Numerical modeling and analysis of micro-porous layer effects in polymer electrolyte fuel cells

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ABSTRACT

It is well known that a micro-porous layer (MPL) plays a crucial role in the water management of polymer electrolyte fuel cells (PEFCs), and thereby, significantly stabilizes and improves cell performance. To ascertain the exact roles of MPLs, a numerical MPL model is developed in this study and incorporated with comprehensive, multi-dimensional, multi-phase fuel-cell models that have been devised earlier. The effects of different porous properties and liquid-entry pressures between an MPL and a gas diffusion layer (GDL) are examined via fully three-dimensional numerical simulations. First, when the differences in pore properties and wettability between the MPL and GDL are taken into account but the difference in the entry pressures is ignored, the numerical MPL model captures a discontinuity in liquid saturation at the GDL|MPL interface. The simulation does not, however, capture the beneficial effects of an MPL on cell performance, predicting even lower performance than in the case of no MPL. On the other hand, when a high liquid-entry pressure in an MPL is additionally considered, the numerical MPL model predicts a liquid-free MPL and successfully demonstrates the phenomenon that the high liquid-entry pressure of the MPL prevents any liquid water from entering the MPL. Consequently, it is found from the simulation results that a liquid-free MPL significantly enhances the back-flow of water across the membrane into the anode, which, in turn, helps to avoid membrane dehydration and alleviate the level of GDL flooding. As a result, the model successfully reports the beneficial effects of MPLs on PEFC performance and predicts higher performance in the presence of MPLs (e.g., an increase of 67 mV at 1.5 A cm^{-2}). This study provides a fundamental explanation of the function of MPLs and quantifies the influence of their porous properties and the liquid-entry pressure on water transport and cell performance.

1. Introduction

It has been widely observed experimentally that the performance of polymer electrolyte fuel cells (PEFCs) is significantly stabilized and improved by adding a micro-porous layer (MPL) to the interface between a gas diffusion layer (GDL) and a catalyst coated membrane (CCM) [1–8]. Therefore, the choice of the proper GDL–MPL combination is critical to achieve favorable PEFC performance and durability. An MPL is made of a mixture of carbon black powder and a hydrophobic agent, usually polytetrafluoroethylene (PTFE), yielding a relatively finer pore structure and a highly hydrophobic feature than GDLs. While the use of MPLs in PEFCs has been a common practice due to the resulting dramatic effects, the exact role of an MPL is uncertain due to several inherent difficulties and, in particular, the complicated multi-phase transport and flooding behaviour between the MPL and its neighboring components. These components may be either GDLs or catalyst layers (CLs), in of which the morphological structures of the pores and the wetting characteristics are all different from those of the MPL. Therefore, recently published studies on MPLs focus mostly on a more precise investigation and analysis of the role of the MPL on water transport and the relevant PEFC performance.

The effects of MPL composition, morphology, and wettability on reactant gases and product water transport in PEFCs have been experimentally investigated [9–15]. Wang et al. [9,10] observed the influence on PEFC performance of carbon powders that were employed to fabricate MPLs. They reported the dual role of the GDL–MPL pore structure in the transport of reactant gases and product water, where the hydrophobic pores in the GDL and MPL facilitate gas transport whereas the hydrophilic pores allow a pathway for liquid transport. They concluded that an appropriate combination of hydrophilic and hydrophobic pores is crucial for optimizing a GDL–MPL component for the proper water management of PEFCs. Chen et al. [11] focused on MPL preparation methods, i.e., conventional wet-layer and novel dry-layer methods. Given the differences in the surface morphology and pore-size distribution between GDLs that use either dry-layer or wet-layer MPLs, they demonstrated that the former MPLs exhibit better PEFC

Nomenclature

a	water activity or effective catalyst area per unit of total volume ($m^2 \, m^{-3}$)
A	area (m^2)
C_P	specific heat ($kJ \, kg^{-1} \, K^{-1}$)
C	molar concentration ($mol \, m^{-3}$)
D_k	mass diffusivity of species, k ($m^2 \, s^{-1}$)
EW	equivalent weight of dry membrane ($kg \, mol^{-1}$)
F	Faraday constant ($96{,}487 \, C \, mol^{-1}$)
i_0	exchange current density ($A \, m^{-2}$)
j	transfer current density ($A \, m^{-3}$)
j^i	diffusive mass flux of ith phase ($kg \, m^{-2} \, s^{-1}$)
J	Leverett function
h	enthalpy per unit mass ($kJ \, kg^{-1}$)
k	thermal conductivity ($W \, m \, K^{-1}$)
k_r	relative permeability
K	hydraulic permeability (m^2)
M	molecular weight ($kg \, mol^{-1}$)
m	*m*ass fraction (a scalar with no units)
n	number of electrons in electrochemical reaction or diffusivity correction factor
n_c	catalyst coverage coefficient
n_d	electro-osmotic drag coefficient
P	pressure (Pa)
P_c	capillary pressure (Pa)
RH	relative humidification of inlet
R_u	universal gas constant ($8.314 \, J \, mol^{-1} \, K^{-1}$)
s	stoichiometric coefficient in electrochemical reaction or liquid saturation
S	source term in transport equation
t	time (s)
T	temperature (K)
$\mathbf{u}$	fluid velocity and superficial velocity in porous medium ($m \, s^{-1}$)
U_o	thermodynamic equilibrium potential (V)
V	volume (m^3)
V_{cell}	cell potential (V)

Greeks letters

α	transfer coefficient
δ_i	thickness of component i
ε	volume fraction of gaseous phase in porous region
ε_e	volume fraction of ionomer phase in CL
γ	advection correction factor
λ	membrane water content ($mol \, H_2O / mol \, SO_3^-$)
λ^α	relative mobility of phase, α
ϕ	phase potential (V)
η	overpotential (V)
θ	contact angle (°)
μ	viscosity ($kg \, m^{-1} \, s^{-1}$)
ρ	density ($kg \, m^{-3}$)
ρ^{mem}	dry membrane density ($kg \, m^{-3}$)
υ	kinematic viscosity ($m^2 \, s^{-1}$)
σ	surface tension ($N \, m^{-1}$) or electronic conductivity ($S \, m^{-1}$)
τ	viscous shear stress ($N \, m^{-2}$)
κ	ionic conductivity ($S \, m^{-1}$)
ξ	stoichiometric flow ratio

Superscripts

c	cathode or capillary
e	electrolyte
eff	effective value in porous region
mem	membrane
g	gas
l	liquid
ref	reference value
s	solid
sat	saturation value

Subscripts

a	anode
avg	average value
BP	bipolar plate
c	cathode or capillary
CL	catalyst layer
e	electrolyte
g	gas phase
GC	gas channel
GDL	gas diffusion layer
H_2	hydrogen
i	species index
in	channel inlet
m	mass equation
mem	membrane
N_2	nitrogen
O_2	oxygen
ref	reference value
t	total
s	solid
sat	saturation value
w	water
Φ	potential equation
0	standard condition, 298.15 K and 101.3 kPa (1 atm)

performance than the latter. They hypothesized that the beneficial effect of dry-layer MPLs is due to a relatively larger number of meso-pores that remain open for gas transport for PEFC operations under conditions of high humidification. Ong et al. [12] examined the effect of MPLs, which were based on PVDF (polyvinylidene fluoride), as a function of several material-dependent parameters, such as the PVDF concentration, PVDF/electrically conductive filler ratio, and MPL thickness. Ramasamy et al. [13] emphasized the influence of MPLs on PEFC durability. By measuring the water-retention capacities of new and aged GDL samples, it was found that GDL samples continuously lose their hydrophobicity during long-term PEFC operations and that the presence of an MPL mitigates the loss of hydrophobicity. Atiyeh et al. [14] experimentally investigated the effect of MPLs on water transport and PEFC performance. The data indicated that the presence of an MPL on the cathode side induces better overall PEFC performance but does not enhance back-diffusion of water from the cathode to the anode. Therefore, it was concluded that the advantage of using an MPL in PEFCs is associated neither with an enhanced back-diffusion of water nor with a lowered net water drag coefficient through the membrane (this coefficient is the moles of water dragged from the anode through the membrane to the cathode per mole of protons transported). By contrast, with direct methanol fuel cells (DMFCs), Liu and Wang [15] demonstrated that the use of an MPL has a dramatic effect on the net water drag coefficient through the membrane.

On the other hand, the role of MPLs in overall water transport in PEFCs was precisely investigated from a theoretical perspective [16–19]. Several MPL models have been introduced. Nam and Kaviany [16] developed a one-dimensional (1D) fuel-cell model in which an MPL was included between the cathode CL and the GDL. Based on capillary water-transport theory, it was demonstrated that the water transport through a porous medium can be enhanced by