

Three Dimensional Large Scale Numerical Simulation of PEMFC with Low-Pt Loading

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ABSTRACT

The developed multiphase mixture model for low-Pt loading electrode is applied to examine the effects of Pt loading and operating condition on current density and water distribution in realistic scale proton exchange membrane fuel cells. The predicted fuel cell voltage, high-frequency resistance, as well as current density and temperature distributions all show good agreement with the experimental data under various operating conditions and for two Pt loadings of 0.3 mg/cm² and 0.1 mg/cm². In particular, the present study demonstrates quantitative comparisons of the liquid water distribution in the proton exchange membrane fuel cell with the neutron imaging measurements. Such a comprehensive data comparison gives a fundamental understanding of the physical phenomena in the proton exchange membrane fuel cells and findings to design and develop the next generation of proton exchange membrane fuel cell with low-Pt loading.

1. Introduction

In the past decade, significant advancements have been achieved in proton exchange membrane fuel cell (PEMFC) technology. However, commercialization of this promising power source for automotive applications is still hindered by high cost and slow development cycle. Spatially resolved measurements of reaction and transport parameters in a fuel cell, while critical for a basic understanding of the complex electrochemical and transport behaviors, are expensive and challenging, if not impossible, to obtain. Modeling and simulation, therefore, play an important role in meeting the increasing demand for details in fuel cell research and development. Additionally, computer simulations become an increasing part of the discovery and design process for a next generation of highly efficient and compact PEMFCs.

A number of modeling studies have been performed with the computational fluid dynamics (CFD) framework to solve the complete set of transport equations governing mass, momentum, species, energy, and charge conservation in PEMFC⁽¹⁾⁻⁽⁴⁾. However, the majority of prior work is limited to simple geometries such as straight channels, simplified dimensional assumptions

such as 1D, 2D, unrealistic operating conditions such as fully humidified gas feed, or small-scale calculations with computational mesh smaller than a million grid points. While these prior studies helped to understand transport phenomena and reaction occurring in PEMFCs, the current challenge facing PEMFC technology is to address real issues arising in development of next generation fuel cells with low cost and high durability with low-Pt loading. Such PEMFCs of the future usually feature a complex 3D flow field, and have auxiliary components, such as coolant channels and inlet and outlet manifolds. Shimpalee⁽⁵⁾ employed a single-phase model to study the dynamic response of a PEMFC during a 20-second cycle with realistic fuel cells. However, the single-phase computations failed to address water flooding and ensuing mass transport loss inherently existing in the PEMFCs under normal operating conditions. Moreover, there has never been an attempt to validate the realistic fuel cell simulations against a wide range of experimental measurements including distribution data. Until most recently, experimental validation studies were limited to small-scale calculations. For example, Fink et al.⁽⁶⁾ and Carnes et al.⁽⁷⁾ performed validation studies on PEMFCs with parallel serpentine flow field, but only the current density (CD) distribution was examined.

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Table 1 Physical properties and correlations

Parameters	Value	Parameters	Value
Dry membrane density (g/cm ³), ρ_e	1.9	Volume fraction of ionomer in the catalyst layer, ε_e	$\varepsilon_e = (I/C) \varepsilon_c \frac{\rho_c}{\rho_e} \left(1 + \frac{M_w \rho_e}{\rho_w EW} \lambda \right)$
EW of dry membrane (g/mol), EW	950	Proton conductivity of ionomer (S/m), κ	$\kappa = 22.0 \exp \left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{353.15} \right) \right] a^{2.24}$, $E_a = 12$ kJ/mol
Anode Pt loading (mg/cm ²)	0.05	Tortuosity of the ionomer phase in the catalyst layer, τ_e	$\tau_e = \begin{cases} 0.0845 (\varepsilon_e - 0.04)^{1.17} & \varepsilon_e < 0.16 \\ 1.0 & \varepsilon_e \geq 0.16 \end{cases}$
Cathode Pt loading (mg/cm ²)	0.3/0.1	Water uptake in ionomer, λ	$\lambda = \begin{cases} \left[1 + 0.2325 a^2 \left(\frac{T-303}{30} \right) \right] [14.22 a^3 - 18.92 a^2 + 13.41 a] & a \leq 1 \\ 8.71 \left[1 + 0.2325 \left(\frac{T-303}{30} \right) \right] (1-s) + [9.22 + 0.181 (T-273.15)] s & a > 1 \end{cases}$
Anode ionomer carbon weight ratio (I/C)	0.6	Water permeability in the membrane (mol/(m ² Pa s)), p_w	$p_w = 3.2 \times 10^{-11} \exp \left[\frac{E_w}{R} \left(\frac{1}{T} - \frac{1}{363} \right) \right] \exp(3.4a)$, $E_w = 22$ kJ/mol
Cathode ionomer carbon weight ratio (I/C)	0.95	Oxygen permeability in ionomer (mol/(m ² Pa s)), p_{O_2}	$p_{O_2} = p_{dry} \exp(-E_{dry}/RT) + v_w p_{wet} \exp(-E_{wet}/RT)$ $p_{dry} = 0.674 \times 10^{-11}$, $p_{wet} = 5.05 \times 10^{-11}$ mol/(mPa s), $E_{dry} = 21.28$ kJ/mol, $E_{wet} = 20.47$ kJ/mol
GDL porosity, ε_{GDL}	0.625	Water volume fraction in ionomer, u_w	$u_w = 18\lambda / (18\lambda + EW/\rho_e)$
MPL porosity, ε_{MPL}	0.5		
Carbon fraction in CL, ε_c	0.696		
Carbon density (g/cm ³), ρ_c	1.95		
GDL thermal conductivity (W/m K)	0.5		
MPL thermal conductivity (W/m K)	0.25		
CL thermal conductivity (W/m K)	0.2		
Electrical contact resistance (Ω cm ²)	0.012		
Coolant specific heat (J/(g*K))	4.18		

In this work, a series of 3D computations and experimental validation on a PEMFC with realistic scale and geometry used in a U.S. Department of Energy (DOE) project⁽⁸⁾ is performed using the multiphase-mixture model. The predicted cell voltage and high-frequency resistance (HFR), current density and temperature distributions, as well as liquid water distribution are compared to the experimental data under various operating conditions and at two platinum (Pt) loadings of 0.3 mg/cm² and 0.1 mg/cm², respectively. The details of the operating conditions and the corresponding experimental data can be found on the DOE project website⁽⁸⁾.

2. Numerical Model and Procedure

This modeling study employed the non-isothermal, electrochemistry-transport fully coupled model based on the multiphase mixture model⁽¹⁾. The two-phase flow in both porous components and gas flow channels in PEMFCs is taken into account. Conservation equations of mass, momentum, energy, species and charge under two phase condition can be summarized as follows:

Continuity equation:

$$\nabla \cdot (\rho \vec{u}) = 0 \quad (1)$$

Momentum conservation:

$$\nabla \cdot \left(\frac{\rho \vec{u} \vec{u}}{\varepsilon^2} \right) = -\nabla P + \nabla \cdot (\mu \nabla \vec{u}) + S_u \quad (2)$$

Energy conservation:

$$\nabla \cdot (\gamma_T \rho C_p \vec{u} T) = \nabla \cdot (k^{eff} \nabla T) + S_T \quad (3)$$

Species conservation:

$$\nabla \cdot (\gamma_C \vec{u} C^i) = \nabla \cdot (D_g^{i,eff} \nabla C_g^i) - \nabla \cdot \left[\left(\frac{mf_i^i}{M^i} - \frac{C_g^i}{\rho_g} \right) \vec{j}_i \right] + S_C^i \quad (4)$$

Electron conservation:

$$0 = \nabla \cdot (\sigma_s^{eff} \nabla \Phi_s) - j \quad (5)$$

Proton conservation:

$$0 = \nabla \cdot (\kappa_e^{eff} \nabla \Phi_e) + j \quad (6)$$

where, ρ , u , P , T , C^i , j , Φ_s and Φ_e are the density, superficial fluid velocity vector, pressure, temperature, molar concentration of species i , volumetric reaction current, electronic phase potential, and electrolyte phase potential, respectively. More details about this model can be found in references⁽¹⁾ and thus are not repeated here. For low-Pt loading (0.1 mg/cm²) simulations, the microscopic transport resistance of oxygen in cathode catalyst layer (CL) will play an important role on PEMFC performance. We used our recently developed electrode model to account for low-Pt loading effect⁽⁹⁾. The physical parameters relevant to the present study are listed in Table 1.

Figure 1 shows the computational geometry and mesh of the modeled PEMFC in this work. This fuel

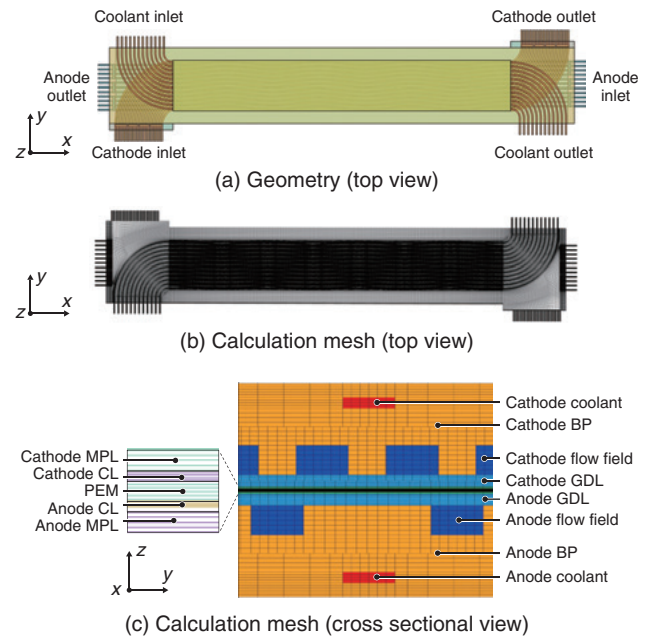


Fig. 1 Computational geometry and mesh of modeled PEM fuel cell

Table 2 Geometry parameters of modeled fuel cell

Parameters	Value
Membrane thickness (μm)	18
CCL thickness (μm)	16
ACL thickness (μm)	6
MPL thickness (μm)	30
GDL thickness (μm)	160
Gas channel width (mm)	0.4
Gas channel height (mm)	0.7
Gas channel length (mm)	183
Coolant channel width (mm)	0.7
Coolant channel height (mm)	0.15
Anode land width (mm)	1.5
Cathode land width (mm)	0.5

cell includes 11 wavy rectangular flow channels on the anode side and twice as many on the cathode side. Each side has 12 coolant channels with the arched part near the inlet and outlet. Due to the complex geometry of the gas flow channels and coolant channels, the bipolar plates (BP) and coolant flow channels, gas diffusion layers (GDL), and membrane electrode assembly (MEA) are meshed separately in order to simplify the meshing process and reduce the mesh element number. This results in the non-conformal meshes in both anode and cathode BP, and in cathode GDL as shown in Fig.1(c). The total number of the mesh elements is about 9.2 million with 95 mesh layers along the through-plane direction of the cell. Details of the geometrical dimensions of the cell are listed in Table 2.

The governing Eqs. (1)-(6) coupled with the low-Pt loaded electrode model for the cathode CL are solved within the commercial CFD software, ANSYS Fluent, using SIMPLE algorithm and algebraic multigrid (AMG) method. User defined functions (UDFs) are added to update the source terms, transport properties, boundary conditions and electrochemical reactions in these equations during calculation. For a typical two-phase simulation case, several thousand iterations are required to reach convergence with the water balance less than 2% and species balance less than 1%.

3. Results and Discussion

3.1. Calculation Condition and Calculation Result

The present validation studies are performed on 8 cases, including 5 cases with 0.3 mg/cm^2 Pt loading and 3 cases with 0.1 mg/cm^2 Pt loading. These cases have different inlet boundary conditions and operating temperatures. Table 3 lists the operating conditions of these cases, in which Letters B and L in Case No. indicate the case with 0.3 mg/cm^2 Pt loading and 0.1 mg/cm^2 Pt loading, respectively. Numerous comparisons with the experiments were conducted. The prediction of water balance between anode and cathode is challenging in the case where cathode inlet gas is dry and anode inlet gas is wet or conversely,

where cathode inlet gas is wet and anode inlet gas is dry. Thus, 8 cases are chosen herein to compare between simulations and experiments here.

Figure 2 shows the contours of the simulated current density (a) and temperature (b) distributions in the membrane, temperature distribution on the cathode BP (c), as well as water saturation distribution in the cathode gas flow channel (d) and GDL (e) for Case B1 at 1.5 A/cm^2 . It can be seen that the current density decreases somewhat with increasing water saturation in the GDL along the cathode flow channels as shown in Fig. 2(e). Some regions with much smaller current density exist near the top and bottom edges where gas flow is detoured by the cathode wavy channels such that it becomes easy to accumulate liquid water. The temperature distribution in the membrane appears to reflect the different patterns of the wavy channels in anode and cathode sides. At the cathode BP, the region with the highest temperature exists near the outlet of the coolant channels. The water saturation in the cathode gas channel and GDL increases along the cathode flow. Although the anode inlet is almost completely dry, the cathode side still accumulates considerable liquid water through condensation, due to the low operating temperature in this case.

The detailed distributions of the reaction current, temperature and water saturation in the PEMFC shown in Fig. 2 are obtained from the 3D computations with fine mesh. However, it is challenging to obtain these distributions with such high spatial resolution from the experiments. In particular, the difference of current density and temperature in the membrane and water saturation in the cathode GDL between the region under the land and under the channel can be clearly observed in the simulation result with high spatial resolution mesh as seen in Fig. 2(a) and (e). As shown in Fig. 2, this developed method can give the deep insight into distributions in the cell such as differences of water, current density, and temperature in the MEA under the lands and under the flow channels which are challenging to measure with experimental approaches.

3.2. Comparison of Current Density and Temperature Distribution between Simulation and Experiment

It is challenging to measure the distributions by experimental approaches with such a high spatial resolution as shown in Fig. 2. According to reference⁽⁸⁾, two 25 (length) $\times$ 4 (width) segmented collectors were used to measure the current density and temperature distributions on anode and cathode BPs, respectively. In order to make direct comparisons, we also divided the simulated results into the same 100 (25 $\times$ 4) segments as in the experiment. In each segment, the simulated values are averaged based on the weight of the mesh area in that segment. Figure 3(a) and (b) show a comparison of the segmented current density and temperature

Table 3 Operating conditions for validation cases

Case	Loading (mg/cm ²)	Current density (A/cm ²)	Cathode			Anode			Cell temperature (°C)	Coolant	
			Stoich.	Inlet Temp. /Dew point (°C)	Inlet pressure (atm)	Stoich.	Inlet Temp. /Dew point (°C)	Inlet pressure (atm)		Inlet T (°C)	Outlet T (°C)
B1	0.3	1.5	2	15.1/9.8	1.6	1.5	18.7/-100.0	1.0	20	11.8	18.9
B2	0.3	1.5	2	36.1/38.2	1.6	1.5	38.7/-100.0	1.0	40	30.9	38.3
B3	0.3	1.5	2	56.8/58.0	1.6	1.5	58.6/-100.0	1.0	60	50.6	58.3
B4	0.3	1.5	2	77.6/77.8	1.6	1.5	78.7/-100.0	1.0	80	73.3	78.5
B5	0.3	1.5	2	37.0/10.1	1.1	1.5	39.9/39.2	1.5	40	33.2	39.8
L1	0.1	1.5	2	35.4/38.1	1.7	1.5	38.7/-100.0	1.1	40	30.1	17.0
L2	0.1	1.5	2	55.9/58.0	1.7	1.5	58.4/-100.0	1.1	60	50.0	58.2
L3	0.1	1.5	2	34.4/10.1	1.2	1.5	38.8/39.2	1.5	40	29.5	18.9

distributions between the simulation and experiment for Case B2, and Fig. 3(c) shows a comparison of the corresponding 1D profiles along the cathode flow channels for the same case. It can be seen that the multiphase-mixture model predictions are in accord with measured current density and temperature

distributions. Moreover, the 1D results successfully capture the trend change of current density and temperature along the cathode channels. Similar agreement is also achieved in other cases considered

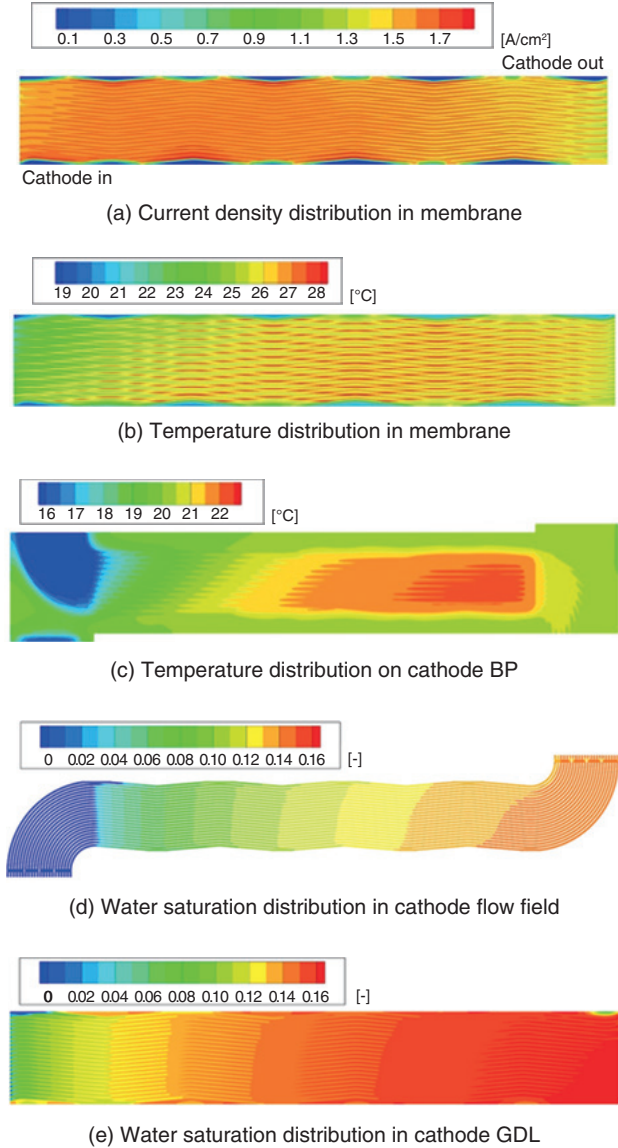


Fig. 2 Contours of calculation results of distributions for Case B1

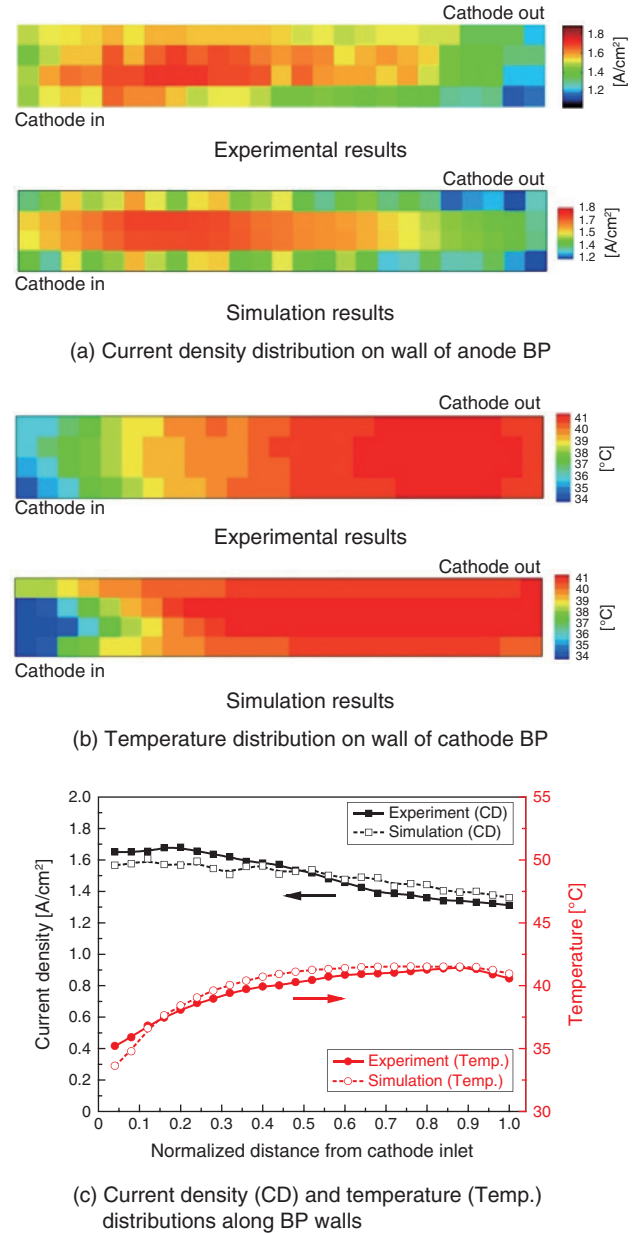


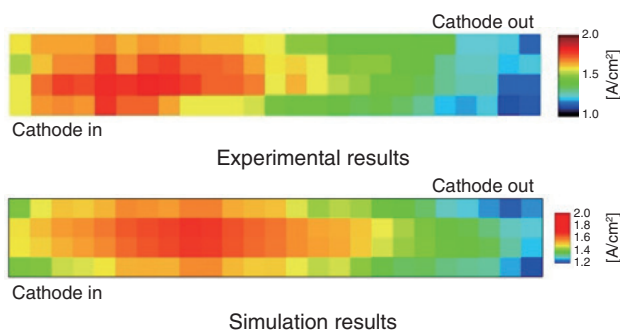
Fig. 3 Current density and temperature distributions for Case B2

as shown in Fig. 4 - Fig. 7 for Case B3, Case B5, Case L2 and Case L3.

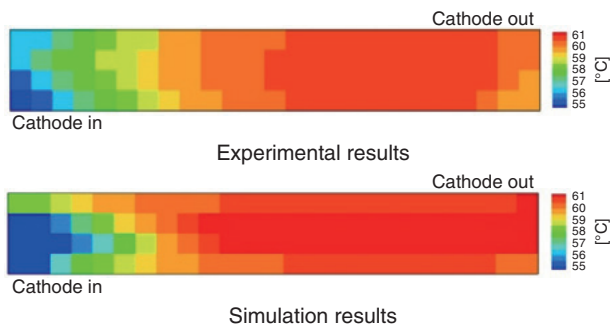
The effects of Pt loading on current density distribution are examined in Fig. 4(c) and Fig. 6(c). The operating conditions of Case B3 and Case L2 are almost same. Although experimental data of current density distribution along the channel doesn't show much difference between 0.3 mg/cm^2 and 0.1 mg/cm^2 cases, the simulation results indicate that current density distribution along the channel becomes more uniform and the peak of the current density is shifted from near the cathode inlet to the middle of the cathode flow path when Pt loading is decreased from 0.3 mg/cm^2 to 0.1 mg/cm^2 . It is assumed that CL with low-Pt loading is unable to deal with high current near

the cathode inlet due to its low active surface area and the peak of the current density is shifted to the downstream of the cathode flow path.

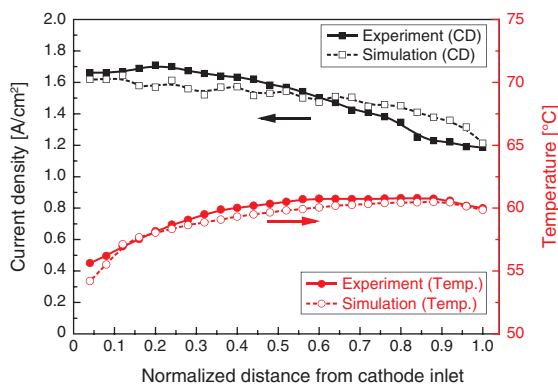
Figures 8 and 9 show the comparisons of the predicted voltage and HFR with the experimental data for all cases with Pt loading of 0.3 mg/cm^2 and 0.1 mg/cm^2 , respectively. From the results of Case B2 and L1, B3 and L2, and B5 and L3, cell voltages are decreased by 50 to 100 mV and HFR is increased by about $10 \text{ m}\Omega\text{cm}^2$ corresponding to the decrease of Pt loading from 0.3 mg/cm^2 to 0.1 mg/cm^2 . The simulations capture the voltage and HFR changes in a wide range of operating conditions for both Pt loadings. Good agreement of the voltage and HFR between simulations and experiments are obtained.



(a) Current density distribution on wall of anode BP

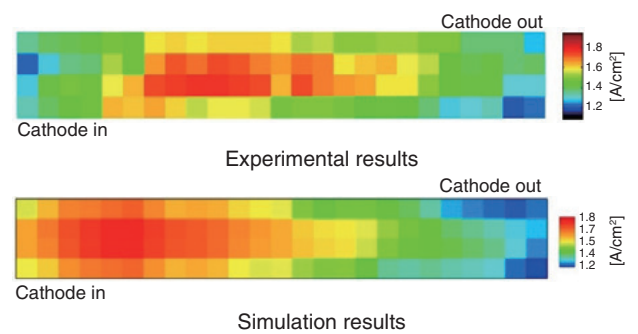


(b) Temperature distribution on wall of cathode BP

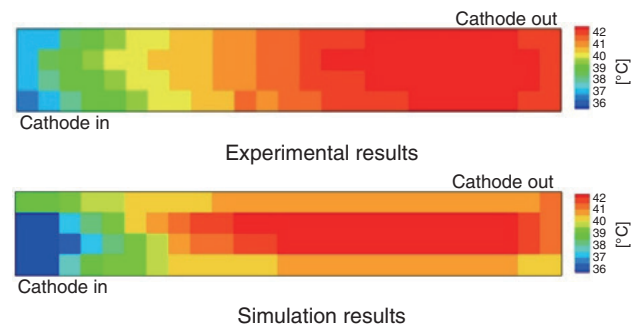


(c) Current density (CD) and temperature (Temp.) distributions along BP walls

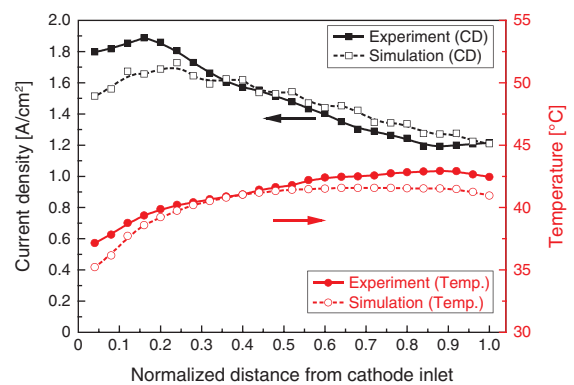
Fig. 4 Current density and temperature distributions for Case B3



(a) Current density distribution on wall of anode BP



(b) Temperature distribution on wall of cathode BP



(c) Current density (CD) and temperature (Temp.) distributions along BP walls

Fig. 5 Current density and temperature distributions for Case B5

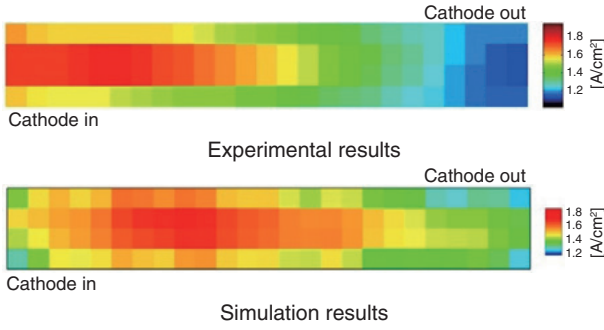
3.3. Comparison of Water Distribution between Simulation and Experiment

Figure 10 compares the water thickness distribution measured by neutron imaging with the simulated one for Case B2, B3, B4 and B5, respectively. The water thickness in the simulations is calculated by,

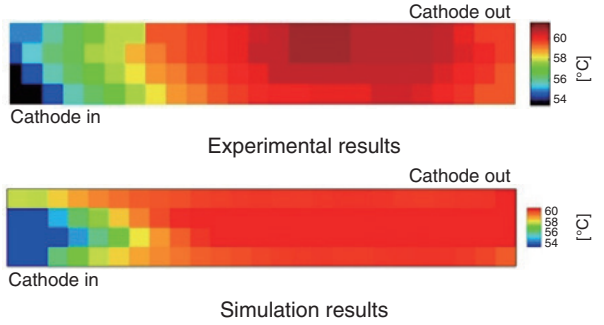
$$t_w = \int s_k \varepsilon_k dx \quad (7)$$

where s_k and ε_k are the water saturation and porosity in the cell components including gas channel, GDL or CL. The integration is performed across the entire thickness of the cell. It is seen from Fig. 10 that the simulated water thickness distribution agrees with the neutron imaging quite well. The liquid water in the cell decreases gradually as the temperature increases.

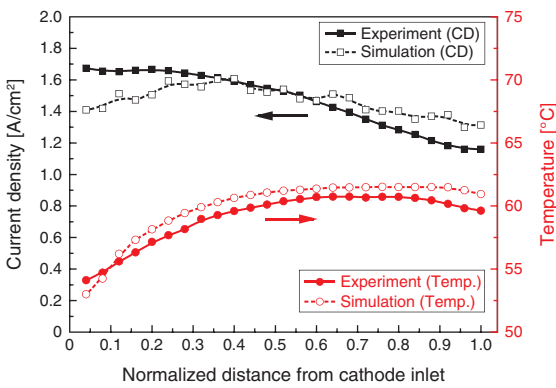
In Case B2 at 40°C, liquid water nearly spreads through the whole cell, while the cell has almost no liquid water in Case B4 at 80°C. In addition, although Case B2 and Case B5 work at the same temperature, different water distribution patterns appear due to the different inlet conditions. In Case B2, the cathode inlet has high relative humidity (RH) and the anode inlet is completely dry. Consequently, there is little liquid water in the region near the anode inlet. In Case B5, the anode inlet is nearly fully saturated, but the cathode inlet RH is very low, thus resulting in a drier region near the cathode inlet. The simulations correctly capture the water distribution change under different operating conditions. The simulation study achieves a quantitative agreement of the water distribution in the cell with neutron imaging measurements, demonstrating that the multiphase-mixture model is quite capable of



(a) Current density distribution on wall of anode BP

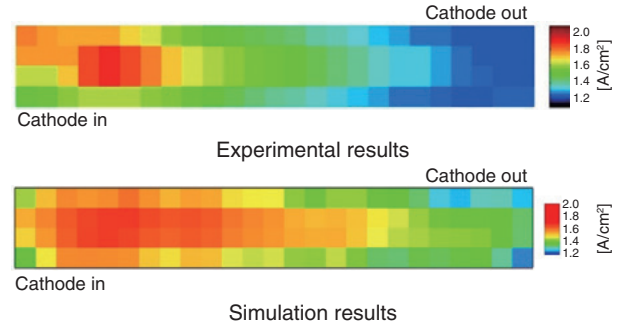


(b) Temperature distribution on wall of cathode BP

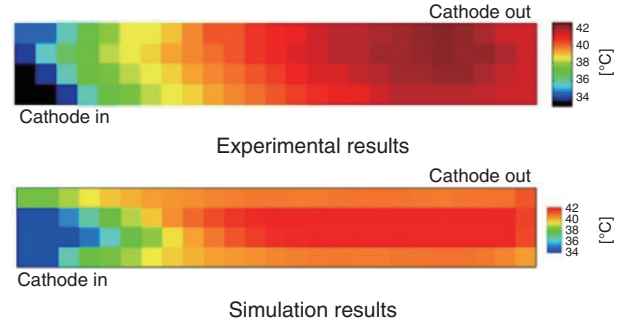


(c) Current density (CD) and temperature (Temp.) distributions along BP walls

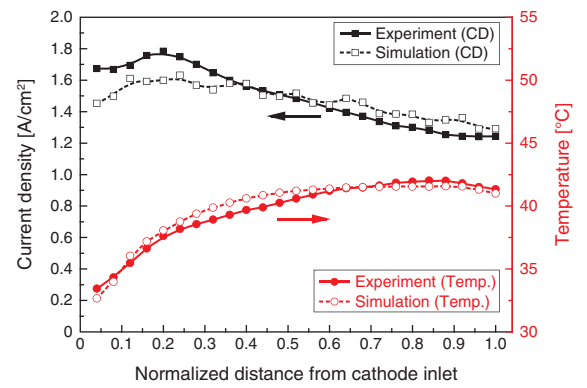
Fig. 6 Current density and temperature distributions for Case L2



(a) Current density distribution on wall of anode BP



(b) Temperature distribution on wall of cathode BP



(c) Current density (CD) and temperature (Temp.) distributions along BP walls

Fig. 7 Current density and temperature distributions for Case L3

predicting water transport and distribution in PEMFCs with realistic flow field geometries. Also, simulation results show the ability of the model to find the

optimal combination of operating condition, flow field and MEA design to utilize a low-Pt loading CL and realize low cost cell.

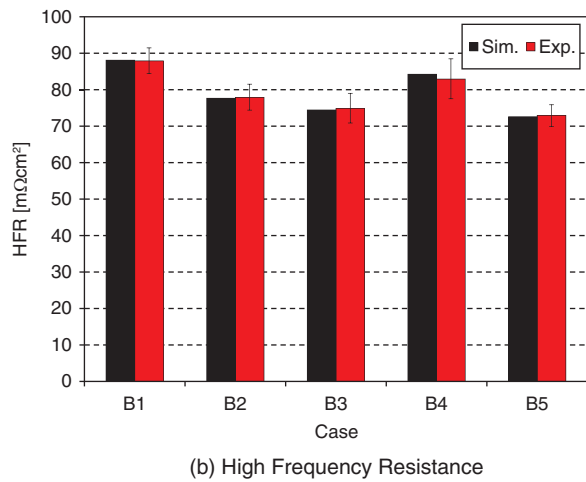
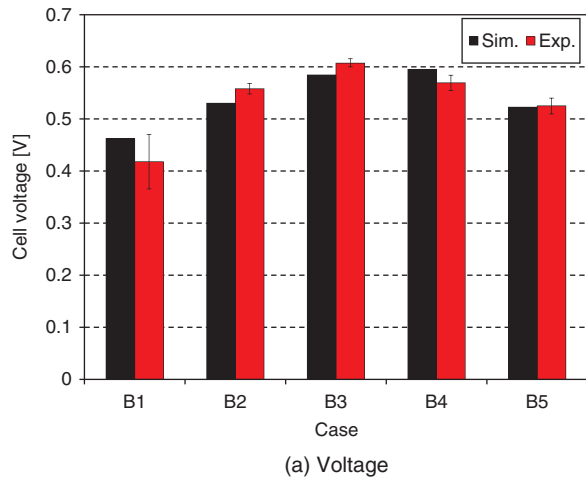


Fig. 8 Comparison of voltage (a) and HFR (b) between simulation and measurement for 0.3 mg/cm² Pt loading cases

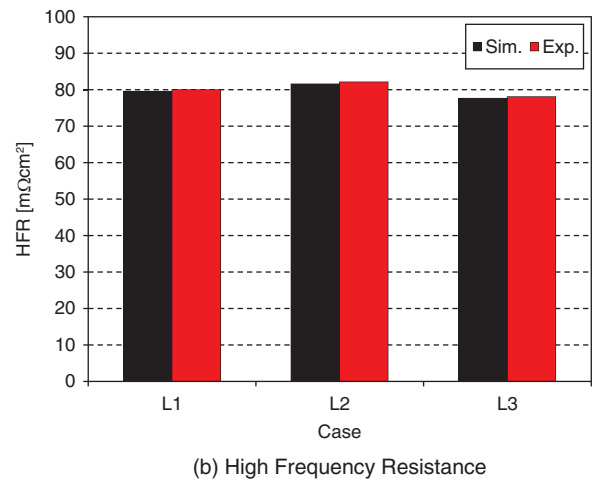
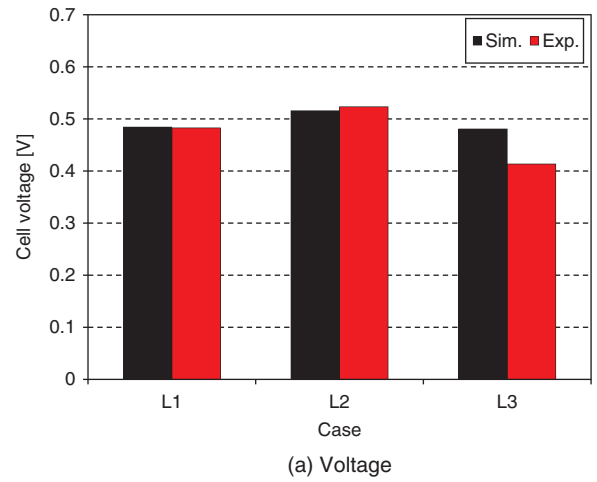


Fig. 9 Comparison of voltage (a) and HFR (b) between simulation and measurement for 0.1 mg/cm² Pt loading case

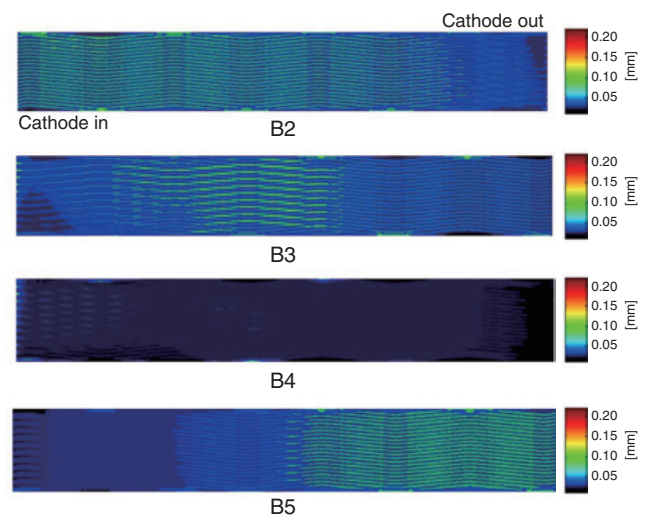
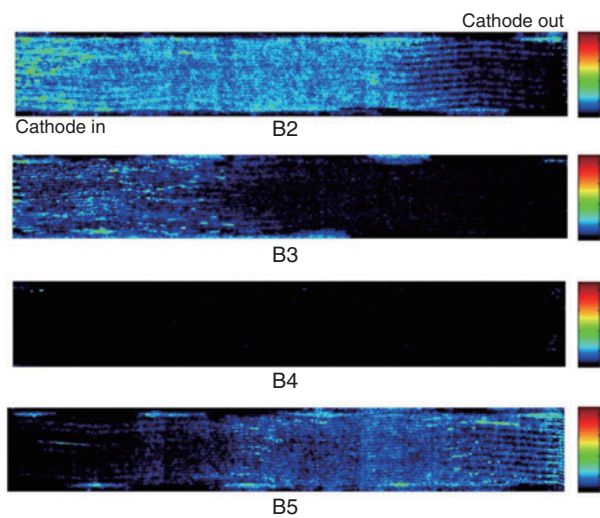


Fig. 10 Comparison of water distribution between simulation and neutron imaging for cases B2, B3, B4, and B5

4. Conclusion

Large-scale computations of a PEMFC with parallel wavy flow field have been carried out using the multiphase-mixture model. We demonstrate the vast computational capability of the model in simulating the comprehensive two-phase phenomena in a PEMFC. Eight case studies are performed to examine the validity of these simulations. Reasonable agreement in cell voltage, HFR, and current density and temperature distributions is achieved between simulations and experiments in these cases under various operating conditions with two Pt loadings of 0.3 mg/cm² and 0.1 mg/cm², respectively. Of particular importance, we obtain a quantitative agreement between the predicted and measured liquid water distributions in a practical PEMFC.

References

- (1) Wang, Y., Wang, C. Y.: A Nonisothermal, Two-Phase Model for Polymer Electrolyte Fuel Cells, Journal of the Electrochemical Society, 153, A1193-A1200, (2006)
- (2) Meng, H.: A Three-dimensional Mixed-domain PEM Fuel Cell Model with Fully-coupled Transport Phenomena, Journal of Power Sources, 164, p.688-696, (2007)
- (3) He, M., Huang, Z., Sun, P., Wang, C.: Modeling and Numerical Studies for a 3D Two-Phase Mixed-Domain Model of PEM Fuel Cell, Journal of the Electrochemical Society, 160, F324-F336, (2013)
- (4) Cao, T. F., Lin, H., Chen, L., He, Y. L., Tao, W. Q.: Numerical Investigation of the Coupled Water and Thermal Management in PEM Fuel Cell, Applied Energy, 112, p.1115-1125, (2013)
- (5) Shimpalee, S., Greenway, S., Spuckler, D., Van Zee, J. W.: Predicting Water and Current Distributions in a Commercial-size PEMFC., Journal of Power Sources, 135, p.79-87, (2004)
- (6) Fink, C., Fouquet, N.: Three-dimensional Simulation of Polymer Electrolyte Membrane Fuel Cells with Experimental Validation, Electrochimica Acta, 56, p.10820-10831, (2011)
- (7) Carnes, B., Spornjak, D., Luo, G., Hao, L., Chen, K. S., Wang, C. Y., Mukundan, R., Borup, R. L.: Validation of a Two-phase Multidimensional Polymer Electrolyte Membrane Fuel Cell Computational Model using Current Distribution Measurements, Journal of Power Sources, 236, p.126-137, (2013)
- (8) <http://pemfcdata.org>.
- (9) Hao, L., Moriyama, K., Gu, W., Wang, C. Y.: Modeling and Experimental Validation of Pt Loading and Electrode Composition Effects in PEM Fuel Cells, Journal of the Electrochemical Society, 162 (8), F854-F867, (2015)

Nomenclature

Latin Symbols

c_p	Specific heat (J/kg K)
C^i	Molar concentration of species i (mol/m ³)

$D^{i,eff}$	Effective diffusivity of species i (m ² /s)
j	Volumetric reaction current density (A/m ³)
P	Pressure (Pa)
S	Source term in transport equations
s	Saturation
T	Temperature (K)
u	Velocity vector (m/s)

Greek Symbols

ε	Porosity
κ	Ionic conductivity (S/m)
λ	Water content in ionomer
ρ	Density (kg/m ³)
σ	Electronic conductivity (S/m)

Subscripts/Superscripts

e	Ionomer
eff	Effective value
g	Gas
i	Species
k	Component in cell
s	Electronic phase

■ 著 者 ■



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