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INFLUENCE OF ANISOTROPIC TRANSPORT PROPERTIES OF THE GDL ON THE PERFORMANCE OF PEMFCS

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A two-dimensional, non-isothermal two-phase model, which includes the full anisotropy of GDL, was developed to investigate the effect of anisotropic ratios on cell performance. Among the four anisotropic ratios, the anisotropic ratio of diffusivity, γ_D , is the most sensitive parameter to cell performance. The present study demonstrated the possibility of improving cell performance by using innovated GDL porous materials with higher anisotropic ratios, especially higher γ_D .

Introduction

The gas diffusion layers (GDLs) of PEM fuel cells, which are porous to allow for gaseous fuels to diffuse to the catalyst side, conduct electricity and heat to or from catalyst side to the current collectors. In addition, the pores of the GDLs provide pathways for removal of liquid water generated by electrochemical reaction and condensation. Although the overall cell performance has significantly been improved in the recent years, a major limitation is still from the mass transport. Cathode GDL plays a critical role in the whole mass transport because generated liquid water will block the open pore paths to impede oxygen transport to the active reaction sites.

A non-isothermal, multicomponent, two-phase diffusion layer model was presented by Senn et al. (1). Natarajan et al. (2) developed a two-dimensional, two-phase, multicomponent transient model for cathode GDL. Both of them discussed the effects of temperature, relative humidity of inlet stream, thickness and porosity of GDL, size of channels and shoulders and channel-to-shoulder ration on cell performance. Their model results provided useful data on optimizing flow field design. However, in their models, they assumed that GDLs were isotropic porous media. The most commonly used GDLs for PEM fuel cells are carbon cloth or carbon paper. Due to the orientation of the underlying fibers, the GDLs show strong anisotropy leading to different transport coefficients in the in-plane and through-plane directions. Therefore, how anisotropic transport properties of GDL affect cell performance of PEMFC becomes an important issue.

Pasaogullari et al. (3) developed a 2-D non-isothermal, multiphase mixture model to investigate the effects of anisotropy of GDL. They found that maximum temperature difference in the GDL was strong function of GDL anisotropy. By a 2-D PEMFC cathode model, Pharoah et al. (4) showed that treating the GDL as an isotropic porous media yielded significant different current density prediction compared to anisotropic treatments. However, they did not take into account the effects of anisotropy of GDL on the performance of PEMFCs. In the present work, we developed a 2-D, non-isothermal, two-phase model with the full anisotropic tensors to investigate the impact of anisotropy of GDL on cell performance. The anisotropic properties of the material are described by permeability, diffusivity, electrical conductivity and thermal conductivity.

Model Description

In this study, the simulation domain was limited to cathode GDL as shown schematically in Figure 1. We assumed symmetry at the channel centerline and the land centerline. We also assumed that main axes of anisotropy overlap with geometrical coordinates and defined that anisotropic ratios γ were in-plane properties divided by through-plane properties. They are:

$$\bar{K} = K_{th} \begin{bmatrix} 1 & 0 \\ 0 & \gamma_K \end{bmatrix}, \bar{D} = D_{th} \begin{bmatrix} 1 & 0 \\ 0 & \gamma_D \end{bmatrix}, \bar{\sigma}_c = \sigma_{c,th} \begin{bmatrix} 1 & 0 \\ 0 & \gamma_{\sigma_c} \end{bmatrix}, \text{ and } \bar{k}_s = k_{s,th} \begin{bmatrix} 1 & 0 \\ 0 & \gamma_{k_s} \end{bmatrix} \quad [1]$$

Figure 1 Schematic diagrams of simulation domain

Two-phase mass and momentum conservation---In porous GDL, two-phase flows follow separated equations for the gaseous mixture and liquid phase.

$$\nabla \rho_l \vec{u}_l = m_{phase} \quad [2]$$

$$\nabla \rho_g \vec{u}_g = -m_{phase} \quad [3]$$

where the term on the right-hand side of above equations (m_{phase}) is the interfacial mass transfer rate of phase change due to evaporation or condensation. ρ_l , ρ_g are the densities of liquid water and gaseous mixture, respectively. The superficial velocities of liquid water and gaseous mixture, $\vec{u}_l$, $\vec{u}_g$, are assumed to be expressed by Darcy's law.

$$\vec{u}_l = -\frac{\bar{K}k_{rl}}{\mu_l} \nabla p_l \quad [4]$$

$$\vec{u}_g = -\frac{\bar{K}k_{rg}}{\mu_g} \nabla p_g \quad [5]$$

where $\bar{K}$ is the absolute permeability tensor of the GDL, while k_{rl} , k_{rg} are the relative permeabilities of the gaseous mixture and the liquid water, which are the function of the liquid water saturation, i.e. $k_{rl} = s^3$ and $k_{rg} = (1-s^3)$ (5). μ_l , μ_g and p_l , p_g are the dynamic viscosities and the partial pressure of liquid water and gaseous mixture, respectively.

The Tomadakis-Sotirchos (TS) model enables the prediction of anisotropic permeability without any fitting parameters (6).

$$K = \frac{\varepsilon}{8(\ln \varepsilon)^2} \frac{(\varepsilon - \varepsilon_p)^{(\alpha+2)} d_f}{(1 - \varepsilon_p)^\alpha [(\alpha + 1)\varepsilon - \varepsilon_p]^2} \quad [6]$$

where d_f is the fiber diameter, α and ε_p are constants that depend on the fiber arrangement and the direction of flow. For 2D arrangement,

$$\begin{aligned} \varepsilon_p &= 0.11, \quad \alpha = 0.785 \text{ (through - plane)} \\ \alpha &= 0.521 \text{ (in - plane)} \end{aligned} \quad [7]$$

$$\gamma_K = \frac{K_{in}}{K_{th}} \quad [8]$$

The capillary pressure, which is the difference between gas phase pressure and liquid phase pressure, is given by (5)

$$p_c = p_g - p_l = \sigma \cos \theta \sqrt{\frac{\varepsilon_i}{K_i}} \mathfrak{Z}(s) \quad [9]$$

where σ is the surface tension, θ is the contact angle, s is the liquid water saturation, $\mathfrak{Z}(s)$ is so called Leverett function.

$$\mathfrak{Z}(s) = \begin{cases} 1.417(1-s) - 2.21(1-s)^2 + 1.263(1-s)^3 & \theta \leq 90^\circ \\ 1.417s - 2.21s^2 + 1.263s^3 & \theta > 90^\circ \end{cases} \quad [10]$$

The interfacial mass transfer rate between two phases m_{phase} is adopted from (5)

$$m_{phase} = \begin{cases} k_{cond} \varepsilon (1-s) \frac{M^{H_2O} p_g}{RT} (x_g^{H_2O} - x_{sat}^{H_2O}) & x_g^{H_2O} \geq x_{sat}^{H_2O} \\ k_{vap} \varepsilon p_g (x_g^{H_2O} - x_{sat}^{H_2O}) & x_g^{H_2O} < x_{sat}^{H_2O} \end{cases} \quad [11]$$

where k_{cond}, k_{vap} are the condensation and evaporation rate constant, respectively. $x_g^{H_2O}$ is the mole fraction of water vapor and $x_{sat}^{H_2O}$ is the saturation molar fraction of water vapor and is a function of the operating temperature T .

Species conservation---The species conservation equations were written in terms of the mass concentration ($w_{O_2}, w_{H_2O}, w_{N_2}$). The species transports based on the diffusion and convection are given by:

$$\nabla \cdot [\rho_g \vec{u}_g w_{O_2} - \varepsilon \rho_g (1-s) \bar{D}_{O_2}^{eff} \nabla w_{O_2}] = 0 \quad [12]$$

$$\nabla \cdot [\rho_g \vec{u}_g w_V - \varepsilon \rho_g (1-s) \bar{D}_V^{eff} \nabla w_V] = -m_{phase} \quad [13]$$

$$w_{N_2} = 1 - w_{O_2} - w_V \quad [14]$$

where $\bar{D}_{O_2}^{eff}, \bar{D}_V^{eff}$ are the effective diffusion coefficients tensor for oxygen and water vapor, respectively. Similar to absolute permeability tensor $\bar{K}$, according to TS model (6),

$$D_i^{eff} = f(\varepsilon) D_i \quad i \in O_2, V \quad [15]$$

$$f(\varepsilon) = \varepsilon \left(\frac{\varepsilon - \varepsilon_p}{1 - \varepsilon_p} \right)^\alpha \quad [16]$$

$$\gamma_D = \frac{D_{i,in}}{D_{i,th}} = \left(\frac{\varepsilon - \varepsilon_p}{1 - \varepsilon_p} \right)^{-0.264} \quad [17]$$

The bulk diffusivities of oxygen and water vapor (D_{O_2}, D_V) are temperature dependent and given by (5):

$$D_{O_2} = 0.1775 \times 10^{-7} \left(\frac{T}{273.15} \right)^{1.823} \quad [18]$$

$$D_V = 0.256 \times 10^{-4} \left(\frac{T}{307.15} \right)^{2.334} \quad [19]$$

Electronic charge conservation---The electronic charge conservation equation is:

$$-\nabla \cdot (\varepsilon_c^{3/2} \overline{\sigma_c} \nabla \psi) = 0 \quad [20]$$

where ε_c is volume fraction of solid phase in GDL, $\varepsilon_c = 1 - \varepsilon$. $\overline{\sigma_c}$ is the electronic conductivity tensor of solid phase. ψ is the electronic potential.

Energy conservation---The energy conservation equation in this model for GDL described the conductive and convective heat transfer in GDL. We assumed that the temperatures of gas phase, liquid phase and solid phase are at local thermal equilibrium ($T_l = T_g = T_s = T$):

$$-\nabla \cdot \left\{ [(1-s)k_g + sk_l + \overline{k_s}] \nabla T \right\} + \rho_l C_p^l \vec{u}_l \cdot \nabla T + \rho_g C_p^g \vec{u}_g \cdot \nabla T = H_{vap} m_{phase} + Q \quad [21]$$

where k_g, k_l, C_p^g, C_p^l are the effective thermal conductivities and effective specific heat capacities of liquid phase and gas phase, respectively. However, $\overline{k_s}$ is the thermal conductivity tensor of the solid phase. The first term on the right-hand side of EQ. 21 is a heat source/sink due to condensation and evaporation. H_{vap} is the latent heat of condensation/evaporation. The second term Q is an internal volumetric source/sink because of the conduction current.

$$Q = \nabla \psi \cdot \varepsilon_c^{1.5} \overline{\sigma_c} \nabla \psi \quad [22]$$

The above conservation equations are for the unknown velocities of gas phase (u_g) and liquid phase (u_l), pressures of gas phase (p_g) and liquid phase (p_l), mass concentration of water vapor (w_v) and oxygen (w_{O_2}) and common temperature (T).

Boundary conditions--- As shown in Figure 1, there are five boundaries or interfaces. The boundary conditions are listed in Table 1.

The interface between the channel and the GDL (B1) is the inlet for the reaction gases. A convective heat transfer boundary is adopted. h is the heat transfer coefficient and T_f is the free-stream temperature(3).

At the interface of GDL and the shoulder of channels (B2), because the current collector is impermeable, the fluxes of species are zero. We assumed that electronic potential at the anode current collector is zero. As the current collector has larger electronic conductivities, i.e., the ohmic loss through the current collector is negligible. Therefore, the electronic potential at the cathode current collector is cell voltage V_{cell} . If we omit the concentration overpotential of the anode hydrogen oxidation reaction (HOR), the cell voltage is

$$V_{cell} = E_{ocv} - |\eta_c| - \left(\frac{i_c}{\sigma_m} \right) L_m \quad [23]$$

where E_{ocv} is the open circuit voltage, σ_m is the membrane conductivity, i_c is the local current density.

TABLE 1 The boundary conditions

	B1	B2	B4	B3&B5
w_j ($j: O_2/V$)	$w_j = w_j^{in}$	$\frac{\partial w_j}{\partial x} = 0$	$-\left[\rho_g u_{g,x} w_{O_2} - \varepsilon \rho_g (1-s) D_{O_2,th} \frac{\partial w_{O_2}}{\partial x}\right]$ $= -\frac{i_c}{4F} M_{O_2}$ $-\left[\rho_g u_{g,x} w_V - \varepsilon \rho_g (1-s) D_{V,th} \frac{\partial w_V}{\partial x}\right]$ $= (1-\beta) \frac{i_c}{4F} (2+4\alpha) M_{H_2O}$	$\frac{\partial w_j}{\partial y} = 0$
p_i ($i: g/l$)	$p_i = p_i^{in}$	$\frac{\partial p_i}{\partial x} = 0$	$-\rho_l \frac{K_{th} k_{rl}}{\mu_l} \left(\frac{\partial p_l}{\partial x}\right)$ $= \beta \frac{i_c}{4F} (2+4\alpha) M_{H_2O}$ $\rho_g \frac{K_{th} k_{rg}}{\mu_g} \frac{\partial p_g}{\partial x} = -\frac{i_c}{4F} M_{O_2}$ $+ (1-\beta) \frac{i_c}{4F} (2+4\alpha) M_{H_2O}$	$\frac{\partial p_i}{\partial y} = 0$
ψ	$\frac{\partial \psi}{\partial x} = 0$	$\psi = V_{cell}$	$-\varepsilon_c^{1.5} \sigma_{c,th} \frac{\partial \psi}{\partial x} = i_c$	$\frac{\partial \psi}{\partial y} = 0$
T	$q = h(T - T_f)$	$T = T_o$	$\left[(1-s)k_g + sk_l + k_{s,th}\right] \frac{\partial T}{\partial x}$ $= i_c \left(-\frac{T _{IV} \Delta S_c^{Pt}}{4F} - \eta_c\right)$	$\frac{\partial T}{\partial y} = 0$

The oxygen reduction reaction (ORR) is described via Tafel kinetics (2):

$$i_c = I_{c,ref} \frac{C_{O_2}}{C_{O_2}^{ref}} (1-s) \exp\left(-\frac{\alpha_c F \eta_c}{RT}\right) \quad [24]$$

Here η_c is the cathode overpotential, $I_{c,ref}$ is the reference exchange current density, α_c is the cathode transfer coefficient.

At the interface of GDL and CL (B4), in the same way of ref. (5), we assumed α is the net water transport coefficient across the membrane and β is the liquid water percentage to the all of the water across the interface of B4. B3 and B5 are the symmetrical boundary conditions.

The above described governing equations and boundary conditions are solved by using COMSOL Multiphysics base on the finite element technique.

Results and Discussion

Table 2 lists the important parameter values used as the base case. To investigate the impact of GDL anisotropy on the cell performance, different GDLs with varied anisotropic ratios were simulated at the same operating conditions at 333.15 K cell temperature and 1 atm operating pressure. The relative humidity of inlet air was 100%.

TABLE 2 Parameters used in the model

Parameters/properties	Value
GDL thickness, L	370 μm
Fiber diameter of GDL, d_f	9.2 μm
<i>Toray carbon paper</i> : GDL porosity, ε	0.55
GDL contact angle, θ	110°
Half rib width, $b/2$	500 μm
Half channel width, $h/2$	500 μm
Catalyst layer thickness, L_c	16 μm
Membrane thickness, L_m	50 μm
Electronic conductivity, σ_c ($\gamma_{\sigma_c} = 14.28$)	1250 S/m (through-plane) 17857 S/m (in-plane)
Thermal conductivity, k_s ($\gamma_{k_s} = 12.35$)	1.7 W/m K (through-plane) 21 W/m K (in-plane)
Membrane conductivity σ_m	7 S/m
Entropy of ORR, ΔS_c^{Pt}	-326.36 J/(mol K)
Cathodic transfer coefficient, α_c	1
Reference oxygen concentration, $C_{ref}^{O_2}$	40.88 mol/ m ³
Condensation constant, k_{cond}	100 1/s
Evaporation constant, k_{vap}	100 1/(atm s)
Net water transport coefficient, α	0.25
Liquid water percentage, β	0.5

Figure 2 shows the dependence between power density and anisotropic ratio at the cathode overpotential $\eta_c = -0.4V$. Because we assumed that membrane is fully hydrated with higher proton conductivities ($\sigma_m = 7 \text{ S/m}$), the current density is mainly dependent on oxygen concentration at GDL/CL interface (B4). As shown in Figure 2, because γ_{σ_c} has no effect on the mass transport, cell performance does not change while γ_{σ_c} increases. However, it affects the distribution of electronic phase potential significantly as shown in Figure 3.

Figure 2 Dependence between power density and anisotropic ratio at $\eta_c = -0.4V$

Figure 3 Electronic potential distributions at the GDL-CL interface at $\eta_c = -0.4V$

The permeability directly affects the distribution of saturation. As γ_K increases, because the in-plane permeability is higher, it requires a smaller pressure gradient to

drive liquid water. Therefore, the distribution of saturation in the GDL is more uniform and has lower values as shown in Figure 4. Due to the lower saturation at higher value of γ_K , the less reaction areas are covered by liquid water. This leads to slightly higher power density as shown in Figure 2.

Figure 4 Saturation distributions at the GDL-CL interface at $\eta_c = -0.4V$

Because heat transfer from GDL is mainly through the current collector shoulder, when γ_{ks} increases, higher thermal conductivity in in-plane direction results in the more uniform temperature distribution and lower temperature in the GDL as shown in Figure 5. According to Equation [24], lower temperature leads to lower gas diffusivities and higher saturation, which makes current density decrease. However, the exponential term of the equation leads to current density increase. Therefore, at different current density, γ_{ks} shows different impacts on cell performance although Figure 2 shows that as γ_{ks} increases from 1 to 10, cell performance increases a few and then tends to be a constant at $\eta_c = -0.4V$.

Figure 5 Temperature distributions at the GDL-CL interface at $\eta_c = -0.4V$

Figure 6 Oxygen mass concentration distributions at the GDL-CL interface at $\eta_c = -0.4V$

Compared to above three anisotropic ratios, γ_D shows significant impact on cell performance. When $\gamma_D < 1$, due to lower transport coefficients in the in-plane direction, less oxygen could reach the regions underneath the current collectors. This means that the distribution of oxygen at interface of GDL with catalyst layer is less uniform as shown in Figure 6. This results in lower power density. When $\gamma_D > 1$, for example, γ_D changes from 1 to 2, power density increases about 6% as shown in Figure 2. This is an extremely interesting case, because compared to the other anisotropic ratios, γ_D is the most sensitive parameter for cell performance. For popular used Toray carbon paper, γ_D is around 1.2. This indicates that it is possible to improve cell performance by using higher γ_D materials for GDLs.

Conclusions

A two-dimensional, non-isothermal two-phase model, which includes the full anisotropy of GDL, was developed to investigate the effect of anisotropic ratios on cell performance. Among the four anisotropic ratios, γ_D is the most sensitive parameter for cell performance. The present study demonstrated the possibility of improving cell performance by using innovated GDL porous materials with higher anisotropic ratios, especially higher γ_D .

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