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Numerical Analysis of Water Transport Through the Membrane Electrolyte Assembly of a Polymer Exchange Membrane Fuel Cell

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The effects of water transport through membrane electrolyte assembly of a polymer exchange membrane fuel cell on cell performance has been studied by a one-dimensional, nonisothermal, steady-state model. Three forms of water are considered in the model: dissolved water in the electrolyte or membrane, and liquid water and water vapor in the void space. Phase changes among these three forms of water are included based on the corresponding local equilibria between the two involved forms. Water transport and its effect on cell performance have been discussed under different operating conditions by using the value and the sign of the net water transport coefficient, which is defined by the net flux of water transported from the anode side to the cathode side per proton flux. Optimal cell performance can be obtained by adjusting the liquid water saturation at the interface of the cathode gas diffusion layer and flow channels.

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Keywords: proton exchange membrane fuel cell, membrane electrolyte assembly, water transport, fuel cell model, net water transport coefficient

1 Introduction

Successful water management in the proton exchange membrane (PEM) fuel cell plays a critical role in terms of reducing the mass transport limitation. Too much water causes flooding in the cathode region, which inhibits oxygen from diffusing to the reaction sites of the cathode catalyst layer of a PEM fuel cell. On the other hand, too little water makes the membrane dry out and results in lower proton conductivity because the membrane's transport properties are highly dependent on water content. One common phenomenon occurring in a PEM fuel cell is that cell performance is low under low humidity conditions. Cell performance gradually improves with an increase in humidity. Once the humidity and liquid water saturation reach certain values, cell performance cannot be improved anymore. Instead, further increases in humidity and liquid water saturation will reduce cell performance.

Numerous researchers have studied improvement to PEM fuel cell performance through experiments, modeling, and optimization design [1–5]. A mathematical model is a powerful tool to understand water transport in PEM fuel cells [6]. Water in a PEM fuel cell either is generated in the cathode catalyst layer as a result of oxygen reduction reaction (ORR) or can be brought in by humidified gaseous reactants. Water may desorb/adsorb in electrolyte or membrane, or condense/evaporate between vapor and liquid phases, depending on the operating conditions of the cell. Most of previous developed PEM fuel cells or cell component models are single-phase models that consider the total water amount without distinguishing liquid water from water vapor [7–11]. These models are valid for low liquid water saturation conditions and are suitable for PEM fuel cell simulation under low humidity. However, when the PEM fuel cell operates in a fully

humidified condition, the gaseous reactants inside the fuel cells become oversaturated and water vapor may condense into liquid water, resulting in a possibly high performance loss due to mass transport limitation. In single-phase models, the effect of liquid water on cell performance cannot be investigated, which is critical for PEM fuel cell operation, especially in high current density range. Therefore, numerous two-phase models have been developed to take into account liquid water transport in PEM fuel cells [12–27]. Previous published two-phase models are able to predict cell performance, as well as the distributions of liquid water saturation and gaseous reactants in the cell. However, most of the parametric studies carried out in these two-phase models did not clearly show the above evolution of cell performance with the variation of liquid water condition in the cathode side of a PEM fuel cell.

Bernardi and Verbrugge [12] developed the hydraulic model with assumptions that the membrane is fully hydrated with liquid water. They analyzed the effects of different operating conditions on water balance in fuel cells. However, this model is not suitable for a partially dry membrane. Recently, Janssen [13] developed a two-dimensional phenomenological model based on concentrated solution theory to describe the transport of water in the membrane, and of water vapor and liquid water in the electrodes. This model gave a clear description of water transport in a partially dry membrane as well as in a fully hydrated membrane, but it was a water transport model only and did not couple with a cell model to thoroughly understand the effect of water transport on cell performance. Therefore, to further understand water transport through the membrane electrolyte assembly (MEA) of a PEM fuel cell, a model should include two-phase transport in the electrodes and gas diffusion layers, describe fully water transport in a cell operating with saturated and unsaturated gases, and couple with a cell model.

More recently, a number of multidimensional, multiphase, and nonisothermal models have been published. Berning and Djilali [21] developed a 3D, two-phase model considering momentum

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Fig. 1 Schematic of simulation domains

transport in the liquid and gas phases through separate transport equations and including exchange terms between phases. However, they treated catalyst layer as an interface without thickness. Wang and Wang [28] expended their multiphase mixture (M2) model to a 3D, nonisothermal two-phase model, where each species or phase in the porous electrode is modeled by a separate mass conservation equation, but one momentum equation is solved to get the mixture velocity. They do not include mass transport between phases. Siegel et al. [17] presented a 2D model to account for the transport of liquid water in the electrode and treat all three forms of water as a separate phase and allow mass transport among them. However, Schroeder's paradox was neglected. Steinkamp et al. [29] presented a 2D dynamic two-phase flow model accounting for all important transport processes in a PEM fuel cell. Unfortunately, the computational cost for simulation was quite high because of the high complexity of the model.

Overall, the focus of this paper is to formulate a model that accounts for most of the important transport processes in a PEM fuel cell with 1D simplification. Using this one-dimensional, nonisothermal, two-phase, steady-state model, we numerically studied the effect of liquid water saturation on cell performance to capture the whole picture of water transport by changing the boundary conditions of liquid water saturation at the cathode side of the cell. The water balance is characterized by the net water flux per proton flux from the anode side through the membrane to the cathode side. Based on the value and sign of the net water flux through the MEA, we analyzed cell performances under different operating conditions and obtained the optimal cell performance by adjusting liquid water saturation at the interface of a cathode gas diffusion layer (GDL) and channels.

2 Model Description

The model presented here is a one-dimensional, two-phase, nonisothermal model of a cell sandwich including five subdomains: anode and cathode gas diffusion layers, anode and cathode catalyst layers, and membrane. A schematic of the model domain is showed in Fig. 1. A fuel cell is a complex system coupling transport processes and the electrochemical reaction. For simplicity, we made the following assumptions.

- (1) The PEM fuel cell operates under steady state.
- (2) A one-dimensional approximation is used in the model formulation by neglecting the variation of reactant concentrations in flow channels.
- (3) Gas species (O_2 , H_2 , N_2 , and water vapor) diffuse through the pores of the GDLs and catalyst layers (CLs). O_2 and H_2 also dissolve into electrolyte as species.
- (4) Three types of water are considered: dissolved water in the electrolyte/membrane, water vapor, and liquid water in pores. The mass transports among these three types of wa-

ter are dictated by the deviation from the local equilibrium. Dissolved water transport in the electrolyte is assumed through diffusion and electro-osmotic drag.

- (5) Generated water from ORR in the cathode catalyst layer is either in liquid or in vapor form, depending on the local vapor pressure.
- (6) Agglomerate model is employed in both anode and cathode catalyst layers.
- (7) Gas species and liquid water cannot penetrate the membrane.

2.1 Model Equations. To thoroughly understand water transport through the whole MEA, we should use a two-fluid, multi-component model to solve individual transport equations for each phase and specie. Abriola and Pinder [30] developed a full system of conservation equations. Here we adopted Abriola and Pinder's general equation systems [30] to the five subdomains of our model by modifying the source/sink terms to reflect the corresponding physical phenomena in each subdomain. Based on the conservation principles of mass, momentum, energy, specie, and charge, the general governing equations can be obtained as follows.

2.1.1 Mass Conservation of Each Specie in Gas Phase. Taking into account electrochemical reaction, diffusion, and convection, the mass conservation equations are given as

$$\frac{d}{dx}(u_g C_j) = \frac{d}{dx} \left[\varepsilon_i (1-s) D_j^{\text{eff}} \frac{dC_j}{dx} \right] - S_j \quad (1)$$

where s is the water saturation and defined as the volume fraction of liquid water in the total void space of the porous media, ε_i is the porosity of subdomain i , and $i \in \{\text{cathode GDL and CL, and anode GDL and CL}\}$. $j \in \{O_2, H_2, N_2, V\}$ and x is the coordinate from the anode side to the cathode side. C_j and D_j^{eff} denote the concentrations and the effective diffusion coefficients of each gas specie in the pore space, respectively. u_g is the superficial velocity of gas phase. S_j is the source/sink term for each gas specie. Because the terms of inertial and bulk viscous can be neglected, we assumed that the gas velocity followed Darcy's law

$$u_g = - \frac{K_i k_{rg}}{\mu_g} \frac{dp_g}{dx} \quad (2)$$

where K_i is the absolute permeability of subdomain i , k_{rg} is the relative permeability of gas phase, μ_g is the dynamic viscosities of gas phase, and p_g is the partial pressure of gas phase. Here, gas phase denotes the mixture of oxygen, nitrogen, and water vapor at the cathode side, and the mixture of hydrogen and water vapor at the anode side. Using the ideal gas law,

$$p_g = \begin{cases} (C_{O_2} + C_{N_2} + C_V^c)RT & \text{at the cathode GDL and CL} \\ (C_{H_2} + C_V^a)RT & \text{at the anode GDL and CL} \end{cases} \quad (3)$$

Source terms S_{O_2} and S_{H_2} are zero at the cathode and anode GDL because of no electrochemical reaction. However, S_{O_2} and S_{H_2} are the oxygen consumption at the cathode CL and the hydrogen consumption at the anode CL, which are related to the cathode and anode reaction rates.

$$S_{O_2} = \frac{1}{4} |RR_c| \quad (4)$$

$$S_{H_2} = \frac{1}{2} |RR_a| \quad (5)$$

where RR_c and RR_a are the reaction rates of the ORR and the hydrogen oxidation reaction (HOR), and given by Butler–Volmer law as

$$RR_k = \frac{a_k i_j^{\text{ref}}}{F} \left(\frac{C_{j,e}^s}{C_j^{\text{ref}}} \right) \varepsilon_{N,k} (e^{\alpha_a F \eta_k / RT} - e^{-\alpha_c F \eta_k / RT}) \quad (6)$$

where $j = \text{O}_2$ and $k = c$ or $j = \text{H}_2$ and $k = a$. $i_{\text{O}_2}^{\text{ref}}$ and $i_{\text{H}_2}^{\text{ref}}$ are the cathode and anode exchange current densities and are estimated by [1]

$$i_{\text{O}_2}^{\text{ref}} = 1 \times 10^{-3} \exp \left[\frac{73,269}{R} \left(\frac{1}{303} - \frac{1}{T} \right) \right] \quad (7)$$

$$i_{\text{H}_2}^{\text{ref}} = 1 \times 10^1 \exp \left[\frac{9500}{R} \left(\frac{1}{303} - \frac{1}{T} \right) \right] \quad (8)$$

$C_{\text{O}_2}^{\text{ref}}$ and $C_{\text{H}_2}^{\text{ref}}$ are the oxygen and hydrogen reference concentrations, α_c and α_a are the cathodic and anodic transfer coefficients, R is the universal gas constant, and η_c and η_a are the surface overpotentials for the cathode and anode sides, respectively.

$$\eta_c = \psi - \phi - U_0, \quad \eta_a = \psi - \phi \quad (9)$$

where U_0 is the open circuit potential and is given by [31]

$$U_0 = 1.23 - 0.9 \times 10^{-3} (T - 298.15) \quad (10)$$

a_c and a_a are the surface areas of catalyst per unit volume of catalyst layer

$$a_k = a_k^{\text{Pt}} m_k^{\text{Pt}} \text{Pt}_k^{\text{eff}} / L_k, \quad k \in c, a \quad (11)$$

where a_k^{Pt} ($\text{m}^2 \text{kg}^{-1}$) is the specific Pt surface area, m_k^{Pt} is the Pt loading, Pt_k^{eff} is the utilization rate of specific Pt surface area, and L_k is the thickness of the catalyst layer.

$$a_k^{\text{Pt}} = 3 / (r_{\text{Pt}} \rho_{\text{Pt}}) \quad (12)$$

where r_{Pt} is the platinum radius and ρ_{Pt} is the density of platinum.

In the Butler–Volmer expressions, Eq. (6), $C_{\text{O}_2,e}^s$ and $C_{\text{H}_2,e}^s$ are oxygen and hydrogen concentrations at the surface of agglomerates where the reaction takes place. They are related to the bulk values ($C_{\text{O}_2,e}$ and $C_{\text{H}_2,e}$). According to Henry's law,

$$C_{\text{O}_2,e} = H_{\text{O}_2} C_{\text{O}_2}, \quad C_{\text{H}_2,e} = H_{\text{H}_2} C_{\text{H}_2} \quad (13)$$

We denote $\varepsilon_N^{\text{in}}$ as the nafion volume fraction inside the agglomerate, and ε_a is the total volume fraction of carbon, Pt, and small pores inside the agglomerates. If the thickness of the electrolyte thin film that covers the agglomerate is δ_e , the agglomerate radius is r_{ag} , then the number of agglomerates per unit volume of the catalyst layer is

$$N = (\varepsilon_a + \varepsilon_N^{\text{in}}) / \left(\frac{4}{3} \pi r_{\text{ag}}^3 \right) \quad (14)$$

The nafion film volume fraction, ε_N^f , is

$$\varepsilon_N^f = \frac{4}{3} \pi [(r_{\text{ag}} + \delta_e)^3 - r_{\text{ag}}^3] N \quad (15)$$

Then the total nafion volume fraction is the sum of the volume fractions of nafion inside the agglomerates and the nafion thin film,

$$\varepsilon_N = \varepsilon_N^{\text{in}} + \varepsilon_N^f \quad (16)$$

Therefore, the porosity of the catalyst layers should be

$$\varepsilon_{\text{CL}} = 1 - \varepsilon_a - (\varepsilon_N^{\text{in}} + \varepsilon_N^f) \quad (17)$$

When liquid water covers the agglomerates, the thickness of the liquid water film δ_l is

$$\delta_l = \left[(r_{\text{ag}} + \delta_e)^3 + \frac{S \varepsilon_{\text{CL}}}{4 \pi N} \right]^{1/3} - (r_{\text{ag}} + \delta_e) \quad (18)$$

The total film thickness would be $\delta = \delta_e + \delta_l$.

We assumed that reactants diffuse in the electrolyte according to Fick's law of diffusion. First we consider one agglomerate in

Fig. 2 The agglomerate structure

the cathode catalyst layer as shown in Fig. 2. For spherical diffusion, the quantity of diffusing oxygen, which passes through the spherical wall per unit time, is given by [32]

$$q = 4 \pi D_{\text{O}_2}^w \frac{(r_{\text{ag}} + \delta_l + \delta_e)(r_{\text{ag}} + \delta_e)}{\delta_l} (C_{\text{O}_2,e} - C_{w-e}) \quad (19)$$

in the water film

and

$$q = 4 \pi D_{\text{O}_2}^e \frac{(r_{\text{ag}} + \delta_e) r_{\text{ag}}}{\delta_e} (C_{w-e} - C_{\text{O}_2,e}^s) \quad \text{in the nafion film} \quad (20)$$

where C_{w-e} is the concentration of oxygen at the interface of the water film and the nafion film. $D_{\text{O}_2}^w$ and $D_{\text{O}_2}^e$ are the diffusivities of oxygen in water and electrolyte, respectively. By summation of Eqs. (19) and (20), we get

$$q = \chi_{\text{O}_2} (C_{\text{O}_2,e} - C_{\text{O}_2,e}^s) \quad (21)$$

where we define

$$\chi_{\text{O}_2} = \frac{\chi_w \chi_e}{\chi_w + \chi_e} \quad (22)$$

$$\chi_w = 4 \pi D_{\text{O}_2}^w \frac{(r_{\text{ag}} + \delta_l + \delta_e)(r_{\text{ag}} + \delta_e)}{\delta_l} \quad (23)$$

$$\chi_e = 4 \pi D_{\text{O}_2}^e \frac{(r_{\text{ag}} + \delta_e) r_{\text{ag}}}{\delta_e} \quad (24)$$

Because the number of agglomerates per unit volume is N , the total quantity of diffusing oxygen, which passes through the water film and the nafion film per unit time, is Nq . We assumed that the total quantity of diffusing oxygen was consumed in the agglomerate. Therefore,

$$N \chi_{\text{O}_2} (C_{\text{O}_2,e} - C_{\text{O}_2,e}^s) = \frac{1}{4} |RR_c| \quad (25)$$

Similar to the cathode catalyst layer, because no water is generated in the anode catalyst layer,

$$\chi_{\text{H}_2} = 4 \pi D_{\text{H}_2}^e \frac{(r_{\text{ag}} + \delta_e) r_{\text{ag}}}{\delta_e} \quad (26)$$

and

$$N \chi_{\text{H}_2} (C_{\text{H}_2,e} - C_{\text{H}_2,e}^s) = \frac{1}{2} |RR_a| \quad (27)$$

where $D_{\text{H}_2}^e$ is the diffusivity of hydrogen in the electrolyte.

S_V is the source/sink for water vapor. At the GDLs, water vapor only comes from phase change $S_V = S_{e/c}$. When local water vapor pressure $p_V = C_V RT$ larger than the saturation pressure of water

vapor p_{sat} , water vapor will condensate to liquid water. Otherwise, liquid water will evaporate to water vapor. The term $S_{e/c}$ due to the evaporation and condensation is given by [14,18]

$$S_{e/c} = \begin{cases} \kappa_e \frac{\varepsilon_i s p_l}{W_l} (p_{\text{sat}} - p_v) & p_v < p_{\text{sat}} \\ \kappa_c \frac{\varepsilon_i (1-s) X_V}{RT} (p_{\text{sat}} - p_v) & p_v \geq p_{\text{sat}} \end{cases} \quad (28)$$

where κ_e and κ_c are the evaporation and condensation rate constants, p_{sat} is the saturation pressure of water vapor, X_V is the molar fraction of water vapor, and

$$X_{V,c} = \frac{C_V^c}{C_{O_2} + C_{N_2} + C_V^c}, \quad X_{V,a} = \frac{C_V^a}{C_{H_2} + C_V^a} \quad (29)$$

At the cathode catalyst layer, water vapor comes from three parts: evaporation/condensation term due to phase change $S_{e/c}$, absorption/desorption term $S_{d/v}$, and water production term due to the chemical reaction S_{pw} .

$$S_V = S_{e/c} + \gamma_{d/v} S_{d/v} + \gamma_{e/c} S_{pw} \quad (30)$$

$$S_{pw} = \begin{cases} \frac{1}{2} |RR_c| & \text{cathode catalyst layer} \\ 0 & \text{anode catalyst layer} \end{cases} \quad (31)$$

where γ is the switch function and will be discussed in Sec. 2.1.5.

We assumed that the mass transfer term $S_{d/v}$ between vapor and dissolved water was driven by concentration gradient $C_d - C_{d,v}^*$ [23],

$$S_{d/v} = \begin{cases} h_{a,v} (C_d - C_{d,v}^*) \lambda (1-s) & C_d < C_{d,v}^* \\ h_{d,v} (C_d - C_{d,v}^*) \lambda (1-s) & C_d > C_{d,v}^* \end{cases} \quad (32)$$

where $h_{a,v}$ and $h_{d,v}$ are the mass transfer coefficients for absorption and desorption of water vapor, C_d is the concentration of dissolved water, and λ is the water content. $C_{d,v}^*$ is the concentration of dissolved water in equilibrium with water vapor and related to the vapor equilibrium water content λ_v^* [7] as follows:

$$C_{d,v}^* = \frac{\rho_{m,\text{dry}}}{W_{m,\text{dry}}} \lambda_v^* \quad (33)$$

where $\rho_{m,\text{dry}}$ is the dry membrane density and $W_{m,\text{dry}}$ is the dry membrane equivalent weight. Hinatsu et al. [33] got the relationship between the vapor equilibrium water content and the water vapor activity a_w at 80°C as follows:

$$\lambda_v^* = 0.3 + 10.8 a_w - 16 a_w^2 + 14.1 a_w^3 \quad (34)$$

and

$$a_w = \frac{C_V^k RT}{p_{\text{sat}}}, \quad k \in (c, a) \quad (35)$$

2.1.2 Mass Conservation of Liquid Water. According to mass conservation equation of liquid phase,

$$\frac{d}{dx} (\rho_l u_l) = m_l \quad (36)$$

where m_l represents the interfacial mass transfer rates from other phases to liquid phases. If W_l is the molar mass of water

$$m_l = \begin{cases} [-S_{e/c} + \gamma_{d/l} S_{d/l} + (1 - \gamma_{e/c}) S_{pw}] W_l & \text{CLs} \\ -S_{e/c} W_l & \text{GDLs} \end{cases} \quad (37)$$

In a similar fashion to $S_{d/v}$, mass transfer term between liquid and dissolved water, $S_{d/l}$, is [23]

$$S_{d/l} = \begin{cases} h_{a,l} (C_d - C_{d,l}^*) & C_d < C_{d,l}^* \\ h_{d,l} (C_d - C_{d,l}^*) & C_d > C_{d,l}^* \end{cases} \quad (38)$$

where $h_{a,l}$ and $h_{d,l}$ are the mass transfer coefficients for absorption and desorption of liquid water in electrolyte, and $C_{d,l}^*$ is the concentration of dissolved water in equilibrium with liquid water and related to the liquid equilibrium water content λ_l^* by

$$C_{d,l}^* = \frac{\rho_{m,\text{dry}}}{W_{m,\text{dry}}} \lambda_l^* \quad (39)$$

The water content at liquid equilibrium has the value of 22.

u_l is the superficial velocity of liquid. We also assumed that the liquid velocity followed Darcy's law

$$u_l = - \frac{K_l k_{rl} dp_l}{\mu_l dx} \quad (40)$$

where k_{rl} is the relative permeability of liquid phase, μ_l is the dynamic viscosity of liquid phase, and p_l is the partial pressure of liquid phase.

By introducing capillary pressure, the liquid water pressure p_l can be replaced and the mass conservation equation for liquid water, Eq. (36), can be transformed into an equation in which the liquid water saturation s needs to be solved.

Capillary pressure is defined as the difference between gas pressure and liquid pressure,

$$p_c = p_g - p_l \quad (41)$$

Substituting Eq. (40) into Eq. (36) with Eq. (41) results in

$$- \frac{d}{dx} \left[\rho_l \frac{K_l k_{rl}}{\mu_l} \left(\frac{dp_g}{dx} - \frac{dp_c}{ds} \frac{ds}{dx} \right) \right] = m_l \quad (42)$$

2.1.3 Electronic and ionic charge transfers.

$$- \frac{d}{dx} \left(\varepsilon_c^{3/2} \sigma_c \frac{d\psi}{dx} \right) = S_{\psi,i} \quad (43)$$

$$- \frac{d}{dx} \left(\varepsilon_N^{3/2} \sigma_e \frac{d\phi}{dx} \right) = S_{\phi,i} \quad (44)$$

where ψ is the electronic potential in carbon phase, ϕ is the protonic potential in electrolyte or membrane phase, σ_c and σ_e are the electron and proton conductivities, ε_c is the volume fraction of carbon phase, ε_N is the volume fraction of nafion, and S_{ψ} and S_{ϕ} are the source/sink terms of electron and proton, respectively.

$$S_{\phi} = \begin{cases} -FRR_c & \text{cathode catalyst layer} \\ FRR_a & \text{anode catalyst layer} \end{cases} \quad (45)$$

$$S_{\psi} = \begin{cases} FRR_c & \text{cathode catalyst layer} \\ -FRR_a & \text{anode catalyst layer} \end{cases} \quad (46)$$

2.1.4 Mass Balance for Dissolved Water in the Electrolyte. We assumed that water transport through membrane or electrolyte by diffusion and electro-osmotic drag. The mass balance for dissolved water in the electrolyte is written as follows:

$$- \frac{d}{dx} \left(D_d \frac{dC_d}{dx} \right) - \frac{d}{dx} \left(n_d \frac{\sigma_e^{\text{eff}}}{F} \frac{d\phi}{dx} \right) = M_d \quad (47)$$

where C_d is the water diffusivity in electrolyte, C_d is the concentration of dissolved water in electrolyte, n_d is the electro-osmotic drag coefficient, which is related to the water content of electrolyte by $n_d = (2.5/22)\lambda$ [7]. F is Faraday's constant, and M_d is the interfacial mass transfer from liquid water or water vapor to dissolved water. In membrane, $M_d = 0$. In the anode and cathode catalyst layers,

Fig. 3 A schematic of mass transfer among the three forms of water

$$M_d = -\gamma_{dlv}S_{dlv} - \gamma_{dll}S_{dll} \quad (48)$$

where γ is the switch function and will be discussed in Sec. 2.1.5.

2.1.5 Switch Function of Mass Transfer Among the Phases (Liquid Water, Water Vapor, and Dissolved Water). The model developed here assumes that the three phases of water, liquid water, vapor, and dissolved water, are in local equilibrium. The driving forces from liquid water to vapor, liquid water to dissolved water, and water vapor to dissolved water are the relative humidity $RH = p_v/p_{\text{sat}}$, the deviation of C_d from $C_{d,l}^*$, and the deviation of C_d from $C_{d,v}^*$, respectively. When $RH > 1$, the vapor pressure exceeds the saturation pressure, the produced water from the ORR becomes a source term in liquid water equation, i.e., $\gamma_{elv} = 0$; otherwise, $\gamma_{elv} = 1$.

In this paper, we adopted a critical saturation value of liquid water [23], denoted by s^* , and set to be the value of the immobile saturation. When liquid water saturation is under s^* , water droplets are in the noncontiguous status. Based on this value, we define two switch functions to describe the mass transfer from vapor or liquid to dissolved water. When the local liquid saturation is smaller than s^* , liquid water is immobile and has less chance to contact with electrolyte; the processes of absorption and desorption between liquid phase and dissolved phase are off, i.e., $\gamma_{dll} = 0$; while the process of absorption and desorption between vapor phase and dissolved phase is on, i.e., $\gamma_{dlv} = 1$. When local liquid saturation is larger than s^* , liquid water droplets connect together and cover the agglomerates; the transfer route from water vapor to dissolved water is closed, $\gamma_{dlv} = 0$; while the processes of absorption and desorption between liquid phase and dissolved phase are on, $\gamma_{dll} = 1$. Figure 3 shows these processes clearly. The mass transfer coefficients between liquid or vapor and dissolved are given in Table 2.

2.1.6 Energy Conservation in Liquid and Gas Phases. We assumed that gas phase, liquid phase, and solid phase participate in energy transfer and local thermal equilibrium among these three phases, that is, $T_g = T_l = T_s = T$. The conversation equation is as follows:

$$-\frac{d}{dx}\left(k_i^{\text{eff}}\frac{dT}{dx}\right) + \frac{d}{dx}(\rho_l c_p^l u_l T + \rho_g c_p^g u_g T) = Q \quad (49)$$

where k_i^{eff} stands for the effective thermal conductivity of subdomains i , and Q is the sum of the volumetric heat source/sink, including Ohmic heat, irreversible electrochemical reaction heat, entropic reaction heat, and phase change heat.

$$Q = \begin{cases} Q_{\text{Ohm}}^c + Q_{\text{Ohm}}^e + Q_{\text{entropic}} + Q_{\text{reaction}} + Q_{e/c} & \text{CLs} \\ Q_{\text{Ohm}}^c + Q_{e/c} & \text{GDLs} \\ Q_{\text{Ohm}}^c & \text{membrane} \end{cases} \quad (50)$$

Each heat source/sink term is expressed as follows:

$$Q_{\text{Ohm}}^c = \begin{cases} (1 - \varepsilon_g)^{3/2} \sigma_c \left(\frac{d\psi}{dx}\right)^2 & \text{GDLs} \\ \varepsilon_c^{3/2} \sigma_c \left(\frac{d\psi}{dx}\right)^2 & \text{CLs} \end{cases} \quad (51)$$

$$Q_{\text{Ohm}}^e = \begin{cases} \sigma_e \left(\frac{d\phi}{dx}\right)^2 & \text{membrane} \\ \varepsilon_{\text{CL}}^{3/2} \sigma_e \left(\frac{d\phi}{dx}\right)^2 & \text{CLs} \end{cases} \quad (52)$$

$$Q_{\text{entropic}} = \begin{cases} \frac{\Delta s_c T}{4} RR_c & \text{cathode CL} \\ \frac{\Delta s_a T}{2} RR_a & \text{anode CL} \end{cases} \quad (53)$$

$$Q_{\text{reaction}} = \begin{cases} -F\eta_c RR_c & \text{cathode CL} \\ -F\eta_a RR_a & \text{anode CL} \end{cases} \quad (54)$$

$$Q_{e/c} = h_{gl} S_{e/v} \quad (55)$$

Table 1 Source/sink terms

Catalyst layers		Gas diffusion layers	Membrane
S_{O_2}	S_{O_2}	0	-
S_{H_2}	S_{H_2}	0	-
S_{N_2}	0	0	-
S_V	$S_{e/c} + \gamma_{dlv} S_{dlv} + \gamma_{elc} S_{pw}$	$S_{e/c}$	-
M_d	$-\gamma_{dlv} S_{dlv} - \gamma_{dl} S_{dl}$	-	0
m_l	$[-S_{e/c} + \gamma_{dl} S_{dl} + (1 - \gamma_{elc}) S_{pw}] W_l$	$-S_{e/c} W_l$	-
Q	$Q_{e/c} + Q_{Ohm}^c + Q_{Ohm}^c + Q_{entropic} + Q_{reaction}$	$Q_{Ohm}^c + Q_{e/c}$	Q_{Ohm}^c
$S_{\phi,i}$	$S_{\phi,i}$	-	0
$S_{\psi,i}$	$S_{\psi,i}$	0	-

where h_{gl} is the liquid-vapor enthalpy change, and Δsc and Δsa are the entropies associated with ORR and HOR, respectively.

In summary, the expressions of the source/sink terms of the model equations in different subdomains are listed in Table 1.

2.2 Constitutive Relations

2.2.1 Effective Diffusion Coefficient. Bruggeman relation is used here to estimate the effective diffusion coefficients of gas species in porous media, respectively.

$$D_j^{\text{eff}} = \varepsilon_i^{1.5} D_j, \quad j \in O_2, H_2, N_2, \text{ and } V \quad (56)$$

where the bulk diffusivities are temperature and pressure dependent [34]

$$D_{O_2} = 3.8 \times 10^{-9} T^{1.5} / p_g \quad (57)$$

$$D_{H_2} = 1 \times 10^{-9} T^{1.5} / p_g \quad (58)$$

$$D_{N_2} = 3.6 \times 10^{-9} T^{1.5} / p_g \quad (59)$$

$$D_V = 4.1 \times 10^{-9} T^{1.5} / p_g \quad (60)$$

The diffusivity of oxygen through the electrolyte has the following form [35]:

$$D_{O_2}^e = 3.1 \times 10^{-7} e^{-2768/T} \quad (61)$$

and the diffusivity of hydrogen through the electrolyte is taken a constant value, shown in Table 2.

The diffusivity of dissolved water through the electrolyte is related to the water content and temperature [36]

$$D_d = \begin{cases} 3.1 \times 10^{-7} \lambda (e^{0.28\lambda} - 1) e^{-2436/T} & 0 < \lambda < 3 \\ 4.17 \times 10^{-8} \lambda (1 + 161 e^{-\lambda}) e^{-2436/T} & 3 < \lambda < 22 \end{cases} \quad (62)$$

2.2.2 Permeability. The absolute permeability can be approximated by Kozeny–Carman law

$$K_i = \frac{d_i^2 \varepsilon_i^3}{16 k_K (1 - \varepsilon_i)^2}, \quad i \in \text{different subdomains} \quad (63)$$

where k_K is a Kozeny–Carman constant and d_i is the mean pore diameter of subdomain i .

The relative permeabilities of liquid and gas phases are related to the liquid water saturation as [15]

$$k_{rl} = s^3 \quad \text{and} \quad k_{rg} = (1 - s)^3 \quad (64)$$

2.2.3 Capillary Pressure. The capillary pressure is given by [16]

$$p_c = \sigma \cos \theta_i \sqrt{\frac{\varepsilon_i}{K_i}} \mathcal{I}(s) \quad (65)$$

where σ is the surface tension, θ_i is the contact angle of subdomain i , and $\mathcal{I}(s)$ is the Leverett function and estimated as

$$\mathcal{I}(s) = \begin{cases} 1.417(1 - s) - 2.21(1 - s)^2 + 1.263(1 - s)^3 & \theta_i < 90^\circ \\ 1.417s - 2.21s^2 + 1.263s^3 & \theta_i > 90^\circ \end{cases} \quad (66)$$

2.2.4 Membrane Conductivity. The membrane conductivity is highly dependent on the water uptake of the membrane and given by Springer et al. [7] as

$$\sigma_e = \exp\left(1268\left(\frac{1}{303} - \frac{1}{T}\right)\right)(0.514\lambda - 0.326) \quad (67)$$

$$\sigma_e^{\text{eff}} = \varepsilon_N^{1.5} \sigma_e \quad (68)$$

2.2.5 Properties of Gas and Liquid Phases. The enthalpy of water evaporation h_{gl} (J/mol) as a function of temperature is fitted based on the data in [37]

$$h_{gl} = 3.5912 \times 10^4 - 2.4253 \times 10^2 T + 1.4453 T^2 - 2.6968 \times 10^{-3} T^3 + 3.5228 \times 10^{-6} T^4 - 1.872 \times 10^{-9} T^5 \quad (69)$$

The density of gas mixture can be expressed as

$$\rho_g^k = \frac{p_g^k \sum_j X_j^k W_j^k}{RT} \quad (70)$$

where

$$X_j^k = \frac{C_j}{\sum_j C_j} \quad (71)$$

The dynamic viscosities of gas mixture are

$$\mu_g^k = \frac{\sum_j X_j^k \mu_j \sqrt{W_j}}{\sum_j X_j^k \sqrt{W_j}} \quad (72)$$

when $k=c$, then $j=O_2, N_2$, and V , or when $k=a$, then $j=H_2$ and V .

2.3 Boundary Conditions. According to our assumptions, gas species and liquid water cannot penetrate the membrane and then their fluxes should be zero at the interfaces of the anode CL and the membrane, and the membrane and the cathode CL, respectively.

$$\begin{aligned} \left. \frac{dC_{O_2}}{dx} \right|_{x=x_{\text{MEM}}} &= \left. \frac{dC_{N_2}}{dx} \right|_{x=x_{\text{MEM}}} = \left. \frac{dC_V}{dx} \right|_{x=x_{\text{MEM}}} \\ &= \left. \frac{ds}{dx} \right|_{x=x_{\text{MEM}}} = 0 \end{aligned} \quad (73)$$

and

$$\left. \frac{dC_{H_2}}{dx} \right|_{x=x_{\text{ACL}}} = \left. \frac{dC_V}{dx} \right|_{x=x_{\text{ACL}}} = \left. \frac{ds}{dx} \right|_{x=x_{\text{ACL}}} = 0 \quad (74)$$

Since there is no proton conducting material in either the anode GDL or the cathode GDL, the proton fluxes at the interfaces between the GDLs and the CLs should be zero,

Table 2 Physical parameters and properties

Symbol	Definition	Value/Reference
Physical constant and properties		
F	Faraday's constant (C mol^{-1})	96,485
R_g	Universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)	8.314
W_{O_2}	Molar mass of oxygen (kg mol^{-1})	0.032
W_{N_2}	Molar mass of nitrogen (kg mol^{-1})	0.028
W_l	Molar mass of water (kg mol^{-1})	0.018
W_{H_2}	Molar mass of hydrogen (kg mol^{-1})	0.002
ρ_l	Liquid water density (kg m^{-3})	1,000
ν	Fixed charge site concentration of nafion (mol m^{-3})	1,800
Δsc	Entropy of ORR ($\text{J mol}^{-1} \text{K}^{-1}$)	326.36
Δsa	Entropy of HOR ($\text{J mol}^{-1} \text{K}^{-1}$)	-0.208
k_c	Thermal conductivity of catalyst layer ($\text{W m}^{-1} \text{K}^{-1}$)	0.27 [39]
k_g	Thermal conductivity of GDL ($\text{W m}^{-1} \text{K}^{-1}$)	1.7 [39]
k_m	Thermal conductivity of membrane ($\text{W m}^{-1} \text{K}^{-1}$)	0.12 [39]
$\rho_l C_p^l$	Heat capacitance (liquid water) ($\text{J m}^{-3} \text{K}^{-1}$)	4.13×10^6
C_p^g	Specific heat capacity of air ($\text{J kg}^{-1} \text{K}^{-1}$)	1.01×10^3
μ_l	Dynamic viscosity of liquid water ($\text{kg m}^{-1} \text{s}^{-1}$)	1×10^{-4}
σ	Surface tension of liquid water (N m^{-1})	0.07
μ_{O_2}	Dynamic viscosity of oxygen ($\text{kg m}^{-1} \text{s}^{-1}$)	2.34×10^{-5}
μ_{N_2}	Dynamic viscosity of nitrogen ($\text{kg m}^{-1} \text{s}^{-1}$)	2.01×10^{-5}
μ_v	Dynamic viscosity of water vapor ($\text{kg m}^{-1} \text{s}^{-1}$)	1.2×10^{-5}
μ_{H_2}	Dynamic viscosity of hydrogen ($\text{kg m}^{-1} \text{s}^{-1}$)	9.93×10^{-6}
k_K	Kozeny–Carman constant	6
ρ_{Pt}	Density of platinum (kg m^{-3})	21,450
$\rho_{m,\text{dry}}$	Density of dry membrane (kg m^{-3})	2,000
$W_{m,\text{dry}}$	Equivalent weight (kg mol^{-1})	1.1
$D_{\text{H}_2}^e$	Diffusivity of hydrogen in the electrolyte ($\text{m}^2 \text{s}^{-1}$)	7.9×10^{-10}
σ_c	Conductivity of carbon phase (S m^{-1})	1,000
Geometry properties		
L	Catalyst layer thickness (μm)	25
L_m	Membrane thickness (μm)	50
LG	GDL thickness (μm)	200
ε_g	Porosity of GDL	0.75
ε_a	Total volume fraction of carbon, Pt, and small pores	0.3
$\varepsilon_N^{\text{in}}$	Nafion volume fraction located inside agglomerates	0.1
ε_c	Carbon volume fraction in catalyst layer	0.2
r_{ag}	Agglomerate radius (nm)	200
δ_e	Thickness of nafion layer coating agglomerates (nm)	15 ^a
θ_g	Contact angle of GDL	110 deg [1]
θ_c	Contact angle of CCL	82 deg [1]
d_c	Mean pore size in CCL (μm)	1 ^a
d_g	Mean pore size in GDL (μm)	10 ^a
r_{Pt}	Platinum radius (nm)	2
Electrochemical properties		
α_c	Cathodic transfer coefficient	1
α_a	Anodic transfer coefficient	1
$C_{\text{O}_2}^{\text{ref}}$	Oxygen reference concentration (mol m^{-3})	1.18 [17]
$C_{\text{H}_2}^{\text{ref}}$	Hydrogen reference concentration (mol m^{-3})	22.6 [17]
Pt_c^{eff}	Utilization rate of specific Pt surface area	0.5
Pt_a^{eff}	Utilization rate of specific Pt surface area	0.5
m_{Pt}^c	Platinum loading on the cathode (kg m^{-2})	4×10^{-3}
m_a	Platinum loading on the anode (kg m^{-2})	4×10^{-3}
Transport properties		
H_{O_2}	Oxygen Henry's law constant (dimensionless)	0.64 [17]
H_{H_2}	Hydrogen Henry's law constant (dimensionless)	0.19 [17]
κ_c	Condensation constant (s^{-1})	100 [14]
κ_a	Evaporation constant ($\text{atm}^{-1} \text{s}^{-1}$)	100 [14]
$h_{d,l}$	Desorption coefficient between dissolved/liquid (s^{-1})	3 ^a
$h_{a,l}$	Adsorption coefficient between dissolved/liquid (s^{-1})	0.1 ^a
$h_{d,v}$	Desorption coefficient between dissolved/vapor (s^{-1})	0.1 ^a
$h_{a,v}$	Adsorption coefficient between dissolved/vapor (s^{-1})	0.01 ^a
$D_{\text{O}_2}^w$	Oxygen diffusivity in liquid water (60°C) ($\text{m}^2 \text{s}^{-1}$)	4.82×10^{-9} [14]
$D_{\text{H}_2}^e$	Hydrogen diffusivity in nafion ($\text{m}^2 \text{s}^{-1}$)	1×10^{-10} [14]
Operating conditions (base case)		

Table 2 (Continued.)

Symbol	Definition	Value/Reference
T_c	Cathode channel temperature (K)	353
T_a	Anode channel temperature (K)	353
RH_c	Cathode channel relative humidity	100%
RH_a	Anode channel relative humidity	100%
P_c	Cathode channel pressure (atm)	1
P_a	Anode channel pressure (atm)	1
x_{O_2}	Oxygen mole fraction	0.21
x_{H_2}	Hydrogen mole fraction	1.0

^aEstimated.

$$\left. \frac{d\phi}{dx} \right|_{x=x_{\text{AGDL}}} = \left. \frac{d\phi}{dx} \right|_{x=x_{\text{CCL}}} = 0 \quad (75)$$

Similarly, the dissolved water only exists in membrane or electrolyte; its flux must be zero at the interfaces between GDLs and CLs.

$$\left. \frac{dC_d}{dx} \right|_{x=x_{\text{AGDL}}} = \left. \frac{dC_d}{dx} \right|_{x=x_{\text{CCL}}} = 0 \quad (76)$$

Since the membrane is not an electron conducting material, the fluxes of electrons at the interfaces between the CLs and membrane are zero.

$$\left. \frac{d\psi}{dx} \right|_{x=x_{\text{ACL}}} = \left. \frac{d\psi}{dx} \right|_{x=x_{\text{MEM}}} = 0 \quad (77)$$

At the interface between the cathode/anode flow channels and the cathode/anode GDL, the concentration of each gas species is prescribed as follows:

$$C_j|_{x=x_{\text{CGDL}}} = C_{j,\text{mean}}, \quad j \in O_2, N_2, V \quad (78)$$

$$C_j|_{x=0} = C_{j,\text{mean}}, \quad j \in H_2, V \quad (79)$$

where subscript “mean” represents the average value between the inlet and outlet because of one-dimensional assumption. The values of the gas concentrations at the boundaries are calculated from the relative humidity of the cathode/anode channels. If p_c and p_a are the total gas pressure in the cathode and anode channels, the concentration of water vapor at the boundaries of the anode and cathode sides can be derived as

$$C_{V,\text{mean}} = \frac{RH p_{\text{sat},k}}{p_k} C_k \quad (k \in a, c) \quad (80)$$

and the total gas molar concentration would be

$$C_k = \frac{p_k}{RT_k} \quad (k \in a, c) \quad (81)$$

where $p_{\text{sat},k}$ is the saturation pressure of water vapor at the cathode/anode flow channels and is a function of temperature [23]

$$\begin{aligned} \log_{10} p_{\text{sat},k} = & -2.1794 + 0.02953(T_k - 273) - 9.1837 \\ & \times 10^{-5}(T_k - 273)^2 + 1.4454 \times 10^{-7}(T_k - 273)^3 \end{aligned} \quad (82)$$

Oxygen and nitrogen concentrations in the cathode flow channels are

$$C_{O_2,\text{mean}} = X_{O_2}(C_c - C_{V,\text{mean}}) \quad (83)$$

$$C_{N_2,\text{mean}} = C_c - C_{V,\text{mean}} - C_{O_2,\text{mean}} \quad (84)$$

and hydrogen concentration in the anode flow channels is

$$C_{H_2,\text{mean}} = X_{H_2}(C_a - C_{V,\text{mean}}) \quad (85)$$

The boundary conditions for temperature in the anode flow channels and cathode flow channels are both specified as

$$T|_{x=0} = T_a \quad (86)$$

Fig. 4 Reaction rate profile in the cathode catalyst layer for the base case

Fig. 5 Oxygen concentration profile in the cathode catalyst layer for the base case

Fig. 6 Net water transport coefficient versus current density for the base case

$$T|_{x=x_{\text{CGDL}}} = T_c \quad (87)$$

Because water is not generated at the anode side, we assume that liquid water saturation at the interface of the anode GDL/channels is zero,

$$s_a = s|_{x=0} = 0 \quad (88)$$

As the result of the ORR, water is produced at the cathode side. If the gas flow rates in the cathode flow channels are not fast enough, liquid water may be accumulated. In this paper, we set the liquid water saturation at the interface of the cathode GDL and the cathode flow channels, s_c , as a control parameter. By changing the value of s_c , we can simulate the evolution of cell performance and discuss optimal strategy for water management.

3 Results and Discussion

This work is focused on water transport issues in the MEA of a PEM fuel cell. The governing equations and boundary conditions described above are solved using the finite-element method implemented in COMSOL 3.3. The primary set of parameter values used for the numerical simulation of the base case is listed in Table 2. A parametric study regarding water management in PEM fuel cells is discussed in the following.

Fig. 7 Water content distribution through the whole MEA for the base case

Fig. 8 Temperature profile through the MEA for the base case

3.1 Base Case. The base case was run at 80°C, 1 atm, and 100% humidity on both sides of the anode and the cathode. The boundary conditions of liquid water saturation at the interfaces between the anode/cathode channels and the GDLs (s_a and s_c) are both set to be zero. Simulation is done by decreasing cell voltage from open circuit potential U_0 to 0.

Most numerical models presented in literatures [17,18,23] were validated by comparison of simulated and measured cell polarization curves. However, the polarization curve is the result of many physical and chemical processes that occurred in a PEM fuel cell, such as proton transport, oxygen transport, or both of them. It would be very helpful for the design engineers to identify what is

Fig. 9 The various heat sources as a function of current density in the cathode catalyst layer for the base case

the dominating or limiting process that leads to the cell performance degradation, where this limiting process occurs and how the water distributes through the whole MEA.

To answer these questions, first of all, the distributions of the reaction rate and oxygen concentration in the cathode catalyst layer for base case are shown in Figs. 4 and 5. At low current density, the reaction rate is distributed evenly in the cathode CL. However, at high current density, the reaction rate is highly close to the membrane side, but the concentration of oxygen does not decrease significantly. It is clearly shown that the proton transport is the limiting factor for the cell's lack of performance.

Second, the net water transport coefficient through the membrane and distributions of water content in the CLs (anode and cathode sides) and in the membrane at different current densities are drawn in Figs. 6 and 7, respectively.

The net water transport coefficient, denoted by β , is defined as the net flux of water transported from the anode to the cathode N_{H_2O} per proton flux N_{H^+} , $\beta = N_{H_2O}/N_{H^+}$.

Two mechanisms are considered here regarding the water transport through the membrane: one is diffusion due to water concentration gradient across the membrane; another is electro-osmotic drag due to proton flux. According to the sign of β values, we can tell the direction of net water transport through the membrane. $\beta > 0$ means that the flux of the electro-osmotic drag is larger than

Fig. 10 Polarization curves for different accumulation levels of liquid water at the cathode side

the flux of the back diffusion and net water transport is from the anode side across the membrane to the cathode side. This will probably lead to drying out of the anode or aggravate the cathode flooding. On the other hand, $\beta < 0$ indicates that the flux of water

Fig. 11 Water content distributions through the MEA at different current densities for different s_c values

Fig. 12 Oxygen concentration at the interface of the cathode catalyst layer and membrane

back diffusion is larger than the flux of the electro-osmotic drag and the net water moves from the cathode side through the membrane to the anode side.

As current density increases, more water is produced at the cathode side. Because produced water leads to higher water fluxes of back diffusion, β value will decrease. However, the flux of the back diffusion is still less than the flux of the electro-osmotic drag. Therefore, as shown in Fig. 6, β is positive, meaning that the net water transport in the MEA is always from the anode side to the cathode side at all current densities for the base case. This may lead to membrane dehydration. The distributions of water content through the electrolyte and membrane at different current densities in Fig. 7 show that at low current densities the water content almost evenly distributed through the MEA. However, when the current density increases, the water content in the anode side decreases dramatically due to the net water transport from the anode side to the cathode side. This results in the anode side membrane dehydration, and meanwhile, the water content in the cathode side increases to the value that equilibrates with the cathode side's relative humidity. Therefore, the limiting proton transport process for the base case occurs actually in the anode catalyst layer and part of the membrane close to the anode CL.

The temperature distribution through the whole cell for base case is shown in Fig. 8. At low current density, such as 0.1 A/cm², the temperature distribution is almost uniform because the heat generation is small. For higher current densities of

Fig. 13 The net water transport coefficient β , as a function of current density at different saturation boundary conditions

Fig. 14 Optimal liquid water saturation versus the immobile saturation

0.5 A/cm² and 1.5 A/cm², the temperature distribution is non-linear because of the heat sources in each subdomain. Since the largest heat source is in the cathode catalyst layer, the position of the highest temperature is at the interface between the membrane and the cathode catalyst layer. Heat sources due to the reaction heat including entropic heat of reaction and irreversible reaction heat, Ohmic heat, and phase change heat versus current density in the cathode catalyst layer are shown in Fig. 9. Compared with the other heat sources, reaction heat is dominant in the cathode catalyst layer. Because the relative humidity of the reactant gas is already 100%, higher temperature will result in the evaporation of liquid water. Therefore, phase change heat becomes negative at high current density as shown in Fig. 9.

3.2 Effect of Liquid Water Accumulation in Cathode Flow Channels. Water is generated in the cathode catalyst layer and may be accumulated in cathode flow channels due to an imperfect water management. The liquid water saturation at the interface of the cathode GDL and the cathode flow channels, s_c , affects the accumulation of liquid water. The larger the s_c value is, the easier the cathode flooding happens. Figure 10 demonstrates the effect of the liquid water accumulation at the interface of the cathode flow channels and the cathode GDL on cell performance. From Fig. 10, when the s_c value increases, cell performance increases due to the proton conductivity improvement by higher water content in the membrane and anode electrolyte. Once s_c reaches a certain value (here is 0.15), increasing s_c further will result in cell performance decrease because of the oxygen transport limitation caused by cathode side flooding. Therefore, the optimal value of s_c , which depends on the design and operation of the cell, exists.

The distributions of water content through the MEA at different current densities under different s_c values are plotted in Fig. 11.

Fig. 15 Value of β versus current density for different relative humidities for the base case

Fig. 16 Performance dependence on relative humidities for the base case

When $s_c \leq 0.15$, at a same current density value the water content is higher for a large s_c than that for a small s_c . It means that the proton conductivity is improved with the increase in s_c . In addition, when $s_c \geq 0.15$, the water content distribution at same current

density remains the same for different s_c values. It means that further increasing the s_c value cannot improve the proton conductivity. When current density increases, due to the water production in the cathode catalyst layer, water content at the cathode catalyst layer increases to the level at a local water balance holding for liquid, vapor, and dissolved water. On the contrary, because of the electro-osmotic drag, water content at the anode catalyst layer decreases and leads to dry out at a high current density level.

A large s_c value will easily cause the cathode side flooding, which leads to a dramatic drop of oxygen concentration in the cathode side, as shown in Fig. 12. The net water transport coefficient β , as a function of current density at different s_c , is given in Fig. 13. At lower current density, when $s_c > 0$, because the back diffusion is larger than the electro-osmotic drag, $\beta < 0$. Along with the increase in current density, both back diffusion and electro-osmotic drag increase, but the increment of electro-osmotic drag is bigger than that of the back diffusion. Therefore, β increases from a negative value to a positive one. After $s_c > 0.15$, since the membrane has reached a fully hydrated status at the cathode side (see Fig. 11), the value of β remains the same even at a higher s_c value.

As discussed in Sec. 2, immobile saturation (s^*) plays an important role in terms of phase change among the three forms of water. According to the experimental investigation in Ref. [38], s^*

Fig. 17 Water content distributions in the membrane for different relative humidity combinations in the anode and cathode channels

is an inherent property of porous media and is determined from the wetting properties and the structure of porous media, such as contact angle, pore shape, porosity, pore size distribution, and heterogeneity. Figure 14 shows the dependences of the optimal liquid water saturation on the interface of the cathode GDL and the cathode flow channels on the immobile saturation. The optimal saturation of liquid water at the interface of the cathode GDL and cathode flow channels increases if the immobile saturation value increases. Therefore, based on the immobile saturation of the porous material, we can adjust the gas flow rate in the cathode flow channels to keep the liquid water saturation at the interface of the cathode flow channels and the GDL close to the optimal value to obtain the best cell performance.

3.3 Effect of the Relative Humidity. Relative humidities at both sides of the MEA also have a noticeable impact on the net water transport through the membrane of the MEA. Figures 15 and 16 present the net water transport coefficients and the polarization curves for different sets of relative humidity combination of the anode and cathode sides when $s_a = s_c = 0$, respectively. From Fig. 15, when relative humidity at the anode side is greater or equal to the value at the cathode side, the direction of the diffusion flux is from the anode side to the cathode side, so the β value is positive and decreases as the current density increases, such as the cases of ($RH_a=1, RH_c=1$), ($RH_a=1, RH_c=0.5$), and ($RH_a=0.5, RH_c=0.5$). However, for the case of ($RH_a=0.5, RH_c=1$), at low current densities, the flux of back diffusion is much larger than the flux of the electro-osmotic drag due to a high water concentration at the cathode side. Therefore the value of β is negative and then increases to positive values with the increase in the current density and stays stable when the current density is high enough. In addition, the positive value of β means that the net water transport is from the anode side to the cathode side. This will eventually result in the anode side dehydration and the cathode side flooding if the cathode flow channels are not well managed. Because here we assume that there is no liquid water accumulation both in the anode and the cathode sides ($s_a = s_c = 0$), the water content in the membrane and the electrolyte is mainly determined by the relative humidity condition of both sides. High relative humidity means higher water content, corresponding to higher proton conductivity, especially in the cathode CL. The water content distributions are given in Fig. 17 for the above mentioned four cases of relative humidity combinations in the anode and cathode flow channels. This is the reason why cell performances of the two cases of ($RH_a=1, RH_c=1$) and ($RH_a=0.5, RH_c=1$) exceed to the performances of the other two cases, as shown in Fig. 16.

4 Conclusions

A one-dimensional, nonisothermal, steady-state model including mass transport among liquid water, water vapor, and dissolved water has been developed to study water transport through the MEA of a PEM fuel cell under different saturation boundary conditions and different sets of feed relative humidities at both anode and cathode sides. We found that when there is no liquid water accumulation at both sides of the MEA or the relative humidity at the anode side is no less than the relative humidity at the cathode side, the net water transport through the membrane is from the anode side to the cathode side and net water transport coefficient decreases to a stable level as the current density increases. However, when the relative humidity at the anode side is less than that at the cathode side, or the liquid water saturation at the interface of the cathode GDL and the cathode flow channels is bigger than the immobile saturation value, the net water transport through the membrane starts from the cathode side to the anode side at low current density level, then changes the transport direction from the anode side to the cathode side and net water transport coefficient finally stabilizes at a positive constant level as the current density increases. Changing the liquid water accumulation level in the cathode channels definitely affects the net water transport in the

MEA and cell performance as well. We also found that when the liquid water saturation in the cathode flow channels increased from 0 to a certain value, cell performance will increase. However, when the liquid water saturation in the cathode channels increases further, cell performance will decrease. This indicates that there is an optimal liquid water saturation level in the cathode flow channels and that optimal saturation level is strongly related to the immobile saturation level of the porous media.

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