

A Pore-Scale Multiphysics Method to Study PEMFC Catalyst Layers

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ABSTRACT

Three dimensional pore-scale numerical approach to study the effects of structural parameters, material properties, and operating conditions on the performance of catalyst layer of proton exchange membrane fuel cell is developed. The proposed approach includes a novel stochastic reconstruction method and a pore-scale fully coupled simulation model. The pore-scale simulation model is based on a hybrid lattice Boltzmann-Finite Difference method. Multi-physics phenomena are taken into account and fully coupled in the model including the electrochemical reactions, water generation and evaporation, mass transport through electrode pores and ionomer, electron transport through carbon support and catalyst particles, and proton transport through ionomer. The proposed method is validated with experimental data and shows good agreement. The case studies show that the structure of catalyst layer and operating condition impacts on the overall electrode performances.

1. Introduction

To achieve high performance with a low-Pt loading electrode is an important issue for the mass production of low cost Proton Exchange Membrane Fuel Cells (PEMFCs) and has been intensively studied through experiments and computation⁽¹⁾. Among the main issues to realize ultra-low Pt loading is optimizing the microstructure of the catalyst layer (CL). As in Fig. 1, the PEMFC CL is composed of four components: carbon agglomerate, ionomer, Pt particles, and pore-space. Water is generated by electrochemical reaction on the Pt surface by use of oxygen, proton, and electron. Oxygen is transported in pore and is dissolved and diffused in the ionomer, electron is transported in Pt and carbon support, and proton is transported in the ionomer. Therefore, transport of reactants and products strongly depends on the CL microstructure. In particular, at high current density operating conditions, the substantial oxygen mass transport loss caused by liquid water, ionomer transport resistance, and interfacial resistances between different phases significantly limits the output power density. The variation of ionomer morphology also affects the Ohmic loss due to proton transport.

To find an optimal CL structure, pore scale modeling has been a focus of attention⁽²⁾⁻⁽⁴⁾. However, no previous work on pore scale modeling has considered complex phenomena such as two phase flow including phase change, which impact the

performance substantially.

Therefore, we propose a novel pore-scale modeling platform to study the influences of various CL microstructures on the performance. It was developed to perform a detailed analysis to understand physico-chemical processes in the CL, and to evaluate the influence of pore-scale structures. The computational platform consists of a novel stochastic reconstruction method and a pore-scale fully-coupled simulation model. The reconstruction method is designed to generate 3-D geometries of the CLs including all the components, at a high level of details. A number of pore-scale and macroscopic structural properties are introduced and specified in advance, leading to a customized CL reconstruction method. In addition,

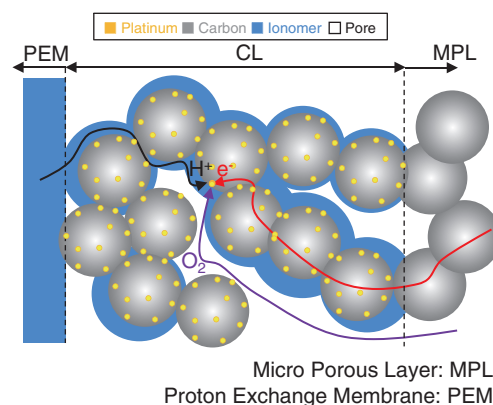


Fig. 1 CL in PEMFC

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anisotropic CLs with graded structural properties can also be reconstructed. In such structures, the electrochemical and transport properties vary along the thickness of the CL. The multi-physics pore-scale model describes important physical and chemical processes in different components of the CL, including liquid water generation, transport, and phase-change. A hybrid lattice Boltzmann-Finite Difference (LBFD) method is used to describe multiphase reactants and products transport. Several new models and methods are introduced to describe processes related to mass transport and Ohmic losses. Furthermore, results from validation and case studies are presented.

2. Stochastic Reconstruction of Catalyst Layer

Pore scale modeling needs the information on the detailed three dimensional structures to predict the phenomena in the CL microstructure. However, it is challenging to measure the real three dimensional geometries due to the weak material characteristics of ionomer to electron beam. So, a numerical reconstruction method based on the knowable structural properties is necessary. In the literature, the efforts on numerical reconstruction of CLs are mainly focused on reproducing CL structures resembling the digitized ones obtained by a microscope. However, due to the technical limitations, it is challenging to distinguish the ionomer from carbon components. The CL reconstruction study was therefore mainly limited to carbon structure reconstruction. The ionomer is added in the system following simple rules, such as uniform thickness⁽²⁾⁻⁽⁵⁾. Pt size distribution has not been considered.

In order to optimize the electrode structure and enhance the fuel cell performances in an efficient way, it is helpful to develop a customized CL reconstruction approach, such that we can stochastically reconstruct the CLs not only having the overall desired statistical properties but also having numerous detailed structural features, including ionomer thickness variations and Pt loading. In addition to isotropic CLs, it is also desirable to reconstruct graded anisotropic ones, which are often observed in real experiments. In this study, we extended a previously proposed stochastic reconstruction method⁽⁵⁾ to provide such features. Numerous structural properties can be flexibly specified in advance, such as volume fraction of each phase, Pt loading, ionomer distribution form and coverage, Pt dispersion and coverage, etc. The structural properties can be globally or locally adjusted and the reconstructed CL can have various graded anisotropic properties.

2.1. Carbon Structure Reconstruction

For the generation of carbon structures, a sphere-based simulated annealing method⁽⁵⁾ is used. Among several approaches which are used to virtually construct a porous media structure, the sphere-based simulated annealing method has recently become

popular due to its outstanding features in generating the CL microstructures.

The sphere-based simulated annealing method is based on the stochastic optimization method to minimize the structural differences between the specified and generated carbon structures. Initially, spherical particles representing primary carbon particles are stochastically added and located in a computational domain until their volume fraction reaches a prescribed limit. Then, the spheres are moved arbitrarily and relocated to a new position according to certain distribution functions and restrictions. This optimization process continues until the structure reaches a status that satisfies the prescribed statistical status. In this study, the status is described by a two-point correlation function⁽⁵⁾.

2.2. Ionomer Distribution

Ionomer is used to transport proton to the catalyst surfaces and is used same polymer with PEM. In the cathode CL, the structure of the ionomer thin film strongly affects the performance. An ideal coverage and thickness will provide the maximum active catalyst sites and mass transport. In a real manufacturing process, the ionomer may not distribute uniformly on the surface of the agglomerates and even it is not uniform on each carbon particle⁽⁶⁾. In order to mimic these real scenarios to the largest extent, we introduce five parameters to guide the reconstruction of ionomer layers: ionomer average thickness $\delta_{i,avg}$, ionomer to carbon mass ratio I/C , ionomer coverage percentage (i.e. percentage of carbon particles covered by ionomer) c_i , maximum offset value between an ionomer layer center and its covered carbon particle center $d_{i,max}$, and the Relative Humidity RH .

The ionomer layer was added in the CL according to multiple restrictions with these controlling parameters. The reconstructed ionomer layer has non-uniform thickness on different carbon particles with the average thickness $\delta_{i,avg}$. By defining the ionomer coverage percentage and the maximum offset value $d_{i,max}$, we are able to reproduce carbon particles that are not covered with ionomer or that are partially covered as in Fig. 2.

During fuel cell operation, the thickness of the ionomer layer changes due to humidification. In this work, this ionomer swelling effect is taken into account. By defining the RH and I/C ratio, the ionomer volume fraction $\varepsilon_{i,RH}$ is calculated as⁽⁷⁾,

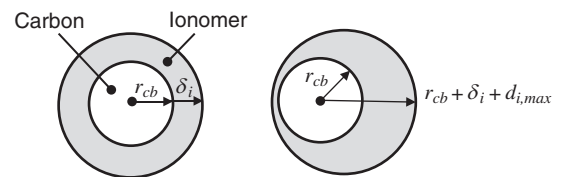


Fig. 2 Schematics of ideal uniform ionomer layer coverage and non-ideal coverage on carbon particle

$$\varepsilon_{i, RH} = \left(\frac{I}{C} \right) \frac{10}{f_i \rho_{i, dry}} \left(1 + \frac{M_w \rho_{i, dry} \lambda}{\rho_w EW} \right), \quad (1)$$

where $f_i = 28 \pm 2 \text{ mg/cm}^2$ for $I/C < 3$, $\rho_{i, dry}$ is the density of dry ionomer, ρ_w is the density of water, M_w is the mole number of water, λ is the water content of the ionomer at a specific RH , and EW is the equivalent weight of ionomer material. The ionomer layers are added to the reconstructed CL according to the RH -dependent volume fraction given by Eq. (1).

2.3. Catalyst Particle Distribution

To represent or control the characteristics of the catalyst particle distribution in the CLs, four controlling parameters are introduced: Pt loading m_{Pt} , Pt weight percentage $Pt_{wt\%}$, Pt/C ratio c_{Pt} , and Pt distance η_{Pt} . The m_{Pt} is the total amount of Pt particles distributed in a unit area of the CL with the unit of mg/cm^2 . The $Pt_{wt\%}$ is the ratio between the weight of Pt and that of carbon and Pt in the CL. The c_{Pt} describes the fraction of carbon particles that contain Pt particles. The η_{Pt} is used to specify the minimum distance between any arbitrarily distributed Pt particles on the surface of carbon agglomerates.

Based on these controlling parameters, the volume fraction of Pt particles ε_{Pt} can be calculated as,

$$\varepsilon_{Pt} = \varepsilon_s \frac{Pt_{wt\%}}{\rho_{Pt}} \left(\frac{Pt_{wt\%}}{\rho_{Pt}} + \frac{1 - Pt_{wt\%}}{\rho_{cb}} \right)^{-1}, \quad (2)$$

where ρ_{Pt} and ρ_{cb} are the density of platinum and carbon, respectively, and ε_s is the total volume fraction of carbon and Pt particles. This amount of Pt catalyst voxels is distributed in a stochastic way according to specified restrictions. Assuming the solid carbon, the Pt particles are located at the surface of each carbon particle. If c_{Pt} is unity, then the Pt particles will have a nearly uniform distribution in the system. The minimum distance between every two Pt particles can be specified to control the degree of particle dispersion. The c_{Pt} can be adjusted flexibly, giving a specific percentage of bare carbon particles are introduced. No catalyst particles are attached to the bare carbon particles. The bare carbon particles are randomly selected among the carbon agglomerate, until the specific percentage is reached. In this way, the Pt distribution will be reproduced to mimic the real situation to the largest extent.

If the percentage of bare carbon particles is 0, and considering the Pt supported carbon has constant $Pt_{wt\%}$, then the $Pt_{wt\%}$ is equal to the ratio between the total Pt weight and the total Pt and carbon weight. Therefore, the $Pt_{wt\%}$ and Pt loading have the following relationship:

$$Pt_{wt\%} = \left[\left(\frac{\varepsilon_s L}{m_{Pt}} - \frac{1}{\rho_{Pt}} \rho_{cb} + 1 \right) \right]^{-1}, \quad (3)$$

where L is the thickness of the CL.

2.4. Anisotropic Graded Structure

The manufactured CLs can easily be inhomogeneous and anisotropic. In order to capture this property, we also extended the current reconstruction method. In the literature, no study has been reported to reconstruct such CLs. In order to reconstruct such structures, two approaches can be considered. The first is to design a reference trial two-point correlation function that describes correctly the graded structure characteristics in the whole system. The second is to generate several different CL domains that have customized properties in each domain and then to combine them together. The first method needs a lot of time to obtain the structure. On the other hand, the second method is more straight forward and easy to realize. However, the main issue for this second approach is the abrupt change of carbon structures, e.g., broken carbons, at the domain boundaries. In order to solve this issue, we propose the following method. First, the carbon agglomerate structure for the first domain is generated. When generating the second domain, the carbon particles in the interfacial region between the first and second domains are subject to some constraints to maintain the continuity of the structure. Specifically, the carbon particles are restricted from relocation or addition. In addition, all the other carbon particles in the bulk region are required to skip the interfacial region when they have to be relocated in the optimization process. After stochastically reconstructing all the domains, good continuity property is obtained at the domain interfaces in the final graded structure.

3. Multiphysics Pore-scale Modeling

In this study, multiphase reacting flows and transport phenomena in different components of the CL are simulated by using a hybrid LBFD method. The velocity field is solved by using the lattice Boltzmann method. The liquid-gas interface is described by using the finite difference phase-field method. The species transport is solved using the macroscopic conservation equation supplemented by the Knudsen diffusion correction. The electrochemical reactions, water generation, and evaporation are fully coupled with the mass transport through pores and ionomer. In the experiments, it has been observed that ionomer layer geometry and transport properties are strongly influenced by the RH and the liquid water in the pores. Ionomer swells and ionic conductivity increases when the ionomer uptakes water. The effects of ionomer swelling are considered in the CL reconstruction process, while the ionic conductivity variation is taken into account in the pore-scale modeling.

3.1. Multiphase Reactive Flow with Phase Change

The phase-field method for two-phase flows with phase change has been developed in this research. The equation for the order parameter C that describes the

liquid-gas interfaces is given as,

$$\frac{\partial C}{\partial t} + u_\alpha \frac{\partial C}{\partial x_\alpha} = \frac{\partial}{\partial x_\alpha} \left(M \frac{\partial \phi}{\partial x_\alpha} \right) + \beta_p \frac{c_{w,sat} - c_{w,g}}{c_{w,sat}} C^2 (1 - C^2), \quad (4)$$

where M is the mobility. ϕ is the chemical potential. The parameter β_p is related to the water evaporation and condensation rate. $c_{w,g}$ is the concentration of water vapor in the gas phase. $c_{w,sat}$ is the saturation concentration of water vapor, and is evaluated by the Clausius-Clapeyron equation⁽⁸⁾.

The continuity, momentum, species, and energy equations can be written as,

$$\frac{\partial u_\alpha}{\partial x_\alpha} = \frac{\Delta p}{\rho} \omega_c, \quad (5)$$

$$\rho \frac{\partial u_\beta}{\partial t} + \rho u_\alpha \frac{\partial u_\beta}{\partial x_\alpha} = - \frac{\partial p}{\partial x_\beta} + \frac{\partial}{\partial x_\alpha} \left[\nu \left(\frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial u_\alpha}{\partial x_\beta} \right) \right] + \rho F, \quad (6)$$

$$\frac{\partial C_i}{\partial t} + u_\alpha \frac{\partial C_i}{\partial x_\alpha} = \frac{\partial}{\partial x_\alpha} \left(D_i \frac{\partial C_i}{\partial x_\alpha} \right) + \omega_i, \quad (7)$$

$$\frac{\partial T}{\partial t} + u_\alpha \frac{\partial T}{\partial x_\alpha} = \frac{\partial}{\partial x_\alpha} \left(k \frac{\partial T}{\partial x_\alpha} \right) + \omega_T \frac{\rho \omega_c h_{fg}}{\rho c_p}, \quad (8)$$

where

$$\omega_c = \beta_p \frac{c_{w,sat} - c_{w,g}}{c_{w,sat}} C^2 (1 - C^2), \quad (9)$$

and $\omega_{H_2O} = a_{C,H_2O} \omega_c$. The parameter a_{C,H_2O} is the conversion factor between the order parameter and the water vapor concentration. ω_i and ω_T are the source terms of species conservation equation and temperature equation, respectively. The velocity field is solved by using the lattice Boltzmann method, while the finite difference method is used to solve other scalar equations. The details of the hybrid LBFD method will be presented in future publications.

3.2. Oxygen Reduction Reaction (ORR)

At high potentials, O and OH coverages on the Pt surface are significant⁽⁹⁾⁻⁽¹¹⁾. The adsorbed O and OH therefore block available reaction sites on which O_2 can sit. As a result, the available reaction sites decrease as the potential increases. The oxygen reduction reaction considering the oxide coverage effect can be expressed by the following kinetic model⁽¹²⁾:

$$j = j_0 \left(\frac{p_{O_2}}{p_{O_2,0}} \right)^\gamma (1 - \theta) \exp \left(- \frac{\alpha F}{RT} \eta \right) \exp \left(- \frac{\omega \theta}{RT} \right), \quad (10)$$

where η is the overpotential, F is the Faraday constant, R is the gas constant, j_0 is the exchange current density, and γ is the oxygen reaction order.

ω is the energy parameter for the Temkin isotherm, which defines the coverage-dependent rate of change of the apparent Gibb's energy of adsorption of adsorbing species. The cumulative oxygen coverage θ is a function of potential and was given by experimental data (refer to Fig. 6(a) of Ref. (13)).

3.3. Coupling of Electrochemistry and Transport

3.3.1. Water production and transport

In the particle-type CL, water is produced at the catalyst particle surface, transports through the ionomer, and finally emerges at the ionomer-pore interface. A simple water transport model involving only diffusion is solved since water production at Pt surface and emergence in the pores is of major interest. On Pt surfaces, the water production is considered as a flux boundary condition:

$$\omega_{w,Pt} = j / 2F, \quad (11)$$

where $\omega_{w,Pt}$ is the water production rate.

At the ionomer-pore interface, water emerges from the ionomer. The water flux on the ionomer-pore boundary is modeled as,

$$\omega_w = c_{lf} (c_{w,i} - c_{w,sat}), \quad (12)$$

where $c_{w,i}$ is the water concentration at the ionomer-pore boundary. c_{lf} is the coefficient that controls the water emergence speed and can be written as,

$$c_{lf} = c_{lf,0} D_{w,i} / l_i^2. \quad (13)$$

The $c_{lf,0}$ is an adjustable parameter, $D_{w,i}$ is the diffusivity of water in ionomer, l_i is the characteristic thickness of the ionomer. Hence, $D_{w,i} / l_i$ represents the velocity scale of the process. Currently we set $c_{lf,0} = l_i$ assuming the water emergence speed has a similar order to that of water diffusion in the ionomer.

In this work, when water emerges from ionomer or Pt to the pores, it is assumed that water is in the liquid phase. As of now, there is no clear evidence of whether the emerging water is in gas phase or in liquid phase. However, when the RH is less than 100%, the emerged liquid water evaporates, which is considered in the present modeling.

Since the order parameter is unity for liquid water, the velocity at the water-emerging boundary can be given as,

$$v_c = \omega_c / C_l, \quad (14)$$

where C_l is the order parameter for liquid water, and it is unity. ω_c is the water flux of $\omega_{w,i}$ in the unit of the order parameter.

3.3.2. Electron and proton transport

The potentials for the solid and electrolyte phases are governed by the Poisson's equation. The boundary conditions are set as follows. For the cathode MPL/CL

interface,

$$\phi_s = V_{cell}, \quad \partial\phi_e / \partial n = 0, \quad (15)$$

where V_{cell} is the potential at the MPL/CL interface. For the cathode PEM/CL interface,

$$\phi_e = \phi_{e,0}, \quad \mathbf{n} \cdot \nabla\phi_s = 0, \quad (16)$$

where $\phi_{e,0}$ is the electrolyte-phase potential at the PEM/CL interface and $\mathbf{n}$ is the surface normal vector. At the ionomer/carbon interface,

$$\mathbf{n} \cdot \nabla\phi_e = 0, \quad \mathbf{n} \cdot \nabla\phi_s = 0. \quad (17)$$

At the electrochemically active surface,

$$-k_e \nabla\phi_e \cdot \mathbf{n} = -j, \quad -k_s \nabla\phi_s \cdot \mathbf{n} = j. \quad (18)$$

In the simulation, Ohmic losses from other components of fuel cells are also calculated based on the electronic and ionic resistance. The resistances are converted from the Ohmic loss of each component predicted by the down-the-channel model⁽¹⁴⁾.

3.3.3. Ionomer humidification and relative humidity

The water plays an important role in CL. It emerges at the ionomer/pore interface, evaporates from liquid water to vapor in the pores, and it can be taken up by ionomer again. It alters the oxygen transport by blocking the pores directly or by making the ionomer swell. It also influences the RH in the CL and proton conductivity in the ionomer. The interactions among these processes are important and are modeled as follows.

When the water concentration in the ionomer $c_{i,w}$ is lower than the saturated concentration, the ionomer uptakes water. The saturated water concentration in the ionomer $c_{i,w,sat}$ is calculated as below⁽¹⁵⁾.

$$c_{i,w,sat} = \lambda / (\lambda \bar{V}_w + EW / \rho_{i,dry}), \quad (19)$$

where $\bar{V}_w$ the molar volume of water, $\rho_{i,dry}$ is density of dry ionomer, and the water content λ is a function of temperature and RH :

$$\lambda = \begin{cases} \left[1 + 0.2325RH^2 \left(\frac{T-30}{30} \right) \right] \times \\ [14.22RH^3 - 18.92RH^2 + 13.41RH], & \text{if } RH < 100\%, \\ 9.22 + 0.181T, & \text{if } RH > 100\%. \end{cases} \quad (20)$$

The RH is calculated based on the water vapor concentration $c_{w,g}$ and temperature T . When the water concentration $c_{i,w}$ in the ionomer becomes larger than $c_{i,w,sat}$, the water emerges from the ionomer and appears in the pores at the ionomer/pore interface. The liquid water evaporates, which increases the RH simultaneously. When the RH varies, the ionomer saturated water concentration $c_{i,w,sat}$ is calculated accordingly in the next time step. The water emergence rate from the ionomer varies accordingly.

Table 1 Parameters of CL sample for studying pore size distribution and transport properties

Parameter	Value	Unit
Thickness	1	μm
Porosity	42	%
Carbon volume	28	%
Structure parameter d	40	nm
Carbon particle diameter	40	nm
Pt loading	0.0129	mg/cm ²
$Pt_{wt\%}$	19	%
Pt particle diameter	5.7	nm
Pt/C ratio c_{Pt}	100	%
ESA	45	m ² /g-Pt
I/C	1	-
EW	900	g/cm ³
Ionomer volume fraction	29.5 (RH0%)	%
	32 (RH20%)	%
	34 (RH45%)	%
	39 (RH85%)	%
Ionomer coverage c_i	100	%
Voxel size	5×5×5	nm ³
Grid number	200×200×200	-

4. Validation Study

4.1. Validation Study: Reconstruction

We reconstructed cathode CLs (CCLs) by applying the proposed method. For validation, we examined the structural and transport properties of the reconstructed CLs and compared with experiments and literature data at different RH values. These properties include Pore Size Distribution (PSD), Electrochemical Surface Area (ESA), proton resistivity, electronic conductivity and gas diffusivity. The ionomer thickness and volume fraction vary with RH , which changes the porosity and tortuosity accordingly. This volume variation effect was taken into account in the reconstruction process. The CLs were reconstructed with the setup specified in Table 1.

The reconstructed CL is presented in Fig. 3. The pore size distribution at dry condition ($RH=0\%$) was evaluated and compared with experimental data in Fig. 4. At different RH conditions, the ionomer volume fraction was calculated in advance and used for the reconstruction. Several macroscopic properties of the CLs were evaluated based on the reconstructed CLs.

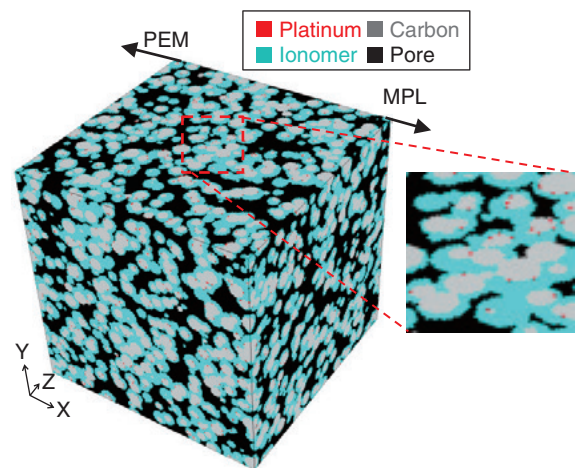


Fig. 3 Reconstructed CL using proposed general stochastic reconstruction method

ESA is about 45 m²/g-Pt. For each CL sample at different *RH*, single phase simulations were conducted to examine the transport properties. In Fig. 5, the proton resistivity with respect to *RH* is shown. The results predicted by the model are in good agreement with the experimental data. In Fig. 6, the gas diffusivities and electronic conductivity at *RH*=30% are compared with literature data⁽¹⁶⁾. The simulation results of gas diffusivity and electronic conductivity also agree with the experimental data.

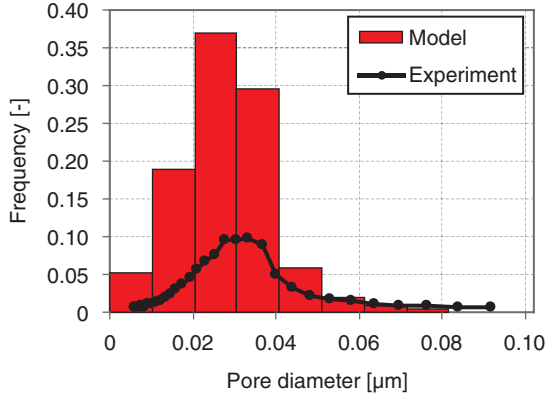


Fig. 4 Pore size distribution

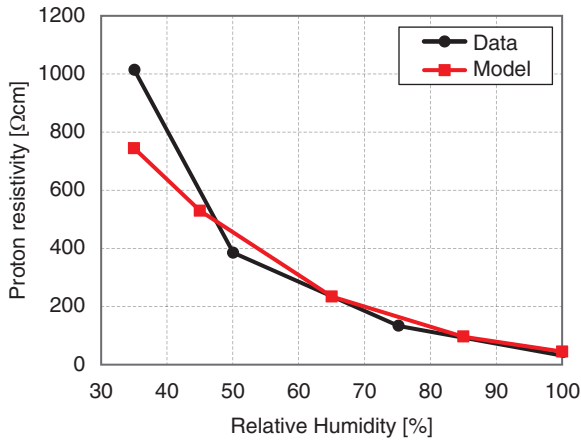


Fig. 5 Validation study: proton resistivity of reconstructed CL

Table 2 Parameters of CL reconstruction for validation

Parameter	Value	Unit
Thickness	15.5	μm
Porosity	42	%
Carbon volume	28	%
Structure parameter <i>d</i>	90	nm
Carbon particle diameter	60	nm
Pt loading	0.2	mg/cm ²
<i>Pt</i> _{wt%}	23.4	%
Pt particle diameter	5.7	nm
Pt/C ratio <i>c_{Pt}</i>	100	%
ESA	45	m ² /g-Pt
<i>I/C</i>	1	-
<i>EW</i>	900	g/cm ³
Ionomer volume fraction	29.5 (RH0%)	%
	35.5 (RH65%)	%
Ionomer coverage <i>c_i</i>	100	%
Voxel size	16×16×16	nm ³
Grid number	960×64×64	-
<i>RH</i>	65	%
Cathode inflow	Air	-
Anode inflow	Pure hydrogen	-
Temperature	353	K
Pressure	150	kPa

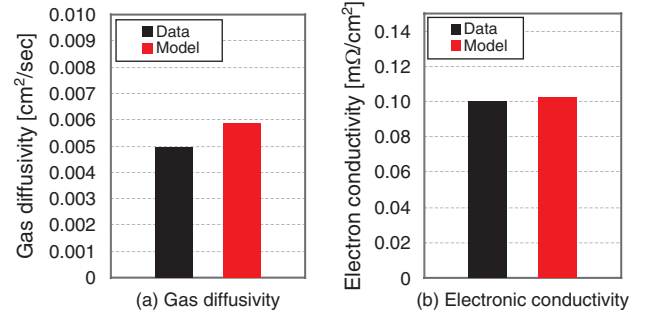


Fig. 6 Data comparison of gas diffusivity and electronic conductivity of reconstructed CL at *RH*=30%

4.2. Validation Study: Simulation

In this case, a cathode CL with full thickness from PEM to MPL was reconstructed and used for fully coupled multi-physics simulations. Numerical results of the model are compared with experimental data. In Fig. 7, the reconstructed structure is demonstrated with the view of the X-Y cross-section at the center of Z-coordinate. The parameters of CL reconstruction are given in Table 2. Carbon particle diameter is measured to be approximately 40 nm. Due to limited resolution in the numerical reconstruction, 60 nm was used. Similarly, the agglomerate structure parameter *d* is set to be 90 nm. At the interface between CCL and MPL, the boundary value of oxygen concentration, *RH* and temperature were all defined with the values predicted with the down-the-channel model⁽¹⁴⁾. In the

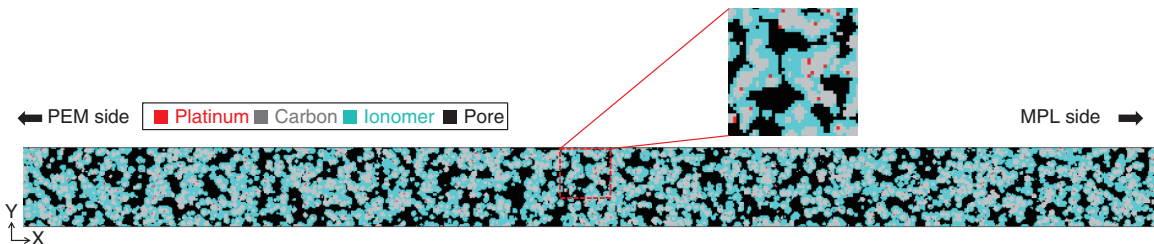


Fig. 7 Validation study: 2-D view of XY plane at center of Z-coordinate of reconstructed 3D CCL structure

simulation, single-phase calculation was conducted first to get the converged ionic potential field. Then, the multiphase simulation is performed by using the single phase results as the initial condition.

In Fig. 8, the V-I polarization curves are shown. The predicted results are in good agreement with experimental data, while at high current density ($1.5 \text{ A/cm}^2 - 2 \text{ A/cm}^2$) the model slightly under-predicts the current density. In CCLs, the water generation rate changes with current density. The relationship between water saturation and current density is shown in Fig. 8. The saturation increases with current density. At the current density of 1.5 A/cm^2 , the saturation level is about 12%. The distributions of liquid water, water vapor concentration, oxygen concentration, electrolyte-phase potential, and temperature are shown in Fig. 9. The average saturation and current density profiles along the CCL thickness (X-direction) are shown in Fig. 10. The results of two cases are shown, the higher current density case at $I = 1.5 \text{ A/cm}^2$ and the lower current density case at $I = 0.4 \text{ A/cm}^2$.

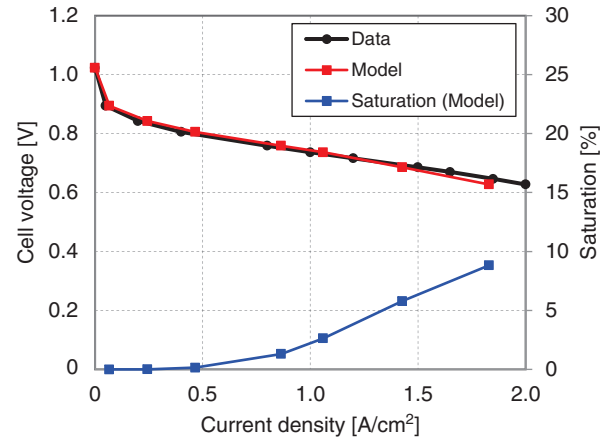


Fig. 8 Validation study: comparison of V-I polarization curve between simulation and experimental data, and simulation result of water saturation

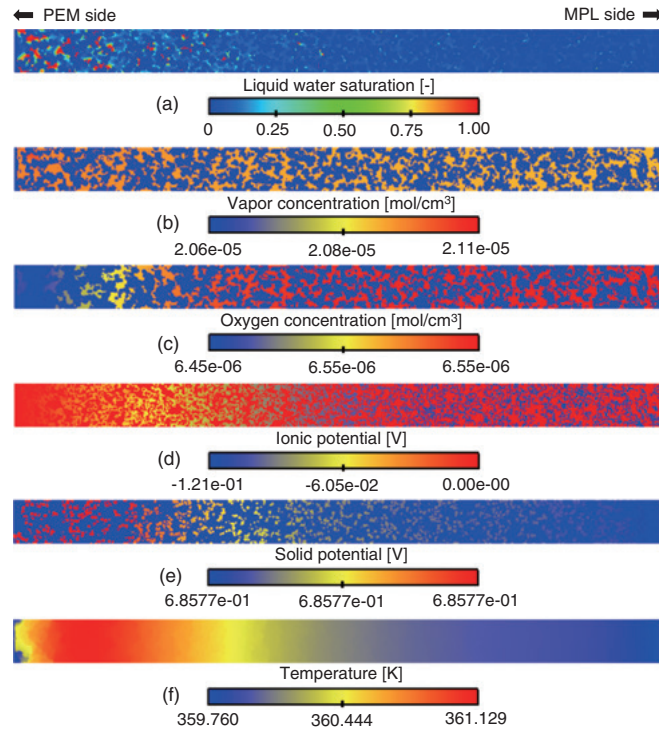


Fig. 9 Validation case: 2-D profiles of flow and electronic field properties on center XY plane of CCL

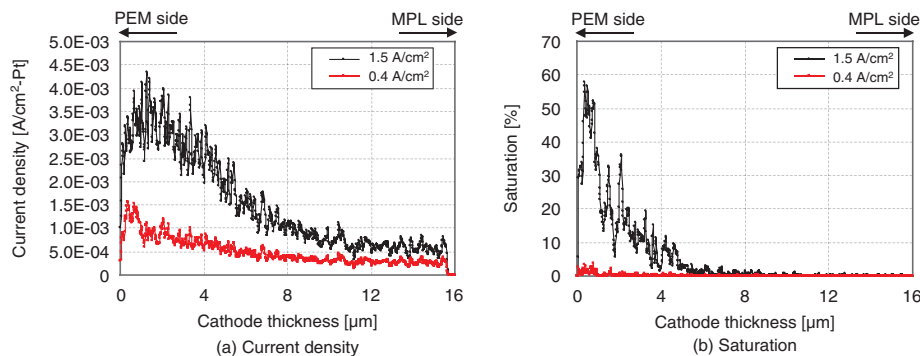


Fig. 10 Current density and saturation distribution along thickness of CL at $I = 1.5 \text{ A/cm}^2$ and 0.4 A/cm^2 ($RH=65\%$)

In Figs. 9 and 10, the left end corresponds to PEM, while the right end MPL. The ionic potential is the highest at the PEM boundary. The maximum current density occurs slightly away from PEM. This is because most of the liquid water exists near PEM. The oxygen concentration is significantly decreased in this region due to the blockage of the pathways by liquid water.

5. Case Study

In order to evaluate the impact of various CL structure properties on the electrode performance, CL samples with different specifications were reconstructed to conduct the case study. Here, results for 4 representative non-graded CLs (N1-N4) and 4 graded CLs (G1-G4) are summarized.

5.1. Non-graded CLs

In the reconstruction process, we adjusted only one parameter for each case, while keeping other structure properties the same. The base non-graded CL sample, N1, was generated with the parameters shown in Table 3. The difference of N2, N3, and N4 from N1 is only RH to examine the effect of *RH* on the CL structure, water saturation, and performance. *RH* of N2, N3, and N4 are 95%, 70%, and 30%, respectively.

The fully coupled multiphase simulation results for all cases are collected and compared. In Fig. 11, V-I polarization improves according to the increase of *RH* due to the increase of proton conductivity. And the polarization curves show that 95% RH case has the best performance due to the best balance between oxygen transport and proton transport. As shown above, the developed model can be applied to show the optimal combination of CL structure and operating condition with the understanding of liquid water and current density distributions.

5.2. Graded CLs

Three graded CLs (G2 to G4) and a reference CL (G1) are reconstructed and simulated with low-

Table 3 Parameter setup of reconstruction and simulation for reference CL sample, N1

Parameter	Value	Unit
Thickness	12	μm
Porosity	42	%
Carbon volume	28	%
Structure parameter d	90	nm
Carbon particle diameter	60	nm
Pt loading	0.2	mg/cm^2
$Pt_{wt\%}$	23.4	%
Pt particle diameter	5.7	nm
Pt/C ratio c_{Pt}	100	%
ESA	45	$\text{m}^2/\text{g-Pt}$
I/C	1	-
EW	900	g/cm^3
Ionomer volume fraction	29 (RH0%)	%
	42 (RH100%)	%
Ionomer coverage c_i	80	%
Computational domain	$16 \times 16 \times 16$	nm^3
Grid number	$760 \times 64 \times 64$	-
RH	100	%
Cathode inflow	Air	-
Anode inflow	Pure hydrogen	-
Temperature	353	K
Pressure	150	kPa

Table 4 Changed reconstruction parameters for non-graded CL samples, G1-G4, from reference CL

Cases	Parameter	Value (6 domains from PEM to MPL)	Unit
G1		Uniform	
G2	I/C	1.2, 1.1, 1.0, 0.9, 0.9, 0.9	-
	Porosity	23.2, 26.1, 29.0, 31.9, 31.9, 31.9	%
G3	$Pt_{wt\%}$	13.1, 13.1, 7.0, 7.0, 0.0, 0.0	%
G4	$Pt_{wt\%}$	0.0, 0.0, 7.0, 7.0, 13.1, 13.1	%

Pt loading CL, 0.05 mg-Pt/ cm^2 . The main parameters, which are different from those for the non-graded case N1, are listed in Table 4. G1-G4 have the same overall I/C ratio, carbon volume fraction, and Pt loading, but their structures are graded and locally different from each other. G2 is chosen to examine the effect of I/C ratio and porosity distribution, and G3 and G4 are chosen to examine the effect of Pt distribution on the performance and water and current density distribution.

Figure 12 shows the performance and water saturation comparison for cases G1 and G2 at 100%

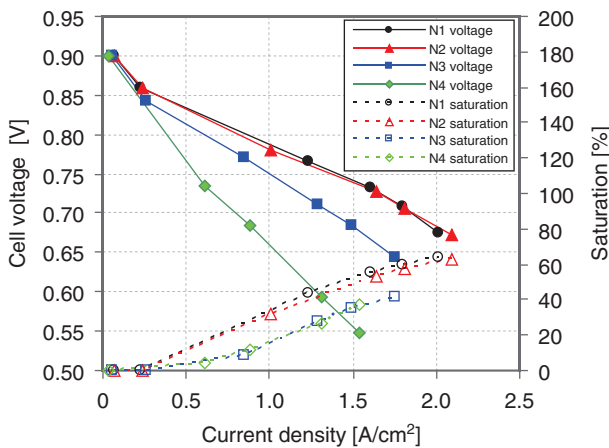


Fig. 11 Case study for N1-N4: Effects of *RH* on CL performance

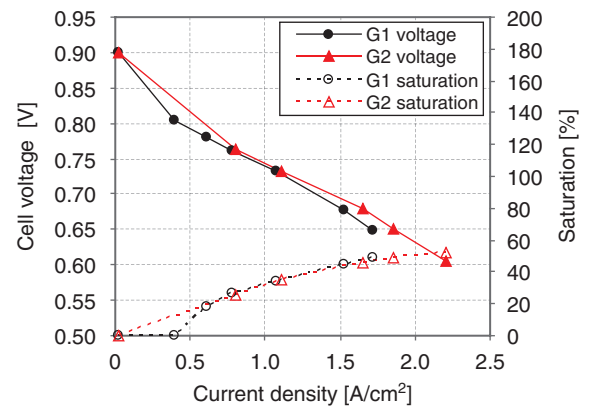


Fig. 12 Case study at *RH* 100%: Effects of graded I/C ratio and porosity on CL performance

RH. The performance of the CL with I/C ratio and porosity gradient (G2) is found to be better due to its high proton conductivity from PEM to MPL and high gas diffusivity from MPL to PEM.

Figure 13 shows the performance and water saturation comparison for cases G1, G3, and G4 at 100% RH. And Fig. 14 shows water saturation and current density per Pt surface distribution along the CL thickness for cases G1, G3, and G4. The performance of CL structure with no Pt loading near the PEM (G4) is found to be the lowest because there is no electrochemical reaction near PEM and proton transport path gets longer and proton transport resistance gets higher. The performance of CL structure with high Pt loading near the PEM (G3) is found to be not better than uniform structure because more liquid water accumulates and the reactive sites are not utilized effectively near the PEM. To examine the effect of RH on the performance and water saturation for G1 and G3, comparison at $RH = 65\%$ is conducted as Fig. 15. At low relative humidity condition, the performance of case G3 is better than

case G1 due to less liquid water accumulation and lower proton transport resistance, and the reactive sites are utilized effectively near the PEM accordingly. As shown above, the developed model can be applied to show the direction of low-Pt loading CL structure and optimal operating conditions for it with the understanding of the phenomena to improve the CL performance.

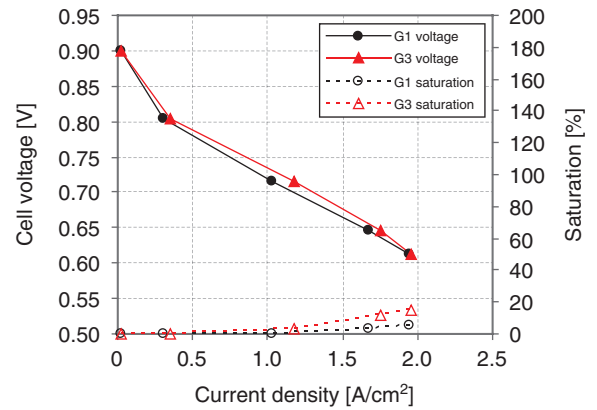


Fig. 15 Case study G1 and G3 at RH 65%: Effects of graded Pt loading on CL performance

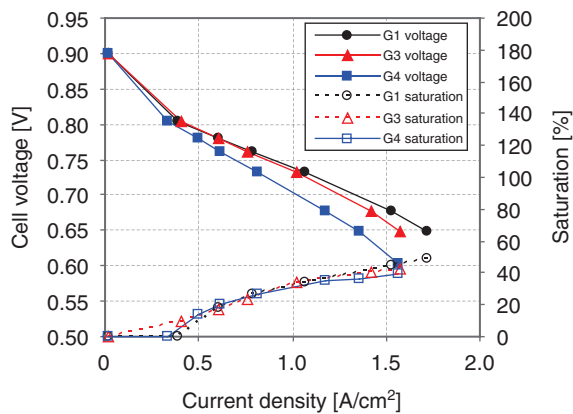


Fig. 13 Case study G1, G3, and G4 at RH 100%: Effects of graded Pt loading on CL performance

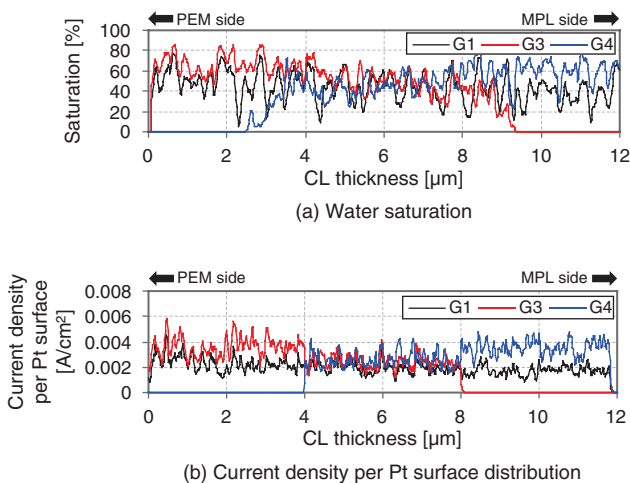


Fig. 14 Water saturation and current density per Pt surface distribution along CL thickness

6. Conclusion

We have proposed a novel computational framework to simulate the detailed physico-chemical processes in the reconstructed CLs of PEMFC. First, a general stochastic reconstruction method was developed based on the sphere-based simulated annealing method. This method is the general stochastic reconstruction method that can generate customized uniform and graded CLs with specified structural parameters. Second, a 3-D pore-scale multi-physics simulation model has been proposed. It can simulate fully coupled multiphase reactive flows and electrochemical phenomena in PEMFC CLs. The model was developed based on the hybrid lattice Boltzmann-Finite Difference method. All important processes occurring in the CL are taken into account, including the electrochemical reactions, water generation and evaporation, mass transport through electrode pores and ionomer, and the electron transport through carbon and catalysts, and proton transport through ionomer.

Reconstruction method is validated by the experimental data of PSD, gas diffusivity, proton resistivity, and electron conductivity. And the fully-coupled model is validated for the experimental V-I polarization curve. The simulation results demonstrate that this approach can be used to predict the performance of the electrode and to investigate detailed transport phenomena in the pore structures including distributions.

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