDL) on water crossover. The results indicate that the flow-channel rib coverage on the GDL surface and the deformation of the GDL can cause an uneven distribution of the water-crossover flux along the in-plane direction, especially at higher current densities. It is also found that both the contact angle and the permeability of the cathode GDL can significantly influence the water-crossover flux. The water-crossover flux can be reduced by improving the hydrophobicity of the cathode GDL.

Copyright © 2011, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

A direct methanol fuel cell (DMFC) directly converts the chemical energy stored in methanol to electricity. Due to its significant advantages including the simple structure, easy handling and high specific energy of the liquid fuel, the DMFC has been regarded as one of the most promising contenders to compete with conventional battery technology for powering portable electronic devices [1–4]. Although promising, the commercialization of the DMFC technology is still hindered by several technical problems, among which water management is one of the key issues. The proper water management is of vital importance to ensure the high performance and operating stability of the DMFC system [2,5–10].

It has been well understood that the supply of diluted methanol solution to the DMFC anode leads to the high water transfer rate from the anode through the polymer electrolyte membrane (PEM) to the cathode, termed as ‘water crossover’. Usually, the term of net water transport coefficient, α, is employed to indicate the magnitude of water crossover, which is defined as the net water flux across the membrane normalized by the protonic current:

\[ \alpha = \frac{N_w F}{I} \]  

(1)

On one hand, water crossover results in the loss of anode water, limiting the use of high concentration methanol solution [11,12]. It is common for an active DMFC to have \( \alpha = 3 \). According to Eq. (1), the methanol fuel solution should be kept blow 3.0 M. On the other hand, water crossover exacerbates the cathode water ‘flooding’ problem, degrading the cell performance and operating stability. As a result, it is critically
important to suppress the rate of water crossover such that both the problems of the anode water loss and cathode flooding can be minimized. To this end, it is essential to gain a deep understanding of the water transport behavior through the membrane electrode assembly in a DMFC.

Extensive efforts have been made to experimentally investigate on water crossover in DMFCs [5,6,11–18] and PEMFCs [19–31]. In general, previous work can be divided into three categories: the measurement of the water-crossover flux [5,6,13], mechanism analyses of water transport through the membrane [14–17], and the visualization of water distribution in DMFCs [19–26]. Xu et al. [5,6] measured the water crossover flux through the membrane and examined the effects of structure design of MEA components on water transport in a DMFC. They found that the use of a hydrophobic GDL and micro porous layer (MPL) could substantially reduce the water-crossover flux. Ren et al. [14,15] experimentally obtained the electro-osmotic drag coefficient of water in the membrane of the DMFC. Based on the experimental and modeling investigations, some innovative designs of the MEA structure were reported [11,12,16,17]. These new designs can help to achieve a lower water-crossover flux, commonly referred to as a “low-α MEA” design. Some MEA designs can even achieve a water neutral state, in which the neat methanol can be used as fuel [16,17], meaning α = −1/6. The visualization study of liquid water in channels of a PEMFC was performed by Yang et al. [19]. The emergence and growth of water droplet on the surface of GDL were observed. Recently, advanced techniques were employed to probe the water distribution in the MEA, such as the fluorescence microscopy technique [20], high resolution X-ray [21,22], and the neutron radiography [23,24]. These new techniques enable the capture of the transient water accumulation behavior. However, the application of these techniques is still limited by the complicated microstructure of the porous materials of the MEA.

It is well understood that the water transport through the membrane is attributed to three mechanisms: molecular diffusion due to the water content gradient across the membrane, convection due to the pressure difference between the anode and cathode, and the electro-osmotic drag caused by the proton migration. However, it is difficult to experimentally reveal each water transport mechanism because the water transport through the membrane is inherently coupled with other transport processes as well as the electrochemical reactions. As a powerful tool, the mathematical modeling can shed light on the complicated water transport processes occurring in DMFCs.

Over the past decades, extensive efforts have been devoted to develop the two-phase models for simulating the liquid–gas two-phase flow and mass transport processes in the liquid-feed DMFCs [32–36]. It is noticed that most of the two-phase DMFC models reported in the open literature assume that the membrane in the liquid-feed DMFC is fully hydrated, which thus ignores the diffusion transport of water through the membrane. Relatively, only a few papers take all of the three water transport mechanisms into account [37–40]. Liu and Wang [37] developed a 3D two-phase mass transport model to investigate water crossover in the DMFCs. They found that the interfacial liquid coverage at the cathode GDL surface greatly influences the net water transport coefficient through the membrane. In this model, however, the liquid and gas phases are assumed to be in thermodynamic equilibrium. Shaffer and Wang [38] numerically studied the effect of the anode micro-porous layer on water crossover with a 1D, two-phase model. In the model, the gas-phase pressure is assumed uniform across the entire anode and cathode porous regions. Recently, Xu et al. [39], and Yang and Zhao [40] also numerically investigated the effects of MEA structure on water crossover in a liquid DMFC by a 1D two-phase mass transport model. The contribution of each water transport mechanism to the total water crossover flux was analyzed in detail.

Our literature review indicates that previous experimental investigations have shown that the GDL design can significantly affect the overall water crossover behavior in DMFCs. However, it is difficult and expensive to experimentally examine all the design parameters of the GDL on water transport through the MEA in DMFCs. In this regard, numerical modeling can play an important role to provide insights into mass transport mechanisms and optimize the GDL design. However, there is still a lack of a sound mathematical model that can take into account the influences of all the GDL design parameters including material properties and geometric size. The objective of this work is to numerically study how the GDL design affects the water crossover behavior in a DMFC. Emphasis is placed on the distribution of the local water crossover flux in the membrane and the effects of physical properties of the GDL including the deformation of the GDL, the electrical contact resistance, the contact angle of the cathode GDL and the permeability of the cathode GDL.

2. Mathematical model

Consider a two-dimensional physical domain, as sketched in Fig. 1, which represents the typical geometry of a MEA that consists of a pair of GDLs, MPLs and CLs on both the anode and cathode, and a polymer electrolyte membrane. The MEA is sandwiched between two parallel flow fields. Since both

![Fig. 1 – Schematic of the computational domain.](image-url)
channel width and rib width in the parallel flow field are symmetrical with respect to their middle points, only a half-rib width and a half-channel width need to be considered. A two-phase mass transport model, as outlined below, is employed to investigate the water transport behavior through the MEA of the DMFC. The anisotropy of the GDL, including the inherent anisotropy, deformation of the GDL, and electrical contact resistance, is taken into account in this model. More details on the model development can be found elsewhere [41,42].

2.1. Mass and heat transport in the porous region

The governing equations of the liquid–gas counter-flow and mass transport in both the anode and cathode porous regions are given by:

\[
\frac{\partial}{\partial x} \left( \frac{K_x\rho_x k_{xg} \partial p_x}{\mu_x} \right) + \frac{\partial}{\partial y} \left( \frac{-K_y\rho_y k_{yg} \partial p_y}{\mu_y} \right) = \dot{m}_g
\]

(2)

\[
\frac{\partial}{\partial x} \left( \frac{-K_x\rho_x k_{xg} \partial p_x}{\mu_x} \right) + \frac{\partial}{\partial y} \left( \frac{-K_y\rho_y k_{yg} \partial p_y}{\mu_y} \right) = \dot{m}_l - n_m M_W \dot{n}_{lm}
\]

(3)

where \( \dot{m}_l \) is the local generation rate of proton in the anode and cathode CLs. In the classical two-phase flow theory in porous media, the liquid-phase and gas-phase pressures are related to the capillary pressure, i.e.,

\[
p_l = p_g - p_l = a \cos \theta_l (\gamma / \kappa)^{1/2} (s)
\]

(4)

where \( a \) and \( \theta_l \) denote the surface tension between liquid and gas phases and the contact angle of the porous media, respectively. The Leverett function, \( J(s) \), is employed to account for the effect of liquid saturation on the capillary pressure, which is given by:

\[
J(s) = \left\{ \begin{array}{ll}
1.417(1-s) - 2.12(1-s)^2 + 1.263(1-s)^3 & 0 \leq s < 90°

1.417s - 2.12s^2 + 1.263s^3 & 90° \leq s < 180°
\end{array} \right.
\]

(5)

The conservation of species transport in liquid and gas phases are, respectively, written as:

\[
\frac{\partial}{\partial x} (u_i C_{Mi}) + \frac{\partial}{\partial y} (v_i C_{Mi}) = \frac{\partial}{\partial x} \left( D_{Mi}^{\text{eff}} \frac{\partial C_{Mi}}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_{Mi}^{\text{eff}} \frac{\partial C_{Mi}}{\partial y} \right) + \dot{R}_M
\]

(6)

\[
\frac{\partial}{\partial x} (u_g C_{Mg}) + \frac{\partial}{\partial y} (v_g C_{Mg}) = \frac{\partial}{\partial x} \left( D_{Mg}^{\text{eff}} \frac{\partial C_{Mg}}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_{Mg}^{\text{eff}} \frac{\partial C_{Mg}}{\partial y} \right) + \dot{R}_g
\]

(7)

where \( i \) in Eq. (7) represents different gas species, including the gas oxygen, water vapor and methanol vapor. The terms on the left-hand sides of Eqs. (6) and (7), denote the convective transport of liquid species and gas species due to the macroscopic fluid motion, respectively. Note that the velocities of liquid and gas phases can be calculated from the gradient of phase pressures. The former two terms on the right-hand sides of Eqs. (6) and (7) represent the diffusion transport of liquid and gas species. The diffusion coefficients are expressed as:

\[
D_{ij}^{\text{eff}} = D_{ij}^0 (1 - s)^{1.5}
\]

(8)

where \( j \) denotes the different species in liquid and gas phases. Eq. (8) is limited in CLs and MPLs. For the calculation of diffusion coefficients in GDLs, the anisotropy of GDLs are considered, and the expression is modified as follows [43–45],

\[
D_{ij}^{\text{eff}} = D_{ij}^0 \left( \frac{1 - s}{1 - s_0} \right)^{\alpha} (1 - s)^{1.5}
\]

(9)

where the constant \( \alpha \) is 0.521 and 0.785 for in-plane and through-plane diffusions, respectively. Liquid saturation in Eqs. (8) and (9) is obtained from Eq. (4).

The non-equilibrium interfacial mass transfer of water and methanol between the liquid and gas phases is also taken into account in the present model. Simply, the interfacial species transfer rates are expressed as follows [46,47]

\[
\dot{R}_W = \left\{ \begin{array}{ll}
K_{pg} \frac{p_{Mg}^{\text{sat}} - y_{uv} p_g}{h} & p_{Mg}^{\text{sat}} \geq y_{uv} p_g

K_{pg} \frac{p_{Mg}^{\text{sat}} - y_{uv} p_g}{RT} & p_{Mg}^{\text{sat}} < y_{uv} p_g
\end{array} \right.
\]

(10)

\[
\dot{R}_M = A_{pg} h_g s (1-s) \frac{p_{Mg}^{\text{sat}} - p_{Mg}}{RT}
\]

(11)

where \( p_{Mg}^{\text{sat}} \) and \( p_{Mg}^{\text{sat}}^\text{int} \), respectively, denote the saturation pressure of water vapor and methanol vapor.

Let us now consider the heat transfer process through the porous region. Assuming, the thermal equilibrium between the liquid and gas phases, the general conservation of energy in the porous regions can be written as:

\[
\frac{\partial}{\partial x} \left( c_p C_{pg} u_j T + \rho C_{pg} u_j T \right) + \frac{\partial}{\partial y} \left( c_p C_{pg} u_j T + \rho C_{pg} u_j T \right)
\]

\[
= \frac{\partial}{\partial x} \left( \kappa^{\text{eff}} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \kappa^{\text{eff}} \frac{\partial T}{\partial y} \right) + \dot{R}_T
\]

(12)

where \( C_p \), \( \kappa^{\text{eff}} \) and \( \dot{R}_T \) represent the heat capacity, thermal conductivity and local heat generation rate in the DMFC, respectively. Note that Eq. (12) is also applied to model the heat transfer in the membrane region.

2.2. Water and methanol crossover through the membrane

In the CLs, water can transfer through the pores of the CL as liquid and gas phases, it also can dissolve into the electrolyte phase. Thus, the transfer of dissolved water in the electrolyte of the CLs and the membrane need to be taken into account. As mentioned earlier, the transport of the dissolved water in the electrolyte phase primarily depends on three mechanisms: diffusion, back convection and electro-osmotic drag. The expression of water flux can be given as:

\[
N_{uw} = -D_{uw}(\lambda) \nabla C_{w,\text{CN}} - \frac{h_l}{M_w \mu_l} K \nabla p_l + n_{aw}(\lambda) \frac{1}{F}
\]

(13)

where \( D_{uw}(\lambda) \) and \( n_{aw}(\lambda) \) denote the diffusivity and electro-osmotic drag coefficient of dissolved water in the electrolyte phase. Detailed expressions can be found in Table 2. Note that the concentration of dissolved water \( C_{w,\text{CN}} \) is related to the water content of the membrane, which is given by:

\[
\lambda = \frac{C_{w,\text{CN}} \varepsilon W}{\rho_{\text{dry}}}
\]

(14)

The distribution of water content in the membrane can be obtained by solving the conservation equation of dissolved water:
Table 1 — Expressions of source terms and coefficients of the governing equations.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Expressions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole generation rate of species</td>
<td>( R_m = \begin{cases} \frac{-i_a}{6F} &amp; \text{ACL} \ \frac{-i_p}{6F} &amp; \text{CCL} \ 0 &amp; \text{ADL, MEM} \end{cases} )</td>
</tr>
<tr>
<td>Generation rate of mass in gas and liquid phase</td>
<td>( m_g = \begin{cases} M_w \delta \theta_w + M_a \delta \omega_w &amp; \text{ADL} \ M_w \delta \theta_w + M_a \delta \omega_w + M_{CO} \delta \omega_{CO} &amp; \text{CCL} \ M_w \delta \theta_w - M_o \delta \theta_o + M_{CO} \delta \omega_{CO} &amp; \text{CDL} \end{cases} )</td>
</tr>
<tr>
<td>Generation rate of heat</td>
<td>( R_T = \frac{</td>
</tr>
<tr>
<td>Generation rate of charges</td>
<td>( \dot{i}_m = \begin{cases} i_a &amp; \text{ACL} \ i_c - i_p &amp; \text{CCL} \ 0 &amp; \text{MEM} \end{cases} )</td>
</tr>
<tr>
<td>Relative permeabilities</td>
<td>( k_{ri} = s^3, \quad k_{rg} = (1-s)^3 )</td>
</tr>
<tr>
<td>Thickness of the GDL under inhomogeneous compression</td>
<td>( L(y) = \begin{cases} L_{\text{comp}} = 2.5 \times 10^{-4} \text{m} &amp; \text{under - rib} \ 19.30314 \log_2((y - 0.0005) \times 10^6 + 1) \times 10^{-4} + L_{\text{comp}} &amp; \text{under - channel} \end{cases} )</td>
</tr>
<tr>
<td>Porosity of the GDL under inhomogeneous compression</td>
<td>( \iota(y) = 1 - (1 - \iota_0) \frac{L_0}{L(y)} )</td>
</tr>
<tr>
<td>In-plane permeability of the GDL</td>
<td>( K_{\text{in-p}} = 5 \times 10^{-13} \frac{L(y)^3}{[1 - L(y)]^2} )</td>
</tr>
<tr>
<td>Electrical conductivity of the GDL</td>
<td>( \sigma_{\text{in-p}} = -1.159 \times 10^3 L(y) + 6.896 \times 10^1, \quad \sigma_{\text{in-p}} = -8.385 \times 10^3 L(y) + 3.285 \times 10^3 )</td>
</tr>
<tr>
<td>Interfacial electrical contact resistance</td>
<td>( r_{\text{MCL}} = 5.83 \times 10^{-10} \exp(2.06 \times 10^L(y)) )</td>
</tr>
</tbody>
</table>

\( \nabla \cdot (N_W) = 0 \) \hspace{1cm} (15)

In the CLs, the thermodynamic equilibrium state of water in liquid, gas and electrolyte phase is assumed for simplicity. As such, the water content in the electrolyte phase of the CLs can be calculated by:

\[ \lambda_{CL} = s \lambda_{\text{eq}} + (1-s) \lambda_{\text{wbv}} \] \hspace{1cm} (16)

where \( \lambda_{\text{eq}} \) is water content in electrolyte phase when the polymer electrolyte is directly contacted with liquid water. The term \( \lambda_{\text{wbv}} \), is the water content when the water in electrolyte phase is in thermodynamic equilibrium with saturated water vapor. Detailed expressions of \( \lambda_{\text{wbv}} \) can be found elsewhere [39].

In a similar fashion to the transport of dissolved water in the membrane, dissolved methanol transport through the membrane also depends on diffusion, back convection and electro-osmotic drag. The flux of methanol crossover can be expressed as:

\[ N_m = -D_m \nabla C_m - \left( \frac{K_{\text{mem}}}{\mu_i} \nabla p_i \right) C_m + n_{M} \frac{I}{F} \] \hspace{1cm} (17)

### 2.3. Electrochemical kinetics

In the anode CL of the DMFC, the Tafel-like expression is used to describe the kinetics of the methanol oxidation reaction (MOR), given as follows:

\[ i_a = A_{\text{ref}} \rho_{\text{sta}} \left( \frac{C_m}{C_m^{\text{sta}}} \right)^\gamma \exp \left( \frac{a_i F}{RT} i_{\text{ref}} \right) \] \hspace{1cm} (18)

where \( \gamma \) is the reaction order related to methanol concentration at the active sites of the catalyst particles.
Table 2 – Physicochemical properties and parameters used in simulation.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbols</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion volume fraction in ACL and CCL</td>
<td>( \varepsilon_{N,ACL}/\varepsilon_{N,CL} )</td>
<td>0.4, 0.4</td>
<td></td>
</tr>
<tr>
<td>Conductivity in membrane phase</td>
<td>( \sigma_m )</td>
<td>((0.5139 - 0.326)e^{268(\frac{1}{kT} - \frac{1}{2})})</td>
<td>(\Omega^{-1}\cdot m^{-1})</td>
</tr>
<tr>
<td>Conductivity in CLs permeability</td>
<td>( \sigma_s )</td>
<td>300</td>
<td>(\Omega^{-1}\cdot m^{-1})</td>
</tr>
<tr>
<td>ADL</td>
<td>( K_{b-p} )</td>
<td>(3 \times 10^{-12})</td>
<td>m²</td>
</tr>
<tr>
<td>MPL</td>
<td>( K_{MPL} )</td>
<td>(7 \times 10^{-13})</td>
<td>m²</td>
</tr>
<tr>
<td>CLs</td>
<td>( K_s )</td>
<td>(3 \times 10^{-14})</td>
<td>m²</td>
</tr>
<tr>
<td>MEM</td>
<td>( K_{mem} )</td>
<td>(7 \times 10^{-18})</td>
<td>m²</td>
</tr>
<tr>
<td>Contact angle of the anode GDL</td>
<td>( \theta_{c,ADL} )</td>
<td>120°</td>
<td></td>
</tr>
<tr>
<td>Contact angle of the cathode GDL</td>
<td>( \theta_{c,CL} )</td>
<td>95°</td>
<td></td>
</tr>
<tr>
<td>Contact angle of the cathode GDL</td>
<td>( \theta_{c,CL} )</td>
<td>(-140°)</td>
<td></td>
</tr>
<tr>
<td>Viscosity of gas phase</td>
<td>( \mu_g )</td>
<td>(2.03 \times 10^{-5})</td>
<td>kg m(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>Viscosity of liquid phase</td>
<td>( \mu_l )</td>
<td>(4.06 \times 10^{-4})</td>
<td>kg m(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>Electro-osmotic coefficients of water and methanol</td>
<td>( n_a )</td>
<td>(2.5 \times 10^{-5})</td>
<td></td>
</tr>
<tr>
<td>Diffusivities</td>
<td>( \mathcal{D}_{M,L} )</td>
<td>(10^{-5} \times 4163 - 999.778/T)</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>Methanol in Nafion</td>
<td>( \mathcal{D}_{M,N} )</td>
<td>(4.9 \times 10^{-8}e^{2486(1/333 - 1/T)})</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>Oxygen in gas phase</td>
<td>( \mathcal{D}_{O2,g} )</td>
<td>(1.775 \times 10^{-6}(T/273.15)^{1.823})</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>Oxygen in Nafion</td>
<td>( \mathcal{D}_{O2,N} )</td>
<td>(1.844 \times 10^{-10})</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>Water vapor in gas</td>
<td>( \mathcal{D}_{W,sv} )</td>
<td>(2.56 \times 10^{-3}(T/307.15)^{2.334})</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>Methanol vapor in gas</td>
<td>( \mathcal{D}_{MV,g} )</td>
<td>(-6.954 \times 10^{-6} + 4.596 \times 10^{-8}T + 9.4979 \times 10^{-11}T^2)</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>Liquid water in the membrane</td>
<td>( \mathcal{D}_{W,N} )</td>
<td>(4.17 \times 10^{-5}(1 + 161e^{-3})e^{-2436/T})</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>Interfacial transfer rate for methanol</td>
<td>( \mathcal{A}_{LM} )</td>
<td>1 \times 10^{5}</td>
<td>m(^{-1})</td>
</tr>
<tr>
<td>Specific interfacial area between liquid and gas</td>
<td>( \rho_{w} )</td>
<td>0.096g/mol (T - 273) atm</td>
<td>atm</td>
</tr>
<tr>
<td>Henry law constant for oxygen</td>
<td>( \rho_{H} )</td>
<td>0.3125 \times 101325/(RT)</td>
<td>atm</td>
</tr>
<tr>
<td>Saturation pressure of vapor</td>
<td>( \log_{10} \rho_{w} )</td>
<td>(-2.1794 + 0.02953(T - 273) - 9.1837)</td>
<td>atm</td>
</tr>
<tr>
<td>Evaporation rate constant of water</td>
<td>( k_s )</td>
<td>(5 \times 10^{-3})</td>
<td>atm(^{-1}) s(^{-1})</td>
</tr>
<tr>
<td>Condensation rate constant of water</td>
<td>( k_c )</td>
<td>50</td>
<td>s(^{-1})</td>
</tr>
<tr>
<td>Electrochemical kinetics parameters</td>
<td>( i_{ref} )</td>
<td>0.04222e^{23300(1/7353 - 1/T)} ( A m^{-3})</td>
<td>A m(^{-3})</td>
</tr>
<tr>
<td>Reference concentration of oxygen</td>
<td>( \rho_{O2} )</td>
<td>0.04222e^{23300(1/7353 - 1/T)} ( A m^{-3})</td>
<td>mol m(^{-3})</td>
</tr>
<tr>
<td>Transfer coefficient of cathode</td>
<td>( \alpha_c )</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Thermodynamic voltage</td>
<td>( V_0 )</td>
<td>1.21</td>
<td>V</td>
</tr>
</tbody>
</table>

\( \gamma = \begin{cases} 0 & \text{if } C_{M,ADL} > C_{M,CL} \\ 1 & \text{if } C_{M,ADL} \leq C_{M,CL} \end{cases} \) (19)

The oxygen reduction reaction (ORR) in the cathode CL of the DMFC described by the Tafel-like expression with a modification factor \( \xi_{O_2} \), which is obtained from the agglomerate model [34,41].

\[ i_c = A_{ref} \exp \left( \frac{C_{O2}}{C_{O2 ref}} \right) \exp \left( \frac{\alpha_c F}{RT\eta_c} \right) \xi_{O_2} \] (20)

Overpotentials in Eqs. (18) and (20) are determined by profiles of solid phase potential and electrolyte phase potential in CLs, which are calculated from the governing equations for electrons and protons, listed as Eqs. (23) and (24).

\[ \eta_a = \varphi_{a,a} - \varphi_{m,a} \] (21)

\[ \eta_c = V_0 + \varphi_{m,c} - \varphi_{a,c} \] (22)

\[ \frac{\partial}{\partial x} \left( \sigma_m \frac{\partial \varphi_m}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma_m \frac{\partial \varphi_m}{\partial y} \right) = i_m \] (23)

\[ \frac{\partial}{\partial x} \left( \sigma_s \frac{\partial \varphi_s}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma_s \frac{\partial \varphi_s}{\partial y} \right) = i_a \] (24)

Up to this point, all the governing equations have been presented. Detailed expressions of the source terms and coefficients used in these equations are listed in Tables 1 and 2. Some parameters are picked from the open published works [48–50].

2.4. Current balance and cell voltage

In a working fuel cell, electrons and protons generated in the anode CL are all consumed in the cathode CL. The mean current densities at the anode and cathode electrodes can be calculated by:


\[
I_a = \frac{\int \int i_a \, dx \, dy}{h_c + h_r} \quad (25)
\]

\[
I_c = \frac{\int \int i_c \, dx \, dy}{h_c + h_r} \quad (26)
\]

Note that the ‘parasitic’ current density due to methanol crossover, given as \( I_p = 6N_{\text{M},a} \), is involved in the integration expression in Eq. (26). Hence, the cell output current density and cell voltage can be determined by:

\[
I_{\text{cell}} = I_a = I_c - I_p \quad (27)
\]

\[
V_{\text{cell}} = \varphi_{\text{a,c}} \quad (28)
\]

### 2.5. Boundary conditions

As shown in Fig. 1, the boundary conditions at twelve interfaces should be specified. Boundaries 1 and 5 represent the interface between the channels and the GDLs. At these two boundaries, the conditions are specified according to the operating conditions as listed in Table 3. The conditions at the internal interfaces between adjacent components of the MEA are specified based on the continuity principle and flux balance of mass, charges and heat. Detailed information about these boundary conditions can be found in our former work [41].

With respect to the calculation of water crossover through the membrane, according to the balance of water flux through the interfaces between the membrane and CLs, boundary conditions for the governing equation of liquid pressure at interface 9 and 10 are given as follows,

- **Boundary 9:**
  \[
  \frac{\rho_l \cdot K_{\text{diff}}}{M_{\text{H}_2\text{O}} \cdot \mu_l} \left|_{\text{9}} \right. = N_{\text{W, diffusion}} \left|_{\text{9}} \right. - N_{\text{W, back convection}} \left|_{\text{9}} \right. \quad (29)
  \]

- **Boundary 10:**
  \[
  \frac{\rho_l \cdot K_{\text{diff}}}{M_{\text{H}_2\text{O}} \cdot \mu_l} \left|_{\text{10}} \right. = N_{\text{W, diffusion}} \left|_{\text{10}} \right. - N_{\text{W, back convection}} \left|_{\text{10}} \right. \quad (30)
  \]

As the contribution of the electro-osmotic drag flux of water to the total water crossover flux is considered in the source term of liquid pressure governing equation, herein only diffusion and back convection mechanisms are taken into account at boundaries 9 and 10.

### 3. Results and discussion

Using a self-written computer code based on the Finite-Volume-Method, all the governing equations are numerically solved under the baseline operating conditions listed in Table 3. It is noticed that the present model is extended from the DMFC model presented in our previous work [41], in which the details of the model validation against the experimental data can be found. In the following, the model is used to investigate the water transport mechanisms through the MEA of a liquid-feed DMFC.

#### 3.1. Liquid saturation distribution

The water saturation in a capillary porous medium is related to the capillary pressure, which represents the difference between the gas-phase pressure and liquid-phase pressure. The distributions of the liquid saturation in the anode porous layers are presented in Fig. 2a–c. It is noted that the distribution of the liquid saturation exhibits a jump at the interface between two adjacent capillary porous layers in the MEA, although the continuities of mass flux, liquid pressure, gas pressure and capillary pressure are all satisfied at the interface between different layers. This is due to the discontinuity of the physical properties of different porous layers, including the porosity, the contact angle and the hydraulic permeability. The figures also clearly show that the higher hydrophobicity of the anode MPL due to the smaller permeability and larger contact angle, results in a lower liquid saturation compared to those in the anode GDL and the anode CL. It is also seen that the distribution of the liquid saturation in the anode GDL along the in-plane direction is not uniform. The liquid saturation in the region under the rib is lower than that in the region under the flow channel. This can be explained as follows. The gas carbon dioxide produced by the anode MOR has to transport from the anode CL to the anode flow channel. Due to the longer transport path (i.e., larger transport resistance) from the under-rib region to the flow channel, the gas carbon dioxide tends to accumulate in the under-rib region, resulting in a relatively lower liquid saturation in the region under the rib as compared with that in the region under the channel.

### Table 3 – Cell geometric dimensions and base case of the model.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbols</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity, thickness</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GDL</td>
<td>( \epsilon_{\text{GDL},c} )</td>
<td>0.7, 3.8 × 10⁻⁸</td>
<td>m</td>
</tr>
<tr>
<td>MPL</td>
<td>( \epsilon_{\text{GDL},c} )</td>
<td>0.3, 0.3 × 10⁻⁴</td>
<td>m</td>
</tr>
<tr>
<td>CL</td>
<td>( \epsilon_{\text{CL}} )</td>
<td>0.3, 0.2 × 10⁻⁴</td>
<td>m</td>
</tr>
<tr>
<td>MEM</td>
<td>( \epsilon_{\text{MEM},c} )</td>
<td>0.3, 1.3 × 10⁻⁴</td>
<td>m</td>
</tr>
<tr>
<td>Height of a half-rib</td>
<td>( h_r )</td>
<td>0.5 × 10⁻³</td>
<td>m</td>
</tr>
<tr>
<td>Height of a half-channel</td>
<td>( h_c )</td>
<td>0.5 × 10⁻³</td>
<td>m</td>
</tr>
<tr>
<td>Operation temperature</td>
<td>( T )</td>
<td>333.15</td>
<td>K</td>
</tr>
<tr>
<td>Anode channel press.</td>
<td>( p_{\text{in,a}} )</td>
<td>101,325</td>
<td>pa</td>
</tr>
<tr>
<td>Cathode channel press.</td>
<td>( p_{\text{in,c}} )</td>
<td>101,325</td>
<td>pa</td>
</tr>
<tr>
<td>Anode channel liquid sat.</td>
<td>( s_{\text{L,a}} )</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>Cathode channel liquid sat.</td>
<td>( s_{\text{L,c}} )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Anode flow rate</td>
<td>( Q_{\text{a,in}} )</td>
<td>1</td>
<td>ml min⁻¹</td>
</tr>
<tr>
<td>Inlet methanol conc.</td>
<td>( C_{\text{m}} )</td>
<td>2000</td>
<td>mol m⁻³</td>
</tr>
<tr>
<td>Inlet oxygen conc.</td>
<td>( C_{\text{O}_2} )</td>
<td>7.68</td>
<td>mol m⁻³</td>
</tr>
</tbody>
</table>
Fig. 2d–f displays the liquid saturation in the cathode porous layers. Generally, the liquid saturation in the cathode porous regions is much lower than that in the anode since the air is supplied to the cathode, whereas the liquid methanol solution is delivered to the anode. The liquid water that is generated from the cathode ORR, together with the water that permeates from the anode, transfers through the cathode porous regions to the cathode flow channel. The low liquid saturation in the cathode porous regions results in the higher mass transfer resistance of the liquid water because of the lower relative permeability, which consequently builds up a much high liquid pressure in the cathode CL. Also, it is found that the in-plane distribution of the liquid saturation is much more uniform at the anode than that at the cathode. We define the largest relative difference of liquid saturation in a region, i.e., the difference between the largest liquid saturation and the smallest liquid saturation normalized by the largest liquid saturation. It can be seen from Fig. 2 that the largest relative differences of liquid saturation at anode GDL, MPL and CL are 9.6%, 1% and 1.5%, respectively, while 71%, 20% and 20% in cathode GDL, MPL and CL.

3.2. Effect of cell current density

In this section, the effects of the cell current density on the distributions of the relative liquid pressure, relative gas pressure, liquid saturation in the porous regions, the water content in the membrane, and the flux of water crossover are explored. Fig. 3a shows the profiles of the relative gas and liquid pressures across the anode porous regions at various current densities. Clearly, the liquid pressure drop from the anode channel to the anode CL is much smaller than the gas pressure drop from the anode CL to the anode channel. For example, at the current density of 400 mA cm$^{-2}$, a pressure drop of 3 Pa is resulted as the liquid methanol solution permeates through the anode GDL and MPL to the anode CL. As for the gas phase, however, the pressure drop of gas CO$_2$ between the anode CL and the anode channel reaches about 2100 Pa. The higher gas
pressure drop means the higher gas flow resistance through the anode porous regions, which is mainly due to the lower gas-phase density and the lower relative permeability of gas phase in the anode porous regions. Also, it is seen from Fig. 3a that with the increase in the cell current density, the gas pressure drop across the anode porous regions increases because of the increased CO2 generation rate. Besides, Fig. 3b also presents the distributions of the liquid saturation across the anode porous region at various current densities. Clearly, with the increase in the cell current density, the whole liquid saturation level in the anode porous regions decreases because much more gas CO2 is generated at higher current density. In addition, the distributions of the gas and liquid pressures across the cathode porous regions at various current densities are also displayed in Fig. 3c. Different from that in the anode porous regions, the pressure drop of the gas phase across the cathode porous regions is much smaller. On the contrary, the liquid pressure varies greatly from the cathode CL to the

Fig. 3 – Effect of the current density on the profiles of (a) relative anode liquid and gas pressures, (b) anode liquid saturation, (c) relative cathode liquid and gas pressures, (d) cathode liquid saturation, (e) water content in CLs and PEM, and (f) water crossover flux.
cathode channel. Comparing Fig. 3a with 3c, it is seen that a much higher liquid-phase pressure is built up in the cathode CL, which can drive part of the liquid water back flow through the membrane to the anode, thus suppressing the total water crossover flux to the cathode. Also, it is found that with the increase in the current density, the liquid pressure drop across the cathode porous regions increases, implying that the liquid water flux across the cathode porous region is increased with the cell current density. Fig. 3d also shows the corresponding profiles of the cathode liquid saturation at various cell current densities. Clearly, as shown in the figure, the liquid saturation in the cathode porous regions increases with the cell current density. Besides, Fig. 3e presents the profiles of water content in the membrane for various current densities. As shown in the figure, the water content is much higher in the region near the anode CL than that in the region near the cathode CL because the water content in the membrane closely relates to the liquid saturation in the anode and cathode CLs. For example, at the current density of 200 mA cm\(^{-2}\), the water content at the interface between the anode CL and the membrane approaches about 19, while it is only about 11 at the interface between the cathode CL and the membrane. With the increase in the cell current density, the water content at the anode CL/PEM interface increases due to the increased liquid saturation in the anode CL. However, the water content at the cathode CL/PEM interface is not sensitive to the change of the cell current density. The effect of the cell current density on the water crossover flux is shown in Fig. 3f. Generally, the trend of water crossover flux by each of the three water transport mechanisms, the total water crossover flux and the net water transport coefficient predicted in this work are qualitatively consistent with the experimental results [5,6] and the numerical results [39,40] reported in the open literature. It can be seen from Fig. 3f that water diffusion through the membrane contributes to a large part of the total water crossover flux, especially at the lower cell current densities. With the increase in the cell current density, the diffusion flux of water decreases significantly because the water content in the membrane at the current density of 200 mA cm\(^{-2}\), the water content at the interface between the anode CL and the membrane is lowered resulting from the decreased liquid saturation in the anode CL at the higher cell current densities. Different from the diffusion flux of water, the electro-osmotic flux of water almost linearly increases with the cell current density as indicated by Eq. (13). As for the back-convection flux of water, the negative value of the back-convection flux indicates that the water flows from the cathode through the membrane to the anode. With the increase in the cell current density, the liquid pressure in the cathode CL is slightly enhanced which in turn forces more liquid water back flow to the anode as indicated in Fig. 3f. Overall, the total water crossover flux increases with the cell current density. With respect to the net water transport coefficient, it decreases sharply in the low cell current density region. The variation in the net water transport coefficient then slows down at moderate and high current density regions.

### 3.3. Effect of rib coverage on the surface of GDL

In this section, we examine the effects of the rib coverage on water transport behaviors. Fig. 4 presents the distributions of the water content in the electrolyte phase of the anode and cathode CLs and the membrane. As mentioned earlier, the variation in the liquid water saturation in the anode CL along the in-plane direction is negligible and the mean saturation level in the cathode CL is very low, which thus only slightly influences the water content level in the membrane near the cathode. As a result, the variation in the water content along the in-plane direction is much smaller, and an almost one-dimensional distribution of the water content contour in the electrolyte phase (anode CL, membrane and cathode CL) is occurred as shown in Fig. 4. Fig. 5 presents the distributions of the diffusion flux of water crossover, electro-osmotic drag flux of water crossover, and the total water crossover flux in the membrane at the current density of 400 mA cm\(^{-2}\). As indicated in Fig. 5a, the variation in the diffusion flux of water along the in-plane direction is much small since the diffusion flux of water is proportional to the gradient of water content across the membrane. However, as indicated in Fig. 5b, the electro-osmotic drag flux of water crossover exhibits a non-uniform distribution along the in-plane direction mainly due to the non-uniform distribution of the local current density as presented in Fig. 6. Black lines in Fig. 6 represent the profiles of the local current densities in the anode and cathode CLs at the mean cell current density of 400 mA cm\(^{-2}\). Clearly, the local current density in the region under the channel is higher than that in the region under the rib. Correspondingly, it can be seen in Fig. 5b that the electro-osmotic flux through the membrane in the region under the channel is also higher than that in the region under the rib. For example, the electro-osmotic flux at the anode CL/PEM interface decreases from 9.5 \(\mu\)mol cm\(^{-2}\) s\(^{-1}\) in the under channel region to 7.5 \(\mu\)mol cm\(^{-2}\) s\(^{-1}\) in the under rib region. The relative difference is about 21%.

As shown in Fig. 5a and b, the water diffusion flux and the electro-osmotic drag flux along the through-plane direction in the membrane are also non-uniform. The variation of water diffusion flux in the membrane along the through-plane...
direction is due to the nonlinear distribution of water content across the membrane as illustrated in Fig. 4 and the variation of water diffusion coefficient with the water content. As for the electro-osmotic drag flux, the decrease in the water content across the membrane from anode to the cathode leads to the decrease in the electro-osmotic drag coefficient, \( n_{d,W}(\ell) \), thus resulting in the variation of the electro-osmotic drag flux across the membrane. It is seen in Fig. 5b that the electro-osmotic flux gradually decreases from the anode side to the cathode side, which is consistent with the variation of the water content. Fig. 5c shows the distribution of the total water crossover flux in the membrane. As shown in the figure, the distribution of the total water flux is also non-uniform along the in-plane direction because of the variation of electro-osmotic flux. For example, the total water crossover flux at the anode CL/PEM interface varies from 12.4 \( \mu \text{mol cm}^{-2} \text{s}^{-1} \) in the region under the channel to about 10.2 \( \mu \text{mol cm}^{-2} \text{s}^{-1} \) in the region under the rib.

In addition, Fig. 7 also shows the distribution of the water crossover flux at a moderate current density of 200 mA cm\(^{-2}\). It can be seen that the variation of both the diffusion flux and the electro-osmotic flux along the in-plane direction are much small, indicating that the variation of the water content and the local current densities in the CLs along the in-plane direction is negligible. The variation of the local current density along the in-plane direction at the mean current density of 200 mA cm\(^{-2}\) is also shown in Fig. 6, represented by the dark green lines. It can be seen that the local current densities in the anode and the cathode CLs are nearly constant along the in-plane direction because of the sufficient transport of methanol from the anode channel to the anode CL. The results indicate that the effects of the rib coverage over the surface of GDL are less significant at moderate current densities compared with that at high current densities.

### 3.4. Effect of the deformation of GDLs

When the MEA is sandwiched in the fixtures, the clamping force causes the deformation of the GDLs, as illustrated in Fig. 8. The compression deformation consequently changes the microstructure and the transport properties of the GDL. As the GDL greatly influences the mass transport of reactants and productions in the fuel cell, it is thus necessary to examine the effects of GDL deformation on water transport in the DMFCs. Additionally, the electrical contact resistance also closely depends on the deformation of the GDL, which thus influences the transport of electrons in the cell. In this section, two cases are studied. One is the GDL with deformation but without considering the electrical contact resistance. The other considers both the GDL deformation and the electrical contact resistance.

We first analyze how the GDL deformation influences the water crossover behavior. In our previous work [42], the effects of the GDL deformation on species transport, such as methanol, oxygen, charges, and heat are discussed. It is found that the increased mass transport resistance of methanol

---

**Fig. 5** – Distributions of water flux (\( \mu \text{mol cm}^{-2} \text{s}^{-1} \)) due to (a) diffusion and (b) electro-osmotic drag, as well as (c) total water-crossover flux in the PEM at the current density of 400 mA cm\(^{-2}\).

**Fig. 6** – The local current density distributions in the anode and cathode CLs along the in-plane direction considering various GDL conditions.
resulting from the GDL deformation causes the shortage of methanol in the anode CL at high current densities, especially in the region under the channel. Consequently, the distributions of the local current densities in the CLs are strongly non-uniform. The blue lines in Fig. 6 represent the profiles of the local current densities along the in-plane direction in the anode and cathode CLs. Clearly, the local current densities in the region under the channel are much higher than that in the region under the rib. The higher local current densities lead to the higher electro-osmotic drag flux of water across the membrane. Fig. 9 shows the corresponding distributions of the diffusion flux, electro-osmotic drag flux and total water crossover flux through the membrane. As shown in Fig. 9b, the electro-osmotic flux is much more uneven along the in-plane direction when the GDL is under compression deformation compared with that in Fig. 5, in which the GDL deformation is not considered. As indicated in Fig. 9b, the largest relative difference of the electro-osmotic flux at the anode CL/PEM interface along the in-plane direction reaches about 55%, consistent with the profiles of local current densities shown in Fig. 6. The distribution of the total water crossover flux is also displayed in Fig. 9c. Due to the large variation of the electro-osmotic drag flux, the total water crossover flux is also non-uniform along the in-plane direction. The largest relative variation of total water flux at the anode CL/PEM interface is about 39%.

Fig. 10 presents the distributions of water crossover flux due to diffusion and electro-osmotic drag as well as the total water crossover flux in the membrane with deformed GDLs at the cell current density of 200 mA cm\(^{-2}\). The corresponding profiles of the local current densities in anode and cathode CLs are plotted in the magenta lines in Fig. 6. The distribution of water flux in Fig. 10 is quite similar to the water flux distribution in Fig. 7. This indicates that the 2-M methanol solution is still high enough to guarantee a sufficient methanol flux for the MOR in the anode CL at a moderate cell current density, even that the mass transport resistance of methanol from the anode channel to the under rib region of the anode CL is increased when the GDL is under deformation. However, it is noticed that the 2-M methanol feeding concentration may lead to severe methanol crossover problem, degrading the cathode performance. More efforts should be devoted to develop new MEA designs, which can not only guarantee the sufficient supply of methanol to the anode CL but also suppress the methanol crossover through the membrane.

We now turn our attention to the influences of the electrical contact resistance. Fig. 11 shows the water crossover flux in the membrane at the mean cell current density of 200 mA cm\(^{-2}\) for the case with both the GDL deformation and the electrical contact resistance taken into account. Interestingly, the total water crossover flux, as shown in Fig. 11c, exhibits a gradual decrease from the under-rib region to the under-channel region, which is different from the distribution...
of total water crossover flux shown in Fig. 10c. The reason can be explained by the distribution of the local current densities in the CLs. It is well known that the electrochemical reactions in CLs depend on both the transport of species (such as methanol and oxygen) and the transport of charges (protons and electrons). At higher current densities, the mass transport of methanol dominates the distribution of the cell current density due to the large concentration polarization. At moderate cell current density, however, the transport of electrons becomes dominant. In our former work [42], it is mentioned that the distribution of electrical contact resistance along the in-plane direction is extremely non-uniform. The electrical contact resistance is much higher in the region under the channel than that in the region under the rib. As a result, the electrons generated in the anode CL under the rib region can more easily transfer to the rib collector. The dark yellow lines in Fig. 6 represent the profiles of the local current densities in the anode and cathode CLs for the case with considering both the GDL deformation and the electrical contact resistance. It can be seen that the local current density in the under-rib region is higher than that in the under-channel region. As a result, the electro-osmotic drag flux in membrane under the rib is higher as shown in Fig. 11b. Since the higher CO2 generation rate in the region under the rib will lead to a lower liquid saturation in the under-rib region of the anode CL, the gradient of water content in this region across the membrane is reduced. Consequently, diffusion flux exhibits a gradually increase from the under-rib region to the under-channel region as shown in Fig. 11a.

In the next sections, we focus on how the contact angle and the permeability of the cathode GDL affect water crossover in the DMFC.

**Fig. 9** – Distributions of water flux ($\mu$mol cm$^{-2}$ s$^{-1}$) due to (a) diffusion and (b) electro-osmotic drag, as well as (c) total water-crossover flux in the PEM at cell current density of 400 mA cm$^{-2}$ with the deformed GDL.

**Fig. 10** – Distributions of water flux ($\mu$mol cm$^{-2}$ s$^{-1}$) due to (a) diffusion and (b) electro-osmotic drag, as well as (c) total water-crossover flux in the PEM at the current density of 200 mA cm$^{-2}$ with the deformed GDL.
3.5. Effect of the cathode GDL contact angle

In this section, the effect of the cathode GDL contact angle on water crossover behavior is examined. Fig. 12 shows the profiles of the cathode relative liquid and gas pressures, cathode liquid saturation, water content in CLs and PEM, and water crossover flux at various cathode GDL contact angles at the cell current density of 200 mA cm\(^{-2}\). In the calculation, the...
cathode GDL contact angle is varied from 110° to 140° while the other parameters are kept unchanged. Note that the higher contact angle represents the higher hydrophobic level of the porous material. It can be seen from Fig. 12(b) that the higher contact angle represents the higher hydrophobic level the other parameters are kept unchanged. Note that the cathode GDL contact angle is varied from 110° to 140°. Due to the increase in liquid pressure in the cathode GDL, as shown in Fig. 12a. Due to the increase in liquid pressure in the cathode GDL, the liquid pressures in the cathode CL and MPL also increase. However, it is seen from Fig. 12b that the variation of liquid saturation in the cathode CL at different contact angles is negligible. As a result, the water content at the cathode CL/PEM interface as well as the whole profile of the water content across the membrane is almost unchanged with the variation of the contact angle of the cathode GDL. Fig. 12d also shows the water crossover fluxes by different transport mechanisms and the net water transport coefficient at various cathode GDL contact angles. Clearly, the cathode GDL contact angle exhibits little effect on water transport behaviors through the membrane, and the total water crossover flux and the water flux due to each of the three mechanisms almost remain the same value.

### 3.6. Effect of the cathode GDL permeability

In this section, the effects of the cathode GDL permeability on water transport across the membrane are examined. Fig. 13a presents the profiles of cathode liquid and gas pressures for various cathode GDL permeabilities at the current density of 200 mA cm\(^{-2}\). Clearly, the decrease in the cathode GDL permeability leads to a sharp increase in the liquid pressure, whereas the variation of the gas pressure is much small. As shown in the figure, the cathode liquid pressure at the cathode CL/PEM interface increases from about 2000 Pa to about 5000 Pa when the cathode GDL permeability is decreased from \(K_0\) to \(K_0 \times 0.1\) with \(K_0\) being the GDL permeability under the baseline condition listed in Tables 1 and 2. The above results indicate that a higher cathode liquid pressure can be built up by decreasing the permeability of the cathode GDL, which can drive more water back flow to the anode, thus suppressing the total water crossover flux. Fig. 13b presents the corresponding distribution of liquid saturation in the cathode porous media. As shown in the figure, the decrease in the cathode GDL permeability results in the significant increase in the liquid saturation, especially that in the cathode CL. With the GDL permeability decreasing from \(K_0\) to \(K_0 \times 0.1\), the liquid saturation at the cathode CL/PEM interface increases from about 0.1 to about 0.34. The increase in the liquid saturation at the cathode CL/PEM interface consequently leads to the increase in the.

![Graphs and diagrams showing the effects of cathode GDL permeability](image-url)

**Fig. 13** — Effect of the cathode GDL permeability on the profiles of (a) relative cathode liquid and gas pressures, (b) cathode liquid saturation, (c) water content in CLs and PEM, and (d) water-crossover flux.
water content of the membrane facing the cathode side. Fig. 13c shows the corresponding distribution of water content across the CLs and the membrane. As can be seen in the figure, the water content at the cathode CL/PEM interface varies from 10.5 to 14 with decreasing the cathode GDL permeability from $K_0$ to $K_0 \times 0.1$. The increase in the water content in the cathode CL consequently lowers the water content gradient across the membrane, thus resulting in the decrease in the diffusion flux of water crossover. The water crossover fluxes due to different mechanisms are plotted in Fig. 13(d). When the cathode GDL permeability is lower than $K_0 \times 0.6$, the diffusion flux of water crossover decreases significantly with the decrease in the cathode GDL permeability. At the same time, the back convection flux of water crossover exhibits a sharp increase. However, it is noticed that the variation of cathode GDL permeability does not change the electro-osmotic drag flux much. Overall, the total water crossover flux decreases from 8.4 $\mu$mol cm$^{-2}$ s$^{-1}$ to 4.6 $\mu$mol cm$^{-2}$ s$^{-1}$ with the cathode GDL permeability decreasing from $K_0 \times 0.6$ to $K_0 \times 0.1$, and the corresponding net water transport coefficient exhibits a sharp reduction from 4.1 to 2.2 as shown in Fig. 13d. Thus, it can be concluded that decreasing the cathode GDL permeability is an effective way to suppress the rate of water crossover to the cathode.

4. Conclusions

In this work, a two-phase mass transport model is developed to study the water crossover behavior through the membrane in DMFCs. The anisotropy of GDLs is taken into account in this model. The effects of GDL structure properties on water crossover due to each water transport mechanism, including diffusion, electro-osmotic drag, and convection have been investigated. The main findings are summarized below.

1. Due to the high hydrophobic level of the MPLs, the liquid saturation in MPLs is much lower than that in other porous layers. Generally, the liquid saturation in the anode porous media is much higher than that in the cathode. Water is prone to diffuse from the anode side to the cathode side, while the higher cathode liquid pressure can push part of the liquid water back. The increase in cell current density leads to the increased CO$_2$ generation rate in the anode CL and higher liquid pressure at the cathode side. Consequently the diffusion flux of water becomes lower. And back convection flux becomes larger as more water is forced to flow back under the higher backward pressure gradient. The electro-osmotic flux almost grows linearly with the cell current density. As a result, the net water transport coefficient decreases first rapidly at low cell current densities, and then slowly at high cell current densities.

2. Rib coverage on the GDL surface and the deformation of GDLs can significantly limit the mass transport of methanol from the anode channel to the under rib region of the anode CL at high cell current densities, resulting in non-uniform distribution of local current density along the in-plane direction. The higher local current density in the region under channel leads to the higher water crossover flux in the corresponding region of the membrane. However, the distribution of local water crossover flux through the membrane becomes more uniform at the low cell current densities.

3. Increasing the cathode GDL contact angle leads to the increase in liquid pressure in the cathode GDL. However, it has little effect on the water content level in the region of membrane facing the cathode side. Consequently, water crossover flux almost remains the same value at different cathode GDL contact angles. On the other hand, decrease in the cathode GDL permeability results in a sharp increase in liquid pressure and liquid saturation in the cathode porous media. Hence, decreasing the cathode GDL permeability can greatly reduce the total water crossover flux through the membrane.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Nos. 51176155, 51106128).

Nomenclature

List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>specific area in the catalyst layer</td>
<td>m$^2$ m$^{-3}$</td>
</tr>
<tr>
<td>C</td>
<td>concentration</td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>D</td>
<td>diffusivity</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>F</td>
<td>faraday constant</td>
<td>96,485 C mol$^{-1}$</td>
</tr>
<tr>
<td>I</td>
<td>electrochemical reaction rate</td>
<td>A m$^{-3}$</td>
</tr>
<tr>
<td>I</td>
<td>current density</td>
<td>A m$^{-3}$</td>
</tr>
<tr>
<td>I</td>
<td>current vector</td>
<td>A m$^{-3}$</td>
</tr>
<tr>
<td>K</td>
<td>absolute permeability of porous media</td>
<td>m$^2$</td>
</tr>
<tr>
<td>k$_e$</td>
<td>evaporation rate of water</td>
<td>atm$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>k$_H$</td>
<td>henry’s law constant</td>
<td></td>
</tr>
<tr>
<td>k$_{rg}$</td>
<td>relative permeability of gas phase</td>
<td></td>
</tr>
<tr>
<td>k$_{rl}$</td>
<td>relative permeability of liquid phase</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>length of the channel</td>
<td>m</td>
</tr>
<tr>
<td>m</td>
<td>source terms in mass conservation equations</td>
<td>kg m$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>M</td>
<td>molecular weight</td>
<td>kg mol$^{-1}$</td>
</tr>
<tr>
<td>n$_d$</td>
<td>electro-osmotic drag coefficient</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>molar flux</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>p</td>
<td>pressure</td>
<td>pa</td>
</tr>
<tr>
<td>p$_c$</td>
<td>capillary pressure</td>
<td>pa</td>
</tr>
<tr>
<td>q</td>
<td>switch factor</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>gas constant</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>R</td>
<td>source term in species conservation equations</td>
<td>mol m$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>R$_W$</td>
<td>interfacial transfer rate of water</td>
<td>mol m$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>s</td>
<td>liquid saturation</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>V</td>
<td>thermodynamic equilibrium voltage</td>
<td>V</td>
</tr>
<tr>
<td>V$_{cell}$</td>
<td>cell voltage</td>
<td>V</td>
</tr>
<tr>
<td>Greek</td>
<td>transfer coefficient</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>reaction order</td>
<td></td>
</tr>
</tbody>
</table>
\( r \) porosity of the porous media

\( \mu \) viscosity, kg m\(^{-1}\) s\(^{-1}\)

\( \theta_c \) contact angle (°)

\( \rho \) density, kg m\(^{-3}\)

\( \sigma \) interfacial tension, N m\(^{-1}\)

Superscripts

ef\( f \) effective value

ref reference value

sat saturated

Subscripts

a anode

c catalyst layer

cathode

e electrons

H\(^+\) protons

mem membrane

g gas phase

l liquid phase

m the membrane phase

O\(_2\) oxygen

WV water vapor

MV methanol vapor

REFERENCES


