Analysis of Mass Transfer and Porosity at Catalyst Layer of Polymer Electrolyte Membrane Fuel Cell Based on A Pore-Scale Model

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Abstract. Fuel cells are a promising power source. The catalyst layer is an important part of a low-temperature fuel cell. A three-dimensional pore-scale model is utilized to shed light on the mechanism of mass transfer and reactions inside the catalyst layer. Relationship between porosity and the number of carbon spheres are discussed quantitatively. Water mass fraction at the outlet is discussed in different porosity and reaction rates. Simulation results show that variance of water mass fraction at the outlet is higher when porosity is higher in generating water cases and variance of water mass fraction at the outlet is lower when porosity is higher in consuming water cases.

1. Introduction
Fuel cells have always been treated as a promising alternative to internal combustion engines on automobiles. One of the core parts of a fuel cell is the catalyst layer. In a low-temperature fuel cell, catalyst layer (CL) usually consists of three parts including carbon, ionomer, and pores. Three parts are medias transporting electron, ion, and gas. The performance of the three-phase reaction interface has a large influence on the whole cell performance.

Since in situ experiments on CL are usually difficult to perform, the pore-scale model of CL is a decent way to characterize deep mechanism inside CL. Lange et al offer a 3-dimensional pore-scale model and use the model to calculate effective diffusion coefficient in CL.[1, 2] Leonard et al indicate that catalyst layer thickness has a significant influence on cell performance through a 1-dimensional model.[3] Lei Xing et al offer a 2-dimensional model to indicate that higher cathode temperature decreases the oxygen mole fraction, eventually resulting in a limitation of cell performance.[4] However, the relationship between porosity and effective diffusivity when the different size of the carbon sphere was inside CL remains unknown. Besides, how water mass fraction at the outlet is affected by reaction rate need confirming.
In this study, a 3-dimensional pore-scale model is presented with the finite element method. Model validation is done by comparing model results with other work. The relationship between porosity and the number of carbon spheres are illustrated quantitatively. Simulation with reaction inside CL shows the corresponding relation of water mass fraction at outlet and reaction rate.

2. Mathematical model

2.1. Model assumption

1. Gas species (O$_2$/H$_2$O in the cathode CL) are supposed to be ideal gas;
2. All carbon spheres are supposed to be the same size, covered with the same amount of ionomer;
3. Knudsen flow is not considered in the model for the simplicity of the model;
4. Inlet and outlet are the opposite faces on the cubic computational domain;
5. Ionomer is considered as a pore when calculating porosity;
6. Carbon spheres are randomly inserted into the domain.

It is a 3-dimensional pore-scale model with a cubic computational domain of 100 nm × 100 nm × 100 nm, shown in Figure 1.

2.2. Governing equations

Equations in the model are mostly like a previous model work of bipolar membrane fuel cell[5, 6]. For the transport of gas species in the porous media (CL), diffusion is the main driving force.

Momentum equation:

$$\frac{\rho}{\varepsilon_p} \left( \mathbf{u} \cdot \nabla \right) \frac{\mathbf{u}}{\varepsilon_p} = \nabla \cdot \left[ -p I + \frac{\mu}{\varepsilon_p} \left( \nabla \mathbf{u} + (\nabla \mathbf{u})^T \right) - \frac{2}{3} \frac{\mu}{\varepsilon_p} (\nabla \cdot \mathbf{u}) I \right]$$

(1)

where $p$ is pressure, $\mu$ is dynamic viscosity, $\rho$ is density, $I$ is the identity matrix, $\varepsilon_p$ is porosity.

Continuity equation:
\[ \nabla \cdot (\rho \mathbf{u}) = 0 \] 

(2)

Species equation:

\[
\begin{align*}
\nabla \cdot \mathbf{j}_i + \rho (\mathbf{u} \cdot \nabla) \omega_i &= R_i \\
M_n &= \left( \sum_i \frac{\omega_i}{M_i} \right)^{-1} \\
\mathbf{j}_i &= -\left( \rho D_{i,eff} \nabla \omega_i + \rho \omega_i D_{i,eff} \frac{\nabla M_n}{M_n} \right) \\
D_{i,eff} &= f_{eff} D_i \\
f_{eff} &= \varepsilon_p^{3/2}
\end{align*}
\] 

(3)

Using Bruggeman correction, in which \( \omega_i \) is the mass fraction, \( M_i \) is the molar mass, \( M_n \) is the mean molar mass, \( D_{i,eff} \) is effective diffusivity, \( D_i^f \) is the diffusion coefficient.

Reactions:

\[ \nabla \cdot \mathbf{j}_i + \rho (\mathbf{u} \cdot \nabla) \omega_i = R_i - \omega_i \sum R_i \] 

(4)

\( R_i \) is mass transfer to other phases.

2.3. Model validation

The 3-dimensional pore-scale model has model validation. Effective diffusivity is compared to results from Shin et al[7]. Simulation results show a similar trend no matter in this work or results from Shin et al[7]. Effective diffusivity increases with porosity. It indicates that the pore scale model could express certain characteristics inside CL.

**Figure 2.** Simulation results on the relationship between porosity and effective diffusivity. (a) Carbon sphere’s radius is set to 20 nm; (b) Carbon sphere’s radius is set to 12 nm.
With detailed check with two results. Overall patterns are the same in both 20 nm and 12 nm cases. Variance in Figure 2(b) is much higher than (a) due to the smaller sphere size. However, simulation results of effective diffusivity in this work is slightly higher than the results from Shin et al. Possible reason is that we consider ionomer as part of the pore in this work. This difference in value could not affect the trend of simulation results. Thus, the present pore-scale model can be used to seek a mechanism inside CL.

3. Results and discussion
In a fixed computational domain of 100 nm × 100 nm × 100 nm, as we may easily think, porosity will decrease linearly with a greater number of carbon spheres covered with ionomer in it. However, simulation results in Figure 3 show that the relationship between porosity and the number of carbon spheres are a curve. The curve shows a similar trend with the radius of carbon from 12 nm to 24 nm. A possible explanation of the curve is that when there are too many carbon spheres inside the cubic computational domain, and we try to insert more spheres into the cubic, more spheres are likely to obtain position at the edge, which will be cut to a piece of carbon spheres that was shown in Figure 1.

![Figure 3. Relationship between the number of carbon spheres and porosity with carbon radius from 12 nm to 24 nm.](image)

After the relationship between the number of carbon spheres and porosity is explored, we would expect how the reaction rate of generating water would affect water mass fraction at the outlet at different porosity situation.

Data from Figure 4 is logical since more water would be transferred to the outlet when more water is generated in CL or vice versa. It is conceivable that different distribution of carbon spheres positions leads to slightly different water mass fraction at outlet even in the same porosity, which indicates that geometry has an influence on effective diffusivity.

Based on data shown in Figure 4 (a) and (b), variance increases with porosity getting near 1.0 at the situation of water generating, while variance decreases with porosity getting lower when water consuming. Relationship between water mass fraction at outlet and reaction rate is exponential as shown in Figure 4 (c) and (d).
Figure 4. Water mass fraction at outlet vs porosity or reaction rate. (a) Reaction rate of generating water: $1.0 \times 10^{12}$ kg m$^{-3}$ s$^{-1}$; (b) Reaction rate of consuming water: $1.0 \times 10^{10}$ kg m$^{-3}$ s$^{-1}$; (c) porosity fixed to 0.636, water mass fraction at outlet vs water generating rate; (d) porosity fixed to 0.636, water mass fraction at outlet vs water consuming rate.

4. Conclusion
A pore-scale model based on the finite element method is created to explore reactions and mass transfer inside a cubic area of the catalyst layer. The number of carbon spheres has a non-linear relationship with porosity. When generating water, the variance of water mass fraction at the outlet is higher when porosity is higher. When consuming water, the variance of water mass fraction at the outlet is lower when porosity is higher.

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